

Polymer Science:

A Comprehensive Reference

VOLUME 3 CHAIN POLYMERIZATION OF VINYL MONOMERS

Editors-in-Chief K. Matyjaszewski M. Möller

POLYMER SCIENCE: A COMPREHENSIVE REFERENCE

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VOLUME 3 CHAIN POLYMERIZATION OF VINYL MONOMERS

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Elsevier Radarweg 29, PO Box 211, 1000 AE Amsterdam, The Netherlands The Boulevard, Langford Lane, Kidlington, Oxford OX5 1GB, UK 225 Wyman Street, Waltham, MA 02451, USA

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A catalogue record for this book is available from the British Library

A catalog record for this book is available from the Library of Congress

ISBN: 978-0-444-53349-4

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Printed and bound in Spain

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CONTENTS OF VOLUME 3

Volui	ne Editors	vii
Edito	rs-in-Chief: Biographies	ix
Edito	rs: Biographies	xi
Cont	tibutors of Volume 3	xix
Prefa	ce	xxi
Forev	vord	XXV
Volun	ne 3 Chain Polymerization of Vinyl Monomers	
3.01	Introduction and Overview: Chain Polymerization of Vinyl Monomers <i>GW Coates and M Sawamoto</i>	1
3.02	Fundamental Aspects of Chain Polymerization S Penczek and JB Pretula	3
3.03	Radical Reactivity by Computation and Experiment <i>ML Coote</i>	39
3.04	Radical Polymerization G Moad	59
3.05	Controlled and Living Radical Polymerization – Principles and Fundamentals <i>T Fukuda and A Goto</i>	119
3.06	Degenerative Transfer with Alkyl Iodide P Lacroix-Desmazes and J Tonnar	159
3.07	Radical Addition–Fragmentation Chemistry and RAFT Polymerization <i>G Moad, E Rizzardo, and SH Thang</i>	181
3.08	Other Degenerative Transfer Systems S Yamago and Y Nakamura	227
3.09	Cobalt-Catalyzed Chain Transfer Polymerization: A Review S Slavin, K McEwan, and DM Haddleton	249

3.10 Nitroxide-Mediated Polymerization J Nicolas, Y Guillaneuf, D Bertin, D Gigmes, and B Charleux

3.12 Copper-Mediated Atom Transfer Radical Polymerization

3.11 Organometallic-Mediated Radical Polymerization

K Matyjaszewski and J Spanswick

R Poli

277

351

377

vi Contents of Volume 3

3.13	Transition Metal Complexes for Metal-Catalyzed Atom Transfer Controlled/Living Radical Polymerization K Satoh, M Kamigaito, and M Sawamoto	429
3.14	Vinyl Polymerization in Heterogeneous Systems B Charleux, M Cunningham, and JR Leiza	463
3.15	Cationic Polymerization of Nonpolar Vinyl Monomers <i>R Faust</i>	501
3.16	Cationic Polymerization of Polar Monomers S Kanaoka and S Aoshima	527
3.17	Anionic Polymerization of Nonpolar Monomers RP Quirk	559
3.18	Anionic Polymerization of Protected Functional Monomers T Ishizone, K Sugiyama, and A Hirao	591
3.19	Anionic Polymerization of Polar Vinyl Monomers D Baskaran and AHE Müller	623
3.20	Industrial Catalysts for Alkene Polymerization A Vaughan, DS Davis, and JR Hagadorn	657
3.21	Metallocene Alkene Polymerization Catalysts GH Zohuri, K Albahily, ED Schwerdtfeger, and SA Miller	673
3.22	Chain Shuttling Catalysis and Olefin Block Copolymers PD Hustad, RL Kuhlman, and C Li Pi Shan	699
3.23	Living Transition Metal-Catalyzed Alkene Polymerization: Polyolefin Synthesis and New Polymer Architectures AM Anderson-Wile, JB Edson, and GW Coates	739
3.24	Copolymerization of Alkenes and Polar Monomers by Early and Late Transition Metal Catalysts A Schöbel, M Winkenstette, TMJ Anselment, and B Rieger	779
3.25	Alkene/CO Copolymerization K Nozaki and S Ito	825
3.26	Cycloolefin Polymerization W Kaminsky, L Boggioni, and I Tritto	843
3.27	Alkyne Polymerization F Sanda, M Shiotsuki, and T Masuda	875

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EDITORS-IN-CHIEF: BIOGRAPHIES



Krzysztof Matyjaszewski received his PhD degree in 1976 from the Polish Academy of Sciences under Prof. S. Penczek. Since 1985 he has been at Carnegie Mellon University where he is currently J. C. Warner University Professor of Natural Sciences and director of Center for Macromolecular Engineering. He is also Adjunct Professor at the University of Pittsburgh and at the Polish Academy of Sciences. He is the editor of *Progress in Polymer Science and Central European Journal of Chemistry*. He has coedited 14 books and coauthored more than 70 book chapters and 700 peer-reviewed publications; he holds 41 US and more than 120 international patents. His papers have been cited more than 50 000 times. His research interests include controlled/living radical polymerization, catalysis, environmental chemistry, and advanced materials for optoelectronic and biomedical applications.

Dr. Matyjaszewski has received 2011 Wolf Prize, 2011 Prize of Société Chimique de France, 2009 Presidential Green Chemistry Challenge Award, 2004 Prize from the Foundation of Polish

Science, and several awards from the American Chemical Society (including 2011 Hermann Mark Award, 2011 Applied Polymer Science Award, 2007 Mark Senior Scholar Award, 2002 Polymer Chemistry Award, and 1995 Marvel Creative Polymer Chemistry Award). He is a member of US National Academy of Engineering, Polish Academy of Sciences, Russian Academy of Sciences, and received honorary degrees from l'Institut Polytechnique, Toulouse, France; University of Athens, Greece; Russian Academy of Sciences; Lodz Polytechnic, Poland; and University of Ghent, Belgium.



Martin Möller studied chemistry at Hamburg and Freiburg. He received his PhD degree in 1981 from the University of Freiburg.

He was a Feodor-Lynen Research Fellow of the Alexander von Humboldt Foundation at the Polymer Science and Engineering Department, University of Massachusetts, Amherst, USA. After his habilitation in 1989 at Freiburg University he was professor at the universities of Twente, Enschede, The Netherlands and Ulm, Germany. Since 2002 he is professor of Textile and Macromolecular Chemistry at RWTH Aachen University, and since 2003 also the director of DWI-Interactive Materials Research Institute at RWTH Aachen University. He has served on the editorial board of several polymer journals. His fields of interest include polymers self-organization of macromolecules, surface modification and activation, formation of functional nanostructures, and organic–inorganic hybrid structures. Martin Möller has received the the Körber-Prize 2002. He is a member of the Deutsche Akademie der Technikwissenschaften (acatech) and of the Academy of Sciences of the state of North-Rhine Westphalia.

EDITORS: BIOGRAPHIES



Alexei R. Khokhlov was born in 1954 in Moscow, Russia. He graduated from Moscow State University in 1977, received his PhD in 1979 and Doctor of Science in 1983. He is Full Professor and Head of the Chair of Physics of Polymers and Crystals. He is a Member of Russian Academy of Sciences (2000), Chairman of Polymer Council of Russian Academy of Sciences (2002) and Laureate of the Russian National Award (2007).



Friedrich Kremer is Professor of Molecular Physics, Materials Research Spectroscopy, Institute of Experimental Physics I, University of Leipzig, Germany. His research interests include broadband dielectric spectroscopy, time-resolved Fourier transform infrared (FTIR) spectroscopy, and experiments with optical tweezers. In 2005 he was awarded with the Karl Heinz Beckurts – Prize; in 2011 he received the Wolfgang-Ostwald-Prize from the German Colloid Society.



Takeji Hashimoto received his MS degree in 1969 and PhD in 1971 (with Prof. R. S. Stein) from the University of Massachusetts. He was appointed as an assistant professor at Kyoto University, Japan, in 1971, and was promoted as a full professor in 1994. He was director of the Hashimoto Polymer Phasing Project, ERATO (Exploratory Research for Advanced Technology), supported by JST (Japan Science and Technology Agency), from 1993 to 1998. He served as a group leader and invited researcher for the project 'Neutron Scattering and Structure-Functionality of Soft Matters' at the Advanced Science Research Center (ASRC), Japan Atomic Energy Research Institute (JAEA), Tokai, from 2003 to 2005. Since his retirement from Kyoto University in March 2005, he has been a professor emeritus of Kyoto University, and served as a full-time visiting researcher at ASRC, JAEA, Tokai, from 2005 to 2008 and as a group leader for the physical science and life science group. He has been a visiting scientist at JAEA, Tokai, since 2008 and a visiting professor at the School of Science and Technology, Kwansei-Gakuin University, Sanda, Japan, since 2009.

He has received several awards including the Society of Polymer Science Japan Award (1986), the High Polymer Physics Award (Ford Prize) from the American Physical Society (1987), the award for Young Rheologist from the Society of Rheology, Japan (1989), the Society of Fiber Science Japan Award (1990), the Osaka Science Award (1992), the Turner Alfrey Award from

Midland Molecular Institute, Midland Section of ACS (1997), the Fraser Price Memorial Award from the University of Massachusetts (1997), the Chemical Society of Japan Award (2003), the Japanese Society for Neutron Science Award (2004), and Society of Polymer Science Japan Award for Outstanding Achievement in Polymer Science and Technology (2006).



Hans Wolfgang Spiess, born in 1942, received his doctoral degree in physical chemistry in 1968 from the University of Frankfurt with H. Hartmann. After a postdoctoral stay at Florida State University (with R. K. Sheline), he returned to Germany in 1970 and joined the Max Planck Institute for Medical Research (with K. H. Hausser), taking part in the rapid development of novel NMR techniques for studying molecular motion in liquids and solids. In 1978, he finished his habilitation in physical chemistry at the University of Mainz in the group of H. Sillescu. Subsequently, he held professorships of physical chemistry at the University of Münster (1981–82) and macromolecular chemistry at the University of Bayreuth (1983–84). In 1984, he was appointed a director of the newly founded Max Planck Institute for Polymer Research in Mainz. His research interests include the development of magnetic resonance techniques for elucidating the structure, dynamics, phase behavior, and order of synthetic macromolecules and supramolecular systems. He applies these methods to the study of new polymer materials to

relate their microscopic and macroscopic behavior. Spiess has served as chairman of the European Polymer Federation (1991–92) and as chairman of the Capital Investment Committee of the German Science Foundation (1994–96). From 1999 till 2005, he has been a member of the Scientific Council of the Federal Republic of Germany. His achievements have been honored by several distinctions, including the Leibniz Prize of the German Research Foundation in 1987, the European Ampere Prize, the Liebig Medal of the German Chemical Society, the Award of the Society of Polymer Science (Japan) in 2002, the Walther Nernst Medal of the German Bunsen Society for Physical Chemistry in 2007, and the Paul J. Flory Research Prize in 2010. He is doctor *honoris causa* of the Technical University of Cluj-Napoca, Romania (1997), and of Adam Mickiewicz University, Poznan, Poland (1998).



Mikihito Takenaka received both the master's degree in engineering in 1988 and the doctor's degree in engineering in 1993 with Prof. Takeji Hashimoto from Kyoto University. In 1997, he was appointed as an assistant professor of the Department of Polymer Chemistry in Kyoto University. He was promoted to associate professor in 2011. His research scope includes the dynamics of phase transitions of polymer alloys and the directed self-assembling of block copolymer thin films.



Geoffrey W. Coates was born in 1966 in Evansville, Indiana. He received a BA degree in chemistry from Wabash College in 1989 and a PhD in organic chemistry from Stanford University in 1994. His thesis work, under the direction of Robert M. Waymouth, investigated the stereoselectivity of metallocene-based Ziegler–Natta catalysts. Following his doctoral studies, he was an NSF Postdoctoral Fellow with Robert H. Grubbs at the California Institute of Technology. During the summer of 1997, he joined the faculty of Cornell University as an assistant professor of chemistry. He was promoted to associate professor in 2001 and to professor in 2002. He was appointed to the first Tisch University Professorship in 2008.

The research focus of the Coates Group is the development of new catalysts for the synthesis of macromolecules as well as small molecules. Professor Coates' research concentrates on developing new methods for reacting commodity feedstocks in unprecedented ways. His current research centers on the development of homogeneous catalysts for olefin polymerization, heterocycle carbonylation, epoxide homo- and copolymerization, and utilization of carbon dioxide in polymer synthesis.

Professor Coates is an Alfred P. Sloan Research Fellow and has received awards from the ACS (A. C. Cope Scholar Award, Affordable Green Chemistry Award, A. K. Doolittle Award, Carl S. Marvel – Creative Polymer Chemistry Award, and Akron Section Award), NSF (CAREER), MIT Technology Review Magazine (TR 100 Award), Research Corporation (Innovation Award), Arnold and Mabel Beckman Foundation (Young Investigator Award), David and Lucile Packard Foundation (Fellowship in Science and Engineering), and Dreyfus Foundation (Camille and Henry Dreyfus New Faculty and Camille Dreyfus Teacher-Scholar Awards). In 2006, he received the Stephen and Margery Russell Distinguished Teaching Award at Cornell University and became a member of the American Association for the Advancement of Science. In 2011, he was identified by Thomson Reuters as one of the world's top 100 chemists on the basis of the impact of his scientific research. He is a member of the editorial advisory boards of the *Journal of Polymer Science, Chemical Reviews*, and *ChemCatChem*. He is a member of the editorial board of *Dalton Transactions* and is an associate editor for *Macromolecules*.



Mitsuo Sawamoto was born in 1951 in Kyoto, Japan. He received a BS (1974), an MS (1976), and PhD degrees (1979) in polymer chemistry from Kyoto University, Japan. After a postdoc-toral research at the Institute of Polymer Science, The University of Akron, Akron, OH, USA (1980–81), he joined the faculty of Department of Polymer Chemistry, Kyoto University, Japan in 1981 as a research instructor and is currently Professor of Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Japan since 1994.

He served as President of the Society of Polymer Science, Japan from 2008–10, and is currently an executive member of the Science Council of Japan, a titular member of IUPAC Polymer Division, and one of the Editors of the *Journal of Polymer Science, Part A, Polymer Chemistry*. He is also the principal investigator of a research project "Sequence-Regulated Macromolecules" (2006–10; Grant-in-Aid for Scientific Research: Creation of Novel Academic Disciplines) and the project leader of the Kyoto University Global Center of Excellence (GCOE)

Project "Integrated Materials Science" (2007–11), both granted by the Ministry of Education, Science, Culture, and Sports, Japan via the Japan Society for Promotion of Science.

With over 350 original papers and over 30 reviews, he has received, among others, Award of the Society of Polymer Science, Japan (1992), Divisional Research Award of the Chemical Society of Japan (1999), and Arthur K. Doolittle Award of PMSE Division, the American Chemical Society (2002). His research interest includes development of novel precision polymerizations and catalysis (living cationic polymerization with Lewis-acid catalysts (1984) and living radical polymerization with transition metal complex catalysts (since 1995)), the synthesis of designed functional polymers, the nature of polymerization intermediates, and most recently the sequence regulation in chain growth polymerization for single-chain functional macro-molecules of carbon-based backbones.

The first paper on his living radical polymerization has been cited thus far over 1600 times and is ranked number two in the most cited papers published in *Macromolecules*; a comprehensive review on this discovery published in *Chemical Reviews* has now been cited over 1200 times and has been selected as one of the ACS 2007 Highly Cited Papers (within top 1%) in the latest ten years (1998–2007); and he was ranked number one in Japan and number three in the world among the most cited scientists in organic and polymer chemistry for the period of 1997–2001.



Stanislaw Penczek is Professor of Polymer Chemistry at the Polish Academy of Sciences (Centre of Molecular and Macromolecular Studies in Lodz). He teaches at the Graduate School of the Jagiellonian University (Krakow) as an honorary professor. He has mostly contributed to the kinetics, thermodynamics, and mechanisms of the ring-opening polymerization, publishing over 300 papers in related areas. He was one of the first to observe living and controlled polymerizations in cationic and anionic ROP, including reversibility of deactivation of propagating species. Among other honors from Belgium, Japan, and Germany (the Warburg Prize), he is a member of the Polish Academy of Sciences and foreign member of German (Nordrhein) Academy, Dr *h.c.* of the Pierre and Marie Curie University in Paris and Dr *h.c.* of the Russian Academy of Sciences. He was a member of the International Union of Pure and Applied Chemistry (IUPAC) Bureau for two terms, and former president of European Polymer Federation.



Robert (Bob) Howard Grubbs' main interests in organometallic chemistry and synthetic chemistry are catalysts, notably Grubbs' catalyst for olefin metathesis and ring-opening metathesis polymerization with cyclic olefins such as norbornene. He also contributed to the development of so-called 'living polymerization'.

Grubbs has received many awards including Alfred P. Sloan Fellow (1974–76), Camille and Henry Dreyfus Teacher-Scholar Award (1975–78), Alexander von Humboldt Fellowship (1975), ACS Benjamin Franklin Medal in Chemistry (2000), ACS Herman F. Mark Polymer Chemistry Award (2000), ACS Herbert C. Brown Award for Creative Research in Synthetic Methods (2001), the Tolman Medal (2002), and the Nobel Prize in Chemistry (2005). He was elected to the National Academy of Sciences in 1989 and a fellowship in the American Academy of Arts and Sciences in 1994.



Hans-Werner Schmidt studied chemistry at the University of Mainz (Germany) and ETH Zürich (Switzerland). He received his diploma in chemistry and Dr. rer. nat. degree in macromolecular chemistry with Prof. Helmut Ringsdorf at the University of Mainz. After a stay at the DuPont Central Research in Wilmington, Delaware (USA), he moved to the University of Marburg to obtain his habilitation. From 1989 to 1994, he was Assistant and Associate Professor of Materials with tenure at the Materials Department, College of Engineering at the University of California, Santa Barbara. Since 1994, he has been Full Professor for Macromolecular Chemistry at the University of Bayreuth. He is director of the Bayreuth Institute of Macromolecular Research and founding member of the Bayreuth Centre for Colloids and Interfaces. Since 2009, he has been Vice President of the University of Bayreuth for research and since 2004 chairman of the 'Elite Study Program Macromolecular Science' (Elite Network Bavaria).

His research interest is focused on the synthesis and development of novel organic functional materials in the area of emerging technologies. This includes multifunctional polymers, molecular glasses, and supramolecular polymer additives and gelators. Combinatorial methods to efficiently synthesize and screen materials properties of polymer and supramolecular materials and functions of devices are an additional aspect.



Mitsuru Ueda received his BS and MS degrees in polymer chemistry from Chiba University in 1970 and 1972, respectively, and a PhD degree from Tokyo Institute of Technology in 1978. He joined Yamagata University in 1972 and was promoted to a professor in 1989. He moved to Tokyo Institute of Technology in 1999. His current research interests are the development of new synthetic methods for condensation polymers, polymer solar cells, fuel-cell membranes, photosensitive materials for microelectronics, and new advanced resist materials.



Axel H. E. Müller obtained his PhD in 1977 from Johannes Gutenberg University in Mainz, Germany, for the work on the kinetics of anionic polymerization with G. V. Schulz. Since 1999, he has been professor and chair of macromolecular chemistry at the University of Bayreuth. In 2004, he received the IUPAC MACRO Distinguished Polymer Scientist Award and since 2011, he has been a Fellow of the Polymer Chemistry Division of the American Chemical Society. He is senior editor of the journal *Polymer*. His research interests focus on the design of well-defined polymer structures by controlled/living polymerization techniques and on self-organized nanostructures and hybrids obtained from them. He has coedited five books and published over 400 research papers.



Karen L. Wooley holds the W. T. Doherty-Welch Chair in the Department of Chemistry at Texas A&M University, with a joint appointment in the Department of Chemical Engineering. She received a BS in chemistry from Oregon State University in 1988 and then studied under the direction of Professor Jean M. J. Fréchet at Cornell University, obtaining a PhD in polymer/ organic chemistry in 1993. She began an academic career as an assistant professor of chemistry at Washington University in St. Louis, Missouri; was promoted in 1999 to full professor with tenure; and was installed as a James S. McDonnell Distinguished University Professor in Arts & Sciences in 2006. In 2009, she relocated to Texas A&M University. Research areas include the synthesis and characterization of degradable polymers, unique macromolecular architectures and complex polymer assemblies, and the design and development of well-defined nanostructured materials, for which she has received several awards, including an Arthur C. Cope Scholar Award, a Herman F. Mark Scholar Award, and awards from the National Science Foundation, the Office

of Naval Research, and the Army Research Office. Karen serves as an editor for the *Journal of Polymer Science*, *Part A: Polymer Chemistry*. She directs an NHLBI-supported Program of Excellence in Nanotechnology and also serves on the Scientific Advisory Panel for the NIH Nanomedicine Development Centers and on the International Scientific Advisory Board for the Dutch BioMedical Materials Program.



Professor Eugenia Kumacheva is a Canada Research Chair in Advanced Polymer Materials. Her current research interests are in polymer micro- and nanostructured materials, hybrid materials, biomaterials, inorganic nanoscale materials, and microfluidics.



Thomas Russell is Silvio O. Conte Distinguished Professor, Polymer Science and Engineering Department; Director, Energy Frontier Research Center (EFRC), Polymer-Based Materials for Harvesting Solar Energy. His research interests are polymer-based nanoscopic structures, polymer-based nanoparticle assemblies, electrohydrodynamic instabilities in thin polymer films, surface and interfacial properties of polymers, polymer morphology; kinetics of phase transitions, and supercritical fluid/polymer interactions.



Professor Christopher K. Ober received his BSc in honours chemistry (co-op) from the University of Waterloo, Ontario, in 1978. He received his PhD in polymer science and engineering from the University of Massachusetts (Amherst) in 1982. From 1982 until 1986, he was a senior staff member at the Xerox Research Centre of Canada where he worked on marking materials. Ober joined Cornell University as an assistant professor in the Department of Materials Science and Engineering in 1986. He recently served as Interim Dean of the College of Engineering. He has pioneered new methods in photolithography and studies the biology materials interface. His awards include the 2009 Gutenberg Research Award from the University of Mainz, the 1st Annual FLEXI Award in the Education Category (for flexible electronics) awarded in 2009, the 2007 Humboldt Research Prize, the 2006 ACS Award in Applied Polymer Science, and the Photopolymer Science and Technology Award in 2004. He was elected an ACS Fellow in the 2009 Inaugural Class.



Professor Dr. Klaus Müllen obtained his PhD degree from the University of Basel, Switzerland, in 1972 where he undertook research with Professor F. Gerson on EPR spectroscopy of twisted π -systems. In 1972, he joined the group of Professor J.F.M. Oth at the Swiss Federal Institute of Technology in Zürich where he worked in the field of dynamic NMR spectroscopy and electrochemistry. He received his habilitation from the ETH Zurich in 1977. In 1979, he became a professor in the Department of Organic Chemistry, University of Cologne, and accepted an offer of a chair in organic chemistry at the University of Mainz in 1983. In 1988, he joined the Max-Planck-Society and in 1989 as one of the directors of the Max-Planck Institute for Polymer Research. His current research topics include new polymer-forming reactions, multidimensional polymers with complex shape-persistent architectures, dyes, chemistry and physics of single molecules, polymers for electronic and optoelectronic devices, materials for lithium or hydrogen storage, biosynthetic hybrids, and nanocomposites. In recent years, he has especially focused on

the chemistry and physics of carbon-rich materials such as carbon nanotubes, graphenes, and nanographenes. He has received numerous prestigious awards such as the International Award of the Polymer Society of Japan (2009), the ACS Award for Polymer Chemistry (2011), the ERC Advanced Grant (2011), and the Tsungming Tu Award (2011). Since 2006, he acts as Associate Editor of the *Journal of the American Chemical Society* and in 2008 and 2009 he served as President of the German Chemical Society.



David A. Tirrell is the Ross McCollum-William H. Corcoran Professor of chemistry and chemical engineering at the California Institute of Technology. After earning the BS degree in chemistry at MIT in 1974, he enrolled in the Department of Polymer Science and Engineering at the University of Massachusetts, where he was awarded the PhD degree in 1978 for work done under the supervision of Otto Vogl. After a brief stay with Takeo Saegusa at Kyoto University, he accepted an assistant professorship in the Department of Chemistry at Carnegie Mellon University in the fall of 1978. He returned to Amherst in 1984 and served as director of the Materials Research Laboratory at the University of Massachusetts before moving to Caltech in 1998. He chaired the Division of Chemistry and Chemical Engineering at Caltech from 1999 until 2009. His contributions to chemistry and chemical engineering have been recognized by his election to the National Academy of Sciences, the National Academy of Engineering, the Institute of Medicine, and the American Academy of Arts and Sciences.



Robert S. Langer is the David H. Koch Institute Professor (there are 14 Institute Professors at MIT; being an Institute Professor is the highest honor that can be awarded to a faculty member). Dr. Langer has written nearly 1130 articles. He also has approximately 800 issued and pending patents worldwide. Dr. Langer's patents have been licensed or sublicensed to over 220 pharmaceutical, chemical, biotechnology, and medical device companies. He is the most cited engineer in history. He served as a member of the United States Food and Drug Administration (FDA)'s SCIENCE Board, the FDA's highest advisory board, from 1995 to 2002 and as its Chairman from 1999 to 2002.

Dr. Langer has received over 180 major awards including the 2006 United States National Medal of Science; the Charles Stark Draper Prize, equivalent of the Nobel Prize for engineers; the 2008 Millennium Prize, the world's largest technology prize; and the 2012 Priestley Medal, the highest award of the American Chemical Society. He is the also the only engineer to receive

the Gairdner Foundation International Award; 72 recipients of this award have subsequently received a Nobel Prize. Among numerous other awards Langer has received are the Dickson Prize for Science (2002); Heinz Award for Technology, Economy and Employment (2003); the Harvey Prize (2003); the John Fritz Award (2003) (given previously to inventors such as Thomas Edison and Orville Wright); the General Motors Kettering Prize for Cancer Research (2004); the Dan David Prize in Materials Science (2005); the Albany Medical Center Prize in Medicine and Biomedical Research (2005), the largest prize in the United States for medical research; induction into the National Inventors Hall of Fame (2006); the Max Planck Research Award (2008); and the Prince of Asturias Award for Technical and Scientific Research (2008). In 1998, he received the Lemelson-MIT Prize, the

world's largest prize for invention for being 'one of history's most prolific inventors in medicine'. In 1989, Dr. Langer was elected to the Institute of Medicine of the National Academy of Sciences, and in 1992, he was elected to both the National Academy of Engineering and the National Academy of Sciences. He is one of very few people ever elected to all three United States National Academies and the youngest in history (at age 43) to ever receive this distinction.

Forbes Magazine (1999) and Bio World (1990) have named Dr. Langer as one of the 25 most important individuals in biotechnology in the world. Discover Magazine (2002) named him as one of the 20 most important people in this area. Forbes Magazine (2002) selected Dr. Langer as one of the 15 innovators worldwide who will reinvent our future. Time Magazine and CNN (2001) named Dr. Langer as one of the 100 most important people in America and one of the 18 top people in science or medicine in America (America's Best). Parade Magazine (2004) selected Dr. Langer as one of six 'Heroes whose research may save your life'. Dr. Langer has received honorary doctorates from Harvard University, the Mt. Sinai School of Medicine, Yale University, the ETH (Switzerland), the Technion (Israel), the Hebrew University of Jerusalem (Israel), the Universite Catholique de Louvain (Belgium), Rensselaer Polytechnic Institute, Willamette University, the University of Liverpool (England), Bates College, the University of Nottingham (England), Albany Medical College, Pennsylvania State University, Northwestern University, Uppsala University (Sweden), and the University of California–San Francisco Medal. He received his bachelor's degree from Cornell University in 1970 and his ScD from the Massachusetts Institute of Technology in 1974 (both degrees in Chemical Engineering).



James E. McGrath received his BS in chemistry from Siena College in New York (1956) and his MS (1964) and PhD (1967) in polymer science from the University of Akron, where he worked on emulsion and anionic polymerization of synthetic rubbers, ozone cracking, and triblock copolymer thermoplastic elastomers. After 19 years in industry (Rayonier (cellulose), Goodyear (synthetic rubbers), and Union Carbide (engineering thermoplastics, polyolefins)), he joined the Chemistry Department at Virginia Tech in 1975. He is now Ethyl Chair and a University Distinguished Professor. He was director of the first group of NSF Science and Technology Centers from 1989 to 2000 on Structural Adhesives and Composites and focused on high-temperature polymers including polyimides, polysulfones, and toughened epoxy polymeric matrix resins for carbon fiber composites. He has many contributions to the anionic and ring-opening polymerization of dienes, epoxides, and organosiloxanes. His current focus is on polymeric materials for carbon fibers and membranes, including fuel cells, reverse osmosis water

purification and gas separation systems. He has 50 patents and over 500 publications and has received numerous awards, including election to the National Academy of Engineers (1994), The International SPE award, the Plastics Hall of Fame, and the ACS awards in Applied Polymer Science (2002) and Polymer Chemistry (2008). He has graduated more than 100 PhD chemists and engineers and remains one of the leaders in polymer science and engineering, with a current group (2011) of 13 students and postdoctoral fellows.



Michael A. Hickner received a BS in chemical engineering from Michigan Tech in 1999 and MEng in 2002 and PhD in chemical engineering from Virginia Tech in 2003. In graduate school, he worked under the direction of James E. McGrath and also spent time in the fuel cell group at Los Alamos National Laboratory developing novel aromatic proton exchange membranes for both hydrogen and direct methanol fuel cells. Before joining the Department of Materials Science and Engineering at Penn State in July 2007, he was a postdoctoral researcher and subsequently became a staff member at Sandia National Laboratories in Albuquerque, NM, where he conducted experimental investigations and modeling studies of liquid water transport in fuel cells and porous media and properties of ion-containing membranes, electrochemical reactors, and nanoporous membranes for water treatment applications. His research group at Penn State is focused on the synthesis and properties of ion-containing polymers, measurement of waterpolymer interactions using spectroscopic techniques, and the study of self- and directed assembly

of polymeric nanostructures for fast transport. He has ongoing projects in new polymer synthesis, fuel cells, batteries, water treatment membranes, and organic photovoltaic materials. He is currently an assistant professor and the Virginia S. and Philip L. Walker Jr. Faculty Fellow in the Materials Science Department at Penn State. Hickner's work has been recognized by a Powe Junior Faculty Enhancement Award (2008), Young Investigator Awards from ONR and ARO (2008), a 3M Non-tenured Faculty Grant (2009), and a Presidential Early Career Award for Scientists and Engineers from President Obama in 2009. He has five US and international patents and over 60 peer-reviewed publications since 2001 that have been cited more than 2900 times as of 2011.



Rainer Höfer graduated in Inorganic Chemistry with Professor Oskar Glemser at the Georg-August Universität zu Göttingen in 1973 with work on sulfur-nitrogen-fluorine chemistry. He spent three years at the Technical University of Oran (ENSEP), Algeria, as Maître de Conférences and Directeur de l'Institut de Chimie before joining Henkel in Düsseldorf. With Henkel KGaA and then as Vice President Research & Technology with Cognis GmbH in Monheim, he has assumed global research and development, application technology, technical sales service, strategic business development, and technology scouting responsibilities in oleochemistry, polymer chemistry, and surfactant chemistry for the polymerization, coatings, graphic arts, adhesives, engineering plastics, agrochemical, synthetic lubricants, mining, and pulp and paper markets. He is founder of Editorial Ecosiris with consultancy and publishing activities in the domains of green chemistry, renewable resources, sustainable development, and interculturation.

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PREFACE

Comprehensive Polymer Science was published in 1989 as a set of seven volumes and then supplemented by two additional volumes. This excellent print collection comprehensively covered the entire field of polymer science at that time. Much of the information is currently still as valuable as it was then, although some aspects are seen differently now. Those differences are important in order to understand the enormous development polymer science has taken since 1989. When we developed the concept for an entirely new edition of *Polymer Science:* A *Comprehensive Reference,* we intended not only to update and replace the original edition of *Comprehensive Polymer Science,* (we are pleased to announce that it will be soon available in electronic format) but also to focus on a widely observed transition of polymer science, from exploring only macromolecules, polymeric materials, and polymerization processes to become part of a comprehensive study on molecular soft matter science enabling advancements in other related disciplines.

In 1989, polymer science had just started a second stage of development after completing the scientific and technological evolution of its fundamental principles. This second stage has been driven by the continuously increasing understanding of the complexity in the structural organization of polymer materials and the challenge to understand and to master the fundamental underlying structure formation on exceedingly large length scales. Material functions based on molecular organization have been the focus of outstanding and highly recognized achievements, for example, new concepts for macromolecular architectures, self-assembling properties, electronically conductive polymers, ultrathin films, and hybrid structures or bioconjugates.

We are once again at the beginning of another step forward in the development of polymer science. Based on an increasing understanding of molecular processes, for example, advancements in mastering molecular self-assembly and the interfacing of bottom-up and top-down approaches to molecular organization, the tremendous progress in understanding the molecular basis of biological processes, and the growing ability to describe more and more complex systems with the rigorous approaches of physics, the traditional boundaries between these fields of science are being torn down. At the same time, the differentiation between materials and living organisms is becoming more and more indistinct, that is, machines are becoming biological and biology is becoming engineered. Already a new field of biofunctional materials is emerging, where 'biofunctional' represents the ability to activate and control a biological response. As a consequence, polymer science is facing a shift in paradigm from having been focused on itself, toward creating an enabling science that provides an understanding of a much broader base of 'molecular soft matter science' that reaches out and provides important contributions toward biology and information- and energy-related technologies. This development is seen in the increased worldwide interest in bioinspired materials engineering biomimetic materials and in the creation of smart nanostructures, as well as polymeric electronic and photonic devices.

The great progress that has been made in many areas of polymer science since 1989 is reflected in, and aided by, three major developments: (1) the advancements in precision polymerization and synthetic combination of well-defined (bio)macromolecular building blocks, for example, controlled polymerization processes, and new macromolecular architectures; (2) the progress in characterization methods spanning an enormous increase in length- and timescales, for example, single molecule imaging and spectroscopy that provides an improved insight on slow and cooperative relaxation and ordering; and (3) significant improvement in the understanding of complex macromolecular systems like polyelectrolytes and block and graft copolymers amplified by the dramatically enhanced power of computational simulations. In addition, much interest has been focused on polymers and materials coming from biological sources, or those designed to serve specific functions in a biological system, which is partly driven by environmental and sustainability aspects, but also by the rising interest in smart biomimetic and bioactive materials. Besides the emergence of new biomaterials and biohybrid macromolecules, this also leads to a new interest in waterborne polymers and polymer synthesis in aqueous systems, for example, enzymatic polymerization.

The organization and outline of the ten volumes of this edition of *Polymer Science: A Comprehensive Reference* has been chosen to give consideration to these developments, but also to link the fundamentals of polymer science, as developed over almost 100 years, with the challenges of the ever more complex systems, and introduce connections that will dominate the future development of a polymer-based molecular soft matter science. Besides the classic print edition, this new edition of *Polymer Science: A Comprehensive Reference* is also provided as an e-version, enabled with efficient cross-referencing and multimedia. We invited the top world experts in polymer science to serve as volume editors and this 'dream team' has prepared a ten-volume set with 269 chapters covering both the fundamentals and the most recent advances in polymer science. Volumes 1–5 are directed toward the fundamentals of polymer science, that is, polymer physics and physical chemistry, advanced characterization methods, and polymer synthesis. In spite of the breadth of information collected in these five volumes, it has not been possible to cover all aspects of polymer science. In some cases, the reader must refer to the chapters in volumes 6–10 that address topical developments with a stronger material focus.

The progress in polymer science is revealed in essentially all chapters of this edition of *Polymer Science*: A Comprehensive Reference. In Volume 1, edited by Khokhlov and Kremer, this is reflected in the improved understanding of the properties of polymers in solution, in bulk, and in confined situations such as in thin films. Volume 2, edited by Spiess, Hashimoto, and Takenaka, addresses new characterization techniques that were not covered in the first edition, or did not even exist in 1989, such as highresolution optical microscopy, scanning probe microscopy, and other procedures for surface and interface characterization. Volume 3, edited by Coates and Sawamoto, presents the great progress achieved in precise synthetic polymerization techniques for vinyl monomers to control macromolecular architecture: the development of metallocene and post-metallocene catalysis for olefin polymerization, new ionic polymerization procedures, atom transfer radical polymerization, nitroxide-mediated polymerization, and reversible addition-fragmentation chain transfer systems as the most often used controlled/living radical polymerization methods. Volume 4, edited by Penczek and Grubbs, is devoted to kinetics, mechanisms, and applications of ring-opening polymerization of heterocyclic monomers and cycloolefins (ROMP), as well as to various less common polymerization techniques. Polycondensation and non-chain polymerizations, including dendrimer synthesis and various 'click' procedures, are covered in Volume 5, edited by Schmidt and Ueda. Volume 6, edited by Müller and Wooley, focuses on several aspects of controlled macromolecular architectures and soft nanoobjects including hybrids and bioconjugates. Many of the achievements would have not been possible without new characterization techniques like atomic force microscopy (AFM) that allowed direct imaging of single molecules and nanoobjects with a precision only recently available. An entirely new aspect in polymer science is based on the combination of bottom-up methods such as molecularly programmed self-assembly with top-down structuring such as lithography and surface templating, as presented in Volume 7, edited by Kumacheva and Russell. It encompasses polymer and nanoparticle assembly in bulk and under confined conditions or influenced by an external field, including thin films, inorganic-organic hybrids, or nanofibers. Volume 8, edited by Muellen and Ober, expands these concepts, focusing on applications in advanced technologies, for example, in electronic industry and centers, in combination with the top-down approach and functional properties like conductivity. Another type of functionality that is rapidly increasing in importance in polymer science is introduced in volume 9, edited by Langer and Tirrell. This deals with various aspects of polymers in biology and medicine, including the response of living cells and tissue to the contact with biofunctional particles and surfaces. Volume 10, edited by Höfer, Hickner, and McGrath, is devoted to the scope and potential provided by environmentally benign and green polymers, as well as energy-related polymers. It discusses new technologies needed for a sustainable economy in our world of limited resources. Common to all approaches in this edition of Polymer Science: A Comprehensive Reference is the mastering of an increasing complexity of the polymer material structure needed for a change in focus

from commodities to materials for various advanced applications, related to energy, environment, and biomedicine.

We hope that this new edition of *Polymer Science: A Comprehensive Reference* will provide the readers with state-of-the-art coverage of all important and modern aspects of polymer science. We would like to thank all volume editors, contributing authors, and Elsevier personnel for their efforts, not only in completing the project in a timely fashion but also in ensuring the outstanding quality of the final product.

Krzysztof Matyjaszewski Martin Möller

FOREWORD

Polymer science has experienced a most impressive expansion in depth, breadth, and diversity through developments in its core domains as well as at the interfaces of polymer chemistry and physics with materials science, supramolecular chemistry, nanoscience, biophysics, and biology. These developments are reflected in the evolution from the original edition of *Comprehensive Polymer Science* to the present edition *Polymer Science: A Comprehensive Reference.* None of these areas can nowadays be envisaged without considering the contributions of polymer science to their own progress. At the same time and with increasing impact, scientists from the other fields contribute new findings and concepts to polymer science and many novel and topical approaches are rooted in the areas mentioned above.

The extension of the concepts and features of supramolecular chemistry from discrete species to polymolecular entities has opened novel perspectives in materials science. It defines a field of supramolecular materials that rests on the explicit implementation of intermolecular interactions and recognition processes for controlling the buildup, the architecture, and the properties of polymolecular assemblies as they emerge from their components through self-organization. Such spontaneous but directed self-assembly is of major interest for the supramolecular design, synthesis, and engineering of novel materials presenting novel properties.

Our own connection with polymer science stems from the introduction and progressive establishment of a supramolecular polymer chemistry built on entities generated by polyassociation between molecular 'monomeric' components through dynamic noncovalent interactions with molecular recognition between the components. The more recent development of dynamic covalent chemistry led to the investigation of dynamic covalent polymers formed by polycondensation through reversible reactions between subunits bearing suitable functional groups. The dynamic features of both these molecular and supramolecular polymers characterize dynamic polymers, dynamers, on both levels. Dynamers may be defined as constitutional dynamic polymers, that is, polymeric entities whose monomeric components are linked through reversible connections and have therefore the capacity to modify their constitution by exchange and reshuffling of their components. They may undergo constitutional variation by incorporation, decorporation, and exchange of components. These dynamic properties confer to dynamers the ability to undergo adaptation and driven evolution in response to physical stimuli or chemical effectors. Dynamers are thus constitutional dynamic materials resulting from the application of the principles of constitutional dynamic chemistry to polymer science. As such, they open wide perspectives toward adaptive materials and technologies.

By the nature and the size of its objects, polymer science plays a very important role in nanoscience and nanotechnology, both areas experiencing a profound mutual fertilization. Polymer science has also been subject to major developments at the interface with biology, by the incorporation of biological components into synthetic polymers, as well as by applying its own principles to the understanding of the features of biological macromolecules.

An extremely rich variety of novel architectures, processes, and properties have resulted and may be expected to further emerge from the blending of polymer science with the other areas of materials chemistry and physics, with ongoing developments in chemistry as well as with the investigation of complex molecular behavior in biological sciences. *Polymer Science: A Comprehensive Reference* provides complete and up-to-date coverage of the most important contemporary aspects and fundamental concepts of polymer science. It will become the indispensable reference not only for polymer scientists but also for all researchers in disciplines related to macromolecular systems.

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3.01 Introduction and Overview: Chain Polymerization of Vinyl Monomers

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3.01.1	Introduction	1
3.01.2	Overview	1

3.01.1 Introduction

Vinyl polymers continue to be the most important class of polymeric materials as measured by annual production volume as well as economics. In the two decades since the first edition of Comprehensive Polymer Science, impressive advances have been made regarding new methods for the synthesis of polymers from vinyl monomers. Although the primary modes of polymerization (anionic, cationic, radical, and metal-mediated) have not changed, advances in polymerization catalysts and initiators now allow the synthesis of polymer architectures that were in many cases unimaginable only a few decades ago. This volume presents an up-to-date perspective on key advances in the area of vinyl polymerization since the first edition of Comprehensive Polymer Science. Such advances include the controlled/living polymerization of vinyl monomers, the synthesis of new vinyl polymer architectures (block, graft, star, etc.), the incorporation of functional groups in vinyl polymers, and the control of molecular weight and polymer end-groups. With the exception of a chapter on alkyne polymerization (Chapter 3.27), this volume only includes vinyl polymerizations that result in saturated polymer backbones; alkene metathesis and conjugated diene polymerization will be covered elsewhere in the treatise.

3.01.2 Overview

Following an overview on the fundamental aspects of chain polymerization (Chapter 3.02), the chapters in this volume

are organized sequentially by polymerization mechanism. Chapters 3.03-3.14 focus on the many developments in radipolymerization, including computational cal and experimental fundamentals of radical reactions, fundamentals of controlled/living radical polymerization, degenerative chain transfer with alkyl iodides, reversible additionfragmentation chain transfer polymerization and related degenerative transfer methods, nitroxide, organometallic, and atom transfer-mediated techniques, as well as radical polymerization in heterogeneous media. Chapters 3.15 and 3.16 cover advances in cationic polymerization, including nonpolar and polar monomers. Chapters 3.17-3.19 address recent progress in cationic polymerization, including nonpolar as well as protected and nonprotected polar monomers. Chapters 3.20-3.27 examine important progress in metal-mediated alkene polymerization in both industrial and academic settings, including metallocene-based catalysts, reversible chain transfer mechanisms, living alkene polymerization by nonmetallocene catalysts, alkene/carbon monoxide copolymerization, and polymerization of alkynes and cyclic alkenes. This volume comprehensively documents the exceptional progress in vinyl chain polymerization over the last two decades and highlights promising emerging areas that will yield exciting advances in the coming vears.

Biographical Sketches



Geoffrey W. Coates was born in 1966 in Evansville, Indiana. He received a BA degree in chemistry from Wabash College in 1989 and a PhD in organic chemistry from Stanford University in 1994. His thesis work, under the direction of Robert M. Waymouth, investigated the stereoselectivity of metallocene-based Ziegler–Natta catalysts. Following his doctoral studies, he was an NSF Postdoctoral Fellow with Robert H. Grubbs at the California Institute of Technology. During the summer of 1997, he joined the faculty of Cornell University as an assistant professor of chemistry. He was promoted to associate professor in 2001 and to professor in 2002. He was appointed to the first Tisch University Professorship in 2008.

The research focus of the Coates Group is the development of new catalysts for the synthesis of macromolecules as well as small molecules. Professor Coates' research concentrates on developing new methods for reacting commodity feedstocks in unprecedented ways. His current research centers on the development of homogeneous catalysts for olefin polymerization, heterocycle carbonylation, epoxide homo- and copolymerization, and utilization of carbon dioxide in polymer synthesis.

Professor Coates is an Alfred P. Sloan Research Fellow and has received awards from the ACS (A. C. Cope Scholar Award, Affordable Green Chemistry Award, A. K. Doolittle Award, Carl S. Marvel – Creative Polymer Chemistry Award, and Akron Section Award), NSF (CAREER), MIT Technology Review Magazine (TR 100 Award), Research Corporation (Innovation Award), Arnold and Mabel Beckman Foundation (Young Investigator Award), David and Lucile Packard Foundation (Fellowship in Science and Engineering), and Dreyfus Foundation (Camille and Henry Dreyfus New Faculty and Camille

Dreyfus Teacher-Scholar Awards). In 2006, he received the Stephen and Margery Russell Distinguished Teaching Award at Cornell University and became a member of the American Association for the Advancement of Science. In 2011, he was identified by Thomson Reuters as one of the world's top 100 chemists on the basis of the impact of his scientific research. He is a member of the editorial advisory boards of the *Journal of Polymer Science, Chemical Reviews*, and *ChemCatChem*. He is a member of the editorial board of *Dalton Transactions* and is an associate editor for *Macromolecules*.



Mitsuo Sawamoto was born in 1951 in Kyoto, Japan. He received a BS (1974), an MS (1976), and PhD degrees (1979) in polymer chemistry from Kyoto University, Japan. After a postdoctoral research at the Institute of Polymer Science, The University of Akron, Akron, OH, USA (1980–81), he joined the faculty of Department of Polymer Chemistry, Kyoto University, Japan in 1981 as a research instructor and is currently Professor of Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Japan since 1994.

He served as President of the Society of Polymer Science, Japan from 2008–10, and is currently an executive member of the Science Council of Japan, a titular member of IUPAC Polymer Division, and one of the Editors of the *Journal of Polymer Science, Part A, Polymer Chemistry*. He is also the principal investigator of a research project "Sequence-Regulated Macromolecules" (2006–10; Grant-in-Aid for Scientific Research: Creation of Novel Academic Disciplines) and the project leader of the Kyoto University Global Center of Excellence (GCOE) Project "Integrated Materials Science" (2007–11), both granted by the Ministry of Education, Science, Culture, and Sports, Japan via the Japan Society for Promotion of Science.

With over 350 original papers and over 30 reviews, he has received, among others, Award of the Society of Polymer Science, Japan (1992), Divisional Research Award of the Chemical Society of Japan (1999), and Arthur K. Doolittle Award of PMSE Division, the American Chemical Society (2002). His research interest includes development of novel precision polymerizations and catalysis (living cationic polymerization with Lewis-acid catalysts (1984) and living radical polymeri

ization with transition metal complex catalysts (since 1995)), the synthesis of designed functional polymers, the nature of polymerization intermediates, and most recently the sequence regulation in chain growth polymerization for single-chain functional macromolecules of carbon-based backbones.

The first paper on his living radical polymerization has been cited thus far over 1600 times and is ranked number 2 in the most cited papers published in *Macromolecules*; a comprehensive review on this discovery published in *Chemical Reviews* has now been cited over 1200 times and has been selected as one of the ACS 2007 Highly Cited Papers (within top 1%) in the latest ten years (1998–2007); and he was ranked number 1 in Japan and number 3 in the world among the most cited scientists in organic and polymer chemistry for the period of 1997–2001.

3.02 Fundamental Aspects of Chain Polymerization

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3.02.1	Introduction	4
3.02.2	The Nobel Prize Award Ceremony Speech of A. Ölander on Behalf of the Nobel Committee	4
3.02.2.1	Presentations of the Laureates	5
3.02.2.1.1	Semenov's presentation	5
3.02.2.1.2	Hinshelwood's presentation	5
3.02.3	Bodenstein Observation of the First Chain Reactions	6
3.02.4	Nernst's Mechanism of the $CI_2 + H_2$ Reaction (Finally Accepted as the Correct One)	6
3.02.5	Kinetic Scheme of the Fundamental Chain Reaction: $CI_2 + H_2$	6
3.02.6	Stationary State, Bodenstein Approximation, and Final Solution	7
3.02.7	Definitions Pertinent to Chain Reactions	7
3.02.7.1	Chain Reaction	7
3.02.7.2	Chain Carrier	7
3.02.7.3	Chain Propagating Reaction	7
3.02.7.4	Chain Branching	7
3.02.7.5	Steady State (Stationary State)	7
3.02.8	Definitions Pertinent to Chain Polymerizations	8
3.02.8.1	Chain Carrier	8
3.02.8.2	Chain Polymerization	8
3.02.8.3	Chain Propagation (in Chain Polymerization)	8
3.02.9	Two Kinds of Steady States in Chain Polymerizations	8
3.02.10	Discovery of Living Polymerization by Michael Szwarc	9
3.02.11	Living Polymerization	9
3.02.11.1	Definition of Living Polymerization	9
3.02.11.2	Reversibility in Chain Polymerizations	9
3.02.11.3	Kinetics of Fast Initiation–Propagation Systems	10
3.02.11.3.1	Anionic polymerizations of vinyl monomers: electron transfer initiation	10
3.02.11.4	Living Polymenzation. Two of More Interconversions of Active Species	10
2.02.11.5	Living estimic polymerization; the ease of trimethyletyrane	12
3.02.11.3.1	Living Californic polymerization. The case of himelingistyrene	12
3.02.11.0	Eiving Folymenzation of Gyelic Compounds Steady-State-Living Chain Polymerization of Cyclic Compounds: Identical Reactivities of Ions and Ion Pairs	13
3 02 11 8	Steady-State Living Polymerization with $k > 0$, k^{\pm} Inversion of Reactivities	14
3 02 11 9	Steady-State Living Polymerization with Dormant Species	15
3 02 11 9 1	Reversible chain deactivation	15
3.02.12	Nearly Steady-State Polymerizations: Controlled Polymerizations Involving Quasi-Equilibria between	10
	Active and Dormant Species	18
3.02.12.1	Living versus Controlled Polymerizations	19
3.02.12.1.1	Definitions of controlled polymerizations	19
3.02.12.2	Persistent Radical Effect: Self-Regulation (Internal Suppression of Fast Reactions)	20
3.02.12.3	Simple Description of the CRP	21
3.02.12.3.1	The fate of active centers	22
3.02.12.4	Rate Constants in CRP Based on the PRE: Principle	23
3.02.12.5	NMP and ATRP: Chemistry	23
3.02.12.6	Controlled Cationic Polymerization of Vinyl Monomers	24
3.02.13	Second Kind of the Steady State: The Rate of Formation of Active Centers Balanced by the Rate of Their	
	Disappearance. Classical Radical Polymerization	25
3.02.13.1	Hot Radicals Theory in Radical Polymerization	26
3.02.13.2	The Dependence of Rate Constants on the Chain Length	27
3.02.13.3	Limits of the Steady-State (Bodenstein) Approximation	27
3.02.13.4	Kate Constants in Kadical Polymerization	27
3.02.13.5	Puise Laser Polymenization–Size Exclusion Unromatography: Method of K _p Determination	28
J.UZ.14	Nun-oleauy-olate Fulymenzation	29
J.UZ.14.1 2 02 1/1 1 1	Naulual pulymetization faet propagation in living polymorization: Cold's treatment	20
3.02.14.1.1 3 09 1/1 9	Soow initiation—last propagation in tiving polymenzation. GOID'S treatment	30 20
0.02.14.2	שלמע בחער טואווטוובוובמנוטוו	50

3 02 14 3	Double Nonstationary Polymerization	30
3.02.15	Chain Polymerizations and Structure of Macromolecules	32
3.02.15.1	Stereochemistry of Propagation	32
3.02.16	Condensative Chain Polymerizations: Biopolymers	33
3.02.16.1	Definition	33
3.02.17	Polymerize Chain Reaction. DNA Syntheses	34
3.02.18	Conclusions	34
Appendix: Lif	fetime and Half-Life: Definitions and Their Relationship	35
References		36

3.02.1 Introduction

This chapter describes the fundamental aspects of chain polymerization. 'Fundamental' can be understood in two ways: first, how all that started – that is, in which way the chain reactions in chemistry (and particularly in polymer science) were discovered; second, basic phenomena. Both aspects are presented in this chapter.

The idea of chain reactions started with the works of Bodenstein. Beginning in about 1906, Max Bodenstein (1871–1942, Magdeburg) investigated the thermal and photochemical reactions between hydrogen and bromine and later the corresponding reactions between hydrogen and chlorine. In about 1913, he observed very high quantum yields (up to 10^6) for the photochemical hydrogen–chlorine reactions and proposed several consecutive reactions with the one that started this event. This series of consecutive reactions was named 'chain reactions'.



Max Ernst August Bodenstein

Various sources, usually depending on the country they come from, describe the history of these early days in a slightly different way.

The Nobel Prize was not awarded for the discovery of chain reactions. However, in 1956, Sir Cyril Norman Hinshelwood from Great Britain (1897–1987, London) and Nikolai Nikolaevich Semenov from Russia (1896, Saratov, to Moscow, 1986) were jointly awarded the Nobel Prize for (mostly) developing branched chain reactions. The first monograph on chain reactions was written by Semenov.



Cyril Norman Hinshelwood



Nikolai Nikolaevich Semenov

3.02.2 The Nobel Prize Award Ceremony Speech of A. Ölander on Behalf of the Nobel Committee

At the award ceremony, as is customary, the award speech was given by A. Ölander on behalf of the Nobel Committee. The presentation stressed on the earlier contribution of van't Hoff and Arrhenius to the discovery of chain reactions and their fundamental phenomena.

Ölander's presentation is given below.¹

Award Ceremony Speech:

Presentation Speech by Professor A. Ölander, Member of the Nobel Committee for Chemistry of the Royal Swedish Academy of Sciences (cited *in extenso*):

Your Majesties, Your Royal Highnesses, Ladies and Gentlemen. The Nobel Prize which is now to be given to Sir Cyril Norman Hinshelwood and Academician Nikolai Nikolaevich Semenov 'for their researches into the mechanism of chemical reactions' reminds us of the very first Nobel Prize in Chemistry, which was awarded in 1901 to the Dutchman Jacobus Henricus van't Hoff. He received his prize for 'the discovery of the laws of chemical dynamics', i.e. the velocity of chemical reactions.

Van't Hoff and the Swede Svante Arrhenius had already in the 1880's disclosed that when molecules of two substances collide, the collision must be sufficiently violent if the initial molecules are to break down and their atoms to rearrange into new molecules, that is, for a chemical reaction to take place.

Thirty years ago Hinshelwood studied a number of chemical reactions which allowed him to draw important conclusions concerning the collisions between molecules, which set them in such vibration that they became unstable.

There are some chemical reactions which are extremely sensitive to light. In 1900 Max Planck had found that light was composed of discrete quanta. It was then natural to think that when a light quantum hits a molecule, it could be excited in such a way that it underwent a chemical reaction. But how could one possibly understand that a single absorbed light quantum could cause perhaps a million molecules to react?

In 1913 the German chemist Max Bodenstein put forth an idea which proved to be extremely fertile, the idea of chain reactions. This means, that if two molecules react, not only molecules of the final reaction products are formed, but also some unstable molecules, having the property of being able to react with the parent molecules without the collision being very violent. In this reaction, new unstable molecules are formed besides stable reaction products and so on. We thus obtain a chain of reactions, so when two molecules have reacted, they cause a great number of more molecules to react.

A Danish and a Dutch scientist, Christiansen and Kramers, in 1923 pointed out that such a chain reaction need not start with a molecule excited by light, but could also start with two molecules colliding violently in the way van't Hoff had thought of.

Christiansen and Kramers also set forth another fruitful idea. If in one link of the reaction chain not only one, but two or more unstable molecules are produced, the reaction chain will branch. The result is that the reaction will spread over the whole mixture so it reacts in its entirety extremely rapidly, thus giving rise to an explosion. However, they did not elaborate the idea further, but pursued other researches.

The combustion of phosphorus vapour and oxygen was studied in 1926 by two scientists in Leningrad, Chariton and Valta. The greatest authority of that time on chemical reaction velocities, Bodenstein, whom I just mentioned, said frankly that their results were incomprehensible and must be wrong. They *were* incomprehensible from the point of view of that time, but the essential results were *not* wrong. Semenov reinvestigated the matter and found that it really was so that a mixture of phosphorus vapour and oxygen did not react at all if the gas pressure was too small or too great, but that at intermediate pressures the mixture exploded. Semenov disclosed that the idea of Christiansen and Kramers gave the explanation of this behavior. He and his team could show, that the pressures, at which the mixture exploded, were dependent on the proportion of gases and dimensions of vessel in a way which agreed completely with the assumption that this combustion was a chain reaction.

The mathematical relations in this case were rather simple. There are other combustions with far greater practical importance, but which are much more complicated. I will first mention the combustion of hydrogen with oxygen. This important reaction was studied both by Hinshelwood and his team in Oxford and by Semenov and his team in Leningrad. Of course also many other scientists have contributed to the final elucidation, but the present prize-winners have indicated the principles guiding the work. Another technically important chain reaction is the combustion of carbon monoxide, not to mention the combustion of hydrocarbons.

When it was found that a great number of reactions were chain reactions, many people in the first enthusiasm thought that almost all reactions were chain reactions and that the simpler mechanisms previously thought of were exceptions. But Hinshelwood put the matter in order. He found substances which could simultaneously react in two ways, one part reacting by a chain mechanism and at the same time the rest reacting in the old-fashioned way.

Sir Cyril Norman Hinshelwood, Academician Nikolai Nikolaevich Semenov. More than half a century has elapsed since the first Nobel Prize in Chemistry was awarded to van't Hoff for his discovery of the laws of chemical dynamics. Some of the greatest advances in chemical kinetics since that time have emerged from your researches and they have inspired a great number of scientists to continued fruitful studies. Your results are of equally great importance to technology and to the more theoretical aspects of chemistry.

On behalf of the Royal Swedish Academy of Sciences I wish to extend to you our warmest congratulations. May I now ask you to receive the Nobel Prize for Chemistry for the year 1956 from the hands of His Majesty the King.

3.02.2.1 Presentations of the Laureates

This presentation was followed by lectures from both laureates, published in the same issue of Nobel lectures¹ (also available on the Internet).

3.02.2.1.1 Semenov's presentation

Semenov in his Nobel lecture 'Some problems relating to chain reactions and to the theory of combustion' described research of his groups at the Leningrad Physical-Technical Institute (under the leadership of academician Abram Joffe) and then in the Institute of Chemical Physics of the Russian Academy of Sciences in Moscow. Semenov stressed on the similarities of branched nuclear reactions discovered in the 1930s by physicists, where, like in chemical chain reactions, the size and density are the decisive factors in the transformation of 'safe' inert conditions to explosion.

Graphite retarders play a role identical to that of retarders in the chain polymerizations, described in Semenov's presentation as a special case of chain reactions (mostly radical polymerization). The history and the basic phenomena were summarized for the first time in Semenov's monograph *Chemical Kinetics of Chain Reactions*,² which mentions E.O. Rice³ and S.S. Medvedev to be among the first ones who studied chain polymerization and also mentions the work of M. Szwarc⁴ on the bond strength and formation of radicals – the slowest stage (initiation) of chain polymerizations. Semenov described the dissociation of allyl bromide (C₃H₅Br) and allyl chloride (C₃H₅Cl), splitting of halogen atoms and forming radicals. This is not far from the actual process of Matyjaszewski's atom-transfer radical polymerization (ATRP) (see Chapter **3.12**).

3.02.2.1.2 Hinshelwood's presentation

The Nobel lecture of Sir Cyril Hinshelwood has an entirely different character and structure. Semenov analyzes stepby-step developments and describes chemical details of the chain processes, placing an emphasis on contributions of more than a dozen Russian scientists who would become, in the course of time, world authorities. Sir Cyril's presentation has a rather philosophical character, although it is titled 'Chemical kinetics in the past few decades'. Particularly, some elementary reactions (such as $H_2 + O_2$) and their general significance were presented. He also described the importance of collaboration of scientists, saying: The study of the hydrogen-oxygen reaction was the first point at which the work in Oxford came into close contact with that of Semenov. Our indebtedness to his ideas was at once recognized and the early exchange opened friendly relations between Semenov and myself which have lasted ever since.

And then, he stressed the importance of chain reactions:

Some reactions, at that time, have been shown to be unimolecular without the participation of chains, but they are rare, and are a small minority of the examples presented by Nature.

Then Hinshelwood turned to an intriguing problem of correlation between values of *A* and E_a in kinetics of any elementary reactions, including those that are elementary reactions in chain reactions, and similar expressions for equilibria and related thermodynamic potentials. This similarity is also underlined by Kondratev.⁵ It would be out of the scope of this chapter to further follow the ideas developed by Hinshelwood, as he describes 'the fundamental harmonies of Nature'. There are more than 70 references in Semenov's Nobel lecture, but there are none in Hinshelwood's. Instead, he says at the end (citing Dante): "I found myself in a dark wood where the straightway was lost".

3.02.3 Bodenstein Observation of the First Chain Reactions

Both laureates, as well as anybody working in the chemical kinetics and particularly in chain reactions, have no doubts that the observation of Bodenstein opened the field, leading eventually to the chain polymerization.

At this point the original observation and ideas of the fundamental work of Bodenstein should be presented. The original studies of the apparently simple reaction

$$Cl_2 + H_2 \rightarrow 2HCl$$
 [1]

could have been described as a bimolecular, second-order reaction not opposed at the chosen conditions. However, the pertinent simple kinetic behavior that could have been observed was not detected. Instead, the kinetic equation found experimentally was

$$\frac{d[HCl]}{dt} = \frac{k_{obs(1)}I[Cl_2][H_2]}{[X](k_{obs(2)}[Cl_2] + k_{obs(3)}[H_2])}$$
[2]

where *I* is the intensity of light and [X] is, as was found later, the concentration of oxygen that was adventitiously present or purposely added to the system.

The quantum yield was found to be enormous: 10^{6} ! Thus, for one quantum of light there are up to 10^{6} elementary reactions. According to Bodenstein, a molecule of Cl₂ absorbing one quantum of light is converted into an excited state:

$$\operatorname{Cl}_2 + h\nu \to \operatorname{Cl}_2^*$$
 [3]

Such an activated molecule reacts with a molecule of H_2 and produces two excited molecules of HCl:

$$Cl_2^* + H_2 \rightarrow 2HCl^*$$
 [4]

These excited molecules of HCl^* should have an excess energy, equal to the sum of the excess energy of Cl_2^* and heat of reaction of $Cl_2^* + H_2$. Then, HCl^* should transfer the excess energy to the Cl_2 molecules:

$$\mathrm{HCl}^* + \mathrm{Cl}_2 \to \mathrm{Cl}_2^* \tag{5}$$

Then, this process is repeated until (according to Bodenstein) the excited molecules would lose their excess energy as a result of certain reactions.

3.02.4 Nernst's Mechanism of the $Cl_2 + H_2$ Reaction (Finally Accepted as the Correct One)

Walther Nernst (1864, Briesen, West Prussia (now Wabrzezno, Poland), to 1941, Berlin, Germany; Nobel Prize in 1920) proposed another scheme in which 'active species' (the present definition; cf. 'Glossary')⁶ are Cl[•] atoms (radicals).



Walther Hermann Nernst

It has been experimentally shown that, indeed, under the influence of light, Cl₂ breaks down, giving two atoms. Thus, Nernst's scheme starts with dissociation:

$$Cl_2 + hv \rightarrow 2Cl^{\bullet}$$
 [6]

It is Cl_2 and not H_2 that is first dissociated, since the bond energy of Cl_2 is much lower than the bond energy of H_2 .

3.02.5 Kinetic Scheme of the Fundamental Chain Reaction: Cl₂ + H₂

Thus, the kinetic scheme involving initiation, propagation, and chain termination is as follows: Initiation:

$$\operatorname{Cl}_2 + hv \xrightarrow{k_1} \operatorname{Cl}^{\bullet} + \operatorname{Cl}^{\bullet}$$
 [7]

Chain growth (propagation):

$$\operatorname{Cl}^{\bullet} + \operatorname{H}_{2} \xrightarrow{k_{3}} \operatorname{HCl} + \operatorname{H}^{\bullet}$$
 [8]

$$H^{\bullet} + Cl_2 \xrightarrow{k_2} HCl + Cl^{\bullet}$$
[9]

Termination:

$$\begin{array}{c} \operatorname{Cl}^{\bullet} + X \xrightarrow{k_{4}} \\ H^{\bullet} + X \xrightarrow{k_{5}} \end{array} \right\} \text{ inactive species} \qquad [10]$$

where X is the deactivation molecule.

The pertinent differential equations for this scheme are simply derived and are given below for the educational purposes and completeness of presentation:

$$\frac{d[Cl^{\bullet}]}{dt} = 2k_1 I[Cl_2] + k_2 [H^{\bullet}][Cl_2] - k_3 [Cl^{\bullet}][H_2] - k_4 [Cl^{\bullet}][X]$$
[11]

$$\frac{d[H^{\bullet}]}{dt} = -k_2[H^{\bullet}][Cl_2] + k_3[Cl^{\bullet}][H_2] - k_5[H^{\bullet}][X]$$
 [12]

$$\frac{d[Cl_2]}{dt} = -k_1 I[Cl_2] + k_2 [H^{\bullet}][Cl_2]$$
[13]

$$\frac{\mathrm{d}[\mathrm{H}_2]}{\mathrm{d}t} = -k_3[\mathrm{Cl}^\bullet][\mathrm{H}_2]$$
[14]

$$\frac{d[HCl]}{dt} = k_2[H^{\bullet}][Cl_2] + k_3[Cl^{\bullet}][H_2]$$
 [15]

where I is the intensity of light.

There are five differential equations, six unknown rate constants, and two unknown concentrations of the intermediates (H^{\bullet} and Cl^{\bullet}), which play the role of 'active species' in this system.

3.02.6 Stationary State, Bodenstein Approximation, and Final Solution

Bodenstein proposed a method of stationary states for the solution of such a multistep process. This is an approximate method based on the assumption that starting from a certain moment from the beginning of the reaction, the concentration of the intermediate species becomes invariable. Then the rate of the change of concentrations of these species (active centers) could be approximated by zero, and differential equations could be replaced by simpler algebraic expressions. (Analysis of reaching steady state in chain polymerization is given in Section 3.02.11.)

Thus, if $d[H^{\bullet}]/dt = 0$ and $d[Cl^{\bullet}]/dt = 0$, then

$$[Cl^{\bullet}] = \frac{2k_1k_2I[Cl_2]^2}{[X](k_2k_5[Cl_2] + k_3k_4[H_2])}$$
[16]

and

$$[\mathrm{H}^{\bullet}] = \frac{2k_1k_3I[\mathrm{Cl}_2][\mathrm{H}_2]}{[\mathrm{X}](k_2k_3[\mathrm{Cl}_2] + k_3k_4[\mathrm{H}_2])}$$
[17]

Substituting $[Cl^{\bullet}]$ and $[H^{\bullet}]$ into equations of the rate of the HCl formation, we obtain

$$\frac{d[HCl]}{dt} = \frac{4k_1k_2k_3I[Cl_2][H_2]}{[X](k_2k_3[Cl_2] + k_3k_4[H_2])}$$
[18]

Substituting the rate constants of elementary reactions by effective constants $4k_1k_2k_3 = k_{eff(1)}$, $k_2k_3 = k_{eff(2)}$, and $k_3k_4 = k_{eff(3)}$, we obtain

$$\frac{d[HCl]}{dt} = \frac{k_{eff(1)}I[Cl_2][H_2]}{[X](k_{eff(2)}[Cl_2] + k_{eff(3)}[H_2])}$$
[19]

[X] was later found to be the concentration of oxygen, adventitiously presented in the system as already mentioned. This is exactly the rate equation that has been found by Bodenstein and is given in eqn [2]. This agreement between the experimentally found and derived rate equations for the chain process was another convincing argument in favor of a chain process. Bodenstein used to say that he saw, while dreaming, a chain of his pocket watch when he was intensely thinking of a probable solution.

3.02.7 Definitions Pertinent to Chain Reactions

This section starts with the first part of definitions of the terms most often used in this chapter and defined by IUPAC either in the Gold Book (GB)⁷ or in 'Glossary of terms related to kinetics, thermodynamics, and mechanisms of polymerization' published in 2008.⁶

3.02.7.1 Chain Reaction

A 'chain reaction' is a reaction in which one or more reactive reaction intermediates (frequently radicals) continuously regenerate usually through a repeated cycle of elementary steps (the 'propagation step'). For example, in the chlorination of methane by a radical mechanism, Cl[•] continuously regenerates in the chain propagation steps:

$$Cl^{\bullet} + CH_4 \rightarrow HCl + H_3C^{\bullet}$$
 [20]

$$H_3C^{\bullet} + Cl_2 \rightarrow CH_3Cl + Cl^{\bullet}$$
^[21]

and so on.

3.02.7.2 Chain Carrier

A species, such as an atom or a radical, that is involved in a chain propagating reaction is known as a 'chain carrier'.

3.02.7.3 Chain Propagating Reaction

A 'chain propagating reaction', or more simply a 'propagating reaction', is an elementary step in a chain reaction in which one chain carrier is converted into another. The conversion can be a unimolecular reaction or a bimolecular reaction with a reactant molecule.

3.02.7.4 Chain Branching

When in a chain reaction there is a net increase in the number of chain carriers, it is called 'chain branching'. A simple example of a chain propagating reaction leading to chain branching is

$$O^{\bullet} + H_2 \to HO^{\bullet} + H^{\bullet}$$
 [22]

(Note: GB sometimes does not use dots, at least for atoms.)

3.02.7.5 Steady State (Stationary State)

(also called 'Bodenstein approximation')

(cit. from GB) In the kinetic analysis of a complex reaction involving an unstable intermediate in low concentration, the rate of change of each such intermediate is set equal to zero so that the rate equation can be expressed as a function of chemical species present in macroscopic amounts. For example, let us assume that X is an unstable intermediate in the reaction sequence:

$$A \xrightarrow[k_{-1}]{k_{-1}} X \qquad [23]$$

$$\mathbf{X} + \mathbf{C} \xrightarrow{k_2} \mathbf{D}$$
 [24

The conservation of mass requires that

$$[A] + [X] + [D] = [A]_0$$
[25]

which, since $[A]_0$ is constant, implies

$$-\frac{\mathbf{d}[\mathbf{X}]}{\mathbf{d}t} = \frac{\mathbf{d}[\mathbf{A}]}{\mathbf{d}t} + \frac{\mathbf{d}[\mathbf{D}]}{\mathbf{d}t}$$
[26]

If X is negligibly small, the rate of formation of D is essentially equal to the rate of disappearance of A and the rate of change of [X] can be set equal to zero. Applying the steady-state approximation (d[X]/dt=0) allows the elimination of [X] from the kinetic equations, whereupon the rate of reaction is expressed as

$$\frac{d[D]}{dt} = -\frac{d[A]}{dt} = \frac{k_1 k_2 [A][C]}{k_{-1} + k_2 [C]}$$
[27]

(end of citation from GB).

This is exactly the way Bodenstein derived his equation for the $H_2 + Cl_2$ reaction, assuming steady state in the chain reaction.

In the following sections that describe fundamentals of chain polymerization, some definitions (e.g., for chain carriers) differ from the more general ones given above.

3.02.8 Definitions Pertinent to Chain Polymerizations

3.02.8.1 Chain Carrier

A 'chain carrier' is an intermediate species bearing an active site for the propagation of a chain reaction.

Note: If an active site is on the terminal monomer unit of a chain, the chain carrier is represented by the symbol ...-m*.

3.02.8.2 Chain Polymerization

A 'chain polymerization' is a chain reaction in which the growth of a polymer chain proceeds exclusively by reaction(s) between monomer(s) and active site(s) on the polymer chain with the regeneration of the active site(s) at the end of each growth step.

- Note 1: A chain polymerization consists of chain initiation and chain propagation reactions and may also include chain deactivation or chain transfer reactions, or both.
- Note 2: The adjective 'chain' in chain polymerization denotes 'chain reaction' rather than a 'polymer chain'.
- Note 3: Propagation in chain polymerization usually occurs without the formation of small molecules. However, cases exist where a low-molar-mass by-product is formed, as in the polymerization of oxazolidine-2,5-diones derived from amino acids (commonly termed *N*-carboxy α -amino acid anhydrides (NCAs)). When a low-molar-mass by-product

is formed, the additional adjective 'condensative' is recommended to form the term 'condensative chain polymerization'.

Note 4: The growth steps are expressed by

$$P_x + M \rightarrow P_{x+1}(+L) \quad x \in \{1, 2, \dots, \infty\}$$

where P_x denotes the growing chain of degree of polymerization *x*, M a monomer, and L a low-molar-mass by-product formed in the case of condensative chain polymerization.

- Note 5: The term 'chain polymerization' may be qualified further, if necessary, to specify the kind of chemical reactions involved in the growth step, for example, ring-opening chain polymerization and cationic chain polymerization.
- Note 6: There exist, exceptionally, some polymerizations that proceed via chain reactions that, according to the definition, are not chain polymerizations. For example, the polymerization $HS-X-SH + H_2C = CH-Y-CH = CH_2 \rightarrow (-S-X-S-CH_2-CH_2-Y-CH_2-CH_2-)_n$ proceeds via a radical chain reaction with intermolecular transfer of the radical center.

The growth step, however, involves reactions between molecules of all degrees of polymerization and, hence, the polymerization is classified as a polyaddition. If required, the classification can be made more precise and the polymerization described as a chain reaction.

3.02.8.3 Chain Propagation (in Chain Polymerization)

'Chain propagation' is a chemical reaction between a chain carrier and a monomer that results in the growth of a polymer chain and the regeneration of at least one chain carrier.

Note: The recommended symbol for the rate constant for chain propagation in a homopolymerization is $k_{\rm p}$.

3.02.9 Two Kinds of Steady States in Chain Polymerizations

In the first kind of steady state in chain polymerization, the concentration of active species (active centers) is approximately constant; that is, they are formed fast in comparison with the rate of chain propagation and do not disappear (are not 'killed') at least in the time when the monomer is mostly consumed.

This kind of terminationless chain reaction, discovered by Szwarc (*vide infra*), exists only in chain polymerizations. For instance, Kondratev⁵ stressed that termination is a genuine step of chain reactions.



Michael Szwarc

The second kind of steady state in chain polymerization results from a balance of the rate of formation of active centers and their termination ('killing') and is studied in Section 3.02.11.

3.02.10 Discovery of Living Polymerization by Michael Szwarc

When initiation is fast and there is no termination, polymerization is called 'living polymerization' and also 'controlled polymerization'. The term 'living polymerization' was coined by Michael Szwarc (1909, Bedzin, Poland, to 2000, San Diego, CA, USA) for the process he discovered in 1956 (together with Ralph Milkovich and Moshe Levy). Thus, the discovery of the chain processes in which termination was absent has been revolutionary for the entire field of chemistry and not merely for the polymer field.^{8–10}

There was a vivid discussion on what kind of polymerization should (or could?) be called 'living'. It has been ignored, however, that the problem of naming the different phenomena had already been solved a long time ago by Humpty Dumpty in his discussion with Alice in *Alice in Wonderland* by Louis Caroll:

'When I use a word,' Humpty Dumpty said, in rather a scornful tone, 'it means just what I choose it to mean — neither more nor less.' 'The question is,' said Alice, 'whether you **can** make words mean so many different things.'

'The question is,' said Humpty Dumpty, 'which is to be master — that's all.'

Thus, the IUPAC Polymer Division has decided on the following definition, which is given in 'Glossary'. 6

3.02.11 Living Polymerization

3.02.11.1 Definition of Living Polymerization

'Living polymerization' is the chain polymerization in which chain termination and irreversible chain transfer are absent.

- Note 1: In many cases, the rate of chain initiation is fast compared with the rate of chain propagation, so that the number of kinetic chain carriers is essentially constant throughout the reaction.
- Note 2: In a living polymerization, the reversible (temporary) deactivation of active centers can take place (see Section 3.02.11.9.1).
- Note 3: In a living polymerization, all the macromolecules formed possess the potential for further growth.
- Note 4: The use of the adjectives 'pseudo-living', 'quasi-living', and 'immortal' is discouraged.

Matyjaszewski and Mueller¹¹ prepared a very similar definition for the Nomenclature Committee of the ACS Division of Polymer Chemistry, which is independent of the IUPAC Polymer Division:

'Living polymerization is a chain polymerization without irreversible chain breaking reactions, i.e. transfer and termination'.

The included notes are in agreement with the above given IUPAC definition.

Throughout this chapter these strict definitions will be used, with some consequences in further discussion of radical and cationic polymerizations. The authors also stressed:

The two terms living and controlled have been considerably confused (not to say abused) by many authors due to the lack of agreed definitions.

If there is no termination, then there should be a linear plot of $\ln([M]_0/[M])$ versus time since propagation is a bimolecular reaction with an invariable concentration of active centers:

$$-\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} = k_{\mathrm{p}}[\mathrm{P}_{\mathrm{i}}^{*}][\mathrm{M}]$$
^[28]

Thus,

$$\frac{\ln[\mathsf{M}]_0}{[\mathsf{M}]} = k_{\mathrm{p}}[\mathsf{P}_{\mathrm{i}}^*]t \qquad [29]$$

If there is no transfer, then the degree of polymerization (P_n) should be a linear function of conversion $\alpha = ([M]_0 - [M])/[M]_0$:

$$P_{\rm n} = \frac{[{\rm M}]_0 - [{\rm M}]}{[{\rm P}_{\rm i}^*]}$$
[30]

where $[P_i^*] = [I]_0$.¹²

Penczek *et al.*¹³ proposed to encompass the two requirements for the livingness into one equation:

$$\ln\left(1 - \frac{P_{n}[I]_{0}}{[M]_{0}}\right) = k_{p}[I]_{0}t$$
[31]

In their monograph on anionic polymerization,¹² Hsieh and Quirk have made the following remark concerning this equation:

"The uniqueness of this approach is that Eqn. 4.22 [Eqn. 30 in this chapter] is a diagnostic test for chain transfer, while Eq. 4.23 [Eqn. 28 in this chapter] is a diagnostic test for chain termination; thus, their combination provides a useful criterion for living polymerizations. It is only necessary to determine the dependence of DP_n on time to apply this criterion. If the plot is linear, both chain transfer and chain termination are absent."

On the other hand the actual kinetic (rate) measurements are not necessary. It has to be remembered, that for this treatment initiation has to be faster than propagation. Polymerization may be living, even if initiation is slower and providing throughout polymerization new generations of the living macromolecules.

3.02.11.2 Reversibility in Chain Polymerizations

In chain reactions described above, the propagation step is considered to be practically irreversible. In polymerizations, when long enough chains (polymerization degrees) are involved, monomers are mostly consumed in the propagation step. Propagation, like the majority of chemical reactions, is reversible, and for polymerization to be able to proceed the rate of propagation should be faster than the rate of depropagation.

$$\cdots - (m) \cdot_n m^* + M \underset{k_d}{\overset{k_p}{=}} \cdots - (m) \cdot_{n+1} m^*$$
[32]

and thus $\Delta_{ss}G = \Delta_{ss}H - \Delta_{ss}S^{\circ}RT \ln[M]$, where subscript s denotes 'solution' and ss denotes 'from monomer in solution to polymer in solution'. When equilibrium is reached, $\Delta_{ss}G = 0$.

At a certain temperature, called the ceiling temperature T_c (for polymerization with $\Delta_{ss}H < 0$ and $\Delta_{ss}S^\circ < 0$), there is practically no polymer formed at equilibrium and thus $[M]_e = [M]_c \cong [M]_0$.

The knowledge of the thermodynamics of polymerization is much more important for cyclic compounds than that for vinyl compounds. A detailed analysis of the relationships between thermodynamic potentials and monomer structures has been given by Penczek and Kaluzynski in Chapter **4.02**. It has particularly been stressed that a reasonable way to compare the thermodynamic ability to homopolymerize is to compare ceiling temperatures. T_c could be measured either for bulk conditions (T_c (bulk)) or at 1 mol l⁻¹ (in solution) (T_c (c°)).

 T_c (bulk) gives the highest temperature at the most privileged conditions, where polymerization would still give a polymer. In many instances, however, T_c (bulk) is higher than the temperature at which a polymer would decompose in degradation processes that could only partially involve depolymerization. Moreover, $T_c(c^o)$ (thus, in solution) may depend on the solvent used, and thus the solvent should be indicated. A few values of T_c are given in **Table 1**, which have been taken from the comprehensive sources.

One of the fundamental goals of chemistry in general (and polymerization in our case) is to relate the extent and the rate of a reaction to the structure of reactants. The former depends on the thermodynamics of polymerization and the latter on kinetics. It follows from previous sections that access to the rates is possible in chain processes when the Bodenstein approximation of the steady state is applied.

3.02.11.3 Kinetics of Fast Initiation–Propagation Systems

In this section, systems with fast initiation are considered. Slow initiation–fast propagation systems are studied in the following sections.

3.02.11.3.1 Anionic polymerizations of vinyl monomers: electron transfer initiation

Among the clear-cut systems conforming to the living (steady state of the first kind) systems is the anionic polymerization

Table 1	Ceiling temperatures	$T_{\rm c}$ ($T_{\rm c}$	(<i>c</i> °)) and	$T_{\rm c}({\rm bulk}))$	for some
unsaturated	and cyclic monomers				

	Т _с (°С)		
Monomer	Bulk (lc)	Solution (ss), (ls)	
Ethylene	367		
$(CH_2=CH_2)$ Styrene $(CH_2=CH_2-C_2H_2)$	310	150 (C ₆ H ₆)	
α -Methylstyrene	61	0 (THF)	
$(CH_2=C(CH_3)C_6H_5)$ Methyl methacrylate $(CH_2=C(CH_3)C(0)OCH_3)$	220	156 (1,2-C ₆ H ₄ Cl ₂)	
Tetrahydrofuran	80	23 (C ₆ H ₆)	
1,3-Dioxolane (00)	91	1 (CH ₂ Cl ₂)	
ε -Caprolactam ($C=O$) NH		223 (ls)	

Ic, liquid \rightarrow condensed; ss, solution \rightarrow solution; Is, liquid \rightarrow solution. $T_c(c^{o})$ is usually determined from $\Delta_{ss}S^{o}$ and $\Delta_{ss}H$.

Taken in part from Tables 7 and 8 of Elias, H. G. *Macromolecules, Vol. 1: Chemical Structures and Syntheses*, Wiley-VCH: Weinheim, 2005, p. 213.¹⁴

of styrene in 1,4-dioxane (DIOX) solution. Szwarc in his monograph¹⁰ indicates that the first paper for such a system was published by Gee and co-workers,¹⁵ who determined the rate constant of propagation in DIOX, which initiated with a known amount of naphthalene sodium and the propagation was followed in a dilatometer. Since the conversion of naphthalene sodium into the sodium salt of living polystyrene is practically instantaneous and quantitative, the concentration of living polystyrylsodium was given by the known concentration of the initiator (Scheme 1).



Scheme 1



Scheme 2

It has been later shown that the large majority of chains grow on both ends. The studies of Gee (for Na⁺) were extended by Szwarc for other salts. In these studies, the decrease in the concentration of styrene and the concentration of living polymers was followed spectrophotometrically. Pictures of apparatuses are given in Szwarc's monograph and are reproduced many times. Transport of components proceeded in high vacuum, and measurements were performed in the sealed apparatus. A fundamental result of these studies, at least for nonpolar monomers, is that the rate constants of anionic propagation of styrene in DIOX strongly depend on the nature of cation. According to Szwarc,¹⁰ an ion pair becomes partly separated in the transition state of propagation (Scheme 2).

Thus, there is a partial dissociation, requiring additional energy (over a simple interaction). In poor solvating media (such as DIOX), the partial dissociation is not facilitated by solvation. Then the stronger the coulombic interaction (with 'smaller' cations it is stronger), the lower the reactivity as more energy is needed to reach the transition state.

When counterions are large enough, no partial dissociation is needed in the transition state and the new bond may be formed without preliminary displacement of the cation (Scheme 3).

3.02.11.4 Living Polymerization: Two or More Interconversions of Active Species

In **Table 2**, the data for tetrahydrofuran (THF) solvent based on the results of **Figure 1** indicate the reverse order of reactivities (in comparison with those of DIOX). The reasons, already mentioned above and elaborated in the next section, are fundamental for ionic polymerizations, which appear practically in any textbook on polymer chemistry.



Scheme 3

Table 2 Rate constants (k_p^{\pm}) of styrene propagation on polystyryl anion (–), metal cation (+), and contact ion pair for various cations

	k± (moľ	$k^{\pm} (mol^{-1} I s^{-1})$				
Solvent/cation	Li ⁺	Na⁺	K⁺	Rb⁺	Cs^{+}	
1,4-Dioxane Tetrahydrofuran	0.9 ~160	3.4 8	20 100 (?)	21.5 50	24.6 25	

The electron transfer and other initiation reactions have also been described in detail in the first edition of *Comprehensive Polymer Science* by Fontanille.¹⁶

Measurements of the conductivity of ...-St and Cat⁺ (symbols are self-explanatory) in DIOX and THF solutions have shown that only in the latter are solvent ions (sometimes called 'free ions') present. No conductivity was noticed in DIOX (ion pairs themselves are electrically neutral). The dissociation is due to the exothermicity of solvation; otherwise, the coulombic forces would keep the ions in a pair together, with no reason to go apart. Thus, it became a problem to determine rate constant on ions (k_p^-). Since there are (at least) two kinds of species of different reactivities, the pertinent final kinetic equation (called also 'Szwarc plot') reads as follows:

$$-\frac{d[M]}{[I]_0[M]}dt = k_p^{\pm} + (k_p^{-} - k_p^{\pm})(K_D)^{1/2}[I]^{-1/2}$$
[33]

where $K_{\rm D}$ is the dissociation constant of ion pairs dissociated into ions. (Derivation of equ. 33 is given in the majority of the text books.)

By plotting the left-hand side of eqn [33] as a function of $[I]_0^{-1/2}$, both k_p^{\pm} and k_p^{-} could be determined. This classical plot is copied from the Szwarc's monograph (slightly modified and colors added).

The net result is that at the conditions of the measurements, k_p^{\pm} decreased in the order Li⁺>Na⁺>K⁺>Rb⁺>Cs⁺ (see **Table 2**). Thus, the orders of reactivities differ for DIOX and THF solutions. DIOX does not solvate cations, whereas THF solvates cations. Thus, the smaller the bare cation, the larger they become when solvated.

Actually Cs⁺ is not solvated by THF and therefore its k_p^+ is almost the same in DIOX and THF solvents.^{17,18}

The next fundamental information came from the dependence of k_p^{\pm} on 1/T (the van't Hoff plot). It was observed that only for DIOX and hexamethylphosphortriamide (HMPA) solvents straight lines were observed, as required for elementary reactions. However, the apparent rate constants $(k_p^{app} = d \ln[M]/[I]_0 dt)$ differed by almost 10^4 times. In THF and some other similar solvents, at higher temperatures k_p^{app} was almost equal to k_p^{app} measured in DIOX and at sufficiently low temperatures it was equal to that measured in HMPA.

Hogen-Esch and Smid in studies of UV absorption spectra of fluorenyl sodium in THF solvent observed two absorption peaks of intensities changing with temperature (Scheme 4). After establishing that 'free' ions are not responsible for these changes, they concluded that there are two kinds of ion pairs: contact and solvent separated. This classical dependence that was the first spectroscopic evidence of two kinds of ion pairs is shown in Figure 2.

Thus, in the studied kinetics, ion pairs in HMPA are separated by the solvent and, therefore, are much more reactive than the contact ion pairs in DIOX. In other solvents, decreasing the temperature increased the proportion of solvent-separated ion



Figure 1 Linear dependence of the apparent bimolecular rate constant (k_p^{app}) of living polystyrene propagation on the reciprocal of the square root of living polymer concentration in THF as solvent at 25 °C.^{17,18} Different lines refer to different counterions: Li⁺, Na⁺, K⁺, Rb⁺, and Cs⁺. LE, living ends.



Scheme 4

pairs. Therefore, in a certain temperature range, a negative temperature coefficient was observed – the apparent rate constant increased with decreasing temperature. Thus, the increase in the proportion of the much more reactive solvent-separated ion pairs contributed more to the rate increase than to the decrease in the rates of the two involved elementary reactions.

In anionic polymerization of polar monomers, the steady-state (living-controlled) polymerization was also achieved. The dependence on the cation structure is due to the interaction of the polymer units with cations, such as in anionic polymerization of methyl methacrylate (Scheme 5).

3.02.11.5 Living Olefin Polymerization

In the field of olefin polymerization, the major effort has been concentrated on choosing the most efficient catalysts – 'high mileage' catalysts as well as on choosing the systems providing highly efficient stereoregulation. Nevertheless, living



Figure 2 Absorption spectrum of fluorenyl sodium in THF at different temperatures: 25 °C (blue), -30 °C (green), and -50 °C (red).¹⁹ o.d., optical density.


polymerization in this area has been described first by Doi *et al.* soon after the discovery of anionic living polymerization.²⁰ Kinetically, these studies have not provided fundamental results, although they are of extreme importance for understanding the olefin polymerization.

3.02.11.5.1 Living cationic polymerization: the case of trimethylstyrene

As reported in 2004 by Faust and co-workers, 21,22 the cationic polymerization of 2,4,6-trimethylstyrene in CH₂Cl₂ solvent at sufficiently low temperatures (e.g., below -20 °C) and in the presence of GaCl₄ anion is the first living cationic vinyl polymerization (CVP) free of side reactions (Scheme 6).

The system with $GaCl_3$ gives full ionization (¹H NMR) of the initiator and then growing chains, whereas with BCl_3 (discussed in Section 3.02.11.9.1) a partial ionization occurs, although the polymerization also behaves as a living polymerization but with reversible deactivation.

3.02.11.6 Living Polymerization of Cyclic Compounds

Anionic polymerization of cyclic compounds may also belong to the first category of the steady state, namely, with invariant concentration of the active species and sufficiently high rate of initiation. The polymerization of ethylene oxide has already been known for a long time, and similar approaches (and kinetic plots) were used, such as in vinyl anionic polymerization discussed above. The polymerization of ethylene oxide has already been described in the first edition.²³ The only novel phenomenon is the increase in the rate with conversion because of the solvation of the cation (e.g., Na⁺) by the emerging poly(ethylene oxide) chains (Scheme 7).

The steady value of the rate constants of propagation was observed after four to six repeating units. Also in this polymerization, ions are found to be more reactive than ion pairs.

In Lodz, β -propiolactone was initiated with crowned sodium acetate,²⁴ and in Paris, with the same initiator but with the cryptated cation.²⁵ Both systems behave nicely as living ones and were the first instances (published at the same time) of living polymerization of cyclic esters (lactones) where two kinds of active species could be detected.

3.02.11.7 Steady-State-Living Chain Polymerization of Cyclic Compounds: Identical Reactivities of Ions and Ion Pairs

In the reactivities described above, ions were found to be more reactive than ion pairs. In the cationic polymerization of cyclic monomers, however, in all the known instances ions and ion pairs do not differ in reactivities.

Indeed, in the ring-opening polymerization of THF, which is a living polymerization, it was observed that the rate constants of propagation on ion pairs do not depend on the anion structures and reactivities of ions are the same as of ion pairs. The corresponding plot of the equation

$$\frac{k_p^{\rm app}}{\alpha} = (k_p^+ - k_p^\pm) + \frac{k_p^\pm}{\alpha}$$
[34]

(where α is the degree of dissociation, $\alpha = \frac{|\text{ions}|}{|\text{ions}+|\text{ion pairs}|}$) is shown in **Figure 3**.²⁶ Thus, the intercept, equal to $k_p^+ - k_p^\pm = 0$, indicates that both ions and ion pairs have identical reactivities. This finding seems to be a fundamental finding for all the cationic



Scheme 6



Figure 3 Dependence of the ratio $k_p^{app}\alpha^{-1}$ on α^{-1} (where α is the degree of dissociation) in the polymerization of THF at 25 °C (blue) and at 10 °C (red). Solvent: CH₂Cl₂.²⁶

polymerizations of heterocyclics studied so far. The major difference with anionic polymerization stems from several factors:

- 1. In the anionic polymerization, the charge in both ring-opening and vinyl polymerizations is much more localized than in cationic polymerization. Some anions, such as SbF₆, BF₄, and even ...-COO⁻, are much 'larger' than cations, such as Li⁺, Na⁺, and Cs⁺ (Table 3).
- 2. In the polymerization of THF and perhaps other heterocyclic monomers, there is a particular stereochemical aspect of the monomer approach. The actual propagation step looks like having an anion under the steep roof on which the monomer is sliding. Thus, during monomer addition, the anion may simply change its position not being partially dissociated from the cation in the way from the ground state to the transition state, as described in Section 3.02.11.2 (Scheme 8).

3.02.11.8 Steady-State Living Polymerization with $k_n^c > \text{ or } < k_n^{\pm}$: Inversion of Reactivities

In the so far discussed polymerizations proceeding in the steady state of the first kind, which is in fact equivalent to the

Table 3	Dependence of the counterion size on their structures:
comparison	of the size of cations and anions







Scheme 9

living polymerization with a high rate of initiation (thus 'controlled'), ions were more reactive than ion pairs ($k_p^- > k_p^{\pm}$), and only in cationic ring-opening polymerization, ions and ion pairs have identical reactivities.

However, there were systems where at higher temperatures $k_{\rm p}^- > k_{\rm p}^\pm$ and at low temperatures $k_{\rm p}^- < k_{\rm p}^\pm$. This was observed in the polymerization of β -propiolactone (β -PL) in dimethylformamide (DMF) with crowned potassium acetate (Scheme 9).²⁷

In kinetics of this living polymerization, k_p^- and k_p^{\pm} were determined by using a Szwarc plot for simultaneous propagation on ions and ion pairs (illustrated in **Figures 1** and **2**). The same method was used in studies of anionic polymerization of other cyclic esters. Results are shown in **Figure 4**.

As follows from Figure 4(b), ions are more reactive at higher temperatures, although at low enough temperatures the reversal of reactivities is observed.

 β -PL is the most polar component of the system. The rate constants of propagation on ion pairs, $k_{\rm p}^{\pm}$, are almost the same at lower and higher $[\beta-PL]_{0}$, whereas the rate constants of propagation on ions, k_{p}^{-} , depend very much on $[\beta-PL]_0$. Indeed, $\Delta \neq H_{(-)}$ is equal to 88 ± 9 and $114 \pm 9 \text{ kJ mol}^{-1}$ at lower and higher monomer concentrations, respectively. What is most striking, however, is the appearance of the isokinetic point, that is, a certain temperature at which $k_{\rm p}^{\pm} = k_{\rm p}^{-}$. Above that temperature $k_p^- > k_p^{\pm}$, and below it, $k_p^- < k_p^{\pm}$. A similar phenomenon was observed in the polymerization of ε-caprolactone.²⁸ These facts were explained by a much stronger solvation of ions than of ion pairs with the components of the system, mostly monomer itself. The solvation is highly exothermic; therefore, solvated ions are relatively much stronger at lower temperatures than are ion pairs. It follows that ions decrease 'faster' with decreasing temperature than ion pairs do. Ion pairs are crowned, and solvent molecules are shielded from the direct approach to cations. Eventually, the degree of solvation of ions is so high that the energy of desolvation becomes a major component of the activation energy. Ion pairs have three times lower activation enthalpy, because they are much less prone to solvation and, inevitably, at a certain low temperature, become more reactive than ions; thus, $k_{\rm p}^{\pm} > k_{\rm p}^{-}$. This phenomenon observed for the first time in ionic polymerization was discussed in more detail by Szwarc in his monograph²⁹ and may be significant in polymer synthesis when a polar solvent has to be used and ions are responsible for some side reactions.

In the previous sections, the living chain polymerization process involved either one kind of active species or more than one in a fast interchange and all the active species have been reactive. Both species either have identical activity or one of the two is more or less active than the other one.



Figure 4 Dependence of $\ln k_p^-$ (in blue) and $\ln k_p^{\pm}$ (in red) on T^{-1} : (a) $[\beta - PL]_0 = 5 \times 10^{-1} \text{ mol } I^{-1}$; (b) $[\beta - PL]_0 = 1 \text{ mol } I^{-1}$. Both in DMF solvent.²⁷

3.02.11.9 Steady-State Living Polymerization with Dormant Species

In this section, systems are described that preserve livingness even though the species that are formed in interconversion from active ones are no more active, but dormant. These systems still differ from the ones treated later when termination takes place to some extent. The term 'dormant' appeared for the first time in Szwarc's monograph.¹⁰ Dormant species are formed in reversible chain deactivation; they are defined by IUPAC.⁶

3.02.11.9.1 Reversible chain deactivation

'Reversible chain deactivation' is the deactivation of a chain carrier in a chain polymerization, reversibly converting an active center into an inactive one and then, within the average lifetime of a growing macromolecule, regenerating an active center on the same original carrier.

- Note 1: The temporarily deactivated species created in this process are often described as dormant.
- Note 2: Reversible deactivation involves reversible combination or reversible chain transfer.

This definition was repeated in a more recent IUPAC document.³⁰ The most obvious system belonging to the present category is the polymerization of ethylene oxide (oxirane) in the presence of alcohols (Scheme 10).

However, more kinetic data are available for the cationic polymerization of THF and then of cyclic esters (lactones). These systems were reviewed in 1995 in a paper titled 'Polymerizations with contributions of covalent and ionic species'.³¹ More recently, the cationic polymerization of styrene with the BCl_4^- counterion (discussed below) became a classical example of reversibility in propagation in living CVP.²⁴

In THF polymerization, an equilibrium between ions and covalent species was detected by using NMR. Both are able to add monomers, but the addition to covalent species is so slow that this polymerization can be treated in this section. This could be at the borderline with similar processes involving some termination (e.g., controlled radical polymerization (CRP)).

Schematically this system reads as shown in Scheme 11.

It has particularly been shown that the proportions of ions and covalent species (esters) depend (as could be expected) on the solvent properties. Thus, at 25 °C, in CH_3NO_2 there are more than 90% of ions whereas in CCl_4 less than 10%. In CH_2Cl_2 solvent, there is an intermediate situation. The corresponding ¹H NMR spectra have been published several times; they also appear in textbooks and are given in Reference 32.



Scheme 11

$$..-CH_2CH_2O \xrightarrow{\ominus} + ROH \longrightarrow ...-CH_2CH_2OH + RO^{\ominus}$$

(Cation omitted)

Moreover, since this interexchange is very slow, the kinetics of interconversion of active \neq dormant could be directly observed by using ¹H NMR. The method of 'temperature jump' was applied: from an equilibrium state (cf. **Scheme 12**) at one temperature, kinetics of attaining an equilibrium at another temperature could be measured since the time needed for changing temperature in the NMR tube was much shorter than the time for reaching a new equilibrium (see **Scheme 12**, where k_{td} is the rate constant of temporary deactivation and k_{io} is the rate constant of back activation (ionization)). The actual set of the ¹H NMR spectra at various stages of interconversion is shown in **Figure 5**.³³ At lower temperatures the proportion of ions is higher due to enhanced solvation.

Thus, the complete scheme of THF polymerization in the presence of anions capable of forming covalent bonds (ClO₄⁻, CF₃SO₃⁻, FSO₃⁻) involved (when dissociation of ion pairs can be neglected) the elementary reactions depicted in **Scheme 13** (only the attack on the endocyclic carbon atom is shown, as it is much faster than the attack on the exocyclic carbon; besides $R_{io} >> R_{pv}^{c}$ where *R* stands for 'rate'). Actually, the proportions of ions and esters do not change with monomer conversion, indicating that indeed $R_{io} \gg R_p^{ci}$. The 'covalent propagation' (k_p^c) does not take place, since this would involve pericyclic four-center one-step addition, which is forbid-den according to the orbital symmetry rules.

Thus, the life record does not involve 'covalent propagation' and can be visualized as segments of the line (lengths of these segments are proportional to the time spent in a given state and not to the length of the macromolecule).

Average lifetimes (see the Appendix) of growing ion pairs and macroesters (τ^{ion} and τ^{cov} , respectively), average numbers of monomer molecules added during the lifetime of an ion pair and macroester (χ_p^{ion} and χ_p^{cov} , respectively), and the average number of polymer repeating units depolymerized during the lifetime of a given species ([THF] = 8 mol l⁻¹, 25 °C; time in seconds).³² This kind of presentation, first shown in 1976, became more popular in the kinetics of other polymerizations, discussed in this chapter as well as in chapters of Volume 3 (**Table 4**).



Esters 4.6 4.9 lons С 4.6 4'9 b <u>4</u>'q 4.6 а 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 5.0 δ (ppm)

Figure 5 ¹H NMR (300 MHz) spectra of the region of living ends in the polymerization of THF with $CF_3SO_2O^-$ anion at -18 °C after disrupting an equilibrium established at +18 °C by a sudden change in temperature (time in 10^2 s): (a) 1.5, (b) 5.7, (c) 13.2, (d) 22.8. Monomer: [THF]₀ = 8.0 mol I⁻¹; initiator: [CF_3SO_3CH_3]₀ = 8.0 × 10⁻² mol I⁻¹ in CC1₄ solvent.³³



Scheme 13

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Table 4	Polymerization of T	THF with C	$CF_3SO_3^-$	anion:	ionic and
covalent spe	ecies				

Solvent	τ ^{ion} (S)	τ^{COV} (S)	χ_p^{ion}	χ ^{ion} χd	χ ^{cov a}
CCI ₄	8.1	124	1.2	0.9	0.03
CH ₃ NO ₂	322	8.0	52.8	41.8	0.02

 ${}^{a}\chi_{\rm p}^{\rm cov}$ does not mean covalent \rightarrow covalent, but covalent \rightarrow ion.

THF/CCI ₄		
	$\tau^{\text{ion}} = 8.1 \text{ s}$ $\chi_{\text{p}}^{\text{ion}} = 1.2$ $\chi_{\text{d}}^{\text{ion}} = 0.9$	$\begin{aligned} \tau^{cov} &= 124 \text{ s} \\ \chi^{cov}_p &= 0.03 \end{aligned}$
THF/CH ₃ NO ₂		
	$\tau^{ion} = 322 \text{ s}$ $\chi_p^{ion} = 52.8$ $\chi_d^{ion} = 41.8$	$\begin{aligned} \tau^{cov} &= 8.0 \text{ s} \\ \chi^{cov}_p &= 0.02 \end{aligned}$

Scheme 14

Schematic life records of growing chains could thus be shown as in **Scheme 14** (no change of monomer concentrations was assumed).

The lengths of segments corresponding to the time periods of being in a given state – ionic or covalent – are not identical not only for different chains but for the same chain as well. The distribution of lengths is approximately the most probable one.

There are several other systems in which formation of dormant species takes place in the otherwise living polymerization: for instance, when active species become aggregated and the aggregated form is inactive. The extent of aggregation, *m*, can be determined from the dependence of $\log R_p$ on $\log P_n^*|_{total}$ (=[I]₀) (where the symbols have their traditional meanings).³⁴ In these systems,

$$\begin{array}{c} P_{n}^{*} + M \xrightarrow{K_{p}} P_{n+1}^{*} \\ m (P_{n}^{*}) \xrightarrow{K_{da}} (P_{n}^{*})_{m} \\ (P_{n}^{*})_{n} + M \xrightarrow{} \end{array} \right\} \quad [I]_{0} = [P_{n}^{*}] + m[(P_{n}^{*})_{m}] \quad [35]$$

If $m[(P_n^*)_m] >> P_n^*]$, then $m[(P_n^*)_m]] \approx [I]_0$.

When

$$R_{\rm p} = \frac{\ln([M]_0/[M])}{t(k_{\rm p}[{\rm P}^*])}$$
[36]

we have

$$\log R_{\rm p} = \log \left\{ k_{\rm p} \left(\frac{K_{\rm da}}{m} \right)^{1/m} \right\} + \frac{1}{m} \log \left[{\rm I} \right]_0$$
 [37]

Thus, from $\log R_p$ as a function of $[I]_0$, the aggregation degree *m* could be determined.



Figure 6 External orders in active centers: dependencies of log R_p on log $([P_n]_{tot})$. Polymerization of 2-methoxystyrene with Li⁺ ion, toluene as a solvent, at 20 °C. (experimental data taken from Geerts, J.; van Beylen, M.; Smets, G. *J. Polym. Sci., Part A-1* **1969**, *7*, 2859;³⁵ green). Anionic polymerization of methyl methacrylate with Li⁺ cation, THF as a solvent, at -65 °C (experimental data taken from Kunkel, D.; Mueller, A. H. E.; Janata, M.; Lochman, L. *Makromol. Chem., Macromol. Symp.* **1992**, *60*, 315;³⁶ purple). Polymerization of oxirane on $-CH_2CH_2O^-$, Cs⁺ ion pairs, THF as a solvent, at 70 °C (experimental data taken from Kazanskii, K. S.; Solovyanov, A. A.; Entelis, S. G. *Eur. Polym. J.* **1971**, *7*, 1421;³⁷ blue). Polymerization of D₃ on $-Si(CH_3)_2O^-$, Li⁺ ion pairs, THF as a solvent, at 22 °C (experimental data taken from Wilczek, L.; Kennedy, J. P. *Polym. J.* **1987**, *19*, 531;³⁸ red)

This dependence for a few systems is given in **Figure 6**, which is taken from Reference 34 and references cited there, i.e., Ref. 35–38. As follows from the data in **Figure 6**, the slopes change; at lower concentrations, the slopes approach unity, indicating that at a sufficiently low concentration, aggregation would vanish. Equation [38] allows the determination of $k_{\rm p}$ and $K_{\rm da}$.

$$R_{\rm p}^{1-m} = -m/K_{\rm da}k_{\rm p}^{m-1} + k_{\rm p}[{\rm I}]_0 R_{\rm p}^{-m}$$
[38]

When experimental data are plotted according to the equation $R_p^{1-m} = f([I]_0 R_p^{-m})$, k_p and K_{da} could be determined.³⁹ Equation [38] was also used to determine k_p and K_{da} in the polymerization of ε -caprolactone, where K_{da} could be verified from the ²⁷Al NMR data, giving concentrations of P_n^* and $(P_n^*)_m$ (Scheme 15).

According to kinetic and ²⁷Al NMR measurements for $[I]_0 \approx 10^{-2} \text{ mol } I^{-1}$, $[M] = 2.0 \text{ mol } I^{-1}$ and at 25 °C $[P_n^*]/[I]_0 \approx 0.1$. Both methods gave similar results. This method gave a much

higher proportion of active centers than did a typical CRP.

Another living polymerization with the formation of dormant species has been described in 2005 – cationic polymerization of 2,4,6-trimethylstyrene – the first (and perhaps the only one so far) living CVP with reversible deactivation in the propagation step.

This polymerization was initiated at low temperatures (from -20 to -70 °C) with 2-(1-chloroethyl)-1,3,5-trimethylbenzene cationized reversibly with BCl₃ in CH₂Cl₂ solvent (Scheme 16).

The usual tests for livingness have shown stability of the initiating cations as well as of the cationic growing centers (Scheme 17).





Active

The original kinetic data have shown perfect linearity of the $-\ln([M]_0/[M])$ plot versus time as well as the linear plot of M_n versus time up to almost $M_n = 20\,000$. These data have been recalculated according to eqn [31], encompassing both dependencies (cf. Figure 7).

As follows from the linearity of the plot, this system conforms to living polymerization. However, the observed rate is increasing with decreasing temperature. This result stems from an increased extent of ionization of covalent (nonreactive) species with decreasing temperature. This process contributes more to the increased polymerization rate than to the decrease in the rate of dissociation of ion pairs with decreasing temperature. There are several similar phenomena observed in ionic reactions. The increase in the rate with decreasing temperature was observed in the conversion of contact ion pairs into solvent-separated ion pairs (much more reactive); this is discussed in Section 3.02.11.4.

A successful finding of this living system is due to blocking in the monomer the labile positions 2, 4, and 6 with the methyl groups, eliminating H⁺ transfer. UV spectroscopy was used in determining the ratio $k_i/k_{-i} \approx 2 \times 10^{-3} \,\mathrm{lmol}^{-1}$ as well as k_p (Scheme 18).²⁴

Thus, only a small fraction of covalent species (actually less than 1%) are ionized. The rate constant of the ion-pair collapse was determined from the dependence of dispersity on conversion by using the method of Mueller and Litwinienko⁴⁰. This, in turn, allowed the determination of k_p^{\pm} since the overall rate was low enough. Thus, $k_p^{\pm} = 1.4 \times 10^4 \text{ mol}^{-1} \text{ l s}^{-1}$ (all data at – 70 °C). Besides kinetic analyses, a detailed analysis of dispersities (D_M) for various mechanisms of activity exchange is also available, in particular for active \leftrightarrows dormant, as given by Litvinienko and Mueller.⁴¹ This treatment involves several instances: two-state mechanism with unimolecular isomerization, bimolecular exchange, degenerative transfer of two chain ends of different activities, and aggregation of two chain ends of different activities.

Dormant

3.02.12 Nearly Steady-State Polymerizations: Controlled Polymerizations Involving Quasi-Equilibria between Active and Dormant Species

In the previous sections, simple living polymerizations on one kind of active species or involving equilibria between two kinds



Figure 7 The time dependence of $-\ln(1 - P_n[I]_0/[M]_0)$ for the polymerization of 2,4,6-trimethylstyrene.



Scheme 18



of species (both active or one active and one dormant) were discussed. In these systems the total concentrations of participating species are invariant and equal to the concentration of the used initiator. This simply means that termination was not detected, and this system studied at the given temperature behaves 'ideally'. It may, however, be sufficient to merely change temperature and termination would appear (even for styrene anionic polymerization in THF with a most 'innocent' cation). Thus, for many systems this borderline between living and nonliving polymerization is diffuse. We are aware that some distinguished scientists, who have contributed chapters in this volume, may disagree with the terminology we are using. However, we are strictly following the IUPAC terminology, particularly the Glossary already cited⁶ and the novel document, devoted to polymerizations with reversible deactivations.30

3.02.12.1 Living versus Controlled Polymerizations

In this and many other chapters in this volume as well as in other volumes of this comprehensive, expressions 'living polymerization' and 'controlled polymerization' are used. IUPAC and ACS definitions are given in Section 3.02.11. The expression 'controlled' was not used in its present sense when the first edition of *Comprehensive Polymer Science* was published. In the past decades, there have been a number of discussions on what kind of a process could bear the corresponding names.

The process itself has certain features and it is up to the interested researchers how to name a certain group of processes that all behave kinetically in the same way. Finally, however, $IUPAC^{6}$ gave the definition of controlled polymerization as given below.

3.02.12.1.1 Definitions of controlled polymerizations

The term 'controlled polymerization' indicates control of a certain kinetic feature of a polymerization or structural aspect of the polymer molecules formed, or both.

- Note 1: The expression 'controlled polymerization' is sometimes used to describe a radical or ionic polymerization in which reversible deactivation of the chain carriers is an essential component of the mechanism, increasing the time of propagation to secure control of one or more kinetic features of the polymerization or one or more structural aspects of the macromolecules formed, or both.
- Note 2: The expression 'controlled radical polymerization' is sometimes used to describe a radical polymerization conducted in the presence of reagents that lead to, for example, ATRP, nitroxide-mediated polymerization (NMP), or reversible addition-fragmentation chain transfer polymerization.
- Note 3: Generally, the adjective 'controlled' should not be used without specifying the particular kinetic or structural feature that is subject to control.

More extensive discussion, however, is given in Reference 11, which also describes major criteria for both living and controlled polymerizations. In addition to the IUPAC definitions, the ACS definitions are quoted below. In principle, there is no difference between the viewpoints of these two groups of experts. According to the ACS document, 'controlled polymerization' is defined as follows:

Controlled polymerization is a synthetic method to prepare polymers which

(a) are well-defined with respect to:

- topology (e.g., linear, star-shaped, comb-shaped, dendritic, cyclic),
- terminal functionality,
- composition and arrangement of comonomers (e.g., statistical, periodic, block, graft, gradient),
- (b) have molecular weights predetermined by the ratio of concentrations of reacted monomer to introduced initiator, as well as unimodal and narrow molecular weight distribution.

Controlled polymerization may include transfer and termination but at a proportion low enough not to significantly affect the control of molecular properties given in definition 3. This means the rate of these side reactions should be low enough in comparison with propagation rate to reach a given synthetic goal.

In addition, the following features should be fulfilled:

- (a) the time of mixing reagents should be short compared to the half-life of the polymerization
- (b) the rate of initiation should be at least comparable to that of propagation
- (c) the rate of exchange between various active species should be faster than that of propagation of the fastest species
- (d) the rate of depropagation should be low in comparison to that of propagation.

Living polymerizations are *controlled* if four (a, b, c, d) conditions are fulfilled. *Controlled* polymerizations are *living* if irreversible transfer and termination is below the detection limit using currently available instrumentation.

It is suggested to determine the contribution of transfer and termination reactions in controlled polymerizations (e.g., by working at higher molecular weights or variable temperatures) to distinguish them from living polymerizations.

The term *controlled* is preferred to *apparently living* or '*living*' (with quotation marks) used to indicate synthesis of well-defined polymers under conditions in which chain breaking reactions undoubtedly occur, like in radical polymerization.

The examples given in this reference also further clarify the issue.

Not in all published papers, after the IUPAC and ACS documents appeared, have the authors decided to follow these recommendations. Therefore, even within this comprehensive there is a certain difference in the use of the two terms.

Nevertheless, it is of interest to also see different opinions, as expressed, for instance, in the paper in Reference 42. We would refrain here from any further discussion of pro and contra. Some authors think that if the process they are working on is called 'living' it is like the author is being knighted.

In 2010, F.P. Muller, A.F. Vandome, and J. McBrewster wrote a 76-page book titled *Living Polymerization*. They also authored more than 15 other books ranging from *Fire Sprinkler Systems* to *Foreign Involvement in the Spanish Civil War*. It shows that 'living polymers' have become the universal subject. In the book on living polymerization cited above there are merely 76 pages copied entirely from the Internet.

In previous sections, when two species were involved a simple equilibrium took place (Scheme 19). In this section, polymerizations with quasi-equilibrium are studied. (The term 'quasi-equilibrium' is used mostly for equilibrium with the transition state.) Quasi-equilibrium (Scheme 20) also

A
$$\implies$$
 B (both species active)
A \implies B' (A: active B': inactive)



Scheme 20

describes processes in which equilibrium is preserved, although concentrations of equilibrated species are not invariable, in contrast to equilibria like in **Scheme 19**.

Thus, if the rates of interconversions are higher than the rate of conversion of A' into inactive A'₂, the equilibrium (called quasi-equilibrium) takes place. If, for example, $[A']_0 = [B'']_0$, then with time (*t*) $[B'']_t$ becomes much larger than $[A']_t$ and in such a system the presence of A', B'', and B'' would be mostly observed.

Scheme 21 (related to Scheme 20, plus monomer conversion) describes, in principle, CRP. Disappearance of A' by bimolecular termination in the radical process (termination) could also be unimolecular, in, for example, controlled cationic polymerization.

3.02.12.2 Persistent Radical Effect: Self-Regulation (Internal Suppression of Fast Reactions)

Hanns Fischer elaborated kinetics describing at least some CRPs in terms of 'persistent radical effect' (PRE) (the term coined by Finke).⁴³ This is an application of the theory explaining the phenomena of self-regulation of the radical reactions that are related to **Scheme 21**. The principle, as Fischer⁴⁴ says, is simple.

"If the reversible processes were the only reactions and if at zero time no radicals are present, then the concentrations of R_i and Y [A' and B" in our Scheme 21] increase equally in time and reach equal steady state values in the equilibrium. However the transient radicals R_i also decay [2A' \rightarrow A'₂ in Scheme 21] by the unavoidable irreversible bimolecular self-termination, whereas, ideally, there is no such reaction of Y [B" in Scheme 21]. Hence, the concentration of the transient species reaches a maximum and decreases thereafter. In contrast, the concentration of the persistent radical increases steadily because it must balance the self-termination less of R_i . As time proceeds the decreasing concentration of the transient radicals also renders the product formation by their self-termination loss and becomes less likely. Instead, the cross-reaction of the transient with persistent species becomes the dominant product formation pathway."



$$(CH_3)_2N$$
—NO $(CH_3)_2N$

+ NO

Dimethylnitrosamine

Scheme 22

One of the many radical reactions quoted in the Fischer's paper is shown in Scheme 22. NO[•] radicals are known to be unable to dimerize in contrast to the dimethylamino radical $(CH_3)_2N^{\bullet}$. Therefore, as a result of the continuous photolysis, the (almost) dominating reaction product is the starting compound (cross reaction). In the beginning, $(CH_3)_2N^{\bullet}$ first dimerize and then their concentration falls down to such a level that practically the only observed product is the starting dimethylnitrosamine (DMNO): the NO[•] radicals are in large excess than $(CH_3)_2N^{\bullet}$. Obviously, after a sufficiently long time, only NO[•] radicals and dimers of dimethylamine would result. This prototype of CRPs has been analyzed by a number of authors.

The scenario is at the basis of the major CRPs, namely, stable free radical polymerizations (SFRPs)^{45,46} and ATRP.^{47–50} In these procedures, control is achieved through a dynamic equilibration between a predominant fraction of dormant species and macroradicals. This allows us to complete initiation before propagation starts or is advanced. Some authors state that an additional requirement is the low concentration of propagating radicals. This is not a necessary condition, particularly when lower P_n is a target. The 'low concentration', however, may mean that there is a much higher total number of growing chains in comparison with the concentration of macroradicals (i.e., fraction of chains fitted at a given moment with radicals).

Another method of control is based on 'degenerative chain transfer polymerization' (DT),⁵¹ the term originally introduced a few years earlier.⁵² It is discussed in detail by Moad *et al.*⁵³

Schematically these three fundamental methods can be described as shown in Scheme 23, which appear several times





RP P_n -X + Mt^n/L $\frac{k_a}{k_{da}}$ P_n + Mt^{n+1} -X/L





in various reviews. (For rate constants in this section, Fukuda's formalism is adopted (Chapter 3.05) although in various sources different subscripts are used.)

Of all the three methods, ATRP, first described by Matyjaszewski and Wang in 1995, is the most often used.⁴⁷

3.02.12.3 Simple Description of the CRP

Below a description (with further simplifying assumptions) of CRP of a monomer M is given on the basis of the ATRP (PRE) principle.

Let $[M]_0 = 1 \text{ mol } l^{-1}$ be polymerized to polymer with $P_n = 100$. The concentration of M is kept constant (by the continuous addition of the monomer), that is, $[M]_0 = 1.0 \text{ mol } l^{-1}$. The concentration of the growing chains should thus be $[M^*]_0 = 1.0 \text{ mol } l^{-1}/10^2 (P_n)$, that is, $10^{-2} \text{ mol } l^{-1}$. $[M^*]$ is also kept invariant (for the sake of simplicity of the presentation). The rate constant of the propagation of the monomer M is taken to be $k_p = 10^3 \text{ mol } l^{-1} \text{ ls}^{-1}$ (like, e.g., in styrene polymerization at ~80 °C). Then if initiation is instantaneous, the rate of polymerization $R_p = 1.0 \times 10^3 \times 10^{-2} = 10 \text{ mol } l^{-1} \text{ s}^{-1}$ (assuming also, as indicated above, $[M^*]$ is invariable and equal to $10^{-2} \text{ mol } l^{-1}$).

The rate is equal to 10 mol l^{-1} s⁻¹; thus, the polymerization of 1 mol l^{-1} would take 0.1 s, which is impossible to control. If the time of polymerization is chosen to be 3 h ≈ 10⁴ s, i.e., 10⁵ times larger than 10⁻¹ s, then the concentration of the growing species should be 10⁵ times lower for conversion of 1 mol l^{-1} of monomer. Therefore, $10^{-2} \text{ mol } l^{-1}/10^5 = 10^{-7} \text{ mol } l^{-1}$. Then, however, P_n would be 10⁷. Therefore, there is the following antinomy:

For the required P_n (=10²), there should be 10⁻² mol l⁻¹ chains. For the required rate R_p , there should be 10⁻⁷ mol l⁻¹ chains in order to polymerize 1 mol l⁻¹ in 10⁴ s.

A solution of this antinomy is as follows: Of growing 10^{-2} mol l⁻¹ macromolecules (chains), only 10^{-7} mol l⁻¹ should be instantaneously active.

Inactive
$$\frac{k_{\rm d}}{k_{\rm c}}$$
 Active + PR

Scheme 24

Inactive + Activator
$$\begin{array}{c} k_a \\ \hline k_{da} \end{array}$$
 Active + PR

Scheme 25

Thus, there should be a mechanism for the conversion of active to inactive chains, and vice versa. In the PRE systems, encompassing NMP and ATRP, these interconversions lead to the steady state governed by quasi-equilibrium.

Thus, for the NMP system (dissociation–combination), see Scheme 24 (cf. Scheme 32).

For the ATRP system, see Scheme 25 (cf. Scheme 33).

The active species (macroradicals) participate not only in the interexchange but also in termination, in which two macroradicals give dead species. Thus, if the lifetime of a given macroradical in certain conditions is equal to Ns, then in the controlled process the total time of activity should be N' < N. For the sake of simplicity, in the first part of the following presentation we assume that not only the monomer concentration would be invariant (continuous addition of the monomer) but also that termination would not take place. (Termination is discussed in the second part of this paragraph.) More complete presentation is given in the explanation of **Figure 8** and description of the PRE effect as given by Fischer. Moreover, the detailed and lucid descriptions are given in the chapters by Fukuda (Chapter **3.05**) and Matyjaszewski (Chapter **3.12**).

The solution of the antinomy mentioned above is that from the $10^{-2} \text{ moll}^{-1}$ macromolecules that can be grown, only $10^{-7} \text{ moll}^{-1}$ should be instantaneously active. Moreover, since the average lifetime of the above-mentioned macroradicals (e.g., polystyryl radical) is ~1 s, the total lifetime of



Figure 8 Variations in the concentration of transient (R) and PRs (Y), dormant and the final polymer chains (P), temporarily inactive macromolecules (I), and monomer (M) in relation to time of living polymerization initiated by the homolysis of the R–Y initiator.

macroradicals in the short periods of activity should be much less than 1 s.

Thus, the major requirement for realizing the controlled process is the presence of equilibrium, allowing conversion of active into inactive species, and vice versa (repetition of **Scheme 25**; the activator could be, e.g., as in **Scheme 33**). Then for equilibrium, k_a [inactive][activator] = k_{da} [active][PR], where PR denotes the persistent radical.

Converting the second-order rate equations to the pseudo-first-order equations (using the assumed constancy of concentrations): $k_a \times 10^{-2} \times [activator] = k_{da} \times 10^{-7} \times [PR]$, we could write (following Fukuda's Chapter **3.05**) $10^{-2}k_{act} = k_{deact}[PR]$. In this way the lifetimes (see the Appendix) of macromolecules in the active and inactive states could be determined.

Both k_a and k_{da} may have various values, depending on the structures of inactive (covalent) form and used activators. The same is true for the back process (deactivation-combination). The only requirement is the fulfillment of the conditions of equilibrium. To be closer to reality, the values of k_a and k_{da} should be of the order determined, for example, for ATRP styrene polymerization; for example, $k_a = 0.45 \text{ mol}^{-1} \text{ l s}^{-1}$ and $k_{da} = 1.1 \times 10^7 \text{ mol}^{-1} \text{ l s}^{-1}$ and can be taken from Reference 54. Assuming that $[A] = 10^{-2} \text{ mol } l^{-1}$, we have Scheme 26. Thus, we obtain **Scheme 27**. For $k_{da} = 10^7 \text{ mol}^{-1} \text{ l} \text{ s}^{-1}$, and $[PR] = 10^{-4} \text{ mol } l^{-1}$ the pseudo first order rate constant is equal to 10^3 s^{-1} and the corresponding lifetime is 10^{-3} s . The lifetime of inactive species is 10² s and the number of periods during the required 10^4 s is 10^2 . The lifetime of an average macroradical is 10^{-3} s. In one period, ~ 1 monomer molecule is added; thus, in 10² periods there are 10² monomer molecules added, providing the required $P_n = 100$. Therefore, the lifetimes (the kinetic meaning of lifetimes and half-times of reactions are given in the Appendix) of active and inactive species are

$$\tau_{\text{active}} = 10^{-3} \text{ s and } \tau_{\text{inactive}} = 10^2 \text{ s}$$

The growth of the macromolecules would consist of the start periods of activity, 10^{-3} s, and longer periods of inactivity, 10^{2} s. The addition of one monomer molecule to one macroradical proceeds at the presented conditions every 10^{-3} s (there is an obvious statistical distribution of times).

The length of one period of activity is 10^{-3} s; therefore, there would be on average one short burst of activity needed for one monomer addition.

$$[\text{Inactive}] \quad \underbrace{k_{a}[A]}_{\text{II}} = [\text{active}] \quad \underbrace{k_{da}[PR]}_{\text{II}}$$

$$10^{-2} \text{ mol } |^{-1} \quad \underbrace{Pseudo}_{\text{first-order constant}} \quad 10^{-7} \text{ mol } |^{-1} \quad \underbrace{Pseudo}_{\text{first-order constant}}$$

Scheme 26

 $10^{-2} \times 1 \times 10^{-2} = 10^{-7}$ k_{da} [PR] (Taking k_a = 1 mol⁻¹ l⁻¹s⁻¹)

Scheme 27

 10^{-3} s 10^2 s Active Inactive, etc.

Scheme 28

The life record for one macromolecule (not scaled) is shown in **Scheme 28**. The number of interconversions during the lifetime of one macromolecule can be calculated from the total time of growth and the time of one interconversion. The total time of growth is 10^4 s, and the time of one interconversion is 10^2 s. There are 10^2 periods of activity of 10^{-3} s each; $10^2 \times 10^{-3}$ s = 10^{-1} s is the total time when a macromolecule is active out of 10^4 s; 10^2 units are added during 10^{-1} s. Thus, there is one monomer molecule every 10^{-3} s per chain.

3.02.12.3.1 The fate of active centers

In previous calculations, in order to show what kind of relationships are needed to fulfill the major condition of controlled process (instantaneous initiation) it has been assumed that the concentration of active centers was constant. However, the growing centers are macroradicals, and, along with the process of monomer addition, termination takes place in a bimolecular termination reaction of macroradicals (k_t). The rate constant of termination, k_t , for the polystyryl radical is $10^7 \text{ mol}^{-1} \text{ l s}^{-1}$.

Then

$$-\frac{\mathrm{d}[\mathbf{S}^{\bullet}]}{\mathrm{d}t} = k_{\mathrm{t}}[\mathbf{S}^{\bullet}]^{2}$$
[39]

$$\frac{1}{[S^{\bullet}]} - \frac{1}{[S^{\bullet}]_0} = k_{\rm t}t$$
[40]

$$[\mathbf{S}^{\bullet}] = \frac{[\mathbf{S}^{\bullet}]_0}{1 + k_t t [\mathbf{S}^{\bullet}]_0}$$

$$[41]$$

The total growth time for an average macromolecule is 10^4 s, but only 10^{-1} s (100 periods for 1 ms each) for a macroradical. Thus, after 10^{-1} s, $[S^\bullet] = [S^\bullet]_0/(1+10^7 \times 10^{-1} \times 10^{-7}) = [S^\bullet]_0/1.1$ or $0.9[S^\bullet]_0$.

Thus, when $1 \mod l^{-1}$ of a hypothetical monomer M is converted in 3 h into a polymer with $P_n = 100$, 10% of the original active species would be dead. Ninety percent would still be able to become active. In every next moment after these 3 h, termination will proceed further. The simple formula (eqn [41]) clearly shows what practically could not be done. Obviously, if P_n were 10, then only ~1% would be dead, but if P_n were larger, for example, $P_n = 1000$, then almost all the macroradicals would be dead at the full monomer conversion in a given time of 10^4 s and other conditions adopted in this case. If the k_p/k_t ratio were higher (e.g., by changing temperature or when an appropriate monomer is chosen), then the propagation of macromolecules still being able to propagate would also change.

The situation presented above considers only one aspect of CRP, namely, the interconversions of the inactive and active forms. It has been our intention to show in a lucid form and using realistic rate constants and concentrations how this single feature may provide control. However, in the PRE, no less important (and sometimes more important) is building a higher concentration of PR and suppressing homotermination this way.

In 2011 Matyjaszewski published a paper⁵⁵ titled 'How fast can a CRP be conducted with preserved chain end functionality?' (perhaps not only 'how fast', but also 'to how large P_n '). In this paper the influence of several variables on the preservation of livingness is discussed in depth.

3.02.12.4 Rate Constants in CRP Based on the PRE: Principle

Scheme 29 shows the rate constants that are involved in CRP. The first reaction is the dissociation (activation) of the shortest chain (initiator of the same structure as R_iX). The rate constants of propagation (k_p) and of termination (k_t) are the same as in the traditional radical polymerization (the new method of k_p determination based on the 'pulse laser polymerization–size exclusion chromatography' (PLP-SEC) is discussed in Section 3.02.14.4). Thus, k_a and k_{da} are of major interest. These are discussed in detail in Chapter 3.05 by Fukuda *et al.* where it is separately described for the CRP with nitroxides (e.g., 2,2,6,6-Tetramethylpiperidinooxy (TEMPO) as the PR) and for the ATRP systems (Scheme 30).

Fukuda describes an experiment in which Polystyrene terminated with TEMPO (PSt-T) of $M_n = 1700$ is heated in the presence of styrene, and in the gel permeation chromatography (GPC) of the product, the peaks of unreacted and reacted PSt-T ([I]₀) could be observed separately. Then, $-d[I]/dt = k_d[I]$, giving $\ln([I]_0/[I]) = k_dt$.

It has also been shown that indeed $[PSt^{\bullet}][T^{\bullet}]/[PSt-T] = K, K$ being invariable throughout the time of polymerization, whereas $[T^{\bullet}]$ was determined by using electron spin resonance (ESR); and finally it has been shown that at a certain stage, $[T^{\bullet}] \cong 10^{3}[PSt^{\bullet}]$ because of the PRE.

Another approach was applied to the determination of k_a in the atom transfer polymerization, which was based on the determination of the PSt[•] released from PSt-Br (activated by Cu salt), scavenged by nitroxide, and detected by high-performance liquid chromatography. Then *K* was determined from the studies of the polymerization rate at the condition at which the following equation could be used:

$$(R-X)_{0} \xrightarrow{k_{ia}} R_{0}^{i} + X^{i}$$

$$R_{0}^{i} + M \xrightarrow{k_{p}} R_{1}^{i}$$

$$R_{1}^{i} + (i-1)M \xrightarrow{k_{p}} R_{i}^{i}$$

$$R_{i}^{i} + X^{i} \xrightarrow{k_{da}} R_{i}X$$

$$R_i^* + R_j^* \xrightarrow{\kappa_t} R_j (or R_i + R_j)$$

1.

$$\ln \frac{[M]_{0}}{[M]} = \frac{k_{p}K[I]_{0}}{X_{0}^{\bullet}}t$$
 [42]

Once k_a is known and *K* determined from eqn [42], k_{da} could be computed.

These fast activation/deactivation reactions and the large ratio of inactive (dormant)/active macromolecules are the heart of CRP. Extensive tables with the values of rate constants are given in Chapters **3.05** and **3.08**. It should be added that the ATRP method, discovered by Matyjaszewski,⁴⁷ is most often used in hundreds of laboratories for the synthesis of polymers or various polymer architectures.

To finish this section, the well-known complete analysis of Scheme 29, as described by Fischer,⁴⁴ is shown in Figure 8. Further reevaluation of this scheme is given in References 56 and 57. Nevertheless, in principle, the original scheme as given by Fischer still seems valid, although the introduced corrections may change some numerical values. In this figure, the evolution of concentrations of monomers (M), dormant macromolecules (I), active macromolecules (macroradicals) (R), PRs (Y), and dead polymers (P) are given. The actual polymerization process (monomer conversion) takes place for $10^4 - 10^8$ s. This figure clearly shows the decline of macroradicals (R) well before an appreciable monomer conversion takes place. Indeed, after 10^4 s, 10^{-4} mol l⁻¹ of the PRs and less than 10^{-8} mol l⁻¹ of the macroradicals (R) are already present. The concentration of dormant macromolecules (I) is $\sim 10^{-2}$ mol l⁻¹; its changes are not seen in this figure, although macromolecules (I) compensate for all the time increase in the concentration of PRs according to the quasi-equilibrium and in accordance with Scheme 31 (related to Scheme 21).

Depending on the polymerization conditions, the starting concentrations of the monomer and PRs, and temperature, the fate of I, M, Y, R, and P may differ from evolutions shown in **Figure 8**. However, in principle, the fundamental behavior would be as shown for major PRE-based processes.

3.02.12.5 NMP and ATRP: Chemistry

In the PRE-based processes, there are two major modes of achieving the reversible deactivation: NMP and ATRP. In NMP the most representative PR is TEMPO, although there are dozens of various compounds that provide the PR. Based on their structures, the rate constants for activation and deactivation may differ substantially, depending on the bond strength between a given compound and the polymer's ultimate unit. For TEMPO and styrene monomer, the rate constants⁵⁸ given in **Scheme 32** were determined as discussed above.

For a typical ATRP with Cu^+ as an activating agent and Cu^{2+} playing a role of the PR, see Scheme 33.⁵⁹



Scheme 30

Scheme 31



Scheme 32



Scheme 33

There are several modifications of the classical ATRP, such as an additional route of back conversion of Cu^{2+} to Cu^{+} , which allows the reduction of the total amount of Cu used to the level of a few parts per million.

There is also another method of CRP that leads, as the author says, 'toward living radical polymerization' and is based on the polymer–polymer exchange. This was comprehensively presented in a lucid paper by Moad and Rizzardo (Scheme 34).⁵³

The earlier work by Otsu, titled 'A model for living radical polymerization', should be noted⁶⁰ even if it was not sufficiently successful. Another approach to achieve livingness (not realized in practice so far) was proposed by Kabanov, who considered a possibility of achieving living radical

polymerization at conditions of microassociation in homogeneous systems, taking as the starting point the emulsion polymerizations when a single radical is present in an emulsion droplet particle.⁶¹

3.02.12.6 Controlled Cationic Polymerization of Vinyl Monomers

Closely related to the PRE is controlled cationic polymerization of vinyl monomers. In the field of CVP, there is a deep difference of opinions. The first is related to the reactivity of the 'modified active centers'. Controlled polymerization was achieved in the late 1970s to early 1980s. Some authors, on the basis of the formation of onium ions (well known from















elementary organic chemistry) when carbenium ions react with nucleophiles, proposed that these nucleophiles (esters, ethers, etc.) form reversibly dormant species (Scheme 35).

Doubts have been raised on whether onium ions are formed, although this is a well-known phenomenon where carbenium ions react with nucleophiles, leading to, for example, oxonium or sulfonium ions. It should also be noted that in a number of systems, proton traps provided 'livingness'. If proton traps were necessary, it simply means that the proton traps stopped (and not eliminated) transfer 'halfway' in systems that should be 'free from irreversible transfer', thus not eliminating proper transfer from a growing macrocation but merely stopping transfer of the expelled proton from starting a new chain. However, by this transfer dead macromolecules are formed somehow. In some papers, the proton traps are nevertheless considered as purifying agents, which react with originally present impurities (mostly acids). It has to be stressed that proton traps may also suppress the presence of 'free' ions by the common ion effect. Thus, one way or another, controlled cationic polymerization has indeed been observed. Then it would fall into the same category (from a viewpoint of kinetics and formal mechanism) as CRP. At least in a sense that the interconversions of inactive and active species give a chance to have relatively fast initiation (in comparison with propagation) and provide a high proportion of the tentatively inactive macromolecules. Then, regaining activity allows synthesis of block copolymers and other architectural varieties. In contrast, the difference between CRP and controlled cationic vinyl polymerization (CCVP) is that in CCVP the interchange between the inactive and active species is relatively slow when compared with the very fast propagation⁶² (e.g., for isobutene) (Scheme 36).

The idea of the 'stretched bonds' and 'the whole Winstein spectrum' popular at one point of time is finally put to rest. Extensive discussion on the allegedly living CVP is given in a paper by Matyjaszewski and Sigwalt.⁶³ These authors analyzed the CCVP in terms of reversible deactivation in the propagation step either by the formation of covalent species (Scheme 36) or

by the formation of onium ions – both temporarily inactive (Scheme 37), increasing the overall time of propagation as in the CRP. When after a certain monomer conversion (even complete) and at a usually rather low polymerization degree a new portion of the monomer is added, polymerization restarts with an almost identical rate constant. This stems merely from the fact that a large proportion of active centers have been converted into the temporarily inactive species. In this system the polymers formed in the allegedly 'living' polymerizations have usually lower molar masses than do the polymers prepared at conditions when 'livingness' has not been observed. Thus, let us quote Szwarc from his last monograph:

No new mechanism operates 'living' cationic polymerization. Neither does a new kind of species participate in these reactions. However, judicious choice of conditions and regents is essential for successful operation of this process, especially if narrow MWD polymers are desired.⁶⁴

3.02.13 Second Kind of the Steady State: The Rate of Formation of Active Centers Balanced by the Rate of Their Disappearance. Classical Radical Polymerization

For a long time the only known steady-state processes involved initiation balanced by termination. This was the first postulate of Bodenstein (see Section 3.02.3): when in the reaction $Cl_2 + H_2$, Cl^{\bullet} is formed in the initiation step by Cl_2 dissociation and either $2Cl^{\bullet} \rightarrow Cl_2$ and $Cl^{\bullet} + H^{\bullet} \rightarrow HCl$ or $2H^{\bullet} \rightarrow H_2$ terminates the kinetic chains. A large number of reactions of inorganic or organic compounds have been analyzed in this way. This approach has also been adapted for the chain polymerizations. There were several attempts to analyze not only radical polymerizations but also ionic polymerizations by using for this assumption, example, cationic polymerizations.⁶⁵ Today, these are mostly of historical importance, especially after elaboration of controlled and living polymerizations.

The second kind of the steady-state process is still at the basis of most industrially important radical polymerizations, leading to, for example, polystyrene, poly(methyl methacrylate), poly(vinyl chloride), poly(vinyl acetate), and fluoro polymers. The general understanding of the kinetics and mechanism of radical polymerization has existed for several years. Therefore, in the mid-1960s,66 some leading authors in the field assumed that research and interest in radical polymerization were oriented toward detailed or specific nature. It has been assumed that efforts in this field are merely 'filling-in' unimportant gaps in existing knowledge. However, since then, as often happens in science, entirely new methods in radical polymerization have been developed, as described above. In traditional radical polymerization, the rate of formation of active macroradicals is balanced by the rate of termination (Scheme 38). In the systems shown in Scheme 38, $k_{\rm p}$ decreases progressively for the first few units and then can be considered as a constant value; however, k_t is often diffusion controlled and depends strongly on viscosity (monomer conversion) and the chain length. The Handbook of Radical Polymerization⁶⁷ published in 2002 (with ~1000 pages and 16 chapters) covers problems ranging from the theory of radical reactions to macromolecular engineering, including dependence of the rate constants on the chain length. Scheme 38 is the most simplified radical polymerization as being taught in the elementary polymer courses.

The 'classical' or simply 'radical polymerization' has already been presented in detail in the major textbooks (~200 pages in Odian's *Principles of Polymerization*⁶⁸ with more than 400 references and more than 100 pages in Elias' *Chemical Structures and Synthesis*⁶⁹). Besides, there are monographs and chapters in multiauthor monographs,^{67,70} several books edited by Matyjaszewski in ACS Symposium Series on CRP, and finally a collection of chapters edited by Buback.⁷¹ Nevertheless, more than 2500 papers per year are published still on radical polymerization – one third being on ATRP (these numbers may vary depending on the way of searching).

The radical polymerization has a long history. Certainly the major credit in this area of polymer chemistry should be given to Hermann Staudinger (1881, Worms, to 1965, Freiburg).^{72,73} Since then all the elementary reactions, namely, initiation (including cage effect and related efficiency), chain propagation, chain transfer (to monomer, polymer, solvent),

$$I \xrightarrow{k_{i}} R_{0}^{i}$$

$$R_{0}^{i} + M \xrightarrow{k_{p1}} R_{i}^{i}$$

$$R_{i}^{i} + n M \xrightarrow{k_{p}} R_{j}^{i}$$

$$R_{i}^{i} + R_{j}^{i} \xrightarrow{k_{t}} R_{i}R_{j} \text{ (or } R_{i} + R_{j})$$

Scheme 38

termination (by combination and disproportionation), inhibition, and retardation were studied in great detail and the corresponding rate constants were determined. Rate constants have been described in terms of the collision theory and its extension to the liquid phase.



Hermann Staudinger (1881, Worms–1965, Freiburg)

The generally accepted and fundamental equation for the rate of polymerization follows from **Scheme 38**:

$$R_{\rm p} = k_{\rm p} [M] \left(\frac{R_{\rm i}}{2k_{\rm t}}\right)^{1/2}$$
[43]

This treatment is based on some assumptions. The first assumption is that the energetic state of macroradicals when formed has enough time to be in equilibrium with its immediate vicinity. Usually equilibrium is rapidly established so that for the subsequent chemical reaction the centers are ready in the same energy state; that is, they are equally reactive. For some time this assumption was challenged, assuming (like Bodenstein in his first equation; cf. eqn [2]) that this equilibrium is not established. Thus, Tűdös proposed a theory of hot radicals,⁷⁴ which is also discussed by Kučera.⁷⁵

3.02.13.1 Hot Radicals Theory in Radical Polymerization

This theory assumes that the situation cannot be excluded where the rate of energy equilibration is comparable with the rate of the successive reaction. In such a system, radicals of various reactivities react with the substrate. At the moment of formation, the reaction product contains the heat from the activation energy of the exothermic elementary reaction and it is in a highly excited state.

The vibrationally excited 'hot' radical R^{*} undergoes a series of collisions with the molecules of reaction components. According to the classical theory of chain reactions, the hot radical is first deactivated and the reaction can proceed only after the substrate has accumulated sufficient activation energy by molecular collisions. In the theory of 'hot' radicals, it is assumed that fresh active centers with excess energy are capable of direct reaction $R_i^* + M \rightarrow R_{i+1}^*$.

The activation energy is supplied by the excess energy of 'hot' radicals; therefore, the process does not require external activation.

The Tűdös theory of hot radicals has not finally been introduced into polymer practice, although many scientists working at that time in radical polymerization assumed that in many systems this theory may be more exact (F. Tűdös, private communication with S. Penczek, 1959/1960).

3.02.13.2 The Dependence of Rate Constants on the Chain Length

It has also been assumed (second assumption) that the rate constants of reactions involving macroradicals are essentially independent of the chain length. There are, following North,⁶⁶ two important situations that arise when this assumption is not valid: The first situation arises when polymerization is initiated by radical-containing groups that exert powerful inductive effects and particularly when low-molecular-weight polymer is formed. The other case may occur when it is not apparent that k_p and k_t would depend, in a similar way, on the chain length.

Condition-dependent k_t has already been observed in 1940s and known as the Tromsdorff–Norrish effect. However, it is only in the decades 1980–2000 that the concept of the chain-length-dependent termination started to be studied in more detail. It was due to the new techniques (pulse laser, SEC, EPR) and the power of computers that numerical calculations were possible. A novel method for the detailed study of the termination kinetics of radical polymerization by using single pulse–pulsed laser–electron paramagnetic resonance (SP–PLP–EPR) has been published in 2010 by Barth and Buback.⁷⁶ This method is related to the PLP method (described in the next sections) and is based on measuring the EPR signal decay. This and related phenomena have been reviewed in Reference 77.

3.02.13.3 Limits of the Steady-State (Bodenstein) Approximation

Another fundamental approximation is the steady-state approximation. There is a certain requirement for steady state to be established. In any real system, the concentration of the initiator and the terminating agent (or macroradicals) must decrease during the reaction and only at idealized conditions the change would not upset the steady state, since the concentration of macroradicals must reach its equilibrium 'stationary' value for each value of the concentration of the initiator. Actually, the second kind of the steady state discussed in this section results from two rates that are equal to each other. The rate of initiation is constant since the theory describes only the early stage of polymerization when the concentration of the initiator is almost constant. Then, by the same token, the rate of termination is constant. Two invariant rates producing (first-order kinetics) and consuming (second-order kinetics) macroradicals inevitably lead to the steady state. This is valid, however, only up to a certain conversion of the monomer and may not be true when the initiation is a bimolecular process, involving monomers.

3.02.13.4 Rate Constants in Radical Polymerization

The aim of any kinetic study of a chemical reaction is the elucidation of the mechanism of reaction, followed by a correlation of the reactivities of the species involved with their chemical structures. Expression of any rate constant in an Arrhenius form may then yield information on the enthalpy and entropy changes (and the Gibbs energy change) during the formation of a transition state.

The most easily observed property is the rate of reaction, that is, the rate of disappearance of the monomer:

$$R_{\rm p} = -\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} = k_{\rm p}[\mathrm{P}_{\rm i}^{\bullet}][\mathrm{M}]$$
[44]

The second observable feature is the degree of polymerization defined by an average-number of monomer units linked together in each average polymer chain: P_n .

As it is known that

$$R_{\rm p} = k_{\rm p} [M] R_{\rm i}^{1/2} (2k_{\rm t})^{-1/2}$$
[45]

we have, for disproportionation,

$$\frac{R_{\rm t}}{R_{\rm p}} = \frac{1}{P_{\rm n}} = \frac{R_{\rm i}^{1/2} (2k_{\rm t})^{1/2}}{k_{\rm p}[{\rm M}]}$$
[46]

These two equations have two common unknowns:

$$R_{\rm i}$$
 and $\frac{k_{\rm p}}{\left(2k_t\right)^{1/2}}$ [47]

Consequently, the knowledge of R_i and one value of either k_p or P_n allows an immediate evaluation of the ratio $k_p/(2k_t)^{1/2}$ and finally also k_t .

Over the years, several methods of determination of R_i have been developed. Discussion of these methods is given in the above-cited monographs on radical polymerization as well as in some textbooks. It suffices to mention that it is possible to measure R_i by determining, for example, the inhibition time in the presence of radical scavengers, so that the rate of consumption of the inhibitor is known.

$$R_{\rm i} = \frac{r[{\rm I}]}{t_{\rm i}} \tag{48}$$

where r is the number of radicals removed by each inhibitor molecule, and t_i is the 'inhibition time' and [I] is the concentration of the inhibitor. The ideal inhibitor is a compound that reacts directly with growing radicals much faster than with the monomer and yield products incapable of further reaction. Kinetics of inhibition and retardation is analyzed in detail by several authors, for example, by Bamford.⁷⁸

Thus, knowing R_i and determining R_p for the same conditions, the value of $k_p/k_t^{1/2}$ is known. There are also a number of methods for the determination of k_p . The simplest would be from R_p and $[P_i^{\bullet}]$; the measurement of R_p and the radical concentration $[P_i^{\bullet}]$ would yield a value for k_p that could then be used in conjunction with the ratios of k_p and k_t to derive k_t . Again, the simplest method of determining $[P_i^{\bullet}]$ would be ESR spectroscopy. It has been used several times since the original first papers by Bresler in Leningrad⁷⁹ and Ranby in Stockholm,⁸⁰ although the measurement is difficult because of a very low concentration of radicals. Nevertheless, Kamachi and co-workers in Japan have determined a number of $[P^{\bullet}]$ by using sophisticated EPR equipment.⁸¹ The method of rotating sector and the flow method were often used in the past. Applications of these methods and related difficulties are described by Moad and Solomon in Reference 70 and in the above-cited monograph. The other non-stationary-state measurement is given in the next section.

3.02.13.5 Pulse Laser Polymerization–Size Exclusion Chromatography: Method of k_n Determination

The discovery of the analytical methods, such as SEC, allowing measurements of the degree of polymerization (P_n) by using very low amounts of polymers, opened a way for the elaboration of a novel method of k_p determination, known as PLP-SEC. Its principle is based on the determination of the P_n of the polymer formed in a very short time after the instantaneous initiation by a burst of the initiating laser irradiation when the concentration of the average monomer concentration is used).

The laser pulse width is very short (e.g., 10 ns) compared to both the lifetime of propagating radicals and the time of conversion of primary radicals to propagating radicals ('instantaneous initiation'). The fate of the formed macroradicals is shown in **Figure 9**, explaining the whole process.

From the SEC data (P_n), k_p is calculated in the following way:

$$\ln \frac{[M]_0}{[M]} = k_p[P_i^{\bullet}]t; \qquad \ln \frac{[M]_0}{[M]} \cong \frac{[M]_0}{[M]} - 1 = \frac{[M]_0 - [M]}{[M]} \qquad [49]$$

$$\frac{[M]_0 - [M]}{[M]} = \frac{\Delta[M]}{[M]}$$
[50]

$$\frac{\Delta[\mathbf{M}]}{[\mathbf{M}]} = k_{\mathbf{p}}[\mathbf{P}_{\mathbf{i}}^{\bullet}]t; \quad \text{since } P_{\mathbf{n}} = \frac{\Delta[\mathbf{M}]}{[\mathbf{P}_{\mathbf{i}}^{\bullet}]} \text{ and } \frac{\Delta[\mathbf{M}]}{[\mathbf{M}]} = k_{\mathbf{p}}\left(\frac{\Delta[\mathbf{M}]}{P_{\mathbf{n}}}\right)t$$
[51]

and finally, after rearrangement,

$$k_{\rm p} = \frac{P_{\rm n}}{[{\rm M}]}t$$
[52]

The conversion of the monomer is very low; thus, [M] may be taken as the starting monomer concentration or – more precisely – as an average value, taking into account conversion; *t* is the time between two pulses (e.g., ~ 1 s).

This method was originally elaborated by Olaj *et al.*⁸³ and developed in a number of his papers, although van Herk in his review⁸² mentions Russian scientists (Gerkin, Sokolov, and Aleksandrov) who gave the theoretical basis of the method. In the same review, one could find more than 40 k_p data and corresponding activation parameters as available by 1997.

In 2008, a further improvement of the method, particularly for acrylic monomers, was achieved. In acrylic polymerization, chain transfer obscured the SEC data and application of the high-energy-output lasers with 500-Hz frequencies (used by the authors for the first time) greatly improved the method.⁸⁴ In **Figure 10**, the SEC results of the experiment performed at 100 Hz are compared with the improvement by using laser pulsing at 500 Hz. The difference in the L_p values is also to be noted.

Later on, this method has been taken by the IUPAC group led by Buback, Gilbert, van Herk, Russel, *et al.*, who systematically measured and compared k_p data taken from various groups and for the most often used monomers. Data for styrene and methyl methacrylate taken from laboratories in Eindhoven, Göttingen, Leverkusen, Sydney, Toronto, Vienna,



Figure 9 Description of the PLP-SEC experiment. Taken from van Herk, A. M. J. Macromol. Sci. Rev. Macromol. Chem. Phys. 1997, 37, 633.82



Figure 10 Molar mass distributions and their derivatives of the polymer generated by the PLP of butyl acrylate at 33 °C. The left panel depicts a sample from laser pulsing at 100 Hz, and the right panel depicts a sample from laser pulsing at 500 Hz but otherwise identical conditions.

and Wilmington were compiled by Gilbert and published in 1996 in *Pure and Applied Chemistry*.⁸⁵ Several other results are available as IUPAC reports published in the same journal. Since then, an obvious question is asked: What accuracy of the values of k_p are indeed needed? (This kind of question is often asked, e.g., for the Avogadro number and several other numbers.)

3.02.14 Non-Steady-State Polymerizations

There are two most-often occurring non-steady-state polymerizations: The initiation is slow and finally steady state is achieved; this is the case for a typical radical polymerization and, in fact, for any steady-state process having inevitably a period of building invariable concentration of the active species. It was analyzed for radical polymerization and this case will be described first. A similar situation may arise in, for example, living anionic polymerization, with 'slow initiation– fast propagation,' although, depending on the k_p/k_i ratio, the behavior of the systems may differ substantially.

A second general case of the non-stationary-chain polymerization is when active species are no longer formed but disappear due to termination. The well-known case that will be described here is the 'dead-end polymerization' (discussed in Moad and Solomon's monograph;⁷⁰ 'dead end' means inactive end group in a macromolecule).

The 'dead end' has been known in many ionic polymerizations, mostly cationic. The 'dying' cationic polymerization of styrene will also be described further in the text, following the slow initiation and dead end in radical polymerization. It is possible to create several other systems (e.g., termination from the steady state of the first case involving end-to-end cyclization) and many others. However, the few mentioned above can be considered as the most fundamental.

3.02.14.1 Radical polymerization

Thus, in radical polymerization, for initiation,

$$\mathbf{I} \to 2\mathbf{R}_0^{\bullet}; \quad -\frac{\mathbf{d}[\mathbf{I}]}{\mathbf{d}t} = k_i[\mathbf{I}]; \quad \frac{\mathbf{d}[\mathbf{R}^{\bullet}]}{\mathbf{d}t} = 2k_i[\mathbf{I}]$$
 [53]

In the further derivation, k_p is considered to be independent of the chain length, which is not true in general (as mentioned above) since k_{p1} , k_{p2} , ..., k_{pj} (where index *j* denotes the degree of polymerization) are known to differ from one another in the reactions of R_{ij}^{\bullet} with the monomer. In the further derivation, however, the reactivity of R_0^{\bullet} is distinguished from R_i^{\bullet} .

Thus, $-d[M]/dt = k_p(\sum [R_j^{\bullet}])[M]$ (consumption of M due to R_0^{\bullet} can be neglected):

$$[\mathbf{I}] = [\mathbf{I}]_0 \exp(-k_i t)$$

$$[54]$$

with some simplifications:

$$\frac{\mathrm{d}[\mathrm{R}_{0}^{\bullet}] + \sum[\mathrm{R}_{j}^{\bullet}]}{\mathrm{d}t} = 2k_{\mathrm{i}} - k_{\mathrm{t}}[\mathrm{R}_{0}^{\bullet}] + \sum[\mathrm{R}_{j}^{\bullet}]^{2}$$

$$[55]$$

Since $[R_0^{\bullet}] \ll \sum [R_j^{\bullet}]$,

$$\frac{\mathrm{d}\sum[\mathbf{R}_{j}^{\bullet}]}{\mathrm{d}t} = 2k_{i}[\mathbf{I}] - k_{t}\left(\sum[\mathbf{R}_{j}^{\bullet}]\right)^{2}$$
[56]

Since the derivation is related to the early stage of polymerization, [I] could be taken as invariable and equal to [I]₀. Thus,

$$\frac{\mathbf{d}[\mathbf{R}_{j}^{\bullet}]}{\mathbf{d}t} = 2k_{i}[\mathbf{I}]_{0} - k_{t}[\mathbf{R}_{j}^{\bullet}]$$
[57]

This is the well-known equation of radical polymerization when at steady state $d[R_i^{\bullet}]/dt = 0$. Integration of this equation gives

$$[\mathbf{R}_{j}^{\bullet}] = \left\{\frac{2k_{i}[\mathbf{I}]_{0}}{k_{t}}\right\}^{1/2} \frac{\exp A}{\exp B}$$
[58]

where $A = 8k_ik_t[I]_0^{1/2}t - 1$ and $B = 8k_ik_t[I]_0t + 1$.



Figure 11 The total radical concentration as a function of time for the polymerization of styrene in benzene at 60 °C initiated by AIBN at a concentration of 1×10^{-3} mol I⁻¹.⁸⁶

Therefore, the concentration of macroradicals builds up asymptotically to its maximum steady-state concentration. Margerison and East⁸⁶ analyzed this equation for the polymerization of styrene, in benzene solvent, with 2,2'-diazobisisobutyronitrile (AIBN) and $[I]_0 = 1 \times 10^{-3} \text{ mol}^{1-1}$. For these conditions, taking $k_t = 7.2 \times 10^7 \text{ mol}^{-1} \text{ l s}^{-1}$, the maximum (i.e., steady-state) value of $[R_j^{\bullet}]_{max} = 1.8 \times 10^{-8} \text{ mol}^{1-1}$ is reached in a few seconds. Thus, first $[R_j^{\bullet}]$ increases and when the concentration becomes large enough, the rate of initiation buildup becomes equal to the rate of bimolecular termination and the steady state is reached. This is shown in **Figure 11**.

3.02.14.1.1 Slow initiation–fast propagation in living polymerization: Gold's treatment

In Section 3.02.11, steady-state living polymerization was discussed. Initiation has been assumed to be fast as compared with propagation. This is then a class of polymerizations where the number of propagating chains remains invariant throughout the course of reaction. Such a situation exists, for example, in anionic polymerization of ethylene oxide, described by Flory, who has shown that such a process leads to the Poisson distribution.⁸⁷

Then, starting from Szwarc's discovery of general living polymerization conditions, the Poisson distribution was observed in a large number of works. However, when $k_i < k_p$, dispersity would differ from the one expected for the Poisson distribution. The rate of polymerization steadily increases until the initiator is fully consumed (depending on the k_p/k_i ratio, complete consumption may or may not take place). Kinetic curves could easily be constructed for various k_p/k_i ratios on the basis of two equations: rate of formation of active species and rate of monomer consumption. Gold⁸⁸ in the often-cited paper 'Statistics of polymer molecular size distribution for an invariant number of propagating chains' gave a complete derivation of k_p/k_i . The relation between [M] and [I] is

$$\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}[\mathrm{I}]} = \left(1 - \frac{k_{\mathrm{p}}}{k_{\mathrm{i}}}\right) + \frac{k_{\mathrm{p}}}{k_{\mathrm{i}}} \frac{[\mathrm{I}]_{\mathrm{0}}}{[\mathrm{I}]}$$

$$[59]$$

and after integration and rearrangement, we get

$$[M] - [M]_0 = \left(1 - \frac{k_p}{k_i}\right) ([I] - [I]_0) + \frac{k_p}{k_i} [I]_0 \ln\left(\frac{[I]}{[I]_0}\right) \qquad [60]$$

These are the basic equations derived from the equations of monomer and initiator consumption. Dispersion is given for the k_p/k_i ratio from 10^{-2} to 10^6 in figures presented in this classical work. The effect of the k_p/k_i ratios on dispersity $(\mathcal{D} = M_w/M_n)$ for one $[M]_0/[I]_0$ ratio (=100) is also discussed in a more recent paper by Hogen-Esch and Olah⁸⁹ from where **Figure 12** is reproduced.

As is often mentioned, dispersity is below 1.4 even for a relatively high k_p/k_i (e.g., 10⁴). The cited authors indicate that Gold's calculations are for irreversible initiation only. Reversibility in initiation may change the dispersity as D = f(conversion).

3.02.14.2 Dead-End Polymerization

The nonstationary conditions also appear when the initiator concentration becomes low enough, for example, when the half-lives of the propagating chains and of initiators become equal in the radical polymerization. In the radical polymerization, the rate of initiation could be determined in the following way.

From the general equations of radical polymerization:

$$-\frac{\mathbf{d}[\mathbf{M}]}{\mathbf{d}t} = k_{\mathrm{p}}[\mathbf{M}] \left(\frac{fk_{\mathrm{d}}[\mathbf{I}]}{k_{\mathrm{t}}}\right)^{1/2}$$
[61]

and $[I] = [I]_0 e^{-kdt}$.

$$-\ln(1-\alpha) = 2k_{\rm p} \left(\frac{f[{\rm I}]_0}{k_{\rm t} - k_{\rm d}}\right)^{1/2} (1 - e^{-k_{\rm d}t/2})$$
 [62]

$$n(1-\alpha) = 2k_p \left(\frac{f[I]_0}{k_t k_d}\right)^{1/2} (1-e^{-k_d t/2})$$
 [63]

where $\alpha = ([M]_0 - [M]/[M]_0)$.

1

Polymerization stops at $\alpha = \alpha_{\infty}$; then, $e^{-k_d t/2} = 0$. Thus,

$$-\ln(1 - \alpha_{\infty}) = 2k_{p} \left(\frac{f[I]_{0}}{k_{t}k_{d}}\right)^{1/2}$$
[64]

After dividing eqn [63] by eqn [64], and rearranging, we get

$$-\ln\left\{\frac{1-\ln(1-\alpha)}{\ln(1-\alpha_{\infty})}\right\} = k_{\rm d}\frac{t}{2}$$
[65]

Hence, k_d could be determined from these nonstationary conditions.

3.02.14.3 Double Nonstationary Polymerization

The cationic polymerization of vinyl monomers, particularly of styrene induced by trifluoromethane sulfonic acid (TfOH), provides an interesting case of nonstationary polymerization. The work that describes this case is given in a paper by Kunitake and Takarabe.⁹⁰ The kinetics was studied in the flow system by online monitoring of the concentration of both polystyryl



Figure 12 Effect of the k_p/k_i ratios on the molecular weight distributions at the monomer/initiator ratio of 100:1.⁸⁹

cations and monomers (in a very short time: fraction of a second).

First, a rise in transient absorption of styryl cation due to protonation was observed (Scheme 39). Between the rise and decay (α_{max} = 340 nm), there is a short period of stationary state (or smooth maximum), which is longer at low temperature and shorter at higher temperature.

Termination probably involves deprotonation (see Scheme 40). Deprotonation regenerates the acid and thus a kind of stationary state is attained in which formation of ion pairs is balanced by the deprotonation reaction. The monomer is being consumed, and since initiation is a bimolecular (second-order) reaction of TfOH with the monomer (Scheme 39) and termination is first order on active centers, decay of the transient takes place. Thus, the nonstationary period is followed by a short stationary period (actually, quasi-equilibrium) and with a final second nonstationary state (cf. Figure 13).

The presence of these nonstationary states gives access to all rate constants of elementary reactions: k_i , k_p , and k_t ; [TfOH] may be assumed to be invariant.

+ TfOH $\xrightarrow{k_1}$ CH₃- $\stackrel{\oplus}{CH}$, TfO



Figure 13 Time course of the formation of polystyryl cation and monomer conversion. Polymerization conditions: $10 \,^{\circ}$ C; 1,2-dichloroethane solvent; $[CF_3SO_3H]_0 = 2.4 \,\text{mmol I}^{-1}$; $[styrene]_0 = 0.391 \,\text{mol I}^{-1.90}$



The rate constant of propagation is simply determined from the usual equation:

$$\ln\left(\frac{[\mathbf{M}]_{t_1}}{[\mathbf{M}]_{t_2}}\right) = k_{\mathbf{p}}[\mathbf{P}^+]\Delta t \qquad [67]$$

Integrals can be determined graphically. This example is given since it nicely demonstrates the formation and decay of species absorbed at 340 nm. These species were assumed to be exclusively polystyryl cations. The rate constant of propagation calculated from these data is much lower than that described





by Faust in Chapter 3.15, as well as based on several measurements, including the 'clock' method. However, in his review, Faust quotes the work of Sigwalt and Moreau.⁹¹ It has particularly been taken into account that the cation–nucleophile combination may lead to a two-step reaction: formation of a complex and then its unimolecular rearrangement.

3.02.15 Chain Polymerizations and Structure of Macromolecules

Chain polymerizations often involve asymmetrically substituted monomers: unsaturated or cyclic. The propagation step in radical, ionic, or coordination polymerization may lead to the formation of different regio- and stereosequences and this phenomenon belongs to the fundamental behavior of chain polymerizations, which obviously for a long range does exist exclusively in macromolecules.

While honoring the discovery of stereospecific polymerization at the Nobel Prize awarding ceremony, the following was said for the Nobel laureates Karl Ziegler and Giulio Natta in 1963.⁹³ 'Nature synthesizes many stereoregular polymers, for example, cellulose and rubber. This ability has so far been thought to be a monopoly of Nature operating with biocatalysts known as enzymes. But now Professor Natta has broken this monopoly'.⁹²



There are several sources of differences in stereostructures of macromolecules. In the case of vinyl monomers, the newly formed covalent bond may involve the substituted carbon or methylene group of the monomer. These additions would lead, respectively, to 'head-to-head' or 'head-to-tail' propagation (regiospecificity) (Scheme 41).

The head-to-tail propagation is favored because when the substituents on the monomer molecule are bulky or polar groups, a steric or coulombic repulsion adds markedly to the head-to-head formation and consequently to the activation energy.

The total difference in activation energies is such, that at temperatures normally encountered in polymerizations the propagation proceeds almost entirely by a head-to-tail placement.

3.02.15.1 Stereochemistry of Propagation

Formation of the addition product may provide two stereoisomers when the polymer chain extensions occur in trans conformation ((a) and (b)) or in gauche arrangement ((c) and (d)), as shown in the Newman projection in Scheme 42.

Polymers may either prefer trans conformation or adopt a helical arrangement of gauche conformations. The helical structures of atactic macromolecules in solution could thus be due to the interaction of substituents but much more common is the helical structure of tactic molecules and macromolecules with intramolecular interactions, mostly H bonding. These phenomena are responsible for not only helical structures of polypeptides but also homochiral polylactides, assuming helical conformation due to weak H bonding between H atoms in the CH₃- groups and >C=O units. In contrast, when two centers are discussed, the formed unit is an isotactic or syndiotactic dyad when two carbon atoms from adjacent units have similar or different configurations. Thus, for three units there is either RRR (or SSS) isotactic triad or RSR (or SRS) syndiotactic triad. Four tactic triads could be envisaged. Thus, if the probability of the isotactic placement is α , then the probability of the syndiotactic placement would be $1 - \alpha$. Then the probabilities of the formation of the corresponding triads are α^2 , $(1-\alpha)^2$, and $2\alpha(1-\alpha)$. The relative concentrations of each triad are given by $\alpha/(1-\alpha) = H_t/2S_t = (I_t/S_t)^{1/2}$, where I_t , S_t , and H_t are, respectively, the fractions of monomers in iso-, syndio-, and hetero-triads and Id and Sd are the fractions in meso- and racemo-dvads).

The corresponding ratio of the rate constants k_{pi}/k_{ps} may be found from the physical measurements of H_t/S_t and I_t/S_t . The dependence on temperature would lead to the thermodynamic activation parameters for both kinds of placements.

In Volumes 3 and 4, there are chapters describing stereospecific polymerization of vinyl and cyclic monomers, formation of isotactic and syndiotactic polymers, and polymerization of racemic (as well as meso) cyclic monomers,

$$\dots - CH_2 - \overset{*}{CH} - X + CH_2 = CH - X \longrightarrow \dots - CH_2 - CH - CH_2 - \overset{*}{CH} (Head-tail)$$
$$\dots - CH_2 - \overset{*}{CH} - X + CH_2 = CH - X \longrightarrow \dots - CH_2 - CH - CH - \overset{*}{CH}_2 (Head-head)$$
$$\overset{*}{X} \overset{*}{X} \overset{*}{X}$$



(P denotes a polymer chain)

involving stereoselection and stereoelection. Phenomenal progress has been made and polymers from basic monomers (e.g., propylene and styrene) may be prepared as iso- or syndiotactic. Moreover, the 'metallocene revolution', as Corradini has called the more recent achievements, 93 allowed the understanding of the mechanism of stereocontrol with C2-symmetric and Cs-symmetric catalysts as well as a difference between C_2 -symmetric bridged and its unbridged analogue. Particularly impressive is a class of oscillating metallocene catalysts with rotating components.94 However, further studies have shown that the formation of the multiblock copolymers with stereoregular-stereoirregular blocks takes place only at particular conditions and that the activation energy for ligand rotation is in several originally used catalysts low and comparable to the activation energy of monomer addition.^{95,96} It has also been shown that it is possible to achieve chain growth in which each individual chain alternates the periods of growth on two different transition-metal catalysts with periods of dormancy, bearing formal resemblance to the interconversion in the controlled processes discussed in the previous sections. However, in the present instance, block copolymers are formed from the same monomer, whereas in CRP or CCVP, multiblocks can be formed from different monomers. These and post-metallocene catalysts, leading to living polymerizations, are described in other chapters of this volume.

3.02.16 Condensative Chain Polymerizations: Biopolymers

3.02.16.1 Definition

The definition of condensative chain polymerization is the repetition of Note 3 from the definition of chain polymerization, given in Section 3.02.8. As per Note 3, propagation in chain polymerization usually occurs without the formation of small molecules. However, cases exist where a low-molar-mass by-product is formed as in the polymerization of oxazolidine-2,5-diones derived from amino acids (commonly termed NCAs). When a low-molar-mass by-product is formed, the additional qualifier 'condensative' is recommended to form the term 'condensative chain polymerization'. The condensative chain polymerization (CCP) is discussed at the end of this chapter because of a particular character of the majority of involved processes.

There is a large class of chain polymerizations, already described in the general definition (cf. Section 3.02.8), in which in every step of monomer addition there is formation of a low-molar-mass side product, often removed from the polymerization systems, like in the nonequilibrium polycon-densation. In the general definition of condensative chain







polymerization, one example has been given, namely, polymerization of NCAs, which leads to poly(α -amino acid)s (Scheme 43). It is a chain process in which active species (most often anionic or coordination species) continuously add the NCA monomer molecules. This polymerization is described in detail in Volume 3 in a chapter by Deming. The qualifier 'condensative' comes from a certain similarity to polycondensation since the low-molar-mass side products are formed in both processes.

Closely related to the polymerization of NCA is the polymerization of cyclic carbonates, leading, under some conditions, to simple polyethers along with the evolution of CO_2 (Scheme 44).

Besides these ring-opening condensative chain polymerizations, there is an interesting class of CCP discovered by Yokozawa.⁹⁷ Its principle is based on the activation of the chain end after the monomer addition. If the activation is sufficient, then the rate of the next monomer molecule addition is higher than the rate of the reaction of monomers among themselves. The schematic presentation of this principle, following Yokozawa, is shown in **Scheme 45**. However, as is often forgotten, the major processes of the biopolymer formation, namely, of polypeptides, nucleic acids, and similar macromolecules as well as at least some poly(anhydro sugars) made either in nature or in laboratory, belong to the condensative chain polymerizations. For instance, the Merrifield solid-state method of polypeptide synthesis is based on the reactions illustrated in **Scheme 46**.

Thus, in every next step, repeating units are formed by adding a monomer molecule to the active end of the growing macromolecules. It could be either homopropagation if all the amino



acids are the same or (much more often) a kind of multimer formation when various amino acids are forming the chain. This process occurs automatically in special synthesizers.

3.02.17 Polymerize Chain Reaction. DNA Syntheses

Several methods of DNA synthesis are based on the same principle: addition of the one-end-protected nucleoside (monomer), deprotection, and so on. These methods are mentioned in this chapter only for the sake of completeness of the presentation.

The process bearing a name 'polymerase chain reaction' (PCR) is finally presented briefly. PCR involves several steps that are depicted in Scheme 47. In order to copy a certain part of the DNA molecule, the macromolecule containing this part is put into solution with starters (primers) prepared beforehand. The starters should be complementary to the fragments of the DNA single chains from both ends of the fragment to be copied. These starters are present in large excess to DNA macromolecules in order to avoid back formation of the double strand. All four nucleosides should also be present in the form of triphosphates, which are to be taken in the amount equal to the final desired mass of the DNA segments. The whole 'soup' is mixed in the presence of polymerase capable of surviving at the temperature needed for double-stranded DNA denaturation (95 °C). Indeed, the whole PCR process became possible after the discovery of enzymes capable of surviving at ~95 °C. When the temperature is increased to 95 °C, the double-stranded DNA gives, by denaturation, the individual single chains of DNA. Decreasing the temperature to the required temperature allows starters to take their positions at the complementary DNA fragments. The back formation of the double strands is not possible because the attached starters block this process. Then, at 72 °C the synthesis in the direction from position 3' to 5' starts on both single DNA macromolecules. Now, the primers in the DNA molecules close the corresponding unoccupied sites and the process continues. In this way, the desired segment is finally formed. From this very moment in every next step, only this particular fragment is repeated. Finally, after a certain number of these cycles, only the desired fragments are formed. In every step, the number of the desired units is doubled. Thus, in n cycles 2^n desired DNA macromolecules result. Since one complete event takes \sim 3 min, in 1 h (60 min) \sim 2²⁰ copies are produced. This is the reason why from a small amount of starting DNA macromolecules this PCR can produce millions (in 20 cycles) of copies in a relatively short time. One billion (10¹²) copies require 30 cycles. The above description also explains Scheme 47, thus completing the scheme.

Synthetic polymer chemistry might try to copy the fundamental features of PCR and apply them in polymer synthesis. This would be the most sophisticated of all the known chain polymerization processes.

3.02.18 Conclusions

In this chapter, fundamentals of chain polymerizations have been analyzed, starting from the discovery of a particular kind



of chemical reactions in such an apparently simple reaction, looking as an elementary bimolecular process, as $Cl_2 + H_2$. Although this volume describes the polymerizations of unsaturated monomers, several examples of kinetics of ring-opening polymerizations are given whenever the described processes are unique in fundamental aspects of chain polymerizations.

Several IUPAC and ACS definitions for fundamental phenomena have been quoted and the authors are convinced that while using them an equivalent of the Canon law '*Roma locuta causa finita*' should be applied in polymer chemistry to these definitions.

Chain polymerizations play an important role in the synthesis of industrial polymers; polyolefins, vinyl polymers, and products of ring-opening polymerizations. Moreover, syntheses of biopolymers, both in nature and in laboratory, use certain kinds of chain polymerizations, known as condensative chain polymerizations.

In spite of the spectacular progress in the last few decades, mostly related to the discovery of the living polymerizations of vinyl and cyclic monomers (including ring-opening metathesis) and then controlled radical and cationic polymerizations of vinyl monomers, the precision of the PCR is not yet achieved in other fields.

In a large majority of controlled chain polymerizations (except the living ones), there is a certain level of unavoidable, at least in 2011 onward, side reactions, namely, termination and/or irreversible chain transfers. For the future, one could hope to find ways of modifying the reactivities of the active centers in such a way that it will be possible to change the ratios of the rate constants of propagation and termination in radical polymerization, further decreasing the proportion of the dead chains at the complete monomer conversion. The PCR is the template-controlled polymerization (cf. Chapter 4.33 on template polymerization). Perhaps a combination of the template

and controlled processes in synthetic polymers could provide the PCR-like conditions. Thus, fast multiplication of the exact copies of the desired structures being the ultimate goal for the chain polymerizations of vinyl and cyclic monomers would be achieved.

Appendix: Lifetime and Half-Life: Definitions and Their Relationship

In the text, the term 'lifetime'(τ) has been used several times. The definition of lifetime is given in the GB.

'Lifetime' of a molecular entity, which decays by first-order kinetics, is the time needed for a concentration of the entity to decrease to 1/e of its original value, that is, $c_{(t=\tau)} = c_{(t=0)}/e$.

Statistically, the time period represents the life expectation of the entity. It is equal to the reciprocal of the sum of the first-order rate constants of all processes causing the decay of the molecular entity: $\tau = 1/\Sigma k$.

- Note 1: Mathematical definition: $\tau = 1/k = 1/(\sum_i k_i)$, with k_i being the first-order rate constants for all decay processes of the decaying state.
- Note 2: Lifetime is sometimes used for the processes that are not of first order. However, in such cases, the lifetime depends on the initial concentration of the entity or of a quencher, and therefore, only an initial or a mean lifetime can be defined. In this case it should be called 'decay time'.
- Note 3: Occasionally, the term 'half-life' $(\tau_{1/2})$ is used, representing the time needed for the concentration (*c*) of an entity to decrease to one half of its original value; that is, $c(t = \tau_{1/2}) = c(t = 0)/2$ (i.e., concentration *c* at $\tau_{1/2}$ = half of the original concentration at t = 0). For the first-order reactions, $\tau_{1/2} = \ln 2\tau$.

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3.03 Radical Reactivity by Computation and Experiment

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3.03.1	Introduction	39
3.03.2	Radical Stability	40
3.03.2.1	Definitions of Radical Stability	40
3.03.2.2	Experimental and Theoretical Procedures	41
3.03.2.3	Structure–Reactivity Trends	43
3.03.3	Other Important Properties	47
3.03.3.1	Polar Effects	47
3.03.3.2	Steric Effects	48
3.03.3.3	Bond Strength	50
3.03.4	Tools for Linking Structure to Reactivity	52
3.03.4.1	Overview	52
3.03.4.2	Curve-Crossing Model	52
3.03.4.3	Linear Free-Energy Relationships	54
References	· ·	56

3.03.1 Introduction

In recent decades there have been major advances in the techniques available for measuring the individual rate coefficients in free-radical polymerization processes. The development of pulsed laser polymerization and its many time-resolved variants have helped to provide direct access to the individual propagation and chain length-dependent termination rate coefficients, at least for homopolymerization processes.¹ Improvements in the accuracy, sensitivity, and resolution of analytical techniques such as size-exclusion chromatography, mass spectrometry, nuclear magnetic resonance, and electron paramagnetic resonance have helped to provide complementary data for measuring rate coefficients associated with many of the other reactions and side reactions (such as chain transfer processes) that occur in conventional and controlled radical polymerization processes.² At the same time, thanks to major advances in the accuracy and efficiency of quantum-chemical methods, coupled with rapidly increasing computational power, accurate first-principles prediction of the various individual rate coefficients is also becoming a reality (for a review, see e.g., Reference 3).

Collectively, these developments have been used to provide a wealth of kinetic data for many of the individual reactions in a wide range of radical polymerization processes. Where such data are available, they can be used to build kinetic models for optimizing the outcome of the polymerization process as a function of its reaction conditions. Nonetheless, in such optimization studies, the range of possible outcomes is bounded by the kinetic parameters associated with the specific reagents used (monomer, initiator, chain transfer agent, control agent, etc.). In many situations, and particularly controlled radical polymerizations, it is additionally necessary to optimize the chemical structures of the reagents. Short of performing major combinatorial chemistry inspired surveys of polymerizations involving all conceivable reagents, it is necessary to develop some level of understanding of the relationship between chemical structure and reactivity.

In this regard, it is worth noting that the exact relationship between chemical structure and reactivity is, of course, provided by quantum mechanics. However, due to its complexity, these links are not obvious through simple inspection of the Schrödinger equation itself. To determine the rate of any particular reaction, it is necessary to solve the relevant equations - usually a time-consuming process in its own right. To find the optimal reagent for a particular process, one would have to resort to repeatedly solving the Schrödinger equation for a wide range of chemical structures until a reagent with suitable characteristics was found. Used in this way, computational quantum chemistry is merely trial and error experimentation without the mess. As Roald Hoffman once put it: "(computational quantum chemistry offers) predictability, but ... not understanding".4 To understand the links between chemical structure and reactivity, simpler and more approximate theories are required.

This chapter is about the tools and theoretical frameworks available for performing structure-reactivity studies in radical polymerization. How does one go about explaining the outcome of a chemical process in terms of the properties of the reagents and their substituents? What do we know already about the influence of chemical structure on radical stability and reactivity in conventional and controlled free-radical polymerization? In what follows we first discuss the various methods for defining and measuring radical stability, including the familiar radical stabilization energy (RSE), along with some lesser-known alternatives, and explain the difference between stability and persistence. A large compilation of RSEs for carbon-centered radicals is presented and used to illustrate principal structure-reactivity trends. We then examine some of the other relevant properties of polymer radicals, including their polarities and steric properties, as well as discussing the main factors affecting bond strengths in polymerization-related reactions. Finally, it is shown how the stabilities of the propagating radicals combine with these other factors to determine the kinetics and thermodynamics of the principal radical reactions in both conventional and controlled radical polymerization processes.

3.03.2 Radical Stability

3.03.2.1 Definitions of Radical Stability

The propagating species in most free-radical polymerization reactions is a π -type carbon-centered radical in which the unpaired electron is located in a p-type orbital and, for a monomer of the general form CH₂=CXY, the sp²-hybridized radical center is substituted with the monomer substituents X and Y, and the remaining polymer chain (see Figure 1). The chemistry of free-radical polymerization is profoundly shaped by the effects of these substituents on the stability of the propagating radical, and the broader relationships between its stability and its reactivity in the various possible reactions and side reactions that occur.

In general terms, the stability or reactivity of species refers to its propensity to undergo chemical reactions, as assessed either on a thermodynamic basis or on a kinetic basis. For radicals, the thermodynamic stability is typically termed the stabilization energy, while the kinetic stability is typically termed the persistence.⁵ Strictly speaking, the stability of a species can only be unambiguously defined in the context of a specific balanced chemical reaction. However, through careful choice of the defining reaction, it is sometimes possible to use stabilities, as measured for one class of reactions, to help predict the kinetic and thermodynamic behavior of those species in other types of chemical reactions. In this section we will examine some alternative defining reactions for the RSE; in subsequent sections we will examine how these can be used to predict the kinetics and thermodynamics of radical polymerization processes.

The RSE^{2,5} is the most commonly used thermodynamic measure of relative radical stability. For a carbon-centered radical R•, the RSE is defined as the enthalpy change of the following isodesmic reaction under standard conditions (usually 298.15 K in the gas phase):

$$\mathbf{R} \bullet + \mathbf{H} - \mathbf{C}\mathbf{H}_3 \to \mathbf{R} - \mathbf{H} + \bullet \mathbf{C}\mathbf{H}_3$$
[1]

In essence, one compares the energy of the radical \mathbb{R}^{\bullet} to a reference species \bullet CH₃, and balances the reaction using the corresponding closed-shell species. An alternative (and completely equivalent) method for representing the standard RSE is as the difference of the corresponding R–H and CH₃–H bond dissociation enthalpies (BDEs).

$$RSE = BDE[CH_3 - H] - BDE[R - H]$$
[2]

Defined in this way, when the RSE for radical \mathbb{R}^{\bullet} is positive, \mathbb{R}^{\bullet} is said to be more stabilized than $\bullet CH_3$; if the RSE is negative, \mathbb{R}^{\bullet} is said to be less stabilized. Occasionally in the literature, this sign convention is reversed⁶ and it is therefore important to check the defining equation carefully when examining literature data.

Strictly speaking, the standard RSE measures the thermodynamic stability of the R^{\bullet} radical (relative to $\bullet CH_3$) toward



Figure 1 A π -type carbon-centered propagating radical in the homopolymerization of CH₂ == CXY.

hydrogen atom transfer reactions only, and includes contributions from the relative stabilities of the radicals, and the relative stabilities of the C–H bonds in R–H and CH_3 –H molecules that balance the reaction. However, it is normally assumed that since hydrogen is both small and relatively nonpolar, the differences in stability of the C–H bonds in R–H and CH_3 –H are minor and therefore cancel. Thus, for carbon-centered radicals at least, the RSE is generally regarded as a measure of the relative stabilities of the radicals alone. In support of this assumption, it is worth noting that RSEs have been used successfully in many studies to predict the stability and reactivity of radicals in other types of chemical reactions⁷ and trends in RSEs have been successfully analysed in terms of arguments involving only the radical species itself.⁶

Nonetheless, it should be emphasized that the use of RSEs to measure radical stability is based on an assumption (i.e., that the stabilities of the C-H bonds of the closed-shell species used to balance the reaction are very similar in R-H and CH₃-H), and this assumption may occasionally break down, particularly if polar and/or steric effects in R are significant. As an illustration, Figure 2 shows the relative stabilities of the alkyl radical series Me, Et, i-Pr, and t-Bu, as calculated using the standard RSE, and alternative definitions in which other types of closed-shell species (i.e., R-X and CH_3-X_1 , where $X = CH_{31}$ OH, F) are used to balance the reaction instead.⁸ As is clear from this graph, even the qualitative ordering of the RSEs is highly sensitive to the type of closed-shell species used to balance the reaction, implying that the contribution of the differences in stability of the R-X and CH₃-X bonds to the reaction energy is not insignificant.

In fact, in this example, there is a significant contribution to the stability of the R-X bond from resonance between its covalent (R-X) and ionic forms (R^+X^-), and this stabilization increases with the increasing electron-donating ability of R from Me < Et < i-Pr < t-Bu. This increasing stabilization of the bond counters the concurrent increasing stability of the radical that results from hyperconjugative stabilization of the unpaired electron. For electronegative X groups such as F and OH, the effect on bond strength is dominant, resulting in a decrease in the measured RSE from Me to t-Bu; for the less electronegative X groups (in this case H and CH_3), the effect on radical stability dominates and the expected increase in RSE from Me to t-Bu is observed. While the standard RSE (i.e., X=H) represents a limiting case for which the polar contribution to bond strength is smallest, this does not necessarily imply that polar effects are absent or that they may not be complicating RSE measurements for other radicals. Thus, consideration should always be given to possible substituent effects on the stability of the closed-shell species when analyzing structure-reactivity trends in RSEs.

Instead of assuming that the contributions of substituent effects on the closed-shell species are negligible, an alternative strategy is to correct for them directly. An advantage of this approach is that because we do not have to minimize the influence of the closed-shell species, it is then no longer necessary to choose reference closed-shell species where polar, steric, resonance, and other effects are minimal. As a result, we do not have to restrict our focus to π -type carbon-centered radicals, and hence a broader range of relative radical stabilities can be measured. The disadvantage is that the bond energy corrections themselves rely upon assumptions, and usually require



Figure 2 Radical stabilization energies (RSEs; 0 K, kJ mol⁻¹) for the series Me, Et, *i*-Pr, and *t*-Bu as calculated using various reactions of the general form: $R \cdot + X - CH_3 \rightarrow R - X + \bullet CH_3$, for X = H, CH_3 , 0H, and F. Data taken from Coote, M. L.; Pross, A.; Radom, L. *Org. Lett.* **2003**, *5*, 4689–4692.⁸

additional information to implement. Some of the main schemes that follow this approach include those of Rüchardt⁹ Zavitsas *et al.*¹⁰ and de Vleeschouwer *et al.*¹¹ For the exact implementation of these schemes, the reader is referred to the original references or a recent review.¹²

Broadly speaking, the Rüchardt⁹ scheme uses R-R BDEs to measure the stability of R. The advantage of using R-R in place of R-H is that polar effects in the reference compound are eliminated; the disadvantage is that corrections for steric strain in R-R are instead required, and in Rüchardt's⁹ scheme they are estimated from MM2 force-field calculations. Zavitsas et al.'s¹⁰ scheme also measures the stability of R• from R-R BDEs, but rather than resort to force-field calculations, the 'strainfree' R-R BDEs are estimated by application of Pauling's electronegativity equation¹³ to known values of the BDEs for R-OH, R-CH₃, CH₃-CH₃, CH₃-OH, and HO-OH. The scheme of de Vleeschouwer et al.11 expresses the BDE of compound A-B in terms of the stabilities of radicals A• and B• and a polar correction term. This term is based in part on Pauling's electronegativity scheme (as in Zavitsas et al.'s¹⁰ scheme) and in part on the nucleophilicity indices^{14,15} of A and B. In principle, the scheme can be applied to any A-B bond; in practice, while correcting for polar effects, this scheme ignores steric, resonance, and other contributions to A-B bond strength and this places some practical restrictions on the suitability of A-B.

The above radical stability schemes all measure the stabilization energy of a radical from its contribution to various bond energies; an alternative approach is to use measurements of the extent of delocalization of the unpaired electron. Since π -type carbon-centered radicals are stabilized by substituents that delocalize the unpaired electron, the more delocalized the unpaired electron is, the more stable the radical is likely to be. This allows one to focus solely on the radical, thereby avoiding complications from substituent effects on the closed-shell reference compounds used to balance the chemical reactions in the other radical stability schemes. However, its potential disadvantage is that it is not necessarily clear that alternative mechanisms of delocalization (π -delocalization, hyperconjugation, spin polarization, and anomeric interactions, and combinations thereof) will lead to the same increase in radical stability for the same degree of spin delocalization (π -delocalization energies, which might then be used in quantitative predictions of radical thermochemistry. Nonetheless, measurements of the extent of delocalization provide a useful complementary measure of radical stability that can be used to explore the physical basis of the other RSE schemes.

In summary, all measures of relative radical stability have strengths and weaknesses and should be used cautiously (for a detailed discussion of this problem, see Reference 17). Nonetheless, for simple π -type carbon-centered radicals these problems are relatively minor and a recent study has shown that all of the above schemes predict essentially the same structure-stability trends across a very broad range of primary, secondary, and tertiary carbon-centered radicals.¹² The standard RSE is the most widely used measure of relative radical stability and is the main focus of this chapter. In general, such RSEs are expected to provide an excellent qualitative guide and a reasonable quantitative guide to relative radical stabilities; however, it is important to keep in mind that contributions to the RSE from the closed-shell species can sometimes complicate or obscure structure-reactivity trends, particularly when steric and/or polar effects in R-H are significant.

3.03.2.2 Experimental and Theoretical Procedures

To measure the RSE of a radical R^{\bullet} , one needs to measure the enthalpy change of reaction (1) or equivalently determine the

R-H and CH₃-H bond dissociation enthalpies (BDEs). Experimentally, the equilibrium constant of this reaction can be measured as the ratio of its forward and reverse coefficients, which can in turn be measured using time-resolved laser flash photolysis. The enthalpic and entropic components can be obtained by studying the equilibrium constant as a function of temperature. Alternatively, if more convenient, the R-H BDE can be measured from the equilibrium constant of any hydrogen transfer reaction (e.g., $R - H + X \bullet \rightarrow R \bullet + X - H$) provided the BDE of the reference substrate (i.e., X-H) is already known. In either case, it should be noted that such measurements often carry assumptions that other side reactions (such as bimolecular termination) are either negligible or occur with known rate coefficients. Alternative strategies for accessing gas-phase experimental values of the R-H BDE include use of negative ion cycles whereby the BDE is deduced from separate measurements of the gas-phase acidity of RH and the electron affinity (EA) of R•, the latter available from negative ion photoelectron spectroscopy. The R-H BDE can also be obtained via the use of photoionization mass spectrometry to measure the appearance energy for the dissociation reaction: $RH \rightarrow R^+ + H^{\bullet} + e^-$. This appearance energy is then corrected for the ionization potential of R•, as measured by photoelectron spectroscopy. An excellent summary and evaluation of these experimental methods, together with a number of critically evaluated hydrocarbon BDEs, is provided by Berkowitz et al.¹⁸ A large database of experimental gas-phase BDEs has been published by Luo;19 further experimental thermochemical data including ionization energies and electron affinities of many species have been collected on the Internet by the National Institute of Standards and Technology (NIST).²⁰

Computational quantum chemistry is increasingly able to provide predictions of rates and equilibrium constants for chemical reactions with accuracies that are competitive with experiment.³ A major advantage of quantum chemistry is that reaction and activation-free energies, and their component enthalpies and entropies, can be accessed directly without having to make assumptions about the reaction scheme of the whole process. The disadvantage is that the accuracy of quantum-chemical predictions depends instead on the numerical approximations made in solving the Schrödinger equation. While extremely accurate methods are well known, these require large amounts of computer power and their computational cost scales rapidly with the size of the chemical system. The key to successful computational quantum chemistry is to choose a methodology that provides the best compromise between accuracy and expense.

The computational methodology outlined here has been identified on the basis of several assessment studies for BDEs and radical thermochemistry and kinetics in general,³ and was recently demonstrated to predict a large test set of gas-phase BDEs to within chemical accuracy.¹² Geometries and frequencies can generally be calculated at low levels of theory such as B3-LYP/6-31G(d); however, improved energies should be calculated using high-level *ab initio* procedures. Unfortunately, the DFT methods currently available fail even to predict the correct qualitative ordering in some BDEs and should be avoided for radical thermochemistry.²¹ Instead, the lowest cost methods that reliably deliver chemical accuracy are the *Gn*-type or the CBS-*n* type composite *ab initio* procedures, which approximate CCSD(T) (or equivalent) calculations with a large basis set

(e.g., triple zeta in the case of G3, quadruple zeta in the case of G4, and the extrapolated infinite basis set limit in the case of CBS-*n*) via a series of additivity approximations. In particular, we have found that the variant G3(MP2)-RAD²² usually offers chemical accuracy and is sufficiently economical that it can be applied to chemical systems of up to approximately 17 non-hydrogen atoms.

Where the species involved are too large for practical G3 (MP2)-RAD calculations, we have devised an accurate ONIOM-type approximation to use instead.²¹ In this procedure, the chemical reaction is divided into a reaction core that should contain the reaction center, any α-substituents, and any other groups directly conjugated with the reaction center; the remaining remote substituents are deleted and replaced with hydrogens. The core reaction is then studied at a high level of theory (in this case, G3(MP2)-RAD) and a lower-level ab initio procedure such as R(O)MP2 with a large triple zeta basis set; this latter procedure is also used to study the full system. The full system at the high level of theory is then approximated as the sum of the core system at the high level and the remaining remote substituent, as estimated at the lower level. The method works because the lower-cost procedure is only used to measure remote substituent effects, which are much less theoretically demanding than modeling the reaction center.

Having obtained geometries, frequencies and improved energies, the enthalpies, entropies, and free-energies can be easily calculated using the standard textbook formulae for the statistical thermodynamics of an ideal gas under the harmonic oscillator/rigid rotor approximation.^{23,24} For accurate rate and equilibrium constants, it is usually necessary to correct the harmonic oscillator results by treating all low-frequency torsional modes as hindered internal rotations (for details on how to do this, see e.g., Reference 25). In this chapter, we are primarily interested only in reaction enthalpies, where these corrections are less significant.

When solution-phase data are required, one has to perform additional calculations to obtain the free energies of solvation, which are then added to the accurate gas-phase free energies to obtain solution-phase free energies. Solvation energies are usually evaluated using continuum solvation models in which the effect of the solvent is studied by performing the calculation in the presence and then absence of an applied electric field to mimic the solution and gas phases. Most continuum models also include additional nonelectrostatic terms to model effects such as cavitation and dispersion. The resulting solvation energies depend on various empirical parameters (which, e.g., are used in conjunction with the properties of the solvent to determine the nature of the electric field) and these are obtained by fitting the resulting solvation free energies to an experimental test set. Because of their semiempirical nature, it is essential that a chosen solvation model is applied at the same level of theory at which it was originally parameterized (for a discussion, see Reference 26). Because solvent effects on radical reactions are relatively small (compared with ionic systems), most continuum solvation models usually perform well. However, for highly solvent-sensitive polymerizations, the new generation method COSMO-RS applied at its parameterization level of theory BP/TZP is recommended.²⁷

The experimental and theoretical procedures above can be used to obtain the bond energies for any of the bond

energy-based radical stability schemes. Spin density distributions can be obtained by applying an appropriate electron localization scheme to the wavefunction generated by quantum-chemical calculations. Typical schemes (in order of increasing sophistication) include Mulliken population analyses, Natural bond orbital analyses, and atoms-in-molecules theory. The former should be applied to minimal basis set calculations; the latter can be applied to higher quality wavefunctions, though the results are generally less sensitive to level of theory than are the bond energies. Experimentally, one can use ESR-derived α - and β -proton hyperfine coupling constants, as these are proportional to spin densities for planar carbon-centered radicals.²⁸ Of these, the β -proton hyperfine coupling constant is slightly less sensitive to deviations from planarity and therefore slightly more robust, although both measures give poor results for highly pyramidal radicals.¹⁶

3.03.2.3 Structure–Reactivity Trends

Due to their importance across a wide range of chemical and biological processes, the effects of primary substituents on the stability of carbon-centered radicals have been widely studied.^{6,12,29} A selection of representative RSEs for •CH₂X radicals, as taken from a recent high-level ab initio study of 192 different primary, secondary, and tertiary carbon-centered radicals,¹² are plotted in Figure 3 in order of increasing radical stability. It can be seen that the RSEs cover a 100 kJ mol⁻¹ range according to the nature of the substituent X. The most stable radicals tend to be substituted with π acceptor groups such as allylic double or triple bonds and/or conjugated phenyl groups. Radicals substituted with heteroatom lone-pair donor groups (such as oxygen, nitrogen, sulfur, and halogens) are also generally very stable, though the stabilities cover a broader range. The least stable radicals tend to be substituted only with pseudo- π acceptor substituents, such as alkyl groups and are often heavily fluorinated. In what follows, we explain how these different types of stabilization mechanism operate and result in the principal trends in the stabilities of π -type carbon-centered radical.

In general, a π -type carbon-centered radical is stabilized by substituents that can delocalize the unpaired electron either through donation of an adjacent lone pair into 2p(C•) or through donation of the unpaired electron into an empty π^* orbital or pseudo- π^* orbital. These two types of orbital interaction are illustrated in Figures 4(a) and 4(b), respectively. In addition to these resonance effects, the stability of a radical can also be affected by sigma withdrawal. Thus, an electronegative substituent (such as F) can exert a destabilizing influence by withdrawing electron density from the electron-deficient radical center through the sigma-bonding network (i.e., without the stabilizing benefit of delocalizing the unpaired electron). Many substituents, particularly lone-pair donor groups, exert both stabilizing resonance effects and destabilizing sigma inductive effects, and the net effect on radical stability depends on the competition between these two factors.

If we focus first on π acceptor substituents (Figure 4(a)), we see that the unpaired electron in 2p(C•) interacts with π orbital of an allylic double bond in a net stabilizing interaction that lowers the energy of the filled π orbital and raises the energy of the singly occupied 2p(C•) orbital. The unpaired electron also interacts with the empty π^* orbital in a net stabilizing

interaction that lowers the energy of the singly occupied 2p (C•) orbital and raises the energy of the empty π^* orbital. The overall result is a net stabilization in which the energy of the doubly occupied π orbital is lowered, that of the singly occupied 2p(C•) orbital is unchanged (as the effects of its interactions with π and π^* counter each other), and the energy of the empty π^* is raised. Similar interactions occur when the unpaired electron interacts hyperconjugatively with pseudo- π^* orbital is usually considerably higher than that of a π^* orbital, the strength of the interaction (and hence stabilization) is much weaker.

Among π acceptor substituents, the extent of stabilization depends on the energy differences between the unpaired electron and π and π^* orbitals. Equivalently, one can think in terms of the number and 'energy equivalence' of the resonance structures that can be drawn in which the electron is delocalized. Generally, the stabilization associated with allylic C=C double bonds is strongest, followed by phenyl rings and then C=C triple bonds; stabilization by C=O and C=N bonds tends to be weaker, followed by NO₂, SOR, and SO₂R. This is in part due to the differences in orbital energies and in part because their stabilization is countered to some extent by concurrent sigma withdrawal. Among the carbonyl groups, the order C(O)H>C $(O)R>C(O)OR>C(O)OH>C(O)NR_2$ reflects the increasing competition for the C=O bond from cross-conjugation with the ester substituent, as well the increasing sigma-withdrawal effects as additional oxygens are included.

Similar factors influence the stabilizing effect of the pseudo- π acceptor substituents. These substituents are of course considerably less stabilizing overall than π acceptor substituents as the energy of the pseudo- π (usually, the C–H sigma bond) is much lower than $2p(C\bullet)$ and the pseudo- π^* (the corresponding sigma antibonding orbital) is much higher. Among the pseudo- π acceptor substituents in Figure 3, the simple CH₃ group is the most stabilizing because there are three available C-H bonds, and the group has no additional substituents causing competing effects. Substituted alkyl groups such as CH₂R are usually less stabilizing because there are fewer available C-H bonds to undergo hyperconjugation and because R can potentially interact with the remaining C-H bonds and reduce their effectiveness as pseudo- π acceptors. The fluorinated substituents are least stabilizing of all due to the concurrent destablization through sigma withdrawal.

If we focus next on the lone-pair donor groups (Figure 4(b)), we note that the unpaired electron undergoes a three-electron interaction with the heteroatom pair that results in a lowering of the doubly occupied lone-pair orbital, a raising of the singly occupied 2p(C•) orbital and hence a net stabilization overall. The strength of the interaction depends on the energy difference between the $2p(C\bullet)$ and the heteroatom lone pair, and the stabilizing effect tends to decrease across the periodic table (e.g., from N > O > F, etc.). When one examines trends down the periodic table, the situation is more complex as, on the one hand, the differences in orbital energies decrease, but on the other hand, the overlap between the orbitals becomes less effective. Complicating matters further, most lone-pair donors are also capable of exerting a destabilizing influence through sigma withdrawal. This latter effect increases across and decreases down the periodic table in line with the electronegativities of the atoms involved.



Figure 3 Effect of X on the radical stabilization energies (RSEs; 0 K, kJ mol⁻¹) of •CH₂X. From Coote, M. L.; Lin, C. Y.; Beckwith, A. L. J.; Zavitsas, A. A. *Phys. Chem. Chem. Phys.* **2010**, *12*, 9597–9610.¹²

The net effect of these trends is that for lone-pair donor groups, stabilization decreases across the periodic table (i.e., from N > O > F) as decreasing lone-pair donation and increasing sigma withdrawal reinforce each other. Where sigma withdrawal is less significant (as in group 15 species), stabilization also decreases down the periodic table (i.e., N > P). However, in groups 16 and 17, sigma withdrawal becomes more important and relief of this destabilizing influence as one moves down the periodic table from row 2 to row 3 becomes the

dominant influence on radical stability (e.g., S > O and Cl > F). In all cases, beyond row 3, the benefit from decreasing sigma withdrawal becomes minimal and stability tends to decrease again due to less effective lone-pair donation (e.g., Cl > Br). Among functional groups with the same heteroatom, differences in stability arise due to the presence of additional sigma-withdrawing groups and also through cross-conjugation. Thus, for example, $OCOCH_3$ is less stabilizing than OH or OR due to competition for the lone pair in the former case.



Figure 4 Orbital interaction diagrams showing the stabilizing interaction between an unpaired electron and (a) a π acceptor substituent, and (b) a lone-pair donor substituent. From Bernardi, F.; Epiotis, N. D.; Cherry, W., *et al. J. Am. Chem. Soc.* **1976**, *98*, 469–478;^{29a} Henry, D. J.; Parkinson, C. J.; Mayer, P. M.; Radom, L. J. Phys. Chem. A **2001**, *105*, 6750–6756;^{29b} Coote, M. L.; Lin, C. Y.; Zipse, H. In *Carbon-Centered Free Radicals: Structure, Dynamics and Reactivity*, M. D. E. Forbes, Ed.; Wiley, 2010; pp. 83–104;^{29c} Hioe, J.; Zipse, H. *Org. Biomol. Chem.* **2010**, *8*, 3609–3617;^{29d} Poutsma, M. L. J. *Org. Chem.* **2011**, *76*, 270–276.^{29e}

The above discussion refers to the isolated effect of individual substituents on radical stability, as measured for singly substituted radicals of the form \bullet CH₂X. To predict their effect on radical stability when other substituents are also present, for example, as in a polymeric propagating radical of the form RC(X)(Y) \bullet or an intermediate reversible addition– fragmentation chain transfer (RAFT)-adduct radical of the form RSC \bullet (Z)SR', a few basic rules are helpful. Generally speaking, radical stability increases when additional stabilizing substituents are included; however, the total stability of the radical is not necessarily the sum of its parts. Instead, substituents can have diminished or enhanced effects in the presence of other groups depending on both steric effects and the relevant orbital interactions.

The orbital interaction between an unpaired electron and a lone pair or π system may affect the energy of the unpaired electron, which in turn can have consequences for its interactions with the other functional groups present. This is particularly the case when the interaction occurs with a lone pair, where the interaction results in the unpaired electron occupying a higher energy orbital than $2p(C\bullet)$ (see Figure 4(b)). In the case of the interaction with a π system, the effect on the energy of the unpaired electron is much smaller because interaction with the π bond tends to destabilize the unpaired electron by a similar amount to the stabilization caused by interaction with π^* . In the symmetrical case (as in Figure 4(a)), these effects cancel exactly; in most other cases there is a slight stabilization of the unpaired electron as the interaction with the π^* tends to be stronger.

As a result of these interactions, when an unpaired electron interacts with multiple lone-pair donors the net stabilization tends to be less than the sum of its parts as the rising energy of the unpaired electron increases the energy gap between this orbital and any subsequent lone pair. This has particularly important implications when understanding the stability of RAFT-adduct radicals, which, by their nature, are always substituted with two lone-pair donor substituents. Not only is the stabilizing influence of the two thiyl substituents much less than the sum of their parts (e.g., the RSEs of \circ CH₂SCH₃ and \circ CH(SCH₃)₂ are 40.7 and 61.1 kJ mol⁻¹, respectively),³⁰ but also the influence of any third lone-pair substituent that might be present as a Z-group is usually negligible. As a result, lone-pair donor/sigma acceptor substituents such as fluorine actually become net destabilizers when attached to the RAFT-adduct radical center because their stabilizing lone-pair donor effect is diminished by the presence of the thiyl groups while their concurrent destabilizing sigma-withdrawal effect remains. This technique for destabilizing the intermediate radical in RAFT can be exploited in the design of optimal RAFT agents for controlling monomers with disparate activities.³¹

For the same orbital-based reasons, when an unpaired electron interacts with a lone-pair donor and a π acceptor, the net result is often greater than the sum of its parts. This is because the interaction with the lone-pair donor raises the energy of the unpaired electron, bringing it closer to that of the π^* orbital. The resulting synergistic effect is also known as a captodative effect. Another way of understanding this effect is to note that when donor and acceptor substituents are both present, additional resonance structures are possible that are not present for pairs of lone-pair donors or pairs of π acceptors (see Figure 5). Even when other factors intervene to diminish synergistic effects, the most stabilized carbon-centered radicals tend to be substituted with both lone-pair donor groups and π acceptor groups. Thus, for example, RAFT-adduct radicals of the form RSC•(Z)SR' in which the Z-group is a π acceptor such as phenyl or cyano tend to have RSEs of 100 kJ mol⁻¹ or more.³⁰ Finally, since interaction between an unpaired electron and a π system usually has a minimal effect on the energy of an unpaired electron, the effects of multiple π acceptor groups tend to be reasonably additive except when steric effects are also important.



Figure 5 Resonance structures possible when a radical is substituted with two lone-pair NH_2 groups (donor/donor), two π acceptor CN groups (acceptor/acceptor), and a combination of one NH_2 and one CN group (donor/acceptor). It is clear that the donor/acceptor combination allows for additional resonance structures compared with either the donor/donor or acceptor/acceptor cases.

To understand steric effects on radical stability, it is important to note that when an unpaired electron interacts with π acceptor substituents, the unpaired electron has to orient itself in parallel with the 2p orbitals from which the π and π^* bonds have been formed, and this is usually best achieved when the radical center and π system are co-planar. The presence of multiple bulky groups that destabilize this planar geometry (or even prevent it from forming) will reduce the overall stability of the radical beyond that expected on the basis of the sum of its parts. When an unpaired electron interacts with lone-pair donor substituents, a slightly pyramidal radical center (up to 25° deviation from planarity in some cases) is favored. This type of angle reflects the best compromise between the demands of effective orbital overlap (requiring that the unpaired electron and lone pair are close to parallel with one another) and the fact that pyramidalization helps to lower the energy of 2p(C•), thereby decreasing the energy difference between this orbital and the heteroatom lone pair. Again if multiple bulky groups prevent this optimal geometry from forming, the stability will be less than the sum of its parts. In addition, because lone-pair donor groups and π acceptor groups tend to prefer these different

geometries around the radical center, the compromise that must be reached when both types of substituent are present can sometimes outweigh the synergistic benefits from their captodative orbital interactions.

Finally, the effect of the terminal and penultimate units on the stability of the propagating radical in free-radical polymerization can be understood in terms of the same basic rules above for multiply-substituted radicals. However, given their importance to radical polymerization, it is worth examining a few specific examples. **Figure 6** shows the RSEs for model unimeric (H–M•) and dimeric (H–M–M•) propagating radicals, as well as unimeric radicals bearing a cyanoispropyl group as an end group (Init–M•) (data taken from Reference 32.) These would be the types of radicals formed by initiation with azo-*bis*-isobutyronitrile. The radicals included are those derived from radical addition to the monomers (M): CH₂==CH₂ (Et), CH₂==CHPh (STY), CH₂==CHCOOCH₃ (MA), CH₂==C(CH₃)COOCH₃ (MMA), CH₂==CHCOOCH₃ (VA), CH₂==CHCONH₂ (AM), and CH₂==CHCOOH (AA).

From Figure 6, it is first noted that the basic trends in the stabilities of the propagating radicals are determined by the



Figure 6 Radical stabilization energies (RSEs; ΔH_{298}) for some model unimeric (H–M•) and dimeric (H–M-M•) propagating radicals, relevant to the polymerization of CH₂—CH₂ (Et), CH₂—CHPh (STY), CH₂—CHCOOCH₃ (MA), CH₂—C(CH₃)COOCH₃, CH₂—CHOCOCH₃ (VA), CH₂—CHCONH₂ (AM), and CH₂—CHCOOH (AA). Unimeric radicals with cyanoispropyl chain ends (Init–M•) are also shown. Lin, C.Y.; Coote, M.L. *Aust. J. Chem.* **2011**, *64*, 747–756.³²

primary radical substituents (i.e., the terminal group); subsequent penultimate effects are significant but not usually large enough to alter the basic trends. This is not surprising given that the penultimate unit is not conjugated with the radical center and can thus only exert its influence in an indirect manner. As might have been expected from Figure 3, the propagating radical in Et polymerization is the least stabilized, followed by that in VA polymerization. There is then a substantial increase in stability for propagating radicals in polymerization of non-alpha-methyl-substituted acrylic monomers (i.e., MA, AA, AM), and a further increase for MMA due to the additional alpha-methyl group. The propagating radical in STY polymerization is the most stabilized of those studied. The importance of radical stability in determining radical reactivity is evident in the fact that to a large extent these trends in radical stability are reflected in homopropagation rate coefficients for these monomers.

With two exceptions, VA and AM, the dimer radicals H-M-M• are slightly less stabilized than the corresponding unimer radicals H-M•. This is because in the unimer, which has the general form $CH_3-C(X)(Y)$, the CH_3 group exerts a hyperconjugative stabilizing influence. In the dimer radicals, one of the C-H bonds is replaced by the next monomer unit (i.e., CH₃-C(X)(Y)-CH₂-C $(X)(Y)\bullet$), which reduces the opportunity for hyperconjugative interactions and, at the same time, weakens the strength of those that remain by competing for them. The AM dimer radical provides an exception to this trend because the penultimate unit can undergo hydrogen bonding interactions with the nitrogen on the terminal unit. This in turn weakens the cross-conjugation interaction in the terminal unit, thereby increasing the ability of the carbonyl to stabilize the radical. The VA dimer also provides an exception to this general trend but for different reasons. Because OCOCH₃ group is relatively strong sigma acceptor, its presence in the penultimate position helps to enhance the hyperconjugative interactions of the beta C-H groups by destabilizing their sigma-bonding orbitals. For the same reason, when the penultimate unit of the propagating radical is a sigma-withdrawing cyanoispropyl initiator fragment (i.e., Init-M•), the radical tends also to be greater in stability compared with both the unimer (H–M•) and dimer (H–M–M•).

In summary, the stability of the propagating radical in free-radical polymerization, as well as other relevant radical intermediates, is profoundly affected by the nature of its primary substituents and, to a lesser extent, the nature of its more remote substituents. These effects, which have been widely characterized both experimentally and theoretically for small model radicals, can be readily understood in terms of the relevant orbital interactions and the impact of steric effects and other direct interactions (such as hydrogen bonding). In subsequent sections, we shall examine how these effects on stability translate into effects on reactivity; but in order to do this, we need to first characterize some of the other key properties of propagating radicals and the other reagents involved.

3.03.3 Other Important Properties

3.03.3.1 Polar Effects

In addition to the stability of a propagating radical, its reactivity and particularly its selectivity are shaped by its ability to donate or accept electron density. This so-called polar effect can be separated into a localized contribution and delocalized contribution: the localized contribution comes from a field effect through space or an inductive effect through a bond and the delocalized contribution can be seen as a resonance effect. This distinction is particularly important when considering the role of remote substituents (e.g., penultimate unit effects) in free-radical polymerization. Whereas resonance effects require conjugation to interact with the reaction center, inductive effects can act remotely, albeit with significantly reduced strength.

As in the case of radical stability, the usual method for measuring the polarity of a molecule or functional group is to study its effect on the kinetics or thermodynamics of a chemical reaction, carefully chosen so to be governed primarily by polar effects. The most widely used polar descriptors are Hammett constants, as originally derived from fitting to pK_a values of substituted benzoic acids by Hammett.³³ Hammett's basic eqn [3] relates the equilibrium constant (or rate constant) for a reaction of a species with substituent R to the same quantity for the same reaction but with R = H, where σ is the substituent constant and ρ is the reaction constant.

$$\log\left(\frac{K}{K_0}\right) = \sigma\rho \tag{3}$$

The substituent constants (known as Hammett constants) are measured for the acid-dissociation equilibrium of benzoic acid and its para- or meta-substituted derivatives, for which the reaction constant ρ is set to unity. Positive values of the Hammett constant indicate that the substituent is a better electron acceptor than H and can thus enhance acidity by helping to stabilize the carboxylate ion; negative values indicate that the substituent is a poorer electron acceptor than H (i.e., an electron donor instead). When the substituent R is in the para position, the resulting σ_p values are taken as a measure of the polar effect of the substituent based on its combined resonance and inductive properties. When the substituent R is in the meta position, the resulting σ_m values are taken as a measure of the polar effect of the substituent based largely on its inductive properties. When a substituent is in the ortho position, it is assumed that the substituent effects are influenced by steric properties also.

Hammett's original constants³³ are plotted in Figure 7, from which is seen that on the basis of their para values, CN and NO₂ are strong electron acceptors, followed by the halogens, which are weaker electron acceptors. Methyl (and other alkyl and aryl groups) are weak donors, while the alkoxy and amino substituents are strong electron donors. For CN and NO₂, the para value slightly exceeds the meta value, consistent with the notion that they owe their electron-withdrawing properties to both sigma and resonance effects that reinforce each other in the para position. In contrast, the heteroatom lone-pair donor substituents (including the halogens, O, and N) all have more meta values that are larger (i.e., more positive or less negative) than their para values, consistent with the notion that their lone-pair donor effect (a resonance effect) is countered by sigma withdrawal, the latter being most important for F and O. The methyl group also has a larger meta value than its para value indicating that it too has its electron donation by hyperconjugation countered by sigma withdrawal, though both effects are very small.



Figure 7 Meta- and para-Hammett constants for selected substituents. From Hammett, L. P. J. Am. Chem. Soc. 1937, 59, 96.33

A number of later variants of Hammett's model exist and a review of these and a large listing of the respective constants has been written by Hansch *et al.*³⁴ For example, Taft applied a modified Hammett model to the reaction rates of ester hydrolysis, in which the inclusion of a steric parameter allowed for a better isolation of the respective polar and steric effects of a substituent:

$$\sigma^* = \log\left(\frac{k_s}{k_{\rm CH_3}}\right)_{\rm B} - \log\left(\frac{k_s}{k_{\rm CH_3}}\right)_A$$
[4]

where k_s is the observed rate for the acid-catalyzed ester hydrolysis, k_{CH_3} is the rate of the reference methyl, and *A* and *B* stand for the acid- or base-catalyzed hydrolyses of carbonyl substituted esters, respectively. Charton further refined σ^* into localized and delocalized terms, where σ_U represents the localized inductive term,³⁵ and unknown polar descriptors can be obtained from fitting equations.³⁶ Although values for a large number of species are available and equations can be used to fit many more, use of the σ_U parameter is limited by the availability of experimental data, particularly for the larger species relevant to radical polymerization processes.

The gas-phase EA and ionization energy (IE) are also commonly used as electronic descriptors, and have the advantage that they are easily accessible from experiment as well as theory. The EA of X is defined as the energy required to detach an electron from the singly charged negative ion (i.e., energy change for the process $X^- \rightarrow X + e^-$); the IE is defined as the energy change when an electron is removed from a neutral atom or molecule in its ground state (i.e., energy change for the process $X \rightarrow X^+ + e^-$). Values of EA and IE are referred to as 'vertical' values, if the geometry of the ion is held constant at that of the neutral species, or 'adiabatic' values, if the geometry of the ion is allowed to relax.

The IE and EA both measure the stabilities of their respective ions relative to the neutral species, and hence will contain a significant contribution from the stability of X. As we will see below, this can actually be an advantage in structure-reactivity studies of radical polymerization as the influence of polar effects on radical reactions often depends on the relative energies of the electron configurations associated with X and X⁺ or X and X⁻. The most appropriate polar descriptor (i.e., IE or EA) for a given species in a given chemical direction will depend on the reaction of charge transfer. In cases where this direction can vary and a single descriptor is required, the global electrophilicity, ω , as defined by Parr *et al.*³⁷ is found from the following combination of IP and EA:

$$\omega = \frac{(\mathrm{IP} + \mathrm{EA})^2}{8(\mathrm{IP} - \mathrm{EA})}$$
[5]

Figure 8 shows the calculated gas-phase vertical IE and EA values for a representative set of primary alkyl radicals of the form •CH₂X, as obtained via high-level ab initio molecular orbital theory calculations.³⁸ The effects of the substituent X on the IEs in Figure 8 are broadly consistent with those of the corresponding Hammett values in Figure 7 but with some exceptions due to the complicating influence of radical stability and the enhanced role of sigma inductive effects. As expected, the highest IE values occur for •CH₂CN, because the CN substituent is a strong electron acceptor (through both sigma and resonance effects) is thus a poor stabilizer of the cation, compared with the radical. Radicals substituted with electron accepting carbonyl-containing substituents also have high IE values. At the other end of the spectrum, radicals substituted with heteroatom lone-pair donors (e.g., halogens and oxygens) substituents have lower IEs, as do radicals substituted with alkyl and aryl groups. These latter groups are better stabilizers than one might expect on the basis of their Hammett constants because their effects are not diminished by sigma withdrawal to the same extent as those of heteroatom lone-pair donors.

3.03.3.2 Steric Effects

Steric effects refer to the impact of nonbonded interactions on the kinetics and thermodynamics of chemical reactions. At a qualitative level, it is relatively straightforward to identify substituents that exert large or small steric effects just through


Figure 8 Vertical ionization energies (IEs) and electron affinities (EAs) of primary alky radicals •CH₂X.

examination of the degree of substitution and the bulkiness of the substituents involved. However, actually quantifying their magnitude and impact on a particular reaction is quite difficult, as steric effects rarely occur in the absence of other types of substituent effect. Steric effects were first determined to be an important variable in structure versus reactivity relationships after pioneering work by Taft,³⁹ who systematically studied the connection between steric effects and the rate constants of reactions. It was known that polar effects were not the only influence in Hammett's equation; therefore, Taft proposed that the relative rates of ester hydrolysis should also include a steric effect.³⁹ His first attempt to quantify the steric effect defined the average relative rate of acid-catalyzed ester hydrolysis as:

$$E_s = \log\left(\frac{k_s}{k_{\rm CH_3}}\right)$$
[6]

where k_s is the observed rate for the acid-catalyzed ester hydrolysis and k_{CH_3} is the rate using methyl as reference; these k_s are identical to those described in eqn [4]. Dubois standardized the measurement of conditions for ester hydrolysis and developed an improved steric descriptor, E'_s .⁴⁰ Later, the Charton steric descriptor v was designed from van der Waal's radii for MZ_n type of molecules and used to fit E'_s for asymmetrical molecules.⁴¹

In a similar approach to that for radical stabilization descriptors, isodesmic reactions have also been proposed to describe the steric effect. For example, Rüchardt and Beckhaus⁴² measured steric effects as the energy change of the following reaction:

$$R - CPh_3 + CH_4 \rightarrow R - H + CH_3 - CPh_3$$
[7]

This method proved unsuccessful due to the interference of resonance effects in R–CPh₃. Recently, Böhm and Exner⁴³ proposed a similar approach to evaluate the steric effect by calculating the reaction energy of a different isodesmic reaction:

However, steric constants calculated via this method also differ distinctly from Charton steric parameters,⁴⁴ as they probably contain significant contributions from the polar effect of R.

Spatial parameters offer a more direct approach to modeling the steric bulk of the system. In the field of organometallic chemistry, steric effects are often quantified through various molecular volume-based descriptors. While molecular volume (*V*) itself can be very poor descriptor for steric effect, the Tolman's cone angle, θ , of the molecule (shown in **Figure 9**) has been shown to be more successful.⁴⁵ Its value can be easily calculated using the van der Waal's radius of the relevant atoms. To use Tolman's cone angle to quantify the steric effect in π -type carbon-centered radicals, it is necessary to specify a Cone angle (θ) for •C (R₁) (R₂) (R₃) calculated using optimized structure of X–C (R₁) (R₂) (R₃)



Figure 9 Tolman's cone angle for an alkyl radical $\bullet C(R_1)(R_2)(R_3)$.

distance between the radical center and cone center. In organometallic chemistry, where this parameter is most widely used, a value of 2.28 Å is normally chosen as a typical metal ligand bond length. For radical polymerization applications, we recently showed that good results could be obtained by measuring the cone angle for R• from its optimized R–Cl geometry.⁴⁴ The values obtained in this way showed a good correlation with Charton steric parameters, and provided a useful steric descriptor in the development of linear free-energy relationships (LFERs) for nitroxide-mediated polymerization.

Some typical values of Tolman's cone angle (θ in radian) for a small set of primary, secondary, and tertiary alkyl radicals are provided in **Figure 10**. It is seen that the biggest effect on θ is the degree of substitution of the radical, with •CH₃ having the smallest value of those studied and, for a fixed substituent X, θ increasing from primary (•CH₂X) to secondary (•CH(CH₃)X) to tertiary (•C(CH₃)₂X). For the set of small radicals studied, the variation due to X is much smaller, though one would expect bigger variation if highly hindered species were considered (e.g., the cone angle for •C(C(CH₃)₃)₃ is as much as 3.6 rad).

3.03.3.3 Bond Strength

In simple terms, the thermodynamics of a chemical reaction depends on the energies of the bonds that are broken and the bonds that are formed. To understand structure-reactivity trends, particularly in radical reactions, it is helpful to look one step deeper than this, and to consider separately the contributions of the intrinsic bond strengths (e.g., as determined by orbital overlap, steric effects, polar effects, etc.) and the intrinsic stabilities of the reactants and product radicals (e.g., as measured using their RSEs). Thus, for example, the energy change for a transfer reaction of the form R•+X- $R' \rightarrow R-X + R'$ • is equal to the difference in the R'-X and R-X BDEs. As discussed already, these in turn will depend on any differences in the intrinsic strengths of the R'-X and R-X bonds, and any differences in the stabilities of the R'• and R• radicals. Whereas the contribution of the radical stabilities is the same in each case; when X = H, the contribution of the differences in bond strengths are negligible, but when X is an electronegative atom like fluorine, this contribution can be very significant. Understanding these distinctions is important if one wishes to use structure-reactivity studies in any genuine predictive capacity.

Substituent effects on the radical stabilities are discussed in Section 3.03.2; this section looks briefly at substituent effects on the principal bond energies involved in radical polymerization reactions. Measuring 'intrinsic' bond energies is as fraught as measuring radical stability. Whereas the overall BDE is an unambiguously definable quantity, the contributions to the BDE of intrinsic bond strength and intrinsic radical stability are not. Nonetheless, as we saw in Section 3.03.2, useful definitions of radical stability can be made, and these are helpful in analyzing structure-reactivity trends. In essence, if one can separate the contributions of radical stability and bond strength to the overall BDE, one can then predict the behavior of the relevant species when either the radical or the bond appear in other types of chemical reaction.

Like the RSEs, the most common method for measuring bond strengths is from the energies of carefully chosen chemical reactions. For example, π bond energies are frequently measured from the corrected hydrogenation energies.⁴⁶ In essence, one calculates the energy to destroy the double bond (A=B, say) by hydrogenation to the corresponding saturated compound (in this case, HA–BH). The energy of this reaction is then corrected by subtracting the energy of the H–H bond that is also lost, and adding the energies of the H–A and H–B bonds that are formed in the process. The energies of the H–H, H–A, and H–B bonds are approximated using the BDEs of the



Figure 10 Values of Tolman's cone angle (rad) for •CH₂X, •CH(CH₃)X, and •C(CH₃)₂X for various X. From Lin, C.Y.; Marque, S.R.A.; Matyjaszewski, K.; Coote, M.L., Macromolecules 2011, submitted (ma-2011-014996).³⁸

corresponding saturated compound. This of course raises a problem in that, as we saw in Section 3.03.2, these same energies depend on not only the energies of the H–A and H–B bonds but also on the stabilities of the A• and B• radicals. As a result, these need to be taken into account when analyzing trends in the π bond energies measured in this way. Nonetheless, in analyzing structure–reactivity trends within a homologous series, many of the additional contributions to the reaction energy do cancel and the resulting reaction energies do indeed reflect trends in bond strengths.

Other strategies for measuring bond strength include the examination of the energy difference between the relevant bonding and antibonding orbitals of the sigma or π bond being studied: the larger the energy gap the stronger the bond. As we will see in the next section, these energy gaps, usually approximated as the singlet-triplet excitation energies, are often directly relevant to predicting the barrier heights in radical reactions. For certain types of π bond, it is also possible to estimate π bond strength by rotating the bond by 90° so as to diminish to zero the overlap between the relevant orbitals, thereby 'turning off' the bonding interaction. There also exist a number of quantum-chemical approaches to calculate intrinsic bond energies, based on distributing the energy of a molecule among its constituent atoms, orbitals, and hence bonds.⁴⁷ Unfortunately, there is no unambiguous method for doing this and the existing schemes are not without problems.⁴⁸ This is an exciting but still a rapidly developing area of quantum chemistry, and an analysis of these energy decomposition schemes is beyond the scope of this chapter.

Clearly the most important factor influencing bond strength is the type of bond that is formed (i.e., whether it is a σ or a π bond) and the nature of the bonding atoms. Generally speaking, π bonds are weaker than σ bonds, due to greater overlap in the latter case. This is why most free-radical addition reactions are exothermic: the energy of π bond that is broken tends to be less than that of the σ bond that is formed and this dominates any other contributions (such as the differences in the stabilities of the reactant and product radicals). Based on singlettriplet excitation energies, the π bonds of triple-bonded systems (such as alkynes) are stronger than those of corresponding double-bonded systems (such as alkenes) because the shorter bond length in the former case affords greater overlap.⁴⁹ Overlap is also an important factor when comparing the energies within a series of sigma or π bonds. Usually, the best overlap occurs when orbitals from the same row of the periodic table interact with one another. Thus, for example, C=S double bonds are considerably weaker than C=C or C=O bonds, which is in turn why thiocarbonyl compounds are more reactive to radical addition than typical monomers and therefore function effectively as control agents in free-radical polymerization.50

Additional factors, particularly the opportunity for resonance stabilization, can also have a major impact on the resulting bond strengths. For example, as has already been noted above, the trends in alkyl halide bond strength depend heavily on the ability of the alkyl fragment to support resonance between the covalent (R–X) and ionic ($R^+ X^-$) configurations. Recently we studied this phenomenon, known as charge-shift bonding,⁵¹ for a broad range of group 14 and 15 chlorides and bromides including a large series of alkyl chlorides.⁵² The trends in bond strength were studied by comparing



Figure 11 Relative R–Br to R–H BDEs (gas phase, 298.15 K) for primary ($R^{\bullet} = \bullet CH_2X$), secondary ($R^{\bullet} = \bullet CH(CH_3)X$), and tertiary ($R^{\bullet} = \bullet C(CH_3)_2X$) R-groups.

the R–X halide BDE to the corresponding R–H hydride BDE. In this way, since R• is common, its stability does not affect the results. As an example, the R–Br BDE to R–H BDE ratios for a representative set of alkyl halides are plotted in **Figure 11**,⁵² from which it is seen that the R–Br bond is strengthened compared with the corresponding R–H bond as the electron donation capacity of R improves either through inclusion of additional methyl substituents (•CH₂X<•CH(CH₃)X<•C (CH₃)₂X) or replacing of X with a stronger electron donor. For the same reasons, as well as considerations of the differences in orbital energies and orbital overlap, the ratio of halide bond strength to hydride bond strength increases as one moves down the periodic table.⁵²

The trends within a homologous series of π bond energies are also dominated by the potential for resonance interactions with their substituents. A good example of this is in the RAFT process, where the stability (and hence reactivity) of the C=S double bond, varies considerably according to whether the RAFT agent (S=C(Z)SR) is substituted with Z-groups capable of undergoing resonance with the C=S π bond. Thus, in computational studies, we have shown that the effect of the Z-group on the π bond energy can be estimated from the energy change of the following isodesmic reaction:⁵³

$$S = C(Z)SCH_3 + H - CH_3 \rightarrow S = C(H)SCH_3 + Z - CH_3$$
 [9]

When this is used to calculate relative RAFT agent stabilities for a range of simple Z-groups, it is very clear that the most stable RAFT agents are those substituted with lone-pair groups (see **Figure 12**). These groups stabilize the π bond through resonance interactions of the form:

This interaction (and hence the corresponding RAFT agent stability) increases with the lone-pair donation ability of the substituent (i.e., N > O > S). It is also clear that when the lone-pair donor is imbedded in a π system that can compete



Figure 12 Effect of the Z-group on the stability (0 K, kJ mol⁻¹) of RAFT agents of the form S=C(Z)SCH₃.

for the lone pair (as in the imidazole and pyrrole Z substituents), the stability is greatly reduced. The stabilizing effect is also countered by sigma withdrawal, which is why the fluorine is much less stabilizing than the other lone-pair donor groups. Alkyl- and aryl-substituted RAFT agents are less stabilized as the interactions with the C=S bond are weaker or and those substituted negligible, with strong sigma-withdrawing groups (such as CN and CF₃) are least stable of all. These basic trends, coupled with the stabilities of the radicals involved, are useful for rapid evaluation of the effectiveness of a RAFT agent for a particular polymerization.⁵³ Similar isodesmic reactions can be used to study the effects of substituents on π bond energies in other situations.

3.03.4 Tools for Linking Structure to Reactivity

3.03.4.1 Overview

To establish the link between structure and reactivity for a given chemical reaction one needs to be able to characterize the relevant properties of the constituent reagents or functional groups. In the present chapter, we have introduced some simple techniques for quantifying the stability of a radical and also its polarity and steric properties; similar approaches can be used to quantify the relevant properties of some of the other relevant reagents in a given reaction. We have also introduced some simple rules for quantifying strengths of the various types of bonds that are broken and formed in a chemical reaction. Taken together, these various properties can allow us to predict (at least in qualitative terms) the thermodynamics of radical reactions - whether a particular reaction is likely to be exothermic or endothermic and whether it is likely to become more or less favored as the substituents are varied. In this section, we extend these concepts in two directions. First, we describe a qualitative theoretical framework for predicting the barrier heights of chemical reactions on the basis of the thermodynamics, and the other relevant properties of the reagents. Second, we show how the qualitative tools for predicting thermodynamics and kinetics can be placed on a more quantitative footing using semiempirical LFERs.

3.03.4.2 Curve-Crossing Model

The curve-crossing model, developed by Pross and Shaik, 54,55 is a theoretical framework for explaining barrier formation in chemical reactions. It is largely based on valence bond (VB) theory,⁵⁶ but also incorporates insights from qualitative molecular orbital theory.⁵⁷ The basic premise of the model is to represent the minimum energy path of a chemical reaction in terms of its principal resonance contributors. It is then possible to study the energy changes of each resonance configuration as the geometries of the species are changed from reactants through to the products; it is also possible to study the energy differences between the respective configurations and explain these in terms of the properties of the species involved (e.g., polarity, radical stability, steric factors, orbital overlap, etc.). By limiting the analysis to a small number of the most important resonance configurations, the model is approximate but sufficiently simple to aid qualitative understanding. At the same time, as the model is grounded in quantitative VB theory, it can be extended to a more rigorous and quantitative level through consideration of additional configurations and the interactions between them. In this chapter, we focus on the simple qualitative version of this analysis, as used to explain structure-reactivity trends and develop LFERs.

To understand the curve-crossing model, it is helpful to think of a chemical reaction as being comprised of a rearrangement of electrons, accompanied by a rearrangement of nuclei (i.e., a geometric rearrangement). We can then imagine holding the arrangement of electrons constant in its initial configuration (which we call the reactant VB configuration), and examining how the energy changes as a function of the geometry. Likewise, we could hold the electronic configuration constant in its final form (the product VB configuration), and again examine the variation in energy as a function of the geometry. If these two curves (energy vs. geometry) are plotted, we form a 'state correlation diagram'. The overall energy profile for the reaction, which is also plotted, is formed by the resonance interaction between the reactant and product configurations (and any other important low-lying configurations). State correlation diagrams allow for a qualitative explanation for how the overall energy profile of the reaction arises, and can then be used to provide a graphical illustration of how variations in the relative energies of the alternative VB configurations affect the barrier height. This in turn allows us to rationalize the effects of substituents on reaction barriers, and to predict when simple qualitative rules (such as the Evans-Polanyi rule⁵⁸) should break down.

For example, in a curve-crossing analysis of radical addition to alkenes, the principal VB configurations that may contribute to the ground-state wavefunction are the four lowest doublet configurations of the three-electron three-center system formed by the initially unpaired electron at the radical carbon (R) and the electron pair of the attacked π bond in the alkene (A).⁵⁹



The first configuration (*RA*) corresponds to the arrangement of electrons in the reactants, the second (*RA*³) to that in the products, and the others (R^+A^- and R^-A^+) to possible charge-transfer configurations. The state correlation diagram showing (qualitatively) how the energies of these configurations vary as a function of the reaction coordinate is provided in **Figure 13**.⁵⁹

To construct this plot for a specific system, we first note that the 'anchor points' (i.e., the quantitative energy differences between the various configurations at the reactant or product geometries) are generally accessible from quantum-chemical calculations. For example, the energy difference between the RA configuration at the reactant geometry, and the RA³ configuration at the product geometry, is simply the energy change of the reaction (i.e., the thermodynamics). The energy difference between the RA and RA³ configurations at the reactant geometry is the energy required to decouple the π electrons in C=C bond of the isolated alkene. This quantity can usually be approximated as the vertical singlet-triplet gap of the isolated alkene, since this configuration usually dominates wavefunction of the lowest energy triplet state. At the product geometry, the $RA - RA^3$ energy difference is also an excitation energy, this time relating to the coupling of the electrons in the formed sigma bond and concurrent coupling of one of these electrons with the unpaired electron instead. This quantity is more difficult to access without doing quantitative VB theory calculations, but could be related to the excitation energy of



Figure 13 State correlation diagram for radical addition to alkenes showing the variation in energy of the reactant (*RA*), the product (*RA*³), and the charge-transfer configurations (R^+A^- and R^-A^+) as a function of the reaction coordinate. The dashed line represents the overall energy profile of the reaction.

the relevant excited doublet state. The charge-transfer configurations can be anchored at the reactant geometry, where they are given as the energy for complete charge transfer between the isolated reactants. For example, the energy difference between the R^+A^- and the *RA* configuration at the reactant geometry would be given as the energy change of the reaction: $R+A \rightarrow R^++A^-$. It can be seen that the energy change of this reaction is simply the difference between the IE ($R \rightarrow R^+ + e^-$) of the donor species and EA ($A^- \rightarrow A + e^-$) of the acceptor.

While the anchor points in the diagram are obtained or at least approximated quantitatively, we generally interpolate the intervening points on the VB configuration curves qualitatively, on the basis of spin pairing schemes and VB arguments.⁵⁴ At this point it should be stressed that the overall energy profile for the reaction is of course quantitatively accessible from our quantum-chemical calculations. The objective of the curve-crossing model analysis is not to generate the overall reaction profile but to understand how it arises - and a qualitative approach to generating the VB configuration curves is generally adequate for this purpose. If we consider first the product configuration, its energy is lowered during the course of the reaction due to bond formation between the radical and attacked carbon. At the same time, the relative energy of the reactant configuration increases because the π bond on the attacked alkene is stretched, and this is not compensated for by bond formation with the attacking radical. The energies of the charge-transfer configurations are initially very high in energy, but are stabilized by Coloumb attraction as the reactants approach one another.

The overall energy profile for the reaction can be formed from the resonance interaction of these contributing configurations. In the early stages of the reaction, the reactant configuration is significantly lower in energy than the others and dominates the ground-state wavefunction. However, in the vicinity of the transition structure, the reactant and product configurations have similar energies, and thus significant mixing is possible. This stabilizes the wavefunction, with the strength of the stabilizing interaction increasing with the decreasing energy difference between the alternate configurations. It is this mixing of the reactant and product configurations which leads to the avoided crossing, and accounts for barrier formation. Beyond the transition structure, the product configuration is lower in energy and dominates the wavefunction. The charge-transfer configurations generally lie significantly above the ground-state wavefunction for most of the reaction. However, in the vicinity of the transition structure, they can sometimes be sufficiently low in energy to interact. In those cases, the transition structure is further stabilized, and (if one of the charge-transfer configurations is lower than the other) the mixing is reflected in a degree of partial charge transfer between the reactants. Since the charge distribution within the transition structure is accessible from quantum-chemical calculations, this provides a testable prediction for the model.

Using this state correlation diagram, in conjunction with simple VB arguments, the curve-crossing model can be used to predict the influence of various energy parameters on the reaction barrier. For radical addition to alkenes,⁵⁹ the barrier depends mainly on the reaction exothermicity (which measures the energy difference between the reactant and product configurations at their optimal geometries), the singlet–triplet gap in the alkene (which measures the energy difference between the reactant geometry), and the relative energies of the possible charge-transfer configurations. The effects of individual variations in these quantities are illustrated graphically in **Figure 14**. It can be seen that the barrier height is lowered by an increase in the reaction

exothermicity, a decrease in the singlet-triplet gap, or a decrease in the relative energy of one or both of the charge-transfer configurations (provided that these are sufficiently low in energy to contribute to the ground-state wavefunction).

A strategy for understanding the effects of substituents in the barriers of radical reactions, such as addition, is to calculate these key quantities (i.e., the reaction exothermicity, the singlet-triplet excitation gap of the closed-shell substrate(s), and the energy for charge transfer between the reactants), and look for relationships between these quantities and the barrier heights. In this way, one could establish, for example, the extent of polar interactions in a particular class of reactions. For example, the curve-crossing analysis of radical addition reactions, which is reviewed in detail elsewhere,⁵⁹ indicates that, in the absence of polar interactions, the barrier height depends on the reaction exothermicity, in accordance with the Evans-Polanyi rule.58 However, for combinations of electron-withdrawing and -donating reactants, polar interactions are significant, and cause substantial deviation from Evans-Polanyi behavior. The curve-crossing model has been used to explain the relative reactivity of the C=C, C=O, and C=S bonds (which is of relevance to RAFT polymerization),⁵⁰ and to examine why alkynes are less reactive to addition than alkenes.⁴⁹ In these cases, the differing singlet-triplet gaps of the alternative substrates are also important in governing their relative reactivities. Curve-crossing studies have also been applied to various types of hydrogen abstraction reactions,⁶⁰ and, depending upon the substituents, the singlet-triplet gaps (in this case of both the reactant and product substrates), exothermicities and polar interactions have all been found to be important in governing reactivity in these reactions. As shown below, the insights from curve-crossing model studies such as these can be used to underpin the development of semiempirical LFERs.

3.03.4.3 Linear Free-Energy Relationships

In this chapter, we have outlined a number of qualitative concepts for predicting thermodynamics and kinetics of chemical reactions in terms of the underlying properties of the reagents



Figure 14 State correlation diagrams showing separately the qualitative effects of (a) increasing the reaction exothermicity, (b) decreasing the singlettriplet gap, and (c) decreasing the energy of the charge-transfer configuration. For the sake of clarity, the adiabatic minimum energy path showing the avoided crossing, as in Figure 13, is omitted from (a) and (b).

and their functional groups. We have also shown how these properties can be quantified using various types of descriptors. To turn these qualitative concepts into more quantitative tools for predicting thermochemistry and/or kinetics, one can of course revert to direct calculation via quantum chemistry. However, as such calculations are time consuming and not always convenient, it is often helpful to develop semiempirical equations which are fitted to known experimental data and used then to predict the behavior of new related systems from measurement of their underlying properties alone. These latter equations are generally referred to as LFERs. The term 'linear' in this context refers to the fact that the key underlying assumption of an LFER is that the kinetics and/or thermodynamics of a reaction is determined by the properties of the isolated reagents. That is, the whole is the sum of its parts. This is clearly a simplification that ignores the possibility for specific interactions (such as hydrogen bonding, or particular stereoelectronic effects) that only occur when particular types of reagents are present together. For this reason, LFERs should always be used with caution and their final predictions backed by direct experimental and/or direct quantum-chemical testing. Despite these potential shortcomings, LFERs often describe experimental observations well and in a manner that aids understanding, and often have a significant degree of predictive capacity.

The key to developing an LEFR is to begin with a list of the types of factors that could affect a particular reaction. Thus, based on the work reviewed in this chapter, one might assume that the effect of the alkyl group on the enthalpy of an alkyl bromide bond-dissociation reaction might depend on its radical stability, its polarity, and steric properties. The barrier heights of a series of bromine transfer reactions are likely to depend not only on the enthalpy changes above but also on the intrinsic bond strengths of the breaking and forming alkyl bromide bonds. The potential for charge-transfer interactions in the transition structures would also be potentially important and might entail the inclusion of polar descriptors for the alkyl bromides as well as the alkyl radicals (i.e., as used to model the reaction enthalpy).

Having gathered this list of factors, one would then collect (from the literature or from theory or experiment) the values of the descriptors that quantify these properties. Thus, for an LFER for an alkyl bromide BDE, one might choose to obtain RSE values for the alkyl radicals from one of the large compilations cited in this chapter,^{6,12,19} the IE values of the alkyl radicals from the NIST database,²⁰ and estimates of Tolman's cone angles from simple force-field calculations (that can be performed on a desktop computer using commercial software suitable for a nonexpert user). For an LFER for predicting the barrier height of the corresponding transfer reaction, it might be additionally necessary to obtain values of the EA values of the alkyl bromides (also from NIST²⁰) and their singlet–triplet excitation energies (either from the literature, or from theory or experiment).

Having obtained values of the descriptors for each of the potentially relevant properties, one then constructs an equation in which the reaction energy or barrier height is expressed as a linear combination of the descriptors. Thus, in the alkyl bromide BDE example, one might develop an equation: $BDE = aRSE + bIE + c\theta + d$, where the RSE, IE, and Tolman's cone angle (θ) are the properties of the alkyl radical. The empirical parameters (a, b, c, and d in this case) are then

determined by fitting the LFER to a set of reaction energies or barriers (in this case alkyl bromide BDEs), as obtained from accurate quantum-chemical calculations or experiment. In doing this, one needs to employ standard statistical methods for checking the goodness-of-fit of the equation to the data, and checking the statistical significance of the individual parameters. If an equation fits poorly, one might need to consider the inclusion of additional descriptors (so as to take into account additional properties) and/or improved versions of the existing descriptors (e.g., replacing IE with EA). If descriptors are statistically redundant, they should be removed from an equation and the equation refitted to the data. In developing an LFER, it is important to test its predictive capacity by using it to predict results for systems that are known but which have not been included in the training set.

LFERs have been developed for describing a number of important reactions relevant to radical polymerization. For example, Marque et al.⁶¹ have developed a series of simple equations for predicting the rate coefficients for the forward and reverse combination reactions between alkyl radicals and nitroxides in terms of the Rüchardt radical stability parameter and the Charton polar and steric parameters of the alkyl radical, and the Hammett polar inductive parameters and Taft steric parameters of the nitroxides. The utility of these equations was highlighted when they were used successfully in the design of a nitroxide capable of controlling the polymerization of methyl methacrylate.⁶² Recently, a new version of this LFER has been developed in which the existing descriptors have been replaced with more easily accessible ones, and its predictive capacity has been expanded to include simultaneous variation of the nitroxide and alkyl radical structure.⁴⁴ A further extension of this LFER to other types of controlled radical polymerization process, including atom transfer radical polymerization and RAFT radical polymerization is currently in development.³⁸

Finally, it is worth noting that LFER relationships can be developed in which the descriptors are themselves defined through fitting the same equations to reference data. Thus, for example, the Hammett eqn [3] in Section 3.03.3.1 is an example of a general LFER in which the Hammett parameters are themselves obtained by fitting to a reference set of data for which the reaction constant is arbitrarily set at unity. These Hammett parameters are then used as descriptors and the reaction constant as a fit parameter when fitting to sets of equilibrium or rate constants for other chemical reactions.

In the radical polymerization field, a prominent such example is the Q-e scheme,⁶³ and subsequent variations on this scheme such as the patterns of reactivity.⁶⁴ These schemes were designed for predicting terminal model reactivity ratios in free-radical copolymerization. The terminal model assumes that the propagation rate coefficient in free-radical polymerization depends only on the nature of the terminal unit of the radical and the monomer.⁶⁵ On the basis of this assumption, the propagation kinetics depends on the rates of just four distinct types of propagation reaction in a binary copolymerization, k_{ii} and k_{ii} (which correspond to a propagating radical terminated with a terminal unit i reacting with either monomer i or monomer j, respectively) and k_{ii} and k_{ii} (which correspond to a propagating radical terminated with a terminal unit j reacting with either monomer i or monomer j, respectively). The basic idea in the Q-e scheme is that this propagation rate coefficient in turn depends on the 'intrinsic reactivity' P_i of the

radical, the intrinsic reactivity Q_j of the monomer, and an interaction term dependent on the polarities e_i and e_j of the radical and monomer. These polar descriptors are assumed to be the same regardless of whether '*i*' and '*j*' are acting as monomers or propagating radicals. The resulting propagation rate coefficient for the general reaction of radical *i* reacting with monomer *j* is given by eqn [12] and the terminal model reactivity ratios are thus given by eqn [13].

$$k_{ij} = P_i Q_j \exp(-e_i e_j)$$
^[12]

$$r_{i} = \frac{k_{ii}}{k_{ij}} = \frac{P_{i}Q_{i}\exp(-e_{i}e_{i})}{P_{i}Q_{j}\exp(-e_{i}e_{j})} = \frac{Q_{i}}{Q_{j}}\exp[-e_{i}(e_{i}-e_{j})]$$
[13]

Values of Q = 1.00 and e = -0.80 are then defined for styrene as a reference, and other Q and e values for all other monomers are obtained by fitting the scheme to an experimental data set of terminal model reactivity ratios.

Notwithstanding the demonstrated importance of penultimate unit effects⁶⁶ and solvent effects on propagation,⁶⁷ both of which are neglected in the terminal model and hence the Qe scheme, the basic principles of the Q-e scheme are consistent with the predictions of the curve-crossing model, as outlined in Section 3.03.4.2. By comparison, one might assume that the polarity terms quantify the role of charge-transfer configurations in the transition state, the intrinsic reactivity of the radical is related to radical stability, and the intrinsic reactivity of the monomer might be taken partially as a measure of its singletriplet gap and partially as the overall energy cost of breaking the π bond, both of which are likely to be correlated with one another within a series of propagation reactions. For these reasons, the scheme works reasonably well for most monomers, though with occasional problems. Indeed, this is a common feature of LFERs. In developing such equations it is necessary to make several simplifications and approximations, so as to make the equations tractable. While these simplifications can compromise accuracy, they do aid understanding and, provided they are used cautiously, they do have a useful role to play in radical polymerization.

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Biographical Sketch



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3.04 Radical Polymerization

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3.04.1	Introduction	60
3.04.2	Initiation	63
3.04.2.1	The Initiation Process	64
3.04.2.1.1	Reaction with monomer	64
3.04.2.1.2	Fragmentation	66
3.04.2.1.3	Reaction with solvents, additives, or impurities	66
3.04.2.1.4	Effects of temperature and reaction medium on radical reactivity	67
3.04.2.1.5	Reaction with oxygen	67
3 04 2 1 6	Initiator efficiency in thermal initiation	67
3 04 2 1 7	Photoinitiation	68
3 04 2 1 8	Care reaction and initiator-derived by-products	68
3 04 2 1 9	Primary radical termination	00
2 0/ 2 1 10	Transfer to initiator	60
2.04.2.1.10	Initiation in beterogeneous polymerization	70
3.04.2.1.11	The Initiation	70
3.04.2.2	The miniators	71
3.04.3	Propagation	/ 1
3.04.3.1	Stereosequence isomerism – lacticity	/ 1
3.04.3.1.1	Terminology and mechanisms	/1
3.04.3.1.2	lacticities of polymers	75
3.04.3.2	Regiosequence Isomerism – Head versus Tail Addition	76
3.04.3.2.1	Monoene polymers	76
3.04.3.2.2	Conjugated diene polymers	78
3.04.3.3	Structural Isomerism – Rearrangement	79
3.04.3.3.1	Cyclopolymerization	79
3.04.3.3.2	Ring-opening polymerization	80
3.04.3.3.3	Intramolecular atom transfer	80
3.04.3.4	Propagation Kinetics and Thermodynamics	81
3.04.3.4.1	Polymerization thermodynamics	81
3.04.3.4.2	Measurement of propagation rate constants	83
3.04.3.4.3	Dependence of propagation rate constant on monomer structure	84
3.04.3.4.4	Chain length dependence of propagation rate constants	84
3.04.4	Termination	85
3 04 4 1	Badical–Badical Termination	86
3 04 4 1 1	Termination kinetics	86
3 04 4 1 2	Dispronortionation versus combination	94
3 04 4 2	Inhibition and Retardation	96
3 04 5	Chain Transfer	07
20451	The Chain Transfer Process	07
2 04 5 1 1	Mageuroment of transfer constants	00
2.04.5.1.1	Hemolutia substitutian ahain transfor	101
3.04.3.1.2 2.04.5.1.2	Addition, fragmentation chain transfer	101
3.04.3.1.3 2.04.5.1.4	Audition-Indyneniation chain transfer	101
3.04.5.1.4	Abstraction—iragmentation chain transfer	102
3.04.5.1.5	Catalytic chain transfer	102
3.04.5.1.6	Iranster to monomer	103
3.04.5.1.7	I ranster to polymer	103
3.04.5.1.8	I ransfer to initiator	104
3.04.6	Reversible Deactivation Radical Polymerization	104
3.04.6.1	Living? Controlled? Mediated?	104
3.04.6.2	lests for Living (Radical) Polymerization	105
3.04.6.3	Agents Providing Reversible Deactivation	106
3.04.6.4	Deactivation by Reversible Coupling and Unimolecular Activation	107
3.04.6.4.1	Kinetics and mechanism	107
3.04.6.4.2	Nitroxide-mediated polymerization	108
3.04.6.5	Atom Transfer Radical Polymerization	109
3.04.6.5.1	Molecular weights and distributions	110

3.04.6.6	Reversible Chain Transfer	110
3.04.6.6.1	Molecular weights and distributions	111
3.04.6.6.2	ThiocarbonyIthio RAFT	111
References		113

3.04.1 Introduction

This chapter has been largely compiled, with permission and some minor updating, from the introductory sections of the corresponding chapters in Moad and Solomon's *The Chemistry of Radical Polymerization*.¹ Most of the examples, data, and detailed discussion have been omitted as have the chapters on (small) radical reactions, copolymerization, and control of polymerization. The reader is referred to the original work¹ for more information.

From an industrial standpoint, a major virtue of radical polymerizations is that they can often be carried out under relatively undemanding conditions. In marked contrast to ionic or coordination polymerizations, radical polymerization exhibits a tolerance of trace impurities. A consequence of this is that high-molecular-weight polymers can often be produced without removal of the stabilizers present in commercial monomers, in the presence of trace amounts of oxygen, or in solvents that have not been rigorously dried or purified. Indeed, radical polymerizations are remarkable among chain polymerization processes in that they can be conveniently conducted in aqueous media.

It is this apparent simplicity of radical polymerization that has led to the technique being widely adopted for both indusof the 19th century. However, the concept that these were materials of high molecular weight took longer to be accepted. Staudinger was one of the earliest and most strident proponents of the notion that synthetic polymers were highmolecular-weight compounds with a chain structure and he did much to dispel the then prevalent belief that polymers were composed of small molecules held together by colloidal forces.³ Staudinger and his colleagues are also often credited with coming up with the concept of a chain polymerization. In an early paper in 1920, he proposed that polymer chains might retain unsatisfied valencies at the chain ends (2).⁴ In 1929, it was suggested that the monomer units might be connected by covalent linkages in large cyclic structures (3) to solve the chain-end problem.⁵ In 1910, Pickles⁶ had proposed such a structure for natural rubber. However, by 1935 it was recognized that polymers have discrete functional groups at the chain ends formed by initiation and termination reactions.⁷ IUPAC recommendations suggest that polymers derived from 1,1-disubstituted monomers CXY=CH₂ (or CH₂=CXY) be drawn as 1b rather than as 1a. However, formula 1a follows logically from the traditional way of writing the mechanism of radical addition (e.g., Scheme 1). Because of the focus on mechanism, the style 1a has been adopted throughout this book.



trial- and laboratory-scale polymer syntheses. Today, a vast amount of commercial polymer production involves radical chemistry during some stage of the synthesis, or during subsequent processing steps. These factors have, in turn, provided the driving force for extensive research efforts directed toward more precisely defining the kinetics and mechanisms of radical polymerizations. The aim of these studies has been to define the parameters necessary for predictable and reproducible polymer syntheses and to give better understanding of the properties of the polymeric materials produced. With understanding comes control. Most recently, over the last 15 years, we have seen radical polymerization moving into new fields of endeavor where control and precision are paramount requirements. Indeed, these aspects now dominate the literature.

The history of polymers, including the beginning of addition and of radical polymerization, is recounted by Morawetz.² The repeat unit structure (1) of many common polymers, including polystyrene (PS), poly(vinyl chloride) (PVC), and poly(vinyl acetate) (PVAc), was established in the latter half In the period 1910–50, many contributed to the development of free-radical polymerization.² The basic mechanism as we know it today (Scheme 1) was laid out in the 1940s and 1950s.^{8–10} The essential features of this mechanism are initiation and propagation steps, which involve radicals adding to the less substituted end of the double bond ('tail addition'), and a termination step, which involves disproportionation or combination between two growing chains.

In this early work, both initiation and termination were seen to lead to formation of structural units different from those that make up the bulk of the chain. However, the quantity of these groups, when expressed as a weight fraction of the total material, appeared insignificant. In a polymer of molecular weight 100 000, they represent only $\sim 0.2\%$ of units (based on a monomer molecular weight of 100). Thus, polymers formed by radical polymerization came to be represented by, and their physical properties and chemistry interpreted in terms of, the simple formula (1).

However, it is now quite apparent that the representation (1) while convenient, and useful as a starting point for



Scheme 1

discussion, has serious limitations when it comes to understanding the detailed chemistry of polymeric materials. For example, how can we rationalize the finding that two polymers with nominally the same chemical and physical composition have markedly different thermal stability? Poly(methyl methacrylate) (PMMA; (1, X=CH₃, Y=CO₂CH₃) prepared by anionic polymerization has been reported to be more stable by some 50 °C than that prepared by a radical process.¹¹ The simplified representation (1) also provides no ready explanation for the discrepancy in chemical properties between lowmolecular-weight model compounds and polymers even though both can be represented ostensibly by the same structure (1). Consideration of the properties of simple models indicates that the onset of thermal degradation of PVC (1, X=H, Y=Cl) should occur at a temperature 100 °C higher than is actually found.¹²

Such problems have led to a recognition of the importance of defect groups or structural irregularities. These groups need not impair polymer properties; they are simply units that differ from those described by the generalized formula (1).^{13–17} If we are to achieve an understanding of radical polymerization, and the ability to produce polymers with optimal, or at least predictable, properties, a much more detailed knowledge of the mechanism of the polymerization and of the chemical microstructure of the polymers formed is required.¹⁷

Structural irregularities are introduced into the chain during each stage of the polymerization and we must always question whether it is appropriate to use the generalized formula (1) for representing the polymer structure. Obvious examples of defect structures are the groups formed by chain initiation and termination. Initiating radicals (which are formed from those initiator- or transfer agent-derived radicals that add monomer so as to form propagating radicals (see Section 3.04.3)) are formed not only directly from initiator decomposition (Scheme 1) but also indirectly by transfer to monomer, solvent, transfer agent, or impurities (Scheme 2).



In termination, unsaturated and saturated ends are formed when the propagating species undergo disproportionation and head-to-head linkages when they combine, and other functional groups may be introduced by reactions with inhibitors or transfer agents (Scheme 2). In-chain defect structures (within the polymer molecule) can also arise by copolymerization of the unsaturated by-products of initiation or termination.

The generalized structure (1) also overestimates the homogeneity of the repeat units (the specificity of propagation). The traditional explanation offered to rationalize structure (1), which implies exclusive formation of head-to-tail linkages in the propagation step, is that the reaction is under thermodynamic control. This explanation was based on the observation that additions of simple radicals to mono- or 1,1-disubstituted olefins typically proceed by tail addition to give secondary or tertiary radicals, respectively, rather than the less stable primary radical (Scheme 3) and by analogy with findings for ionic reactions where such thermodynamic considerations are of demonstrable importance.

Until the early 1970s, the absence of suitable techniques for probing the detailed microstructure of polymers or for examining the selectivity and rates of radical reactions prevented the traditional view from being seriously questioned. In more recent times, it has been established that radical reactions, more often than not, are under kinetic rather than thermodynamic control and the preponderance of head-to-tail linkages in polymers is determined largely by steric and polar influences (see Section 3.04.2.2).¹⁸

It is now known that a proportion of 'head' addition occurs during the initiation and propagation stages of many polymerizations (see Section 3.04.3.2). for example, poly (vinyl fluoride) chains contain in excess of 10% head-to-head linkages.¹⁹ Benzoyloxy radicals give ~ 5% head addition with styrene (S) (see Section 3.04.2.1.1).^{20,21} However, one of the first clear-cut examples, demonstrating that thermodynamic control is not of overriding importance in determining the outcome of radical reactions, is the cyclopolymerization of diallyl compounds (see Section 3.04.3.3.1).²²⁻²⁵

Monomers containing multiple double bonds might be anticipated to initially yield polymers with pendant unsaturation and ultimately cross-linked structures. The pioneering studies of Butler and coworkers^{24,25} established that diallyl compounds, of general structure (4), undergo radical polymerization to give linear saturated polymers. They proposed that the propagation involved a series of inter- and intramolecular addition reactions. The presence of cyclic units in the polymer structure was rigorously established by chemical analysis.²⁶ Addition of a radical to the diallyl monomer (4) could conceivably lead to the formation of five-, six-, or even seven-membered rings as shown in Scheme 4. However, application of the then generally accepted hypothesis, that product radical stability was the most important factor determining the course of radical addition, indicated that the intermolecular step should proceed by tail addition (to give 5) and that the intramolecular step should afford a six-membered ring and a secondary radical (7). On the basis of this theory, it was proposed that the cyclopolymer was composed of six-membered rings (9) rather than five-membered rings (8).

It was established in the early 1960s that 5-hexenyl radicals and simple derivatives gave 1,5- rather than 1,6-ring closure



under conditions of kinetic control.²⁷ However, it was not until 1976 that the structures of cyclopolymers formed from 1,6-dienes (4) were experimentally determined and Hawthorne *et al.*²⁸ showed that the intramolecular cyclization step gives preferentially the less stable radical (6) (five- vs. six-membered ring, primary vs. secondary radical) – that is, \geq 99% head addition. Over the past two decades, many other examples of radical reactions that preferentially afford the thermodynamically less stable product have come to light.

The examples described in this chapter serve to illustrate two well-recognized, though often overlooked, principles, which lie at the heart of polymer, and, indeed, all forms of chemistry. These are as follows:

- 1. The dependence of a reaction (polymerization, polymer degradation, etc.) on experimental variables cannot be understood until the reaction mechanism is established.
- 2. The reaction mechanism cannot be fully defined, when the reaction products are unknown.

The recent development of radical polymerizations that show the attributes of living polymerization is a prime example of where the quest for knowledge on polymerization mechanism can take us. Reversible deactivation radical polymerization (RDRP)²⁹ relies on the introduction of a reagent that reversible deactivates with the propagating radicals, thereby converting them to a dormant form (Scheme 5). This enables control of the active species concentration allowing conditions to be chosen such that all chains are able to grow at a similar rate (if not simultaneously) throughout the polymerization. This has, in turn, enabled the synthesis of polymers with low dispersity and a wide variety of block, stars, and other structures not hitherto accessible by any mechanism. Specificity in the reversible initiation-termination step is of critical importance in achieving living characteristics.

The first steps toward RDRP were taken by Otsu and colleagues^{30,31} who in 1982 published a paper entitled "A Model for Living Radical Polymerization".³¹ In 1985, this was taken one step further with the development by Solomon et al.³² of nitroxide-mediated polymerization (NMP). This work was first reported in the patent literature³² and in conference papers but was not widely recognized until 1993 when Georges et al.33 applied the method in the synthesis of low-dispersity PS. In 1995, RDRP was described in detail within a small section entitled "Agents for Controlling Termination" in the first edition of The Chemistry of Free Radical Polymerization. Since that time the area has expanded dramatically. The scope of NMP has been greatly extended³⁴ and new, more versatile, methods have appeared. The most notable are atom transfer radical polymerization (ATRP)^{35,36} and polymerization with reversible addition fragmentation chain transfer (RAFT).^{37,38} From



Figure 1 Publication rate of journal papers on radical polymerization and on living, controlled, or mediated radical polymerization for the period 1975–2008 based on SciFinder[™] search (as of March 2010). It does not distinguish forms of controlled radical polymerization. It includes most papers on ATRP, RAFT, and NMP and would also include conventional, non-RDRP, controlled radical polymerizations. It would not include papers, which do not mention the terms 'living', 'controlled', or 'mediated'.

small beginnings pre-1995, this area now accounts for more than a third of all papers in the field of radical polymerization. Moreover, the growth in the field since 1995 is almost totally attributable to developments in this area (Figure 1).

In the succeeding sections, we detail the current state of knowledge of the chemistry of each stage of polymerization. We consider the details of the mechanisms, the specificity of the reactions, the nature of the group or groups incorporated in the polymer chain, and any by-products. The intention is to create an awareness of the factors that must be borne in mind in selecting the conditions for a given polymerization and provide the background necessary for a more thorough understanding of polymerizations and polymer properties. In the final sections, we descibe the various approaches to RDRP.

3.04.2 Initiation

Initiation is defined as the series of reactions that commences with generation of *primary* radicals and culminates in addition to the carbon–carbon double bond of a monomer so as to form *initiating* radicals (Scheme 6).^{39,40} The term primary radical

Reversible deactivation Active species propagating radical $I = \begin{bmatrix} X \\ -CH_2 - C \\ + \end{bmatrix} = \begin{bmatrix} X \\ + \end{bmatrix}$





used in this context should be distinguished from that used when describing the substitution pattern of alkyl radicals.

Classically, initiation was only considered as the first step in the chain reaction that constitutes radical polymerization. Although the rate and efficiency of initiation were known to be extremely important in determining the kinetics of polymerization, it was generally thought that the detailed mechanism of the process could be safely ignored when interpreting polymer properties. Furthermore, while it was recognized that initiation would lead to formation of structural units different from those that make up the bulk of the chain, the proportion of initiator-derived groups seemed insignificant when compared with total material. For example, in PS the initiator-derived end groups will account for \sim 0.2% of units in a sample of molecular weight 100000 (termination is mainly by combination). This led to the belief that the physical properties and chemistry of polymers could be interpreted purely in terms of the generalized formula - that is, (CH2-CXY)n

This view prevailed until the early 1970s and can still be found in some current-day texts. It is only in recent times that we have begun to understand the complexities of the initiation process and can appreciate the full role of initiation in influencing polymer structure and properties. Four factors may be seen as instrumental in bringing about a revision of the traditional view:

- The realization that polymer properties (e.g., resistance to weathering, thermal or photochemical degradation) are often not predictable based on the repeat unit structure but are in many cases determined by the presence of 'defect groups'.¹³⁻¹⁶
- 2. The development of techniques whereby details of the initiation and other stages of polymerization can be studied in depth.
- 3. The finding that radical reactions are typically under kinetic rather than thermodynamic control. Many instances can be cited where the less thermodynamically favored pathway is a significant, or even the major, pathway.
- 4. The development of RDRP (NMP, ATRP, RAFT). Lack of specificity in initiation can lead to dead chains and in turn to impure block copolymers or defects in complex architectures (stars, dendrimers, etc.).

It is the aim of this section to describe the nature, selectivity, and efficiency of initiation. The intention is to create a greater awareness of the factors that must be borne in mind by the polymer scientist when selecting an initiator for a given polymerization.

3.04.2.1 The Initiation Process

The simple initiation process depicted in many standard texts is the exception rather than the rule. The yield of primary radicals produced on thermolysis or photolysis of the initiator is usually not 100%. The conversion of primary radicals to initiating radicals is dependent on many factors and typically is not quantitative. The primary radicals may undergo rearrangement or fragmentation to afford new radical species (secondary radicals) or may interact with solvent or other species rather than monomer.

The reactions of the radicals (whether primary, secondary, solvent-derived, etc.) with monomer may not be entirely regioor chemoselective. Reactions, such as head addition, abstraction, or aromatic substitution, often compete with tail addition. In the sections that follow, the complexities of the initiation process will be illustrated by examining the initiation of polymerization of two commercially important monomers, S and methyl methacrylate (MMA), with each of three commonly used initiators, azobisisobutyronitrile (AIBN), dibenzoyl peroxide (BPO), and di-*t*-butyl peroxyoxalate (DBPOX). The primary radicals formed from these three initiators are cyanoisopropyl, benzoyloxy, and *t*-butoxy radicals, respectively (Scheme 7). BPO and DBPOX may also afford phenyl and methyl radicals, respectively, as secondary radicals.

3.04.2.1.1 Reaction with monomer

First consider the interaction of radicals with monomers. Some behave as described in the classic texts and give tail addition as the only detectable pathway (Scheme 8). However, tail addition to the double bond is only one of the pathways whereby a radical may react with a monomer. The outcome of the reaction







is critically dependent on the structure of both radical and monomer.

For reactions with S, specificity is found to decrease in the series cyanoisopropyl ~ methyl ~ *t*-butoxy > phenyl > benzoyloxy. Cyanoisopropyl (Scheme 8),⁴¹ *t*-butoxy, and methyl radicals give exclusively tail addition.²⁰ Phenyl radicals afford tail addition and ~ 1% aromatic substitution.²⁰ Benzoyloxy radicals give tail addition, head addition, and aromatic substitution (Scheme 9).^{20,42}

With MMA, these radicals show a quite different order of specificity; regiospecificity decreases in the series cyanoisopropyl \sim methyl > phenyl > benzoyloxy > *t*-butoxy. Cyanoisopropyl and methyl radicals give exclusively tail addition. Benzoyloxy and phenyl radicals also react almost exclusively with the double bond (though benzoyloxy radicals give a mixture of head and tail

addition⁴³) and abstraction, while detectable, is a very minor (<1%) pathway.^{43,44} On the other hand, only 63% of *t*-butoxy radicals react with MMA by tail addition to give 12 (Scheme 10).⁴⁵ The remainder abstract hydrogen, from either the α -methyl (predominantly) to give 13 or the ester methyl to give 14.^{45,46} The radicals 12–14 and methyl (formed by β -scission) may then initiate polymerization.

These examples clearly show that the initiation pathways depend on the structures of the radical and the monomer. The high degree of specificity shown by a radical (e.g., *t*-butoxy) in its reactions with one monomer (e.g., S) must not be taken as a sign that a similarly high degree of specificity will be shown in reactions with all monomers (e.g., MMA).

Radicals can be classified according to their tendency to give aromatic substitution, abstraction, double-bond addition, or



Scheme 9 Initiation pathways for benzoyloxy radical initiation of styrene polymerization (S, styrene).



Scheme 10 Initiation pathways for *t*-butoxy radical initiation of styrene polymerization (MMA, methyl methacrylate).

 β -scission and further classified in terms of the specificity of these reactions. With this knowledge, it should be possible to choose an initiator according to its suitability for use with a given monomer or monomer system so as to avoid the formation of undesirable end groups or, alternatively, to achieve a desired functionality.

The importance of these considerations can be demonstrated by examining some of the possible consequences for radical-monomer systems. For the case of MMA polymerization initiated by a t-butoxy radical source, chains may be initiated by the radicals 12, 13, or 14 (Scheme 10). A significant proportion of chains will therefore have an olefinic end group rather than an initiator-derived end group. These chain ends may be reactive, either during polymerization, leading to chain branching, or afterward, possibly leading to an impairment in polymer properties. PS formed with BPO as initiator will have a proportion of relatively unstable benzoate end groups formed by benzoyloxy radical reacting by head addition and aromatic substitution (Scheme 9).^{20,42} There is evidence that PS prepared with BPO as initiator is less thermally stable^{47,48} and less resistant to weathering and yellowing^{49,50} than that prepared using other initiators.

A comprehensive survey of kinetics, mechanism, and specificity of radical-monomer reactions compiled from the literature through mid-2005 is provided in *The Chemistry of Radical Polymerization*.¹

3.04.2.1.2 Fragmentation

Many radicals undergo fragmentation or rearrangement in competition with reaction with monomer. For example, *t*-butoxy radicals undergo β -scission to form methyl radicals and acetone (Scheme 11).

Benzoyloxy radicals decompose to phenyl radicals and carbon dioxide (Scheme 12).

The reactivity of the monomer and the reaction conditions determine the relative importance of β -scission. Fragmentation reactions are generally favored by low monomer concentrations, high temperatures, and low pressures. Their significance is greater at high conversion. They may also be influenced by the nature of the reaction medium.

Other radicals undergo rearrangement in competition with bimolecular processes. An example is the 5-hexenyl radical (16). The 6-heptenoyloxy radical (15) undergoes sequential fragmentation and cyclization (Scheme 13).⁵¹

The radicals formed by unimolecular rearrangement or fragmentation of the primary radicals are often termed secondary radicals. Often the absolute rate constants for secondary radical formation are known or can be accurately determined. These reactions may then be used as 'radical clocks',^{52,53} to calibrate



Scheme 11







the absolute rate constants for the bimolecular reactions of the primary radicals (e.g., addition to monomers). However, care must be taken since the rate constants of some clock reactions (e.g., *t*-butoxy β -scission⁵⁴) are medium dependent.

3.04.2.1.3 Reaction with solvents, additives, or impurities

A typical polymerization system comprises many components besides the initiators and the monomers. There will be solvents, additives (e.g., transfer agents, inhibitors) as well as a variety of adventitious impurities that may also be reactive toward the initiator-derived radicals.

For the case of MMA polymerization with a source of *t*-butoxy radicals (DBPOX) as initiator and toluene as solvent, most initiation may be by way of solvent-derived radicals^{54,55} (Scheme 14). Thus, a high proportion of chains (>70% for 10% w/v monomers at $60^{\circ}C^{55}$) will be initiated by benzyl rather than *t*-butoxy radicals. Other entities with abstractable hydrogens may also be incorporated as polymer end groups. The significance of these processes increases with the degree of conversion and with the solvent (or impurity):monomer ratio.



Scheme 14 Initiation pathways for *t*-butoxy radical initiation of styrene polymerization in toluene solvent (MMA, methyl methacrylate).

There is potential for this behavior to be utilized in devising methods for the control of the types of initiating radicals formed and hence the polymer end groups.

3.04.2.1.4 Effects of temperature and reaction medium on radical reactivity

The reaction medium may also modify the reactivity of the primary, or other radicals without directly reacting with them. For example, when *t*-butoxy reacts with MMA (Scheme 10), the ratio of addition: abstraction: β -scission varies according to the nature of the solvent⁵⁴ and the reaction temperature.^{56,57}

For *t*-alkoxy radicals, polar and aromatic solvents favor abstraction over addition, and β -scission over either addition or abstraction. Addition, abstraction, and β -scission have quite different Arrhenius parameters. As a further example the temperature dependence of the rate constants for addition of cumyloxy radicals to S, abstraction from isopropylbenzene, and β -scission to give methyl radicals is shown in **Figure 2**. Low temperatures favor abstraction over addition and both of these reactions over β -scission.

3.04.2.1.5 Reaction with oxygen

Radicals, in particular carbon-centered radicals, react with oxygen at near diffusion-controlled rates.⁶¹ Thus, for polymerizations carried out either in air or in incompletely degassed media, oxygen is likely to become involved in, and further complicate, the initiation process.

The reaction of oxygen with carbon-centered radicals (e.g., cyanoisopropyl, **Scheme 15**) affords an alkylperoxy radical (17).^{62,63} This species may initiate polymerization, thus forming a relatively unstable peroxidic end group (18). With respect to most carbon-centered radicals, the alkylperoxy radicals (17) show an enhanced tendency to abstract hydrogen. The alkylperoxy radicals may abstract hydrogen from polymer, monomer, or other components in the system,⁶⁴ forming a potentially reactive



Figure 2 Temperature dependence of rate constants for reactions of cumyloxy radicals: (a) β -scission to methyl radicals (— — —); (b) abstraction from isopropylbenzene (- - - - -); and (c) addition to S (— —). Data are an extrapolation based on literature Arrhenius parameters.^{58,59} Adapted from Moad, G. *Prog. Polym. Sci.* **1999**, *24*, 81–142.⁶⁰





hydroperoxide (19) and a new radical species (R^{\bullet}) that may initiate polymerization. The process is further complicated if 18 or 19 undergo homolysis under the polymerization conditions. The peroxides derived from 18 and 19 may also be active as chain transfer agents.

3.04.2.1.6 Initiator efficiency in thermal initiation

The proportion of radicals that escape the solvent cage to form initiating radicals is termed the initiator efficiency (f) which is formally defined as follows (eqn [1]):

$$f = \frac{\text{Rate of initiation of propagating chains}}{n \times (\text{rate of initiator disappearance})}$$
[1]

where *n* is the number of moles of radicals generated per mole of initiator. In some texts, the initiator efficiency (*f*) is defined simply in terms of the yield of initiator-derived radicals (the fraction of radicals I• that undergo cage escape – Section 3.04.2.1.8). This number will always be larger than that obtained by application of eqn [1].)

The effective rate of initiation (R_i) in the case of thermal decomposition of an initiator (I_2) decomposing by Scheme 16 is given by eqn [2]:

$$R_{i} = k_{i}[I\bullet][M] + k_{i}'[I'][M]$$
[2]

Equation [1] can then be written as follows (eqn [2]):

$$f = \frac{(k_i[\mathbf{I}\bullet][\mathbf{M}] + k_i'[\mathbf{I}'\bullet][\mathbf{M}])}{2k_d[\mathbf{I}_2]}$$
[3]

If, as is usual, the k_i are not rate determining, the rate of initiation is given by eqn [4]:

$$R_{\rm i} = 2k_{\rm d}f[{\rm I}_2] \tag{4}$$

According to eqn [1], the term f should take into account all side reactions that lead to loss of initiator or initiator-derived radicals. These include cage reaction of the initiator-derived radicals, primary radical termination, and transfer to initiator. The relative importance of these processes depends on

 $\begin{array}{cccc} I_2 & & \stackrel{k_d}{\longrightarrow} & [2 \ I \bullet] & \longrightarrow & I \bullet & \text{Primary radical formation} \\ I \bullet + M & \stackrel{k_i}{\longrightarrow} & P_1 \bullet & \text{Initiation} \\ I \bullet & & \longrightarrow & I' \bullet & \text{Secondary radical formation} \\ I' \bullet + M & \stackrel{k_i'}{\longrightarrow} & P_1 \bullet & \text{Initiation} \end{array}$



monomer concentration, medium viscosity, and many other factors. Thus f is not a constant and typically decreases with conversion.

3.04.2.1.7 Photoinitiation

It is worthwhile to consider some of the special features of photoinitiation. The Jablonski diagram provides a convenient description of the events that follow absorption of light (Figure 3). A molecule in its ground state (S_0) absorbs a photon of light to be excited to the singlet state (S_1). As well as being electronically excited, the molecule will be vibrationally and rotationally excited. Certain reactions may take place from the excited singlet state. These will compete with fluorescence, and other deactivation processes that return the molecule to the ground state, and intersystem crossing to the triplet state (T_1). The triplet state is typically of lower energy than the excited singlet state. Chemical reaction then competes with phosphorescence and other deactivation processes.

Azo-compounds and peroxides undergo photodecomposition to radicals when irradiated with light of suitable wavelength. The mechanism appears similar to that of thermal decomposition to the extent that it involves cleavage of the same bonds. It is also worth noting that certain monomers may undergo photochemistry and direct photoinitiation on irradiation of monomer is possible.

Clearly, unless monomer is the intended photoinitiator, it is important to choose an initiator that absorbs in a region of the UV-visible spectrum clear from the absorptions of monomer and other components of the polymerization medium. Ideally, one should choose a monochromatic light source that is specific for the chromophore of the photoinitiator or photosensitizer. It is also important in many experiments that the total amount of light absorbed by the sample is small. Otherwise the rate of initiation will vary with the depth of light penetration into the sample.

In order to define the rate and efficiency of photoinitiation, consider the simplified reaction (Scheme 17).

The quantum yield (Φ) is the yield of initiating radicals produced per photon of light absorbed (eqn [5])

$$\Phi = \frac{\text{Yield of initiating radicals}}{n \times (\text{photons absorbed})}$$
[5]

which can also be expressed in terms of the rate of initiation (eqn [6]):

$$\Phi = \frac{\text{Rate of initiation of propagating chains}}{n \times (\text{intensity of incident irradiation absorbed})} = \frac{R_{\text{i}}}{nI_{\text{abs}}}$$
[6]



Figure 3 Jablonski diagram describing photoexcitation process.

$$l_2 \xrightarrow{h_{\mathcal{V}}} 2 l \bullet$$

$$l \bullet + M \xrightarrow{k_i} P_1 \bullet$$

Scheme 17

where *n* is the number of moles of radicals generated per mole of initiator and I_{abs} is the intensity of incident light absorbed.

The Beer–Lambert law (also often called Beer's law) relates I_{abs} to the total incident light intensity (I_0) (eqn [7]):

$$\frac{abs}{I_0} = 1 - 10^{scd} = 1 - e^{\alpha} cd$$
[7]

and if αcd is small (< 0.1 for < 5% error), then this simplifies to eqn [8]:

$$\frac{I_{\rm abs}}{I_0} \approx \alpha cd \qquad [8]$$

where ε (= $\alpha/2.303$) is the molar extinction coefficient at the given wavelength, *c* is the concentration of the absorbing substance, and *d* is the pathlength. It can be seen that the term Φ embraces the same factors as $k_d f$ in thermal initiation. Care must be taken to establish how the molar extinction coefficient (ε or α) was determined since both decadic and natural forms are in common usage.

If the reaction with monomer is not the rate-determining step, the rate of radical generation in photoinitiated polymerization is given by eqn [9]:

$$R_{i} = 2\Phi I_{abs}$$

= $2\Phi I_{0} \left(1 - e^{\alpha d[I_{2}]} \right) = 2\Phi I_{0} \left(1 - 10^{\varepsilon d[I_{2}]} \right)$ [9]

which for small $\alpha d[I_2]$ simplifies to eqn [10]:

$$R_{\rm i} = 2\Phi I_0 \propto d[{\rm I}_2] \tag{10}$$

3.04.2.1.8 Cage reaction and initiator-derived by-products

The decomposition of an initiator seldom produces a quantitative yield of initiating radicals. Most thermal and photochemical initiators generate radicals in pairs. The self-reaction of these radicals is often the major pathway for the direct conversion of primary radicals to nonradical products in solution, bulk, or suspension polymerization. This cage reaction is substantial even in bulk polymerization at low conversion when the medium is essentially monomer. The importance of the process depends on the rate of diffusion of these species away from one another.

Thus, the size and the reactivity of the initiator-derived radicals and the medium viscosity (or microviscosity) are important factors in determining the initiator efficiency. Thus, the extent of the cage reaction is likely to increase with decreasing reaction temperature and with increasing conversion.^{21,65} The cage reaction, as well as lowering the initiation efficiency, can produce a range of by-products. These materials may be reactive under the polymerization conditions or they may themselves have a deleterious influence on polymer properties. For example, the cage reaction of cyanoisopropyl radicals formed from the decomposition of AIBN produces, among other products (Scheme 18), methacrylonitrile (MAN), which readily undergoes copolymerization to be incorporated into



Scheme 18

the final polymer,^{41,66} and tetramethylsuccinonitrile (20), which is claimed to be toxic and should not be present in polymers used for food contact applications.^{67,68}

In other cases, the cage reaction may simply lead to reformation of the initiator. This process is known as cage return and is important during the decomposition of BPO and DTBP. Cage return lowers the rate of radical generation but does not directly yield by-products. It is one factor contributing to the solvent and viscosity dependence of k_d and can lead to a reduced k_d at high conversion.

A variety of methods may be envisioned to decrease the importance of the cage reaction. One method, given the viscosity dependence of the cage reaction, is to conduct polymerizations in solution rather than in bulk. Another involves carrying out the polymerization in a magnetic field.⁶⁹ This is thought to reduce the rate of triplet-singlet intersystem crossing for the geminate pair.⁷⁰

3.04.2.1.9 Primary radical termination

The primary radicals may also interact with other radicals present in the system after they escape the solvent cage. When this involves a propagating radical, the process is known as primary radical termination. The term also embraces the reactions of other initiator or transfer agent-derived radicals with propagating radicals. Most monomers are efficient scavengers of the initiator-derived radicals and the steady-state concentration of propagating radicals is very low (typically $\leq 10^{-7}$ M). The concentrations of the primary and other initiator-derived radicals are very much lower (typically $\leq 10^{-9}$ M). Thus, with most initiators, primary radical termination has a very low likelihood during the early stages of polymerization.

Primary radical termination may involve combination or disproportionation with the propagating radical. It is often assumed that small radicals give mainly combination even though direct evidence for this is lacking. Both pathways are observed for reaction of cyanoisopropyl radicals with PS• (Scheme 19). The end group formed by combination is similar to that formed by head addition to monomer differing only in the orientation of the penultimate monomer unit.

If the rate of addition to monomer is low, primary radical termination may achieve greater importance. For example, in photoinitiation by the benzoin ether (23), both a fast initiating species (24, high k_i) and a slow initiating species (25, low k'_i) are generated (Scheme 20). The polymerization kinetics are complicated and the initiator efficiency is lowered by primary radical termination involving the dimethoxybenzyl radical (25).^{71,72}

Primary radical termination is also of demonstrable significance when very high rates of initiation or very low monomer concentrations are employed. It should be noted that these conditions pertain in all polymerizations at high conversion and in starved feed processes. Some syntheses of telechelics are based on this process. Reversible primary radical termination by combination with a persistent radical is the desired pathway in many forms of RDRP.

3.04.2.1.10 Transfer to initiator

Many of the initiators used in radical polymerization are susceptible to induced decomposition by various radical species. When the reaction involves the propagating species, the process is termed transfer to initiator. The importance of this reaction depends on both the initiator and the propagating radical.

Diacyl peroxides are particularly prone to induced decomposition (Scheme 21). Transfer to initiator is of greatest importance for polymerizations taken to high conversion or







when the ratio of initiator to monomer is high. It has been shown that, during the polymerization of S initiated by BPO, transfer to initiator can be the major pathway for the termination of chains.41,73

Transfer to initiator introduces a new end group into the polymer, lowers the molecular weight of the polymer, reduces the initiator efficiency, and increases the rate of initiator disappearance. Methods of evaluating transfer constants are discussed in Section 3.04.5.1.1.

3.04.2.1.11 Initiation in heterogeneous polymerization

Many polymerizations are carried out in heterogeneous media, usually water-monomer mixtures, where suspending agents or surfactants ensure proper dispersion of the monomer and control the particle size of the product.

Suspension polymerizations are often regarded as 'minibulk' polymerizations since ideally all reactions occur within individual monomer droplets. Initiators with high monomer and low water solubility are generally used in this application. The general chemistry, initiator efficiencies, and importance of side reactions are similar to that seen in homogeneous media.

Emulsion polymerizations most often involve the use of water-soluble initiators (e.g., persulfate) and polymer chains are initiated in the aqueous phase. A number of mechanisms

for particle formation and entry have been described; however, a full discussion of these is beyond the scope of this book. Readers are referred to recent texts on emulsion polymerization by Gilbert⁷⁴ and Lovell and El-Aasser⁷⁵ for a more comprehensive treatment.

Radicals typically are generated in the aqueous phase and it is now generally believed that formation of an oligomer of average chain length z (z-mer, P_z •) occurs in the aqueous phase prior to particle entry.⁷⁶ The steps involved in forming a radical in the particle phase from an aqueous-phase initiator are summarized in Scheme 22. The length of the z-mer depends on the particular monomer and is shorter for more hydrophobic monomers.

The concentration of monomers in the aqueous phase is usually very low. This means that there is a greater chance that the initiator-derived radicals (I•) will undergo side reactions. Processes such as radical-radical reaction involving the initiator-derived and oligomeric species, primary radical termination, and transfer to initiator can be much more significant than in bulk, solution, or suspension polymerization, and initiator efficiencies in emulsion polymerization are often very low. Initiation kinetics in emulsion polymerization are defined in terms of the entry coefficient (ρ) , a pseudofirst-order rate coefficient for particle entry.

Initiator (aq)	I∙ (aq)	(Initiator-derived radical in aqueous phase		
	$\xrightarrow{M} P_1^{\bullet}$ (aq)	(Initiating radical in aqueous phase)		
	$\xrightarrow{M} P_z^{\bullet}$ (aq)	(z-1 monomer additions to give z-mer)		
	$\xrightarrow{\rho} P_{z}^{\bullet}(p)$	(Transfer to particle phase, entry)		

Microemulsion and miniemulsion polymerization differ from emulsion polymerization in that the particle sizes are smaller $(10-30 \text{ and } 30-100 \text{ nm}, \text{ respectively, vs. } 50-300 \text{ nm})^{74}$ and there is no monomer droplet phase. All monomer is in solution or in the particle phase. Initiation takes place by the same process as conventional emulsion polymerization.

3.04.2.2 The Initiators

Certain polymerizations (e.g., S) can be initiated simply by applying heat; the initiating radicals are derived from reactions involving only the monomer. More commonly, the initiators are azo-compounds or peroxides that are decomposed to radicals through the application of heat, light, or a redox process.

When initiators are decomposed thermally, the rates of initiator disappearance (k_d) show marked temperature dependence. Since most conventional polymerization processes require that k_d should lie in the range $10^{-6}-10^{-5} \text{ s}^{-1}$ (half-life $\sim 10 \text{ h}$), individual initiators typically have acceptable k_d only within a relatively narrow temperature range ($\sim 20-30 \text{ °C}$). For this reason, initiators are often categorized purely according to their half-life at a given temperature or *vice versa*.⁷⁷ For initiators that undergo unimolecular decomposition, the half-life is related to the decomposition rate constant by eqn [11]:

$$t_{1/2} = \frac{\ln 2}{k_{\rm d}}$$
[11]

The Arrhenius relationship can be rearranged as follows (eqn [12]) to enable calculation of the temperature required to give a desired decomposition rate or half-life:

$$T(^{\circ}C) = -273.15 - \frac{E_{a}}{R \ln\left(\frac{k_{d}}{A}\right)} = -273.15 - \frac{E_{a}}{R \ln\left(\frac{\ln 2}{At_{\frac{1}{2}}}\right)}$$
[12]

The temperature at which the half-life is 10 h is then given by the following expression (eqn [13]):

$$T(^{\circ}C) = -273.15 - \frac{0.120277E_{a}}{-10.8578 + \ln\left(\frac{1}{A}\right)}$$
[13]

The initiator in radical polymerization is often regarded simply as a source of radicals. Little attention is paid to the various pathways available for radical generation or to the side reactions that may accompany initiation. The preceding discussion demonstrated that in selecting initiators (whether thermal, photochemical, redox, etc.) for polymerization, they must be considered in terms of the types of radicals formed, their suitability for use with the particular monomers, solvent, and the other agents present in the polymerization medium, and for the properties they convey to the polymer produced.

Many reviews detailing aspects of the chemistry of initiators and initiation have appeared.^{40,77,78} A noncritical summary of thermal decomposition rates is provided in the *Polymer Handbook*.^{79,80} The subject also receives coverage in most general texts and reviews dealing with radical polymerization. References to reviews that detail the reactions of specific classes of initiator are given under the appropriate subheading below.

Some characteristics of initiators used for thermal initiation are summarized in Table 1. These provide some general guidelines for initiator selection. In general, initiators that afford carbon-centered radicals (e.g., dialkyldiazenes, aliphatic diacyl peroxides) have lower efficiencies for initiation of polymerization than those that produce oxygen-centered radicals. Exact values of efficiency depend on the particular initiators, monomers, and reaction conditions.

3.04.3 Propagation

The propagation step of radical polymerization comprises a sequence of radical additions to carbon–carbon double bonds. In order to produce high-molecular-weight polymers, a propagating radical must show a high degree of specificity in its reactions with unsaturated systems. It must give addition to the exclusion of side reactions that bring about the cessation of growth of the polymer chain. Despite this limitation, there is considerable scope for structural variation in homopolymers.

The asymmetric substitution pattern of most monomers means that addition gives rise to a chiral center and their polymers will have tacticity (Scheme 23, Section 3.04.3.1).

Addition to double bonds may not be completely regiospecific. The predominant head-to-tail structure may be interrupted by head-to-head and tail-to-tail linkages (Figure 4, Section 3.04.3.2).

Intramolecular rearrangement of the initially formed radical may occur occasionally (e.g., backbiting – Scheme 24, Section 3.04.3.3.3) or even be the dominant pathway (e.g., cyclopolymerization in Section 3.04.3.3.1, ring-opening polymerization in Section 3.04.3.3.2). These pathways can give rise to branches, rings, or internal unsaturation in the polymer chain.

This section is primarily concerned with the chemical microstructure of the products of radical homopolymerization. Variations on the general structure $(CH_2-CXY)_n$ are described and the mechanisms for their formation and the associated rate parameters are examined. With this background established, aspects of the kinetics and thermodynamics of propagation are also considered (Section 3.04.3.4).

3.04.3.1 Stereosequence Isomerism – Tacticity

The classical representation of a homopolymer chain, in which the end groups are disregarded and only one monomer residue is considered, allows no possibility for structural variation. However, possibilities for stereosequence isomerism arise as soon as the monomer residue is considered in relation to its neighbors and the substituents X and Y are different. The chains have tacticity (Section 3.04.3.1.1). The tacticity of some common polymers is considered in Section 3.04.3.1.2.

The following discussion is limited to polymers of monoor 1,1-disubstituted monomers. Other factors become important in describing the types of stereochemical isomerism possible for polymers formed from other monomers (e.g., 1,2-disubstituted monomers).⁸¹

3.04.3.1.1 Terminology and mechanisms

Detailed discussion of polymer tacticity can be found in texts by Randall,⁸² Bovey,^{81,83} Koenig,^{84,85} Tonelli⁸⁶ and Hatada.⁸⁷ In order to understand stereoisomerism in polymer chains formed from mono- or 1,1-disubstituted monomers, the terminology considers four idealized chain structures:

Table 1 Guide to Properties of Polymerization Initiators

Initiator Class	Example	Section ^a	Radicals generated ^b	Efficiency ^c	Transfer ^d
dialkyldiazenes	CN CN H ₃ C-C-N=N-C-CH ₃ CH ₃ CH ₃ AIBN	3.3.1.1	1° alkyl	low	low
hyponitrites	CH_3 CH_3 $H_3C-C-O-N=N-O-C-CH_3$	3.3.1.2	1° alkoxy, 2° alkyl	high	low
diacyl peroxides	CH ₃ CH ₃ O O CH ₂ (CH ₂) ₂ CH ₂ -C-O-O-C-CH ₂ (CH ₂) ₂ CH ₃ L DO	3.3.2.1	(1° acyloxy), 2° alkyl	low	high
diaroyl peroxides	O B B B C C C C C C B B B C C C C C B B B C C C B	3.3.2.1	1° aroyloxy, 2° aryl	high	high
peroxydicarbonates	$H_{3}C$ O O CH ₃ CH-O-C-O-O-C-O-CH $H_{3}C$ CH ₃	3.3.2.2	1° alkoxycarbonyloxy, (2° alkoxy)	high	high
peroxyesters	СН₃ О СН₃ Н₃С−Ċ-О-О-С−Ċ-CН₃	3.3.2.3	1° alkoxy, acyloxy, 2° alkyl	med.	med.
peroxyoxalates	ĊH ₃ ĊH ₃ ĊH ₃ O O CH ₃ H ₃ C-Ċ-O-O-Ċ-Ċ·O-O-Ċ-CH ₃ ĊH ₃ CH ₃ DBPOX	3.3.2.3	1° alkoxy, 2° alkyl	high	med.
dialkyl peroxides	СН ₃ СН ₃ H ₃ C-C-O-O-C-CH ₃ CH ₃ CH ₃ DTBP	3.3.2.4	1° alkoxy, 2° alkyl	high	low
dialkyl ketone peroxides	\bigcirc O-O-C(CH ₃) ₃	3.3.2.5	1° alkoxy, 2° alkyl	med.	low
hydroperoxides	С-С(СН ₃) ₃ СН ₃ H ₃ C-С-О-О-Н СН ₃	3.3.2.5	1° hydroxy, alkoxy, 2° alkyl	high	high
persulfate	0 -0-S-0-0-S-0-	3.3.2.6	1° sulfate radical anion	low	low
disulfides	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	3.3.2.5	1° thiyl	high	high

^aSection in *The Chemistry of Radical Polymerization*¹ where the properties of the initiator are described in detail.

^b1° = primary radical from initiator decomposition, 2° = secondary radical-derived by fragmentation of 1° radical. Species shown in parentheses may be formed under some conditions but are seldom observed in polymerizations of common monomers. ^cEfficiency decreases as the importance of cage reactions increases.

^dSusceptibility to radical-induced decomposition



Scheme 23



Head-to-head linkage

Figure 4 Definition of 'tail-to-tail' and 'head-to-head' linkages.

- The isotactic chain (Figure 5) where the relative configuration of all the substituted carbons in the chain is the same. For the usual diagrammatic representation of a polymer chain, this corresponds to the situation where similar substituents lie on the same side of a plane perpendicular to the page and containing the polymer backbone.
- 2. The syndiotactic chain (Figure 6) where the relative configuration of centers alternates along the chain.
- 3. The heterotactic chain (Figure 7) where the diad configuration alternates along the chain.
- 4. The atactic chain (Figure 8) where there is a random arrangement of centers along the chain. (In the literature the term atactic is sometimes used to refer to any polymer that is not entirely isotactic or not entirely syndiotactic.)

For polymers produced by radical polymerization, while one of these structures may predominate, the idealized structures do not occur. It is necessary to define parameters to more precisely characterize the tacticity of polymer chains.

It should be stressed that this treatment of polymer stereochemistry only deals with relative configurations, whether a substituent is 'up or down' with respect to that on a neighboring unit. Therefore, the smallest structural unit that contains stereochemical information is the diad. There are two types of diad: meso (m), where the two chiral centers have like configuration (are enantiomeric), and racemic (r), where the centers have opposite configuration (**Figure 9**).

Confusion can arise because of the seemingly contradictory nomenclature established for analogous model compounds with just two asymmetric centers.⁸⁸ In such compounds, the diastereoisomers are named as in the following example (Figure 10).

It is usual to discuss triads, tetrads, pentads, and so on in terms of the component diads. For example, the *mrrrmr* heptad is represented as shown in Figure 11.

It is informative to consider how tacticity arises in terms of the mechanism for propagation. The radical center on the propagating species will usually have a planar sp² configuration. As such it is achiral and it will only be locked into a specific configuration after the next monomer addition. This situation should be contrasted with that which pertains in anionic or coordination polymerizations where the active center is pyramidal and therefore has chirality. This explains why stereochemical control is more easily achieved in these polymerizations.

The configuration of a center in radical polymerization is established in the transition state for addition of the next monomer unit when it is converted to a tetrahedral sp³ center. If the stereochemistry of this center is established at random (Scheme 25; $k_m = k_r$), then a pure atactic chain is formed and the probability of finding a *meso* diad, *P*(*m*), is 0.5.

Polymers formed from monosubstituted monomers (X=H) under the usual reaction conditions (e.g., 60 °C, bulk) appear almost atactic with only a slight preference for syndiotacticity and values of P(m) in the range 0.45–0.52.

If the reaction center adopts a preferred configuration with respect to the configuration of the penultimate unit in the chain (Scheme 25; $k_m \neq k_r$), then Bernoullian statistics apply. The stereochemistry of the chain is characterized by the single parameter, P(m) or P(r) [=1–P(m)]. The *n*-ad concentrations can be calculated simply by multiplying the concentrations of the component diads. Thus the relative triad concentrations are given by the following expressions (eqns [14]–[16]):

$$mm = P(m)_2$$
[14]

$$mr = rm = 2P(m)P(r) = 2P(m)[1-P(m)]$$
 [15]

$$rr = P(r)(r)^2 = [1 - P(m)]^2$$
 [16]

Higher *n*-ads are calculated similarly. Thus for the *mrrrmr* heptad

$$mrrrmr = 2 P(m) P(r) P(r) P(r) P(m) P(r) = 2 P(m)^{2} P(r)^{4}$$

The factor 2 is introduced in the case of asymmetric *n*-ads that can be formed in two ways (*mrrrmr* = *rmrrrm*).

Where the nature of the preceding diad is important in determining the configuration of the new chiral center (Scheme 26), first-order Markov statistics apply. Propagation is subject to a penpenultimate unit effect (also called an antepenultimate unit effect). Two parameters are required to specify the stereochemistry, $P(m|\mathbf{r}) [=1 - P(m|m)]$ and $P(r|\mathbf{r}) [=1 - P(r|m)]$, where P(i|j) is the conditional probability that given a *j* diad, the next unit in the chain will be an *i* diad. (In some texts, for example, those by Bovey^{81,86} and Tonelli,⁸⁶ P(i|j) is written P(j/i.) It can be shown that

$$P(m) = \frac{P(m|r)}{P(m|r)} + P(r|m)$$
[17]





Figure 5 Isotactic chain.











Figure 8 Atactic chain.



Figure 9 Representation of meso (*m*) and racemic (*r*) diads with polymer chains.



Figure 10 Representation of meso (*m*) and racemic (*r*) diastereoisomers of low-molecular-weight compounds.

The relative triad concentrations are then given by the following expressions (eqns [18]–[20]):

$$mm = P(m) P(m|m)$$
[18]

$$mr = rm = 2 P(m) P(r|m) = 2 P(m) [1 - P(m|m)]$$
 [19]

$$rr = P(r) P(r|r)$$
[20]

Again the higher *n*-ads are calculated similarly. Thus for the *mrrrmr* heptad

$$mrrrmr = 2 P(m)(m) P(r|m) P(r|r) P(r|r) P(m|r) P(r|m)$$

We can also write expressions to calculate P(m|r) and P(r|m) from the triad concentrations (eqns [21] and [22]):

$$P(m|r) = \frac{mr}{(2\ mm + mr)}$$
[21]

$$P(r|m) = \frac{rm}{(2 rr + rm)}$$
[22]

The Coleman–Fox two-state model describes the situation where there is restricted rotation about the bond to the preceding unit (Scheme 27). If this is slow with respect to the rate of addition, then at least two conformations of the propagating radical need to be considered, each of which may react independently with monomer. The rate constants associated with the conformational equilibrium and two values of P(m) are required to characterize the process.

More complex situations may also be envisaged and it should always be borne in mind that the fit of experimental data to a simple model provides support for but does not prove that model. The power of the experiment to discriminate between models has to be considered.



Figure 11 Representation of *mrrrmr* heptad identifying component *n*-ads.









3.04.3.1.2 Tacticities of polymers

Many radical polymerizations have been examined from the point of view of establishing the stereosequence distribution. For most systems, it is claimed that the tacticity is predictable within experimental error by Bernoullian statistics (i.e., by the single parameter P(m) – see Section 3.04.3.1.1). It should be noted that, in some studies, deviations of 5–10% in expected and measured nuclear magnetic resonance (NMR) peak intensities have been ascribed to experimental error. Such error is sufficient to hide significant departures from Bernoullian statistics.^{96,463}

Tacticity is most often determined by NMR analysis and usually by looking at the signals associated with



the –CXY– group (refer Figure 11). The analysis then provides the triad concentrations (mm, mr, and rr) and the value of m or P(m) is given by eqn [23]:

$$P(m) = mm + 0.5 mr$$
 [23]

Most polymers formed by radical polymerization have an excess of syndiotactic over isotactic diads (i.e., $P(m) \le 0.5$). P(m) typically lies in the range 0.4–0.5 for vinyl monomers and 0.2–0.5 for 1,1-disubstituted monomers. It is also generally found that P(m) (the fraction of isotactic diads) decreases with decreasing temperature.⁹¹

There are exceptions to this general rule. For example, polymerizations of methacrylates with very bulky ester substituents (26–29) show a marked preference for isotacticity, ⁹² whereas polymerizations of MMA show a significant preference for syndiotacticity. Polymerization of the acrylamide (AM) derivative (33) that has a bulky substituent on nitrogen also provides a polymer that is highly isotactic.^{93,94} AM and simple derivatives (*N*-isopropylacrylamide (NIPAM), *N*,*N*-dimethylacrylamide (DMAM)) give polymers that are slightly syndiotactic. Tacticity can be influences by solvent and Lewis acids.⁹⁵



An explanation for the preference for syndiotacticity during MMA polymerization was proposed by Tsuruta *et al.*⁹⁶ They considered that the propagating radical should exist in one of two conformations and showed, with models, that attack on the less hindered side of the preferred conformation (where

steric interactions between the substituent groups are minimized) would lead to formation of a syndiotactic diad while similar attack on the less stable conformation would lead to an isotactic diad.

MMA polymerization is one of the most studied systems and was thought to be explicable, within experimental error, in terms of Bernoullian statistics. Moad *et al.*⁹⁷ have made precise measurements of the configurational sequence distribution for PMMA prepared from ¹³C-labeled monomer. It is clear that Bernoullian statistics do not provide a satisfactory description of the tacticity.⁹⁷ This finding is supported by other work.^{89,98,99} First-order Markov statistics provide an adequate fit of the data. Possible explanations include (1) penpenultimate unit effects are important and/or (2) conformational equilibrium is slow (Section 3.04.3.1.1). At this stage, the experimental data do not allow these possibilities to be distinguished.

It seems likely that other polymerizations will be found to depart from Bernoullian statistics as the precision of tacticity measurements improves. One study¹⁰⁰ indicated that vinyl chloride polymerizations are also more appropriately described by first-order Markov statistics. However, there has been some reassignment of signals since that time.^{101,102}

The triad fractions for PVAc^{103,104} seem to obey Bernoullian statistics. However, the concentrations of higher order *n*-ads cannot be explained even by first- (or second-) order Markov statistics, suggesting either that ambiguities still remain in the signal assignments at this level or that there are unresolved complexities in the polymerization mechanism. Tacticities have been shown to be solvent and temperature dependent, with the degree of syndiotacticity being significantly enhanced in fluoroalcohol solvents and by lower temperatures.^{105,106} Tacticity of vinyl esters is also dependent on the ester group.¹⁰⁷

Devising effective means for achieving stereochemical control over propagation in radical polymerization remains an important challenge in the field.

3.04.3.2 Regiosequence Isomerism – Head versus Tail Addition

Most monomers have an asymmetric substitution pattern and the two ends of the double bond are distinct. For mono- and 1,1-disubstituted monomers (Section 3.04.3.2.1), it is usual to call the less substituted end 'the tail' and the more substituted end 'the head'. Thus the terminology evolved for two modes of addition, head and tail, and for the three types of linkages, head-to-tail, head-to-head, and tail-to-tail. For 1,2-di-, tri-, and tetrasubstituted monomers, definitions of head and tail are necessarily more arbitrary. The term 'head' has been used for that end with the most substituents, the largest substituents, or the best radical stabilizing substituent (Scheme 28).

With 1,3-diene-based polymers, greater scope for structural variation is introduced because there are two double bonds to attack and the propagating species is a delocalized radical with several modes of addition possible (see Section 3.04.3.2.2).

3.04.3.2.1 Monoene polymers

Various terminologies for describing regiosequence isomerism have been proposed.^{81,84} By analogy with that used to describe





stereosequence isomerism (Section 3.04.3.1), it has been suggested that a polymer chain with the monomer units connected by 'normal' head-to-tail linkages should be termed isoregic, that with alternating head-to-head and tail-to-tail linkages, syndioregic, and that with a random arrangement of connections, aregic.⁸¹

For mono- and 1,1-disubstituted monomers, steric, polar, resonance, and bond-strength terms usually combine to favor a preponderance of tail addition, that is, an almost completely isoregic structure. However, the occurrence of head addition has been unambiguously demonstrated during many polymerizations. During the intramolecular steps of cyclopolymerization, 100% head addition may be obtained (Section 3.04.3.3.1).

The tendency for radicals to give tail addition means that a head-to-head linkage will, most likely, be followed by a tail-to-tail linkage (Scheme 29). Thus, head-to-head linkages formed by an 'abnormal' addition reaction are chemically distinct from those formed in termination by combination of propagating radicals (Scheme 30).

In view of the potential problems associated with discriminating between the various types of head-to-head linkages, it is perhaps curious that, while much effort has been put into finding head-to-head linkages, relatively little attention has been paid to applying spectroscopic methods to detect tailto-tail linkages where no such difficulty arises.

Even allowing for the above-mentioned complication, the number of head-to-head linkages is unlikely to equate exactly with the number of tail-to-tail linkages. The radicals formed by tail addition (T^{\bullet}) and those formed by head addition (H^{\bullet}) are likely to have different reactivities.

Consideration of data on the reactions for small radicals suggests that the primary alkyl radical (H^{\bullet}) is more likely to give head addition than the normal propagating species (T^{\bullet}) for three reasons:





Scheme 30

- The propensity for head addition, which usually corresponds with attack at the more substituted end of the double bond, should decrease as the steric bulk of the attacking radical increases. Note that H• (a primary alkyl radical in the case of mono- and 1,1-disubstituted monomers) will usually be less sterically bulky than T•.
- The primary alkyl radical (H•) will be more reactive than T• with no α-substituent to stabilize or delocalize the free spin.

However, head addition is usually a very minor pathway and is difficult to determine experimentally. Analysis of the events that follow head addition presents an even more formidable problem. Therefore, there is little experimental data on polymers with which to test the above-mentioned hypothesis. Data for fluoro-olefins indicate that H• gives less head addition than T• (Section 3.04.3.2.1(iii)). No explanation for the observation was proposed.

The primary alkyl radical, $H\bullet$, is anticipated to be more reactive and may show different specificity to the secondary or tertiary radical, $T\bullet$. In VAc and vinyl chloride (VC) polymerizations, the radical $H\bullet$ appears more prone to undertake intermolecular (Sections 3.04.3.2.1(i) and 3.04.3.2.1(ii)) or intramolecular atom transfer reactions.

3.04.3.2.1(i) Poly(vinyl acetate)

It is generally agreed that $\sim 1-2\%$ of propagation steps during VAc polymerization involve head addition. There is some evidence that, depending on reaction conditions, a high proportion of the head-to-head linkages may appear at chain ends (Scheme 31) and that the number of head-to-head linkages may not equate with tail-to-tail linkages. The extent of head addition in VAc polymerization increases with the polymerization temperature.

The reaction conditions (solvent, temperature) may also influence the amount of head addition and determine whether the radical formed undergoes propagation or chain transfer.

3.04.3.2.1(ii) Poly(vinyl chloride)

Establishment of the detailed microstructure of PVC has attracted considerable interest. This has been spurred by the desire to rationalize the poor thermal stability of the polymer. Many reviews have appeared on the chemical microstructure of PVC and the mechanisms of 'defect group' formation.¹⁰⁸⁻¹¹²

Although head addition occurs during PVC polymerization to the extent of ~ 1%, it is now thought that PVC contains few, if any, head-to-head linkages (<0.05%).^{113,114} Propagation from the radical formed by head addition is not competitive with a unimolecular pathway for its disappearance, namely, 1,2-chlorine atom transfer (see Scheme 32).

$$\begin{array}{c|c} & & & & \\ & &$$

Scheme 31 (VAc, vinyl acetate)



Scheme 32 (VC, vinyl chloride)

3.04.3.2.1(iii) Fluoro-olefin polymers

Propagation reactions involving the fluoro-olefins, vinyl fluoride (VF), $^{19,115-117}$ vinylidene fluoride (VF2), $^{115,117-119}$ and trifluoroethylene (VF3) 120 show relatively poor regiospecificity. This poor specificity is also seen in additions of small radicals to the fluoro-olefins (see Section 3.04.2.3). Since the fluorine atom is small, the major factors affecting the regiospecificity of addition are anticipated to be polarity and bond strength.

3.04.3.2.2 Conjugated diene polymers

There is greater scope for structural variation in the diene-based polymers than for the monoene polymers already discussed. The polymers contain units from overall 1,2- and *cis*- and *trans*-1,4-addition. Two mechanisms for overall 1,2-addition may be proposed. These are illustrated in Schemes 33 and 34:

1. The delocalized allyl radical produced by addition to the 1- (or 4-) position may react in two ways to give overall 1,2- or 1,4-addition (Scheme 33).







Scheme 34 (B, butadiene)

2. By analogy with the chemistry seen with monoene monomers, the propagating species could, in principle, add to one of the internal (2- or 3-) positions of the diene (Scheme 34).

Analyses of polymer microstructures do not allow these possibilities to be unambiguously distinguished. However, electron paramagnetic resonance (EPR) experiments demonstrate that radicals add exclusively to one of the terminal methylenes.¹²¹

When used in conjunction with unsymmetrical dienes with substituents in the 2-position, the term 'tail addition' has been used to refer to addition to the methylene remote from the substituent. 'Head addition' then refers to addition to the methylene bearing the substituent (i.e., head addition \equiv 4,1- or 4,3-addition; tail addition \equiv 1,4- or 1,2-addition) as illustrated below for chloroprene (Scheme 35). Note that 1,2- and 4,3-addition give different structures, while 1,4- and 4,1-addition give equivalent structures and a chain of two or more monomer units must be considered to distinguish between head and tail addition.

Tacticity is only a consideration for units formed by 1,2-addition. However, units formed by 1,4-addition may have a *cis*- or a *trans*-configuration.

In anionic and coordination polymerizations, reaction conditions can be chosen to yield polymers of specific microstructure. However, in radical polymerization, while



Scheme 35

some sensitivity to reaction conditions has been reported, the product is typically a mixture of microstructures in which 1,4-addition is favored. Substitution at the 2-position (e.g., isoprene or chloroprene) favors 1,4-addition and is attributed to the influence of steric factors. The reaction temperature does not affect the ratio of 1,2:1,4-addition but does influence the configuration of the double bond formed in 1,4-addition. Lower reaction temperatures favor *trans*-1,4-addition.

Early work on the microstructure of the diene polymers has been reviewed.⁸¹ While polymerizations of a large number of 2-substituted and 2,3-disubstituted dienes have been reported,¹²² little is known about the microstructure of diene polymers other than polybutadiene (PB),¹²³ polyisoprene,¹²⁴ and polychloroprene.¹²⁵

3.04.3.3 Structural Isomerism – Rearrangement

During most radical polymerizations, the basic carbon skeleton of the monomer unit is maintained intact. However, in some cases the initially formed radical may undergo intramolecular rearrangement leading to the incorporation of new structural units into the polymer chain. The rearrangement may take the form of ring closure (see Section 3.04.3.3.1), ring opening (see Section 3.04.3.3.2), or intramolecular atom transfer (see Section 3.04.3.3.3).

The unimolecular rearrangement must compete with normal propagation. As a consequence, for systems where there is < 100% rearrangement, the concentration of rearranged units in the polymer chain will be dependent on reaction conditions. The use of low monomer concentrations will favor the unimolecular process and it follows that the rearrangement process will become increasingly favored over normal propagation as polymerization proceeds and monomer is depleted (i.e., at high conversion). Higher reaction temperatures generally also favor rearrangement.

3.04.3.3.1 Cyclopolymerization

Diene monomers with suitably disposed double bonds may undergo intramolecular ring closure in competition with propagation (Scheme 36). The term cyclopolymerization was coined to cover such systems. Many systems that give cyclopolymerization to the exclusion of 'normal' propagation and cross-linking are now known. The subject is reviewed in a series of works by Butler.^{22,24,25,126,127}

Intramolecular cyclization is subject to the same factors as intermolecular addition (see Section 3.04.2.3). However, stereoelectronic factors achieve greater significance because the relative positions of the radical and double bond are constrained by being part of the one molecule and can lead to head addition being the preferred pathway for the intramolecular step.

Geometric considerations in cyclopolymerization are optimal for 1,6-dienes. Instances of cyclopolymerization involving formation of larger rings have also been reported, as have examples where sequential intramolecular additions lead to bicyclic structures within the chain. Various 1,4- and 1,5-dienes



are proposed to undergo cyclopolymerization by a mechanism involving two sequential intramolecular additions.

3.04.3.3.2 Ring-opening polymerization

Much of the interest in ring-opening polymerizations stems from the fact that the polymers formed may have lower densities than the monomers from which they are derived (i.e., volume expansion may accompany polymerization).^{128–131} This is in marked contrast with conventional polymerizations that typically involve a nett volume contraction. Such polymerizations are therefore of particular interest in adhesive, mold filling, and other applications where volume contraction is undesirable. Their use in dental composite and adhesive compositions has attracted recent attention.¹³¹

Ring-opening polymerizations and copolymerizations also offer novel routes to polyesters and polyketones. These polymers are not otherwise available by radical polymerization. Finally, ring-opening copolymerization can be used to give end-functional polymers. For example, copolymerization of ketene acetals with, for example, S, and basic hydrolysis of the ester linkages in the resultant copolymer offers a route to α, ω -difunctional polymers.

Reviews on radical ring-opening polymerization include those by Sanda and Endo,¹³² Klemm and Schultz,¹³³ Cho,¹³⁴ Moszner *et al.*,¹³⁵ Endo and Yokozawa,¹³⁶ Stansbury,¹³⁰ and Bailey.¹³⁷ A review by Colombani¹³⁸ and Moad *et al.* on addition–fragmentation processes is also relevant. Monomers used in ring opening are typically vinyl- (e.g., vinylcyclopropane – **Scheme 37**) or methylene-substituted cyclic compounds (e.g., ketene acetals) where addition to the double bond is followed by β -scission.

However, there are also examples of addition across a strained carbon–carbon single bond, as occurs with bicyclobutane¹³⁹ and derivatives.^{140,141} Interestingly, 1-cyano-2,2,4,4-tetramethylbicylobutane is reported to provide a polyketenimine.¹⁴² This is the only known examples of a α -cyanoalkyl radical adding monomer via nitrogen.

For ring opening to compete effectively with propagation, the former must be extremely facile. For example, with $k_{\rm p} \sim 10^2 - 10^3 \,{\rm M}^{-1} \,{\rm s}^{-1}$ the rate constant for ring opening (k_{β}) must be at least $\sim 10^5 - 10^6 \,{\rm s}^{-1}$ to give > 99% ring opening in bulk polymerization. The reaction conditions can be chosen so as to favor ring opening. Ring opening will be favored by dilute reaction media and, usually, by higher polymerization temperatures.

The ring-opening reaction usually results in the formation of a new unsaturated linkage. When this is a carbon–carbon double bond, the further reaction of this group during polymerization leads to a cross-linked (and insoluble) structure and can be a serious problem when networks are undesirable. In many of the applications mentioned above, cross-linking is desirable.

3.04.3.3.3 Intramolecular atom transfer

It has been known for some time that intramolecular atom transfer, or backbiting, complicates polymerizations of E (Scheme 38), VAc, and VC. Recent work has shown that backbiting is also prevalent in polymerization of acrylate esters (Section 3.04.3.3.3(i)) and probably occurs to some extent during polymerizations of most monosubstituted monomers.^{143,144}

Viswanadhan and Mattice¹⁴⁵ carried out calculations aimed at rationalizing the relative frequency of backbiting in these and other polymerizations in terms of the ease of adopting the required conformation for intramolecular abstraction (see Section 3.04.2.4.4). More recent theoretical studies generally support these conclusions and provide more quantitative estimates of the Arrhenius parameters for the process.^{146,147}

Cases of 'addition-abstraction' polymerization have also been reported where propagation occurs by a mechanism involving sequential addition and intramolecular 1,5-hydrogen atom transfer steps (Section 3.04.3.3.3(ii)).

3.04.3.3.3(i) Acrylate esters and other monosubstituted monomers Recent work has shown that backbiting is prevalent in polymerizations and copolymerizations of acrylate esters.^{143,144,148-159} It is also observed in S polymerization at high temperature¹⁴³ and probably occurs to some extent during polymerizations of most monosubstituted monomers. At high temperatures, and at low temperatures in very dilute solution, backbiting may be followed by fragmentation (Scheme 39).^{143,144,148–150,158} At lower temperatures short-chain branch formation dominates.¹⁵¹⁻¹⁵⁴ The backbiting process complicates the measurement of propagation rate constants for acrylates.¹⁶⁰

The high-temperature polymerization of acrylates with the backbiting–fragmentation process has been used to synthesize macromonomers based on acrylate esters.^{143,144,150} Interestingly, fragmentation shows a strong preference for giving the polymeric macromonomer (36) and a small radical (37).^{143,144} An explanation for this specificity has yet to be proposed.

3.04.3.3.3(ii) Addition-abstraction polymerization

Several examples of addition–abstraction polymerization have been reported. In these polymerizations, the monomers are designed to give quantitative rearrangement of the initially formed adduct via 1,5-hydrogen atom transfer (Scheme 40). The monomers (38) are such that the double bond is electron rich (vinyl ether) and the site for 1,5-H transfer is electron deficient. This arrangement favors intramolecular abstraction over addition. Thus compound (38a) undergoes^{161,162} quantitative rearrangement during homopolymerization. For 38b, where the site of intramolecular attack is less electron deficient, up to 80% of propagation steps involve intramolecular abstraction. As expected, higher reaction temperatures and lower









Scheme 40

monomer concentrations favor the intramolecular abstraction pathway.

3.04.3.4 Propagation Kinetics and Thermodynamics

In this section, we consider the kinetics of propagation and the features of the propagating radical $(P_n \bullet)$ and the monomer (M) structure that render the monomer polymerizable by radical homopolymerization (Section 3.04.3.4.1).

In the literature on radical polymerization, the rate constant for propagation, k_{p} , is often taken to have a single value (i.e., $k_p(1) = k_p(2) = k_p(3) = k_p(n)$ – refer **Scheme 41**). However, there is now good evidence that the value of k_p is dependent on chain length, at least for the first few propagation steps (Section 3.04.3.4.1), and on the reaction conditions.

3.04.3.4.1 Polymerization thermodynamics

Polymerization thermodynamics has been reviewed by Allen and Patrick,¹⁶³ Ivin,¹⁶⁴ Ivin and Busfield,¹⁶⁵ Sawada,¹⁶⁶ and Busfield.¹⁶⁷ In most radical polymerizations, the propagation steps are facile (k_p typically > 10² M⁻¹ s⁻¹ – Section 3.04.3.4.2) and highly exothermic. Heats of polymerization (ΔH_p) for addition polymerizations may be measured by analyzing the equilibrium between monomer and polymer or from calorimetric data using standard thermochemical techniques. Data for polymerization of some common monomers are collected in **Table 2**. Entropy of polymerization (ΔS_p) data are more

P ₁ •	+	М	\rightarrow	P ₂ •	$k_{p}(1)[P_{n}\bullet][M]$
P_2^{\bullet}	+	М	\rightarrow	P ₃ •	$k_p(2)[P_n\bullet][M]$
P ₃ •	+	М	\rightarrow	P_4^{\bullet}	<i>k</i> _p (3)[P _n •][M]
P <i>n</i> [●]	+	М	\rightarrow	P_{n+1} •	$k_{p}(n)[P_{n}\bullet][M]$

Scheme 41

scarce. The scatter in experimental numbers for $\Delta H_{\rm p}$ obtained by different methods appears quite large and direct comparisons are often complicated by effects of the physical state of the monomer and polymers (i.e., whether for solid, liquid or solution, degree of crystallinity of the polymer).

The addition of radicals and, in particular, propagating radicals to unsaturated systems is potentially a reversible process (Scheme 42). Depropagation is entropically favored and the extent therefore increases with increasing temperature (Figure 12). The temperature at which the rate of propagation and depropagation become equal is known as the ceiling temperature (T_c). Above T_c there will be net depolymerization.

With most common monomers, the rate of the reverse reaction (depropagation) is negligible at typical polymerization temperatures. However, monomers with alkyl groups in the α -position have lower ceiling temperatures than monosubstituted monomers (**Table 2**). For MMA at temperatures < 100 °C, the value of K_{eq} is < 0.01 (Figure 12). α -Methylstyrene (AMS) has a ceiling temperature of < 30 °C and is not readily polymerizable by radical methods. This monomer can, however, be copolymerized successfully.

The value of T_c and the propagation/depropagation equilibrium constant (K_{eq}) can be measured directly by studying the equilibrium between monomer and polymer or they can be calculated at various temperatures given values of ΔH_p and ΔS_p using eqns [24] and [25], respectively.

$$K_{\rm eq} = \exp\left(\frac{\Delta H_{\rm p}}{RT} - \frac{\Delta S_{\rm p}}{R}\right) = \frac{1}{\left[\mathrm{M}\right]_{\rm eq}}$$
[24]

where [M]_{eq} is the equilibrium monomer concentration.

$$T_c = \frac{\Delta H_p}{\Delta S_p + R \ln[M]}$$
[25]

Note that the value of T_c is dependent on the monomer concentration. In the literature, values of T_c may be quoted for

	X	R	$\Delta H_{\rho} (kJ mol^{-1})$				
Monomer			a	b	C	$\Delta S_{p}^{c} (Jmol^{-1} K^{-1})$	T _c ^d (°C)
AA	CO ₂ H	Н	67	-	-	-	-
MAA	CO ₂ H	CH3	43	65	-	-	-
MA	CO_2CH_3	Н	78	-	-	-	-
MMA		CH ₃	56 (58)	55	56 ^{168,169}	118 ^{168,169}	202
EMA	$CO_2C_2H_5$	CH ₃	60 (58)	-	60 ¹⁷⁰	124 ¹⁷⁰	211
BMA	$CO_2C_4H_9$	CH ₃	58 (60)	-	-	-	-
MEA ¹⁷¹	CO ₂ CH ₃	C_2H_5	32 ^{<i>e</i>}	-	-	-	22
AN	CN	H	75 [†]	-	-	109 ¹⁶⁷	415
MAN	CN	CH ₃	57	-	64 ¹⁷²	142 ^{<i>g</i>,172}	177
S	Ph	Н	69 (73)	70	73 ¹⁷³	104 ¹⁷³	428
AMS	Ph	CH ₃	-	35	45 ¹⁷⁴	148 ¹⁷⁴	31
VAc	$0_2 CCH_3$	Н	88 (90)	-	-	-	-
VC	CI	Н	96	112	-	-	-

 Table 2
 Thermodynamic parameters for polymerization of selected monomers (CH₂=CRX)

^aFrom calorimetry – data are for liquid monomer to amorphous solid polymer or for liquid monomer to polymer in monomer (in parentheses) and are taken from the Polymer Handbook unless otherwise indicated.¹⁶⁷ All data are rounded to the nearest whole number.

^bFrom heat of combustion monomer and polymer – data are for liquid monomer to amorphous solid polymer and are taken from the *Polymer Handbook*.¹⁶⁷ All data are rounded to the nearest whole number.

^cFrom studies of monomer–polymer equilibria – data are for liquid monomer to amorphous solid polymer. All data are rounded to the nearest whole number.

^{*d*}Calculated from numbers of ΔH_p (column *c* except for AN) and ΔS_p shown and [M] = 1.0.

^eBased on a measured T_c of 82 ^eC in bulk monomer and an assumed value for ΔS_p of 105 J mol⁻¹ K^{-1,171} A more reasonable value of ΔS_p of 120 J mol⁻¹ K⁻¹ would suggest a ΔH_p of 40 kJ mol⁻¹.

Partially crystalline polymer.

^gIn benzonitrile solution.

AA, acrylic acid; MAA, methacrylic acid; MA, methyl acrylate; MMA, methyl methacrylate; BMA, butyl methacrylate; MEA, methyl ethacrylate; AN, acrylonitrile; MAN, methacrylonitrile; S, styrene; AMS, α-methylstyrene; VAc, vinyl acetate; VC, vinyl chloride

[M] = 1.0 M, for $[M] = [M]_{eq'}$ or for bulk monomer. Thus care must be taken to note the monomer concentration when

$$P_n^{\bullet} + M \stackrel{K_{eq}}{\longrightarrow} P_{n+1}^{\bullet}$$

comparing values of T_c . One problem with using the above method to calculate K_{eq} or T_c is the paucity of data on ΔS_p . A further complication is that literature values of ΔH_p show variation of ± 2 kJ mol–1 that may in part reflect medium effects.¹⁶⁷ This 'error' in ΔH_p corresponds to a significant uncertainty in T_c .



Figure 12 Dependence of K_{eq} on temperature for selected monomers based on values of ΔH_p and ΔS_p shown in **Table 2** AN, acrylionitrile; S, styrene; MMA, methyl methacrylate; MAN, methacrylonitrile; AMS, α -methylstyrene.

Steric factors appear to be dominant in determining ΔH_p and ΔS_p . The resonance energy lost in converting monomer to polymer is of secondary importance for most common monomers. It is thought to account for ΔH_p for VAc and VC being lower than for acrylic and styrenic monomers.

Evidence for the importance of steric factors comes from a consideration of the effect of α -alkyl substituents. It is found that the presence of an α -methyl substituent raises ΔH_p by at least 20 kJ mol–1 (Table 2, compare entries for acrylic acid (AA) and methacrylic acid (MAA), methyl acrylate (MA) and MAA, acrylonotrile (AN) and MAN, S and AMS). The higher ΔH_p probably reflects the greater difficulty in forming bonds to tertiary centers. This view is supported by the observation that higher alkyl substituents further increase ΔH_p (e.g., ethyl in methyl ethacrylate (MEA),¹⁷¹ Table 2). Increasing the chain length of the α -substituent from methyl to ethyl should not greatly increase the thermodynamic stability of the radical, but steric factors will make the new bond both more difficult to form and easier to break.

Limited data suggest that the entropic term may be as important as the enthalpic term in determining polymerizability. The value of ΔS_p is lowered > 20 J mol⁻¹ K⁻¹ by the presence of an α -methyl substituent (Table 2, compare entries for AN and MAN, S and AMS). This is likely to be a consequence of the polymers from α -methyl vinyl monomers having a more rigid, more ordered structure than those from the corresponding vinyl monomers.

There have been many studies on the polymerizability of α -substituted acrylic monomers.^{171,175–178} It is established that the ceiling temperature for α -alkoxyacrylates decreases with the size of the alkoxy group.¹⁷⁵ However, it is of interest that polymerizations of α -(alkoxymethyl)acrylates (40),¹⁷⁵ α - (acyloxymethyl)acrylates (41),¹⁷⁷ and captodative substituted monomers (42, 43)¹⁷⁹ appear to have much higher ceiling temperatures than the corresponding α -alkylacrylates (e.g., MEA). For example, methyl α -ethoxymethacrylate¹⁷⁵ readily polymerizes at 110 °C, whereas MEA¹⁷¹ has a very low ceiling temperature (Table 2). However, values of the thermodynamic parameters for these polymerizations have not yet been reported.

3.04.3.4.2 Measurement of propagation rate constants

Methods for measurement of k_p have been reviewed by Stickler,^{180,181} van Herk,¹⁸² and more recently by Beuermann and Buback.¹⁸³ A largely noncritical summary of values of k_p and k_t obtained by various methods appears in the *Polymer Handbook*.¹⁸⁴ Literature values of k_p for a given monomer may span 2 or more orders of magnitude. The data and methods of measurement have been critically assessed by International Union of Pure and Applied Chemistry (IUPAC) working parties^{185–191} and reliable values for most common monomers are now available.¹⁸³ The wide variation in values of k_p (and k_t) obtained from various studies does not reflect experimental error but differences in data interpretation and the dependence of kinetic parameters on chain length and polymerization conditions.

Traditionally, measurement of k_p has required determination of the rate of polymerization under steady-state (to give k_p/k_t^2) and non-steady-state conditions (to give k_p/k_t). The classical techniques in this context are the rotating sector^{192–195} and related methods such as spatially intermittent polymerization (SIP).¹⁹⁶

EPR methods that allow a more direct determination of k_p have been developed. These enable absolute radical concentrations to be determined as a function of conversion. With especially sensitive instrumentation, this can be done by direct measurement.^{197–200} An alternative method, applicable at high conversions, involves trapping the propagating species in a frozen matrix^{201,202} by rapid cooling of the sample to liquid nitrogen temperatures.

The radical concentration, when coupled with information on the rate of polymerization, allows k_p (and k_t) to be calculated. The EPR methods have been applied to various polymerizations including those of B, DMA, MMA,^{201–206} S,^{207,208} and VAc.²⁰⁹ Values for k_p are not always in complete agreement with those obtained by other methods (e.g., pulsed laser polymerization (PLP), SIP) and this may reflect a calibration problem. Problems may also arise because of the heterogeneity of the polymerization reaction mixture²⁰⁵ and insufficient sensitivity for the radical concentrations in low-conversion polymerizations²⁰² or very low molecular weights. Some data must be treated with caution. However, the difficulties are now generally recognized and are being resolved.²⁰⁰





Figure 13 Experimental molecular weight distribution obtained by GPC (______) and its first derivative with respect to chain length (------) for PS prepared by PLP. The vertical scales are in arbitrary units. Polymerization of 4.33 M styrene at 60 °C with benzoin 0.006 M and laser conditions: $\lambda = 350$ nm, 80–100 mJ per pulse, $\tau = 0.05$ s.²¹⁴

PLP has emerged as the most reliable method for extracting absolute rate constants for the propagation step of radical polymerizations.¹⁸³ The method can be traced to the work of Aleksandrov *et al.*²¹⁰ PLP in its present form owes its existence to the extensive work of Olaj and coworkers²¹¹ and the efforts of an IUPAC working party.^{185–191} The method has now been successfully applied to establish rate constants, k_p (overall), for many polymerizations and copolymerizations.

In PLP the sample is subjected to a series of short (<30 ns) laser pulses at intervals τ . Analysis of the molecular weight distribution gives the length of chain formed between successive pulses (ν) and this yields a value for k_p (eqn [26]).

$$v = k_{\rm p} \,[{\rm M}]\tau \qquad [26]$$

A molecular weight distribution for a PS sample obtained from a PLP experiment with S is shown in **Figure 13**. Olaj *et al.*²¹¹ found empirically that v was best estimated from the points of inflection in the molecular weight distribution. Kinetic modeling of PLP has been carried out using Monte Carlo methods^{212,213} or by numerical integration.^{214,215} These studies confirm that the point of inflection in the molecular due to k_p becoming limited by the rate of diffusion of monomer. While conversion dependence of k_p at extremely high conversions is known, some data that indicate this may need to be reinterpreted, as the conversion dependence of the initiator efficiency was not recognized.

3.04.3.4.3 Dependence of propagation rate constant on monomer structure

Recent data for k_p are summarized in Table 3. Monomers have been grouped into three series according to the α -substituent (hydrogen, methyl, other). Some trends can be seen.

- 1. The Arrhenius A factor decreases by almost an order of magnitude in going from monomers with an α -hydrogen $(20-80 \times 10^6 \text{ M}^{-1} \text{ s}^{-1})$ to those with an α -methyl $(2-5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1})$ and decreases further for those with a larger α -substituent, dimethyl itaconate (44), and the MA dimer (45), $(0.2-1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1})$ (Table 3). The same overall trend is seen for analogous reactions of small radicals (Table 4) and is predicted by theory.
- Within both the α-hydrogen and α-methyl series, the lowest k_p values (for MAN, S, B) are associated with the highest activation energies and the more stable propagating radicals.
- 3. Within the series of alkyl acrylates and methacrylates, there is a clear tendency for increase in k_p with increase in the length of the alkyl chain. The effect is small and, on the basis of the data shown in **Table 3**, cannot be assigned to a variation in *A* or E_a . However, there are reasonable theoretical grounds to expect that this effect could be assigned to changes in the frequency factor.
- 4. The methacrylic monomers with protic substituents (MAA, 2-hydroxyethyl methacrylate (HEMA)) are associated with higher k_p values that are solvent and concentration dependent. The effect is suggestive of monomer–polymer and/or monomer–monomer association through hydrogen bonding.
- 5. The lowering of k_p with the increase in size of the α -substituent (MA>MMA>44~45) is associated with an increase in *A* and a decrease in E_a .



weight distribution is usually a good measure of *v*. With choice of polymerization conditions, the values of *v* are relatively insensitive to the termination rate and mechanism and the occurrence of side reactions such as transfer to monomer. Some difficulties are experienced with high k_p monomers (acrylates, VAc) but appear to have been resolved through the use of low reaction temperatures and dilute media.²¹⁵ These difficulties may arise through interference from backbiting.¹⁶⁰ Independent determination of the rate of polymerization allows k_p/k_t and hence k_t to be evaluated.²¹⁶

There are some reports that values of $k_{\rm p}$ are conversion dependent and that the value decreases at high conversion

3.04.3.4.4 Chain length dependence of propagation rate constants

It is usually assumed that propagation rate constants in homopolymerization (k_p) are independent of chain length and, for longer chains (length > 20), there is experimental evidence to support this assumption.^{196,207} However, there is now a body of indirect evidence to suggest that the rate constants for the first few propagation steps $k_p(1)$, $k_p(2)$, and so on can be substantially different from $k_p(overall)$ (refer Scheme 41). The effect can be seen as a special case of a penultimate unit effect. Evidence comes from a number of sources, for example:
Table 3	Kinetic parameters for propagation in selected radical
polymerizati	ons in bulk monomer

Monomer	k _p (60 °C) ^a (M ^{−1} s ^{−1})	A^{b} ($M^{-1} s^{1} \times 10^{6}$)	E _a b (kJ mol ⁻¹)	Reference
α-H				
MA	28000	16.6	17.7	217
BA	31000	15.8	17.3	218
DA	39000	17.9	17.0	217
VAc	8300	14.7	20.7	219
S ^c	340	42.7	32.5	189
В	200	80.5	35.7	220
α-Methyl				
MAA	1200	-	-	221
MAA(MeOH) ^d	1000	0.60	17.7	221
MAA(H ₂ O) ^e	6700	1.72	15.3	-
MMA ^c	820	2.67	22.4	188
EMA ^c	870	4.06	23.4	187
<i>n</i> BMA ^c	970	3.78	22.9	187
<i>i</i> BMA	1000	2.64	21.8	222
EHMA	1200	1.87	20.4	222
DMA ^c	1300	2.50	21.0	187
HEMA	3300	8.88	21.9	223
GMA	1600	4.41	21.9	223
MAN	59	2.69	29.7	224
α -Other				
44	25	0.20	24.9	225
45	30	1.25	29.5	226

^aValues are calculated from the Arrhenius parameters shown and given to two significant figures.

^bValues given to three significant figures.

^cIUPAC benchmark value

 $^{\prime\!33}$ vol% MAA in methanol. Values are dependent on solvent and on concentration. $^{\prime\!915}$ vol% in water.

MA, methyl acrylate; BA, butyl acrylate; DA, dodecyl acrylate; VAc, vinyl acetate; S, styrene; B, butadiene; MAA, methacrylic acid; MMA, methyl methacrylate; *n*BMA, *n*-butyl methacrylate; *i*BMA, *iso*-butyl methacrylate; EHMA, 2-ethyhexyl methacrylate; GMA, glycidyl methacrylate; MAN, methacrylate; S, styrene

- 1. Chain transfer constants (k_p/k_{tr}) often show a marked chain length dependence for very short chain lengths, indicating that k_p , k_{tr} , or both are chain length dependent.²²⁷
- 2. The absolute rate constants for the reaction of small model radicals with monomers are typically at least an order of magnitude greater than the corresponding values of $k_{\rm p}$ (Table 4).²²⁸

- 3. Aspects of the kinetics of emulsion polymerization⁷⁶ can be explained by invoking chain length dependence of $k_{\rm p}$.
- 4. The apparent chain length dependence of k_p (average) in PLP experiments (Section 3.04.3.4.2) can be interpreted in this light.²¹⁴ However, Olaj *et al.*²²⁹ have interpreted the same and similar data as suggesting a smaller decrease in k_p over a much longer range of chain lengths. They proposed that chain length dependence was a consequence of a change in the degree of solvation of the polymer chain and thus in the effective monomer concentration in the vicinity of the chain end. The explanation is analogous to that proposed to explain the bootstrap effect in copolymerization. Beuermann¹⁸³ has questioned these interpretations, pointing out that the interpretation of PLP data can be problematical due to the dependence of the shape of the molecular weight distribution on experimental parameters.

There have been attempts at direct measurements of these important kinetic parameters in AN,²³⁰ MA,²³¹ MAN,^{232,233} MMA,²³³ and S²³⁴ polymerizations. When the reaction is compared to a reference reaction, care must be taken to establish the influence of chain length on the reference reaction.

Frequency factors for addition of small radicals to monomers are higher by more than an order of magnitude than those for propagation (Table 4). Activation energies are typically lower. However, trends in the data are very similar, suggesting that the same factors are important in determining the relative reactivities for both small radicals and propagating species. The same appears to be true with respect to reactivities in copolymerization.²²⁸



3.04.4 Termination

In this section we consider reactions that lead to the cessation of growth of one or more polymer chains. Three processes will be distinguished:

1. The self-reaction of propagating radicals by combination and/or disproportionation (e.g., Scheme 43) (Section 3.04.4.1).

Table 4Rate constants (25 °C) and Arrhenius parameters for propagation of monomers $CH_2 = CR^1R^2$ compared with rate constants for addition of small radicals

Monomer	$k_{\rho}^{a} (M^{-1} s^{-1})$	<i>Log</i> A	E _a (kJ mol⁻¹)	Model	$k_a^{\ a}$ ($M^{-1} s^{-1}$)	Log A ^b	E _a (kJ mol−¹)
E	77	7.27	34.3	•CH ₃	12 000	8.5	28.2
S	340	7.63	32.5	•CH ₂ Ph	4700	8.5	30.8
MA	28 000	7.22	17.7	47	1 100 000	8.5	15.6
AN	-	-	-	•CH ₂ CN	410 000	8.5	18.4
MMA	820	6.43	22.4	49	9700	7.5	22.4
MAN	59	6.42	29.7	• $C(CH_3)_2CN$	2 300	7.5	26.4

^a Values at 60 °C calculated from the Arrhenius parameters shown and quoted to two significant figures.

^b Log A values based on recommendations of Fischer, H.; Radom, L. Angew. Chem., Int. Ed. Engl. 2001, 40, 1340–1371.²²⁸

E, ethylene; S, styrene; MA, methyl acrylate; AN, acrylonitrile; MMA, methyl methacrylate; MAN, methacrylonitrile





Scheme 44



Scheme 45

- 2. Primary radical termination (Sections 3.04.3.1.9); the reaction of a propagating radical with an initiator-derived (I•, Scheme 44) or transfer agent-derived radical. The significance of this process is highly dependent on the structure of the radical (I•).
- Inhibition (Section 3.04.4.2); the reaction of a propagating radical with another species (Z•, Scheme 45) to give a dead polymer chain. Z• is usually of low molecular weight. Examples of inhibitors are 'stable' radicals (e.g., nitroxides, oxygen), nonradical species that react to give 'stable' radicals (e.g., phenols, quinones, nitroso compounds) and transition metal salts.

Chain transfer, the reaction of a propagating radical with a nonradical substrate to produce a dead polymer chain and a new radical capable of initiating a new polymer chain, is dealt with elsewhere. There are also situations intermediate between chain transfer and inhibition where the radical produced is less reactive than the propagating radical but still capable of reinitiating polymerization. In this case, polymerization is slowed and the process is termed retardation or degradative chain transfer.

3.04.4.1 Radical–Radical Termination

The most important mechanism for the decay of propagating species in radical polymerization is radical-radical reaction by combination or disproportionation as shown in **Scheme 43**. This process is sometimes simply referred to as bimolecular termination. However, this term is misleading since most chain termination processes are bimolecular reactions.

Before any chemistry can take place, the radical centers of the propagating species must come into appropriate proximity and it is now generally accepted that the self-reaction of propagating radicals is a diffusion-controlled process. For this reason, there is no single rate constant for termination in radical polymerization. The average rate constant usually quoted is a composite term that depends on the nature of the medium and the chain lengths of the two propagating species. Diffusion mechanisms and other factors that affect the absolute rate constants for termination are discussed in Section 3.04.4.1.1(iv).

Even though the absolute rate constant for reactions between propagating species may be determined largely by diffusion, this does not mean that there is no specificity in the termination process or that the activation energies for combination and disproportionation are zero or the same. It simply means that this chemistry is not involved in the rate-determining step of the termination process.

The relative importance of combination and disproportionation in relevant model systems and in polymerizations of some common monomers is considered in Sections 3.04.4.1.2(i) and 3.04.4.1.2(ii), respectively. The significance of the termination mechanism on the course of polymerization and on the properties of polymers is discussed briefly in Section 3.04.4.1.2.

3.04.4.1.1 Termination kinetics

A detailed treatment of termination kinetics is beyond the scope of this book. However, some knowledge is important in understanding the chemistry described in subsequent sections. There are a number of reviews of the kinetics of radical-radical termination of propagating species. Those by North²³⁵ and O'Driscoll²³⁶ provide a useful background. Significant advances in our knowledge of termination kinetics came with the development of pulsed laser methods. Recent reviews include those by Buback *et al.*,²³⁷ Russell,^{238–241} and de Kock *et al.*^{242,243} Many of the issues surrounding termination have been summarized by one IUPAC working party.^{185,186,191} Values of, and methods of determining, termination rate constants are currently being critically assessed by another working party.^{237,244}

In Section 3.04.4.1.1(i), we provide an overview of the classical treatment of polymerization kinetics. Some aspects of termination kinetics are not well understood and no wholly satisfactory unified description is in place. Nonetheless, it remains a fact that many features of the kinetics of radical polymerization can be predicted using a very simple model in which radical-radical termination is characterized by a single rate constant. The termination process determines the molecular weight and molecular weight distribution of the polymer. In Section 3.04.4.1.1(ii), we define the terminology used in describing molecular weights and molecular weight distributions. In Section 3.04.4.1.1(iii), we provide a simple statistical treatment based on classical kinetics and discuss the dependence of the molecular weight distribution on the termination process. Some of the complexities of termination associated

with diffusion control and the dependence on chain length and on conversion are described in Section 3.04.4.1.1(iv).

Termination in heterogeneous polymerization is discussed in Section 3.04.4.1.1(v) and the more controversial subject of termination during RDRP is described in Section 3.04.4.1.1(vi).

3.04.4.1.1(i) Classical kinetics

The overall rate constant for radical-radical termination can be defined in terms of the rate of consumption of propagating radicals. Consider the simplified mechanism for radical polymerization shown in Scheme 46.

Ideally, as long as the rate constants for reinitiation ($k_{\rm iT}$, $k_{\rm iM}$) are high with respect to that for propagation ($k_{\rm p}$), the transfer reactions should not directly affect the rate of polymerization and they need not be considered further in this section. The overall rate constant for radical–radical termination (k_t) can be defined in terms of the rate of consumption of propagating radicals as shown in eqn [27]:

$$R_{\rm t} = -2k_{\rm t}[\mathbf{P}\bullet]^2 \qquad [27]$$

where [P•] is the total concentration of propagating radicals and $k_t = k_{tc} + k_{td}$.

In many works on radical polymerization, the factor 2 is by convention incorporated into the rate constant.^{245,246} In this case, $R_t = -k_t [P\bullet]$.² The termination rate constant is then sometimes expressed as $k_t = k_{tc}/2 + k_{td}$ to reflect the fact that only one polymer chain is formed when two propagating radicals combine while two are formed in disproportionation. In reading the literature and when comparing values of k_t care must be taken to establish which definitions have been used.²³⁶ In accord with the current IUPAC recommendation,²⁴⁷ in the following discussion, eqn [27] and $k_t = k_{tc} + k_{td}$ are used.

Application of a steady-state approximation (that $R_t = R_{ix}$ eqn [28]) and a long-chain approximation (negligible monomer consumption in the initiation or reinitiation steps) provides a number of useful relationships.

$$\frac{-d[\mathbf{P}\bullet]}{dt} = R_{i} - R_{t} = 2k_{d}f[\mathbf{I}_{2}] - 2k_{t}[\mathbf{P}\bullet]^{2} = 0$$
 [28]

3. The total concentration of propagating radicals ([P•]) (eqn [29]):

$$[\mathbf{P}\bullet] = \left(\frac{k_{\rm d}f}{k_{\rm t}}\right)^{0.5} [\mathbf{I}_2]^{0.5}$$
 [29]

4. The mean lifetime of a propagating radical (τ) (eqn [30]):

$$\tau = (2k_{\rm d}f[I_2]k_{\rm t})^{-0.5}$$
[30]

5. The average kinetic chain length ($\bar{\nu}$) (eqn [31]):

$$\bar{\nu} = \frac{R_{\rm p}}{R_{\rm t}} = \frac{R_{\rm p}}{R_{\rm i}} = \frac{k_{\rm p}[M]}{(2k_{\rm d}f[I_2]k_{\rm t})^{0.5}}$$
[31]

6. The number average degree of polymerization in the absence of chain transfer (eqn [32]):

$$\bar{X}_{n} = \frac{k_{\rm p}[{\rm M}]}{\left(1 + \frac{k_{\rm td}}{k_{\rm t}}\right) \left(2k_{\rm d}f[{\rm I}_{2}]k_{\rm t}\right)^{0.5}}$$
[32]

7. The initiator efficiency (eqn [33]):

$$f = \left(1 + \frac{k_{\rm td}}{k_{\rm t}}\right) \frac{R_{\rm p}}{\bar{X}_{\rm n} k_{\rm d} [I_2]}$$
[33]

It also enables elimination of the radical concentration in the expression for rate of polymerization (eqn [34]):

$$R_{\rm p} = \frac{-\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} = k_{\rm p}[\mathrm{P}''][\mathrm{M}] = k_{\rm p} \left(\frac{k_{\rm d}f}{k_{\rm t}}\right)^{0.5} [\mathrm{I}_2][\mathrm{M}]^{0.5} \qquad [34]$$

In eqn [34], the rate of polymerization is shown as being half order in initiator (I_2). This is true for only initiators that decompose to two radicals, both of which begin chains. The form of this term depends on the particular initiator and the

Scheme 46

initiation mechanism. The equation takes a slightly different form in the case of thermal initiation e.g., styrene, redox initiation, diradical initiation, and so on. Side reactions also cause a departure from ideal behavior.

Equation [34] can be recast in terms of the fractional conversion of monomer to polymer as in eqn [35]:

$$\cdot \frac{\mathrm{dln}\left(\frac{[\mathrm{M}]}{[\mathrm{M}]_{\mathrm{o}}}\right)}{\mathrm{d}t} = \left(\frac{k_{\mathrm{d}}fk_{\mathrm{p}}^{2}}{k_{t}}\right)^{0.5} [\mathrm{I}_{2}]^{0.5}$$
[35]

From this we can see that knowledge of $k_d f$ and R_p in a conventional polymerization process readily yields a value of the ratio $k_{\rm p}^{2}/k_{\rm t}$. In order to obtain a value for $k_{\rm t}$, we require further information on $k_{\rm p}$. Analysis of $R_{\rm p}$ data obtained under nonsteady-state conditions (when there is no continuous source of initiator radicals) yields the ratio k_p/k_t . Various non-steady-state methods have been developed including the rotating sector method, SIP, and PLP. The classical approach for deriving the individual values of $k_{\rm p}$ and $k_{\rm t}$ by combining values of $k_{\rm p}^2/k_{\rm t}$. with $k_{\rm p}/k_{\rm t}$ obtained in separate experiments can, however, be problematical because the values of k_t are strongly dependent on the polymerization conditions (Section 3.04.4.1.1(iv)). These issues are thought to account for much of the scatter apparent in literature values of $k_{\rm t}$.^{184,237} PLP and related methods yield absolute values of $k_{\rm p}$ directly (the methods used for extracting $k_{\rm p}$ are discussed in Section 3.04.3.4.2). These values may be combined with either k_p^2/k_t or k_p/k_t to give k_t .

The SP–PLP^{183,242,248} and PS–PLP^{183,249} techniques involve following the monomer conversion induced by a single laser pulse or a sequence of laser pulses. These experiments are usually conducted at high pressure because rates of termination are lower and sensitivities are somewhat higher.¹⁸³

EPR methods can be used to determine the radical concentration [P•] either directly^{199,200} or via trapping methods.²⁰¹ Fluorescence experiments have also been designed to give [P•] for a particular conversion.^{250–252} Given [P•] and the rate of polymerization, k_p can be evaluated using eqn [34]. Given the rate of initiation and [P•], k_t can be calculated using eqn [29].^{199,200,253} It is also possible to estimate k_t from the molecular weight distributions given k_p and [P•] using kinetic simulation.^{251,252}

For low conversions, values of the rate constants k_t for monosubstituted monomers (S and acrylates) are $\sim 10^8 \,\text{M}^{-1} \,\text{s}^{-1}$ and those for methacrylates are $\sim 10^7 \,\text{M}^{-1} \,\text{s}^{-1}$ and activation energies are small and in the range $3-8 \,\text{kJ} \,\text{mol}^{-1}$.¹⁸³ These activation energies relate to the rate-determining diffusion process (Section 3.04.4.1.1(iv)) rather than to radical-radical coupling.

Values of termination constants for sterically hindered monomers may be several orders of magnitude lower than those for S (and methacrylates). Such monomers include various α -substituted methacrylates, itaconates, fumarates, and N-substituted itaconimides and maleimides. Values of k_t for these monomers have been reported to lie in the range $10-10^5 \text{ M}^{-1} \text{ s}^{-1}$ depending on the particular structure.²⁰⁰

3.04.4.1.1(ii) Molecular weights and molecular weight averages

The degree of polymerization of a polymer (X_i) is equal to the chain length *i* (the number of monomer units in the chain). If

we neglect end groups, the number molecular weight (M_n) is given by eqn [36]:

$$M_{\rm i} = X_{\rm i} M_0 \qquad [36]$$

where M_0 is the molecular weight or molar mass of the monomer or repeat unit. By definition, the molar mass of the end groups should be included in the molecular weight of a polymer but the corresponding quantity is not included in the degree of polymerization. In this book, in accord with common usage, we use the term molecular weight rather than molar mass when referring to polymers.

The number average molecular weight (\overline{M}_n) is the average molecular weight of all of the polymer chains that make up a sample and is given by eqn [37]:

$$\bar{M}_{n} = \frac{\sum n_{i} X_{i}}{\sum n_{i}} M_{0}$$
[37]

where n_i is the concentration of chains of length *i* (monomer units)

The weight average molecular weight (\overline{M}_w) is given by eqn [38]:

$$\bar{M}_{w} = \frac{\sum w_{i}X_{i}}{\sum w_{i}}M_{0} = \frac{\sum n_{i}X_{i}^{2}}{\sum n_{i}X_{i}}M_{0}$$
[38]

where w_i is the weight of chains of length *i*.

The z average molecular weight (\overline{M}_z) is provided by eqn [39]:

$$\bar{M}_{z} = \frac{\sum n_{i} X_{i}^{3}}{\sum n_{i} X_{i}^{2}} M_{0}$$
[39]

This term gives some information about the asymmetry of the molecular weight distribution and is important in analyzing sedimentation behavior in ultracentrifugation.

It is also useful to define the moments of the chain length distribution (CLD). The *j*th moment is defined in eqn [40]:

$$\lambda^j = \sum n_i X_i^j \tag{40}$$

The zeroth moment $\lambda^0 = \sum n_i$ can be recognized as the total concentration of polymer chains and the first moment $\lambda^1 = \sum n_i X_i = \sum w_i$ is the total concentration of repeat or monomer units in those chains. The moments can be related to the molecular weight averages as follows:

$$\bar{M}_{\rm n} = \frac{\lambda^1}{\lambda^0} M_0, \ \bar{M}_{\rm w} = \frac{\lambda^2}{\lambda^1} M_0, \ \bar{M}_{\rm z} = \frac{\lambda^3}{\lambda^2} M_0$$

The breadth of the molecular weight distribution is often discussed in terms of the dispersity (D) (also commonly called the polydispersity index or the polydispersity) and is expressed in terms of the moments as shown in eqn [41]:

$$D = \frac{\bar{X}_{w}}{\bar{X}_{n}} = \frac{\bar{M}_{w}}{\bar{M}_{n}} = \frac{\lambda^{0}\lambda^{1}}{(\lambda^{1})^{2}}$$

$$[41]$$

In calculations the moments can be treated as concentrations. Kinetic simulation of radical polymerization to evaluate dispersities typically involves evaluation of the moments rather than the complete distribution. This method of moments is accurate as long as the kinetics are independent of chain length.

3.04.4.1.1(iii) Molecular weight distributions

The simple statistical treatment of radical polymerization can be traced back to Schultz.²⁵⁴ Texts by Flory⁸ and Bamford *et al.*¹⁰ are useful references.

The probability of a propagation event (ϕ) can be defined as shown in eqn [42]:

$$\phi = \frac{R_{\rm p}}{R_{\rm p} + R_{\rm t} + R_{\rm tr}}$$
$$= \frac{k_{\rm p}[{\rm M}]}{k_{\rm p}[{\rm M}] + 2k_{\rm t}[{\rm P}^{\bullet}] + k_{\rm trI}[{\rm I}_2] + k_{\rm trM}[{\rm M}] + k_{\rm trT}[{\rm T}]} \qquad [42]$$

A given chain will undergo *i*-1 propagation steps (each with probability ϕ) before termination (with probability $1-\phi$). Thus, if termination is wholly by chain transfer or disproportionation, the CLD is given by eqn [43] (Figure 14):

$$n_i = \phi^{i-1}(1-\phi)$$
 [43]

This distribution is known as the Schultz–Flory or most probable distribution. $^{\rm 8}$

The moments of the molecular weight distribution are

$$\lambda^0 = 1, \lambda^1 = (1-\phi)^{-1}, \lambda^2 = (1+\phi)(1-\phi)^{-2}$$

and the average degrees of polymerization and dispersity are

$$\bar{X}_{n} = \frac{1}{1-\phi}, \ \bar{X}_{w} = \frac{1+\phi}{1-\phi}, \ \text{ and } D = \frac{\bar{X}_{w}}{\bar{X}_{n}} = 1+\phi$$

and for long chains as $\phi \longrightarrow 1$, $D \longrightarrow 2$.

If termination is wholly by combination, it can be shown¹⁰ that the number distribution is given by eqn [44] (Figure 14):

$$n_i = (i-1)(1-\phi)^2 \phi^{i-2}$$
[44]

The moments of the molecular weight distribution are

$$\lambda^0 = 1, \ \lambda^1 = 2(1-\phi)^{-1}, \ \lambda^2 = (4+2\phi)(1-\phi)^{-2}$$

and the average degrees of polymerization and dispersity are

$$\bar{X}_{n} = \frac{2}{1-\phi}, \ \bar{X}_{w} = \frac{2+\phi}{1-\phi}, \ \text{and} \ D = \frac{\bar{X}_{w}}{\bar{X}_{n}} = \frac{2+\phi}{2}$$

The molecular weight distribution in this case is significantly narrower. For long chains as $\phi \rightarrow 1$ so $D \rightarrow 1.5$.

For the more general case, the molecular weight distribution will be described by a weighted average of eqns [43] and [44] (eqn [45]):

$$n_{i} = \frac{R_{tc}}{R_{t} + R_{tr}} (i-1)(1-\phi)^{2} \phi^{i-2} + \frac{R_{td} + R_{tr}}{R_{t} + R_{tr}} \phi^{i-1}(1-\phi)$$
 [45]

These equations predict that for oligomers with degree of polymerization less than 10, dispersities significantly less than 1.5 will be obtained (Figure 15).

The above treatment applies only to polymerizations where there is negligible conversion of monomer, initiator, and transfer agents. Analytical treatments have been devised to take into account effects of conversion and more complex mechanisms. Discussion of these is beyond the scope of this book.

A common error is to confuse the gel permeation chromatography (GPC) distribution with the weight distribution. The response of a refractive index detector is proportional to the mass of polymer. The GPC elution volume (V) typically scales according to the logarithm of the degree of polymerization (or the logarithm of the molecular weight). Thus, $V \sim a + b \log i$ (where a and b are constants) and a volume increment (dV) will be proportional to di/i. It follows that the *y*-axis of the GPC distribution (e.g., **Figure 14b**) is proportional to iw_i or i^2n_i .

3.04.4.1.1(iv) Diffusion-controlled termination

Termination by self-reaction of propagating radicals is a diffusion-controlled process even at very low conversion.²³⁷ The evidence for this includes the following:

- 1. Analogy with the known chemistry of small radicals. The rate constants for self-reaction of small radicals approach the diffusion-controlled limit and the rate constants can be predicted using the Smoluchowski equation.
- 2. The value of k_t shows an inverse dependence on medium viscosity as anticipated for a diffusion-controlled reaction.
- The value of k_t decreases with increasing pressure (positive activation volume). For a reaction involving the



Figure 14 (a) Number and (b) GPC distributions for two polymers both with $\bar{X}_n = 100$. The number distribution of chains formed by disproportionation or chain transfer (-----, $\Sigma n_i = 1.0$, $\bar{X}_w/\bar{X}_n = 2.0$) is calculated using eqn [43]. The number distribution of chains formed by combination (---, $\Sigma n_i = 1.0$, $\bar{X}_w/\bar{X}_n = 1.5$) is calculated using eqn [44].



Figure 15 Dispersity (D) as a function of \overline{X}_n for polymers formed by (a) disproportionation or chain transfer (——) and (b) combination (-----).

combination of two species, the activation volume is expected to be negative.

However, while it is generally accepted that the rate of radicalradical reaction is dependent on how fast the radical centers of the propagating chains (P_i^{\bullet} and P_j^{\bullet}) come together, there remains some controversy as to the diffusion mechanism(s) and/or what constitutes the rate-determining step in the diffusion process. The steps in the process as postulated by North and coworkers^{255–257} are shown conceptually in Scheme 47.

Center of mass or translational diffusion is believed to be the rate-determining step for small radicals²⁵⁸ and may also be important for larger species. However, other diffusion mechanisms are operative and are required to bring the chain ends together and these will often be the major term in the termination rate coefficient for the case of macromolecular species. These include the following:

- 1. Segmental motion. The internal reorganization of the chain required to bring the reactive ends together.
- 2. Reptation. The snaking of the chain through a viscous medium.
- 3. Reaction diffusion (also called residual termination). Chain end motion by addition of monomer to the chain end.

The relative importance of these mechanisms, and the value of the overall k_t , depends on the molecular weight and dispersity of the propagating species, the medium, and the degree of conversion. The value of k_t is not a constant!

In dealing with radical-radical termination in bulk polymerization, it is common practice to divide the polymerization



Figure 16 Conversion time profile for bulk MMA polymerization at 50 °C with AIBN initiator illustrating the three conversion regimes. Data are taken from Balke, S. T.; Hamielec, A. E. *J. Appl. Polym. Sci.* **1973**, *17*, 905–949.²⁵⁹

timeline into three or more conversion regimes.^{236,260} The reason for this is evident from **Figure 16**. Within each regime, expressions for the termination rate coefficient are defined according to the dominant mechanism for chain end diffusion. The usual division is as follows:

- Low conversion prior to the onset of the autoacceleration phenomenon known as the gel or Norrish–Trommsdorff effect^{261–263} and characterized by highly mobile propagating species. Center of mass and/or segmental diffusion are the rate-determining mechanisms for chain end movement. Initiator efficiencies are high and approximately constant.
- 2. Medium-to-high conversion immediately after the onset of the gel effect. The diffusion mechanism is complex. Large chains become effectively immobile (on the timescale of the lifetime of a propagating radical) even though the chain ends may move by segmental diffusion, reptation, or reaction diffusion. Monomeric species and short chains may still diffuse rapidly. Short–long termination dominates. Initiator efficiencies may reduce with conversion.
- Very high conversion the polymerization medium is a glassy matrix. Most chains are immobile and reaction diffusion is the rate-determining diffusion mechanism. New chains are rapidly terminated or immobilized. Initiator efficiencies are very low.

The precise conversion ranges are determined by a variety of factors including the particular monomer, the molecular weight of the polymeric species, and the solvent (if any). For



Scheme 47

bulk polymerization of S and MMA, (1) is typically < 20%, (2) is 20–85%, and (3) is > 85%. In solution polymerization, or for polymerizations carried out in the presence of chain transfer agents, the duration of the low-conversion regime is extended and the very high-conversion regime may not occur. Cage escape is also a diffusion-controlled process, thus the initiator efficiency (*f*) and the rate of initiation ($k_d f$) generally decrease with conversion and depend on the conversion regime as indicated above.

3.04.4.1.1(iv)(a) Termination at low conversion Most in-depth studies of termination deal only with the low-conversion regime. Logic dictates that simple center of mass diffusion and overall chain movement by reptation or many other mechanisms will be chain length dependent. At any instant, the overall rate coefficient for termination can be expressed as a weighted average of individual chain length-dependent rate coefficients (eqn [46]):²⁶⁴

$$k_{t} = \frac{\sum_{i=1}^{\infty} \sum_{j=1}^{\infty} k_{t}^{i,j}[\mathbf{P}_{i}\bullet][\mathbf{P}_{j}\bullet]}{[\mathbf{P}\bullet]^{2}}$$
[46]

where $k_t^{i,j}$ is the rate coefficient for reaction between species of chain lengths *i* and *j*, and [P•] is the total radical concentration.

Mahabadi and O'Driscoll²⁶⁴ considered that segmental motion and center of mass diffusion should be the dominant mechanisms at low conversion. They analyzed data for various polymerizations and proposed that $h_t^{i,j}$ should be dependent on chain length such that the overall rate constant obeys the expression:

$$k_t \propto \bar{X}_n^{-\alpha}$$
 [47]

where \bar{X}_n is the number average degree of polymerization and $\alpha = 0.5$ for short \bar{X}_n reducing to 0.1 for large \bar{X}_n .

Various expressions have been proposed for estimating how the overall rate coefficient k_t and the individual rate coefficients $k_t^{i,j}$ vary with the chain lengths of the reacting species, ^{236,264–271} simple relationships of the following forms are the most often applied: ^{257,267,271,272}

1. The harmonic mean is said to be of the functional form expected if chain end encounter or coil overlap is ratedetermining:

$$k_{\rm t}^{ij} = k_{\rm to} \left(\frac{2 \cdot i \cdot j}{i+j}\right)^{-\alpha}$$
[48]

 The Smoluchowski mean is of the functional form expected if translational diffusion is rate-determining; it is known to provide a reasonable description of the termination kinetics of small radicals:

$$k_{\rm t}^{i,j} = 0.5k_{\rm to}(i^{-\infty} + j^{-\infty})$$
[49]

or

$$k_{\rm t}^{i,j} = 2\pi \,\sigma \, p_{\rm spin}(D^i + D^j) \tag{50}$$

where σ is a capture radius, p_{spin} is a spin multiplicity term, and D^i and D^j are chain length-dependent diffusion constants. When $\alpha = 1$, the Smoluchowski mean and the harmonic mean approximations are the same 3. The geometric mean has no physical basis but has been suggested to best approximate the functional form of the segmental diffusion process:

$$k_{\rm t}^{i,j} = k_{\rm to}(i \cdot j)^{-\infty/2}$$
 [51]

where α and k_{to} are constants.

While many data are suggestive of chain length dependence, the data are not usually suitable for or have not been tested with respect to model discrimination. Values of $k_t^{1,1}$ have been determined for a variety of small 'monomeric' radicals to be $\sim 10^9 \text{ M}^{-1} \text{ s}^{-1}$.²⁷² Taking k_{to} as $k_t^{1,1}$ and α as 1.0 in the geometric expression yields values of $k_t^{i,j}$ as shown in **Figure 17a**.²¹⁴ Use of the Smoluchowski mean or the harmonic mean approximation predicts a shallower dependence of $k_t^{i,j}$ on the chain length (**Figure 17b**). All expressions yield the same dependence for j = i.

However, it has been pointed out that the value of k_{to} in the expressions (eqns [51]-[49]) should not be confused with the small radical $k_t^{1,1}$, rather, the value of k_{to} represents the termination rate constant of a single unit chain if the implied diffusion mechanism was the rate-determining process.

Recent work has allowed values of $k_t^{i,i}$ and α for bulk polymerization in dilute solution to be estimated. This work suggests values of $k_{to} = k_t^{1,1} \sim 1 \times 10^8 \text{ M}^{-1}$ and $\alpha \sim 0.15 - 0.25$ for both MMA and S.^{183,274} Some values of $k_t^{1,1}$ and α for S and (meth)acrylates estimated from SP–PLP at high pressure experiments are shown in Table 5.

The value of the exponent α obtained in the above-mentioned experiments is in remarkable accord with predictions based on a consideration of excluded kinetic volume effects. Khokhlov²⁷⁵ proposed that for a slow, chemically controlled reaction between the ends of long chains α should be 0.16. The value of α was suggested to increase to 0.28 for chain end-mid-chain reaction and to 0.43 for mid-chain-mid-chain reaction. The latter provides one possible explanation for the greater exponent for higher acrylates (Table 5).²⁷⁶

For the situation where the chain length of one or both of the species is 'small' (not entangled with itself or other chains) and conversion of monomer to polymer is low, the termination kinetics should be dominated by the rate of diffusion of the shorter chain. While the chain remains short, the time required for the chain reorganization to bring the reacting centers together will be insignificant and center of mass diffusion can be the rate-determining step. As the chain becomes longer, segmental diffusion will become more important. Thus, it is expected that $k_t^{i,j}$ should lie between an upper limit predicted by the Smoluchowski mean (eqn [49]) and a lower limit predicted by the geometric mean value for higher chain lengths as shown in **Figure 18**.

Smith *et al.*²⁷⁴ have recently suggested a composite model based on similar considerations to predict $k_t^{i,j}$ over the entire chain length range. Experimental data for $k_t^{1,1}$ for dodecyl methacrylate polymerization consistent with such a model have been provided by Buback *et al.*²⁷⁷

Since shorter, more mobile, chains diffuse more rapidly (by center of mass diffusion or other mechanisms), they are more likely to be involved in termination. For this reason, most termination involves reaction of a long species with a short



Figure 17 Chain length dependence of $k_{t}^{i,j}$ predicted by (a) the geometric mean (eqn [51]) or (b) the harmonic mean approximation (eqn [48]) or the Smoluchowski mean (eqn [49]) with $\alpha = 1.0$ and $k_{to} = 10^9$; *i* and *j* are the lengths of the reacting chains.

 Table 5
 Parameters characterizing chain length dependence of termination rate coefficients in radical polymerization of common monomers

Monomer	Т <i>(°С)</i>	P <i>(bar)</i>	k_{p} ($M^{-1} s^{-1}$)	$k_{to} (M^{-1} s^{-1})$	α	Reference
S MMA DMA MA BA	40 40 40 40	1000 2000 1000 1000 1000	1 600 1 700 1 400 28 600 35 600	7×10^{7} 4×10^{7} 3×10^{6} 2×10^{8} 6×10^{7}	0.16 0.14 0.15 0.15 0.14	248 276 276 276 276

Determined by the SP–PLP technique. Values apply to bulk polymerization at low conversion (up to 15% conversion).

S, styrene; MMA methyl methacrylate; DMA, dodecyl methacrylate; MA, methyl acrylate; BA, butyl acrylate; DA, dodecyl acrylate

species. The lower mobility of long chains ensures that they are unlikely to react with each other. Cardenas and O'Driscoll²⁷⁸ proposed that propagating species be considered as two populations; those with chain length below the entanglement limit and those above. This basic concept has also been adopted by



Figure 18 Chain length dependence of $k_t^{i,j}$ predicted by the Smoluchowski mean (eqn [49]) with $\alpha = 0.5$ and $k_{to} = 10^9$ (upper series) and the geometric mean (eqn [51]) with $\alpha = 0.2$ and $k_{to} = 10^8$ (lower series); *i* and *j* are the lengths of the reacting chains. For low conversions, $k_t^{i,j}$ is expected to lie between the values predicted by eqns [49] and [51] (see text).

other authors.^{251,279–282} Russell²⁷⁹ has provided a detailed critique of these concepts. Direct experimental evidence for the importance of the dispersity of the propagating radicals on termination kinetics has been reported by Faldi *et al.*²⁸⁰ O'Neil and Torkelson questioned the chain entanglement concept pointing out that for low conversions chain entanglements are unlikely even for chain lengths > 100.

For larger species, even though the chains themselves may be in contact, chain end diffusion by segmental motion, reptation, or reactive diffusion will be required to bring the radical centers together. These terms are likely to be more important than center of mass diffusion. North²³⁵ argued that diffusion of the reactive chain end of longer chains by segmental diffusion should be independent of chain length and has presented some experimental evidence for this hypothesis.

Bamford^{270,283–287} has proposed a general treatment for solving polymerization kinetics with chain length dependent on k_t and considered in some detail the ramifications with respect to molecular weight distributions and the kinetics of chain transfer, retardation, and so on.

3.04.4.1.1(iv)(b) Termination at medium-to-high conversions Changes in the population of propagating species and the increase in the polymer concentration mean that the rate coefficient for radical-radical termination will decrease with conversion. The moderate conversion regime is

characterized by the autoacceleration phenomenon known as the gel or Norrish–Trommsdorf effect.^{261–263} Various empirical relationships defining k_t or the rate of diffusion of long chains in terms of either the viscosity^{235,288} or the free volume^{259,260,269,289–293} have been proposed which enable the onset of the gel effect (Figure 16) to be predicted for a number of polymer systems.

Ito,²⁹⁴ Tulig and Tirrell,²⁹⁵ and de Gennes^{296,297} have proposed expressions for k_t based on a reptation mechanism. More recently, the manner in which the termination rate coefficient scales with chain length for entangled systems has been considered in some detail in studies by O'Shaughnessy and coworkers.^{281,282,298,299} For the situation where both chains are long (entangled), the way in which the termination coefficient (or diffusion rates) should scale with chain length means that a long chain is unlikely to terminate by reaction with another long chain. Short-long termination is dominant. Measurements of the diffusion rate constants of oligomers and polymers provide some support for this theory.

The concept of reaction diffusion (also called residual termination) has been incorporated into a number of treatments.^{300,301} Reaction diffusion will occur in all conversion regimes. However, at low and intermediate conversions, the process is not of great significance as a diffusion mechanism. At high conversion, long chains are essentially immobile and reaction diffusion becomes the dominant diffusion mechanism (when *i* and *j* are both 'large' > 100). The termination rate constant is determined by the value of k_p and the monomer concentration. In these circumstances, the rate constant for termination k_t^{ij} should be independent of the chain lengths *i* and *j* and should obey an expression of the form:³⁰⁰

$$k_{\rm t}^{\rm i,j} = k_{\rm t1} k_{\rm p} [{\rm M}]$$
 [52]

where k_{t1} is a constant.

3.04.4.1.1(v) Termination in heterogeneous polymerization

The kinetics of termination in suspension polymerization is generally considered to be the same as for solution or bulk polymerization under similar conditions and will not be discussed further. A detailed discussion on the kinetics of termination in emulsion polymerization appears in recent texts by Gilbert⁷⁴ and Lovell and El-Aasser⁷⁵ and readers should consult these for a more comprehensive treatment.

The steps involved in entry of a radical into the particle phase from an aqueous-phase initiator have been summarized in Section 3.04.2.1.11. Aqueous-phase termination prior to particle entry should be described by conventional dilute solution kinetics (Section 3.04.4.1.1.4(i)). Note that chain lengths of the aqueous-soluble species are short (typically <10 units).

Even though the chemical reactions are the same (i.e., combination, disproportionation), the effects of compartmentalization are such that, in emulsion polymerization, particle-phase termination rates can be substantially different to those observed in corresponding solution or bulk polymerizations. A critical parameter is \bar{n} , the average number of propagating species per particle. The value of \bar{n} depends on the particle size and the rates of entry and exit.

Many emulsion polymerizations can be described by so-called zero-one kinetics. These systems are characterized by particle sizes that are sufficiently small that entry of a radical into a particle already containing a propagating radical always causes instantaneous termination. Thus, a particle may contain either zero or one propagating radical. The value of \bar{n} will usually be less than 0.4. In these systems, radical-radical termination is by definition not rate determining. Rates of polymerization are determined by the rates of particle entry and exit rather than by the rates of initiation and termination. The main mechanism for exit is thought to be chain transfer to monomer. It follows that radical-radical termination, when it occurs in the particle phase, will usually be between a short species (one that has just entered) and a long species.

Treatments (Smith–Ewart,³⁰² pseudo-bulk⁷⁴) have been devised which allow for the possibility of greater than one radical per particle and for the effects of chain length-dependent termination. Further discussion on these is provided in the references mentioned above.^{74,75}

Microemulsion and miniemulsion polymerization processes differ from emulsion polymerization in that the particle sizes are smaller (10–30 and 30–100 nm, respectively, vs. 50–300 nm)⁷⁴ and there is no discrete monomer droplet phase. All monomer is in solution or in the particle phase. Initiation usually takes place by the same process as conventional emulsion polymerization. As particle sizes reduce, the probability of particle entry is lowered and so is the probability of radical-radical termination. This knowledge has been used to advantage in designing living polymerizations based on reversible chain transfer (e.g., RAFT, Section 3.04.6.6.2).^{303–305}

3.04.4.1.1(vi) Termination during RDRP

It remains a common misconception that radical-radical termination is suppressed in RDRP processes such as RAFT, NMP, or ATRP. An issue, in many people's minds, is whether processes that involve an irreversible termination step, even as a minor side reaction, can be called living. The term 'living radical polymerization' appears to be an oxymoron; a contradiction in terms (Section 3.04.6.4.1(i)). In any processes that involve propagating radicals, there will be a finite rate of termination commensurate with the concentration of propagating radicals and the reaction conditions. The RDRP processes that sometimes fall under the heading of living or controlled radical polymerization (e.g., NMP, ATRP, RAFT) provide no exceptions.

In conventional radical polymerization, the CLD of propagating species is broad and new short chains are formed continually by initiation. As has been stated above, the population balance means that, termination, most frequently, involves the reaction of a shorter, more mobile, chain with a longer, less mobile, chain. In well-controlled RDRP, the chain lengths of most propagating species are similar (i.e., $i \sim j$) and increase with conversion. Ideally, in ATRP and NMP no new chains are formed. In practice, some new chains may be formed, as, for example, from thermal initiation in S polymerization. In processes such as RAFT, new small radicals are continuously formed by initiation as in the conventional process but form a much smaller part of the population as they undergo rapid equilibration with longer dormant chains.

Diffusion mechanisms depend on chain length as follows:

1. Very short chains (*X*_n<10 units). Translational diffusion is the most important diffusion mechanism.

- 2. Chains of moderate length ($X_n \sim 10-100$ units). Segmental motion of the chain ends is the rate-determining diffusion mechanism.
- 3. Long chains. Chains immobile, reaction diffusion is rate determining.

Based on this it might be expected that at low conversions the extent of termination would be higher than in a conventional polymerization since all chains are short. Similarly, for higher conversions the extent of termination should be lower than in a conventional polymerization because most chains are long.³⁰³ It has also been proposed that the molecular weight distribution in RDRP might be analyzed to provide values of $k_t^{i,i}$ as a function of molecular weight. Vana *et al.*³⁰⁶ have analyzed RAFT polymerization in this context. Their data suggest a chain length dependence in general agreement with that suggested by other methods. It can also be noted that the SP–PLP experiment is, in some respects, a good model of an RDRP and also provides values of $k_t^{i,i}$.^{183,276,277}

It can also be noted that reversible chain transfer, in RAFT and similar polymerizations, and reversible activation–deactivation, in NMP and ATRP, provide other mechanisms for reaction diffusion.

3.04.4.1.2 Disproportionation versus combination

Even though the rate of radical-radical reaction is determined by diffusion, this does not mean there is no selectivity in the termination step. As with small radicals, self-reaction may occur by combination or disproportionation. In some cases, there are multiple pathways for combination and disproportionation. Combination involves the coupling of two radicals (Scheme 43). The resulting polymer chain has a molecular weight equal to the sum of the molecular weights of the reactant species. If all chains are formed from initiator-derived radicals, then the combination product will have two initiator-derived ends. Disproportionation involves the transfer of a β -hydrogen from one propagating radical to the other. This results in the formation of two polymer molecules. Both chains have one initiator-derived end. One chain has an unsaturated end and the other has a saturated end (Scheme 43).

Since the mode of termination clearly plays an important part in determining the polymer end groups and the molecular weight distribution, a knowledge of the disproportionation: combination ratio (k_{td}/k_{tc}) is vital to the understanding of structure–property relationships. Unsaturated linkages at the ends of polymer chains, as may be formed by disproportionation, have long been thought to contribute to polymer instability and it has been demonstrated that both head-to-head linkages and unsaturated ends are weak links during the thermal degradation of PMMA.^{307–310} Polymer chains with unsaturated ends may also be reactive during polymerization. Copolymerization of macromonomers formed by disproportionation is a possible mechanism for the formation of long-chain branches.^{311–313} Such macromonomers may also function as RAFT agents (Section 3.04.6.6).^{313–315}

Knowledge of k_{td}/k_{tc} is also important in designing polymer syntheses. For example, in the preparation of block copolymers using polymeric or multifunctional initiators, ABA or AB blocks may be formed depending on whether termination involves combination or disproportionation, respectively. The relative importance of combination and disproportionation is also important in the analysis of polymerization kinetics and, in particular, in the derivation of rate parameters.

3.04.4.1.2(i) Model studies

The determination of k_{td}/k_{tc} by direct analysis of a polymerization or the resultant polymer often requires data on aspects of the polymerization mechanism that are not readily available. For this reason, it is appropriate to consider the self-reactions of lowmolecular-weight radicals that are structurally analogous to the propagating species. These model studies provide valuable insights by demonstrating the types of reaction that are likely to occur during polymerization and the factors influencing k_{td}/k_{tc} .

In these model studies, evaluation of k_{td}/k_{tc} is simplified because reactions that compete with disproportionation or combination are more readily detected and allowed for. However, by their very nature, model studies cannot exactly simulate all aspects of the polymerization process. Consequently, a number of factors must be borne in mind when using model studies to investigate the termination process. These stem from differences inherent in polymerization versus simple organic reactions and include the following:

- 1. There may be additional pathways open to the poly- or oligomeric radicals that are not available to the simple model species.³¹⁶
- 2. In polymerization, particular propagating species have only transient existence since they are scavenged by the addition of monomer or other reactions. Model studies are usually designed such that the self-reaction is the only process. This can lead to a very different and sometimes misleading product distribution. A knowledge of the reaction kinetics is extremely important in analyzing the results.
- Reaction conditions (solvent, viscosity, etc.) chosen for the model experiment and the polymerization experiment are often very different.

Model carbon-centered radicals are conveniently generated from azo compounds. These have the advantage that radicals are generated in pairs and that transfer to initiator is generally not a serious problem. All of the major products from thermal or photochemical decomposition in an inert solvent are the products from radical-radical reaction. One frequently observed complication is polymerization of the unsaturated by-products of disproportionation. This problem may be circumvented by conducting experiments in the presence of an inhibitor, the concentration of which can be chosen such that all radicals that escape the solvent cage are trapped and reactions of the initiator-derived radicals with other species are eliminated.³¹² The value of k_{td}/k_{tc} is determined by analyzing the products of cage reaction. Most data indicate no difference in specificity between the cage and encounter (i.e., noncage) processes.³¹²

A comprehensive survey combination:disproportionation ratios complied from the literature through mid-2005 is provided in *The Chemistry of Radical Polymerization*.¹

3.04.4.1.2(ii) Polymerization

A substantial number of studies give information on k_{td}/k_{tc} for polymerizations of S and MMA. There has been less work on other systems. One of the main problems in assessing k_{td}/k_{tc} lies with assessing the importance of other termination mechanisms (i.e., transfer to initiator, solvent, etc., primary radical termination).

Techniques applied in assessing the relative importance of disproportionation and combination include the following:

- 1. The gelation technique. This method was developed by Bamford *et al.*³¹⁷ In graft copolymerization, termination by combination will give rise to a cross-link, while disproportionation (and most other termination reactions) will lead to graft formation. The initiation system based on a polymeric halo-compound (poly(vinyl trichloroacetate)/Mn₂ (CO)₁₀/*hv*) was used to initiate polymerization and the time for gelation was used to calculate k_{td}/k_{tc} . In the original work, the results were calibrated with reference to data for S polymerization, disproportionation may account for 10–20% of chains. Thus the data may require minor adjustment. Systems studied with this technique include AN, MAN, MA, MMA, and S.
- Molecular weight measurement. The mode of termination can be calculated by comparing the kinetic chain length (the ratio of the rate of propagation to the rate of initiation or termination) with the measured number average molecular weight.^{318–320}
- 3. Molecular weight distribution evaluation. This method relies on a precise evaluation of the molecular weight distribution.^{321–324} The mode of termination has a significant influence on the shape of the molecular weight distribution with the instantaneous dispersity (*D* being \sim 2.0 if terminaoccurs exclusively by disproportionation tion of propagating radicals and ~ 1.5 if termination involves only combination (Section 3.04.4.1.1(ii)).³²⁵ Values of *D* are conversion dependent so the method should only be applied to very low-conversion samples. Truncation of the ends of the distribution as a result of baseline selection difficulties will lead to the dispersity being underestimated.³²⁶ A more precise but related method is to fit the entire molecular weight distribution using kinetic modeling methods.
- 4. End group determination. Polymer chains terminated by combination possess two initiator-derived chain ends. Disproportionation affords chains with only one such end. The value of k_{td}/k_{tc} can therefore be determined by evaluating the initiator-derived polymer end groups/molecule by applying eqn [53]:

$$\frac{k_{\rm td}}{k_{\rm tc}} = \frac{(2-x)}{2(x-1)}$$
[53]

where *x* is the number of initiator fragments per molecule. The errors inherent in this technique can be large since the polymer end groups typically comprise only a very small fraction of a polymer sample. The initiator-derived ends may be labeled for ease of detection. It is necessary to allow for side reactions. If there is transfer to monomer, solvent, and so on, the value of k_{td}/k_{tc} will be overestimated. The occurrence of transfer to initiator, primary radical termination, or copolymerization of initiator by-products will lead to k_{td}/k_{tc} being underestimated.

Scheme 48

5. Mass spectrometry. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectroscopy has been used to determine k_{td}/k_{tc} in S and MMA polymerization.³²⁷ Chains formed by disproportionation and chains formed by combination form two distinct distributions.

Evaluation of molecular weights after ultrasonic scission of high-molecular-weight polymers (PMMA and PS) in the presence of a radical trap has been claimed to provide evidence of the termination mechanism.³²⁸ However, scission gives radicals as shown in **Scheme 48**.

3.04.4.1.2(iii) Summary

A comprehensive survey combination:disproportionation ratios for both model systems and polymerizations complied from the literature through mid-2005 is provided in *The Chemistry of Radical Polymerization.*¹ Unequivocal numbers for k_{td}/k_{tc} are not yet available for most polymerizations and there is only qualitative agreement between values obtained in model studies and real polymerizations.

It is tempting to attribute problems in reconciling data from model studies and actual polymerizations to difficulties associated with data interpretation. The polymerization experiments are often complicated by other termination pathways, in particular chain transfer, which must be allowed for when assessing the results. It is notable in this context that the discrepancies are most evident for reactions carried out at higher temperatures.

However, some of the differences may be explicable in terms of an effect of molecular size. For many of the model systems, at least one of the reaction partners is monomeric. Since combination is known to be more sensitive to steric factors than disproportionation, k_{td}/k_{tc} may be anticipated to be higher for the corresponding propagating species. The values of k_{td}/k_{tc} seen for systems involving monomeric model radicals should be considered only as a lower limit for the polymeric system.

Despite these problems in assessing $k_{td}/k_{tc'}$ it is possible to make some generalizations:

- Termination of polymerizations involving vinyl monomers (CH₂=CHX) involves predominantly combination.
- Termination of polymerizations involving α-methylvinyl monomers (CH₂=C(CH₃)X) always involves a measurable proportion of disproportionation.
- 3. During disproportionation of radicals bearing an α -methyl substituent (e.g., those derived from MMA), there is a strong preference for transfer of a hydrogen from the α -methyl group rather than the methylene group.
- 4. Within a series of vinyl or α-methylvinyl monomers, k_{td}/k_{tc} appears to decrease as the ability of the substituent to stabilize a radical center increases. Thus, k_{td}/k_{tc} for radicals ~ C(•)(CH₃)X or ~ C(•)HX decreases in the series where X is CO₂R ≫ CN>Ph.

3.04.4.2 Inhibition and Retardation

Inhibitors and retarders are used to stabilize monomers during storage or during processing (e.g., synthesis, distillation). They are often used to quench polymerization when a desired conversion has been achieved. They may also be used to regulate or control the kinetics of a polymerization process.

Inhibitors have been defined as species that, when added to a polymerization, react to consume and deactivate the initiator-derived radicals.329 Retarders have been similarly defined as species that deactivate the propagating radicals.³²⁹ According to this definition, a nitroxide added to a t-butoxy radical-initiated polymerization of S should be called a retarder since the t-butoxy radicals appear not to react with the nitroxide. However, the initiator-derived and propagating radicals often show similar selectivity in their reactions and the distinction between inhibitors and retarders becomes blurred. In a cyanoisopropyl radical-initiated polymerization of S, an added nitroxide would be called an inhibitor when used in high concentration and a retarder when used at very low concentration. Generally the term inhibitor is used without reference to which radicals are scavenged. With many experimental techniques, it is not possible to discriminate between scavenging of initiator-derived and oligomeric propagating radicals. Thus an inhibitor has come to mean any species that is able to rapidly and efficiently scavenge propagating and/or initiator-derived radicals and thus prevent polymer chain formation. The term retarder is commonly used to define species that slows rather than prevents polymerization.

Inhibitors or retarders that give inert products are called 'ideal'.³²⁹ The term 'ideal inhibitor' has also been used to describe a species that stops all polymerization until such time as it is completely consumed (i.e., the induction period) and then allows polymerization to proceed at the normal rate. However, in many cases the products formed during inhibition or retardation are not inert. Four main pathways for further

reaction following the initial reaction with inhibitor or retarder are distinguished:

- 1. Slow reinitiation with reference to propagation following chain transfer.
- Slow propagation with reference to normal propagation following addition.
- 3. Further reaction of the initially formed species as an inhibitor or retarder.
- 4. Reversal of the reaction associated with inhibition or retardation.

The kinetics and mechanism of retardation and inhibition has been reviewed by Bamford,³²⁹ Tüdos and Földes-Berezsnich,³³⁰ Eastmond,³³¹ Goldfinger *et al.*,³³² and Bovey and Kolthoff.³³³

Common inhibitors include stable radicals, oxygen, certain monomers, phenols, quinones, phenothiazine, nitro and nitroso compounds, and certain transition metal salts. Some inhibition constants (k_z/k_p) are provided in **Table 6**. Absolute rate constants (k_z) for the reactions of these species with simple carbon-centered radicals are summarized in **Table 7**.

Whether a given species functions as an inhibitor, a retarder, a transfer agent, or a comonomer in polymerization is dependent on the monomer(s) and the reaction conditions. For example, oxygen acts as an inhibitor in many polymerizations, yet it readily copolymerizes with S. Reactivity ratios for VAc–S copolymerization are such that small amounts of S are an effective inhibitor of VAc polymerization ($r_s = 0.02$, $r_{Vac} = 22.3$). The propagating chain with a terminal VAc adds to S preferentially even when VAc is present in large excess over S. The resultant propagating radical with a terminal S adds to VAc only slowly. The reactions of many inhibitors with propagating radicals may become reversible under some reaction conditions. In these circumstances, the reagent may find use as a control agent in RDRP (Chapter 3.08).

The effectiveness of inhibitors is measured in terms of the rate constant ratio k_z/k_p and the stoichiometric coefficient. The

Table 6Inhibition constants (k_z/k_p , 60 °C, bulk) for various inhibitors with some commonmonomers

	$k_{\rm z}/k_{ m p}$						
Inhibitor	MMA	MA	AN	S	VAc		
CuCl ₂	1 030	-	100 ^a	10 000	-		
FeCl ₃	5 000 k _n ^a	6800 k _n ^a	3.33 ^a	536	2 300 000 k _n		
<i>p</i> -Benzoquinone	4.5	< 0.15 k _n ^b	0.91 ^b	520	-		
Nitrobenzene	0.00464 ^b	0.00464 ^b	-	0.326	11.2 ^b		
DPPH	2 000	-	-	-	-		
Oxygen	33 000	-	-	14600	-		
Anthracene	-	0.098 ^b	2.67 ^b	2 ^{<i>c</i>}	27.8		
<i>p</i> -Hydroguinone	-	-	-	-	0.7		
Phenol	-	0.0002 ^b	-	-	0.06		
Styrene	-	-	-	-	40.8 ^{b330}		

Data taken from Eastmond, G. C. In *Comprehensive Chemical Kinetics*; Bamford, C. H., Tipper, C. F. H., Eds; Elsevier: Amsterdam, 1976; Vol. 14A, pp 1–103.²⁴⁵ unless otherwise stated and are rounded to three significant figures. ^aIn DMF.

MMA, methyl methacrylate; MA, methyl acrylate; AN, acrylonitrile; S, styrene; VAc, vinyl acetate; DPPH, diphenylpicrylhydrazyl

^b50 °C.

^{°44.4 °}C.

Inhibitor	Radical	Temperature (°C)	k_z ($M^{-1} s^{-1}$)	References
TEMPO	Primary alkyl	60	\sim 1 \times 10 ⁹	334,335,336
p-Benzoquinone CuCl ₂	Benzyi Primary alkyl Primary alkyl	69 25	2.9×10^{-5} 2.0×10^{-5} 6.5×10^{-5}	51 51 51

Table 7Absolute rate constants (k_z) for the reaction of carbon-centered radicals withsome common inhibitors

TEMPO, 2,2,6,6-tetrametylpiperidine-1-oxyl

Initiation				
l ₂	\rightarrow	2 •	$R_{\rm i} = 2 k_{\rm d} f[l_2]$	
I∙+M	\rightarrow	P₁•	$k_{\rm i} \ge k_{\rm p}$	
Inhibition				
l∙+Z	\rightarrow	IZ (dead)	$R_z = k_z[Z][I\bullet]$	
Propagation				
$P_n \bullet + M$	\rightarrow	P_{n+1} •	$R_{\rm p} = k_{\rm p}[{\rm M}][{\rm P}\bullet]$	
Disproportion	atior	า		
$P_n \bullet + P_m \bullet$	\rightarrow	$P_n^H + P_m^=$	$R_{\rm tc} = 2k_{\rm tc}[{\sf P}\bullet]^2$	$R_{\rm t} = R_{\rm tc} + R_{\rm tc}$
Combination				
$P_n \bullet + P_m \bullet$	\rightarrow	P _{<i>n</i>+<i>m</i>}	$R_{\rm tc} = 2k_{\rm tc}[{\sf P}\bullet]^2$	
Retardation				
$P_{n} \bullet + Z$	\rightarrow	P ₂ Z (dead polymer)	$R_7 = k_7[Z][P\bullet]$	

Scheme 49

stoichiometric coefficient is the moles of radicals consumed per mole of inhibitor. These parameters may be determined by various methods. A brief description of the classical kinetic treatment for evaluating k_z/k_p follows. Consider the reaction scheme shown which describes ideal inhibition and retardation (Scheme 49).

With the omission of the reinitiation reaction, this scheme is the same as that for polymerization with chain transfer and an expression (eqn [54]) for the degree of polymerization similar in form to the Mayo equation can be derived:

$$\frac{1}{\bar{X}_{n}} = \frac{\left(1 + \frac{k_{\rm td}}{k_{\rm t}}\right) \left(2k_{\rm d}f[I_{2}]k_{\rm t}\right)^{0.5}}{k_{\rm p}[{\rm M}]} + \frac{k_{\rm z}[Z]}{k_{\rm p}[{\rm M}]}$$
[54]

If the amount of termination by radical–radical reaction is neglected, the degree of polymerization and the kinetic chain length are given by eqn [55]:

$$v \approx \bar{X}_{n} \approx \frac{k_{p}[M]}{k_{z}[Z]}$$
[55]

If chains are very short, we must include an additional term in the numerator for monomer consumption in the initiation step (eqn[56]):

$$\bar{X}_{n} = \frac{k_{p}[M]}{k_{z}[Z]} + 1 \qquad [56]$$

Data on the rate of consumption of the inhibitor as a function of conversion may also be used to obtain k_z/k_p (eqn [57]):

$$\frac{k_z}{k_p} = \frac{[M]}{[Z]} \frac{d[Z]}{d[M]} = \frac{d\log[M]}{d\log[Z]}$$
[57]

It is clear that many procedures used to evaluate chain transfer constants can also be used to evaluate the kinetics of inhibition. The following sections will show that the mechanism for inhibition is often more complex than suggested by Scheme 49

3.04.5 Chain Transfer

Chain transfer is the reaction of a propagating radical with a nonradical substrate (X–Y, **Scheme 50**) to produce a dead polymer chain and a new radical (Y•) capable of initiating a polymer chain. The transfer agent (X–Y) may be a deliberate additive (e.g., a thiol) or it may be the initiator, monomer, polymer, solvent, or an adventitious impurity.

Transfer without reinitiation is called inhibition and is discussed in Section 3.04.4.2. There are also situations where the reaction produces a dead polymer chain and a radical that is less reactive than the propagating radical but still capable of reinitiating polymerization. The process is then termed retardation or degradative chain transfer.

3.04.5.1 The Chain Transfer Process

The general mechanism of chain transfer, as first proposed by Flory,^{8,337} may be written schematically as shown in **Scheme 51**. The overall process involves a propagating chain ($P_n \bullet$) reacting with a transfer agent (T) to terminate one polymer chain and produce a radical (T \bullet) that initiates a new chain ($P_1 \bullet$).

Transfer agents find widespread use in both industrial and laboratory polymer syntheses. They are used to control:

- 1. the molecular weight of polymers
- 2. the polymerization rate and exotherm (by mitigating the gel or Norrish–Trommsdorff effect)
- 3. the polymer end groups.

∽CH₂-ĊH Ph	+ X - Y	Transfer	∽CH₂-CH−X + Y Ph
Y∙ +	CH ₂ =CH	Reinitiation	Y-CH₂-ĊH Ph

Transfer to transfer agent or solvent

P _n •+1	\rightarrow	$P_n + 1 \bullet$	$R_{trT} = K_{trT} [P^{\bullet}][1]$
Reinitiation			
T∙+M	\rightarrow	P ₁ ●	$R_{iT} = k_{iT} [T\bullet][M]; k_{iT} \ge k_p$
Transfer to initia	tor		
$P_n \bullet + I_2$	\rightarrow	$P_n + I \bullet$	$R_{\rm trT} = k_{\rm trT} [P\bullet][I_2]$
Reinitiation			
$I \bullet + M \ \to \\$	P₁●		$R_{iT} = k_{iT} [I\bullet][M]; k_i \ge k_p$
Transfer to mon	omer		
$P_n \bullet + M$	\rightarrow	$P_n + M \bullet$	$R_{\rm trT} = k_{\rm trT} [P\bullet][M]$
Reinitiation			
M∙ + M	\rightarrow	P ₁ ●	$R_{\rm iT} = k_{\rm iT} [M\bullet][M]; k_{\rm iM} \ge k_{\rm p}$

Scheme 51

General aspects of chain transfer have been reviewed by Chiefari and Rizzardo,³³⁷ Barson,³³⁹ Farina,³⁴⁰ Eastmond,³³¹ and Palit *et al.*³⁴¹ The use of chain transfer in producing telechelic and other functional polymers has been reviewed by Boutevin,³⁴² Heitz,³⁴³ Corner,³⁴⁴ and Starks.²²⁷ There are two main mechanisms that should be considered in any discussion of chain transfer: (a) atom or group transfer by homolytic substitution (Section 3.04.5.1.2) and (b) addition-fragmentation (Section 3.04.5.1.3).

Even in the absence of added transfer agents, all polymerizations may be complicated by transfer to initiator, solvent, monomer (Section 3.04.5.1.6), or polymer (Section 3.04.5.1.7). The significance of these transfer reactions is dependent upon the particular propagating radicals involved, the reaction medium, and the polymerization conditions. Thiol-ene polymerization consists of sequential chain transfer and reinitiation steps and ideally no monomer consumption by propagation.

For efficient chain transfer, the rate constant for reinitiation following transfer ($k_{\rm iT}$; refer Scheme 51) must be greater than or equal to that for propagation ($k_{\rm p}$). In these circumstances, the presence of the transfer agent reduces the molecular weight of the polymer without directly influencing the rate of polymerization. If, however, $k_{\rm iT} < k_{\rm p}$, then polymerization will be retarded and the likelihood that the transfer agent-derived radical (T•) will undergo side reactions such as primary radical termination is increased. Thus, retardation is much more likely in polymerizations of high $k_{\rm p}$ monomers (e.g., MA, VAc) than it is with lower $k_{\rm p}$ monomers (e.g., S, MMA). Retardation is discussed in greater detail in Section 3.04.4.2.

Even when $k_{\text{IT}} \ge k_{\text{pr}}$, the rate of polymerization at higher conversions will often be lower that in the absence of a transfer agent due to a reduced gel or Norrish–Trommsdorf effect. One cause of this autoacceleration phenomenon is a reduced rate of radical–radical termination brought about by the immobilization of long chains through entanglement at higher conversions (Section 3.04.4.1.1(iv)). In the presence of a transfer agent, the population of short chains is higher and, because the ultimate molecular weight is lower, there are fewer chain entanglements.

The number average degree of polymerization (\bar{X}_n) of polymer formed at any given instant during the polymerization can be expressed simply as the rate of monomer usage in propagation divided by the rate of formation of polymer molecules (the overall rate of termination). Thus according to classical kinetics, if termination is only by radical-radical reaction or chain transfer, the degree of polymerization is given by eqn [58]:

$$\bar{X}_{n} = \frac{k_{p}[M]}{\left(1 + \frac{k_{td}}{k_{t}}\right)k_{t}[P\bullet] + k_{tr,T}[T] + k_{tr,I}[I] + k_{tr,M}[M]}$$
[58]

This can be rewritten as eqn [59]:

$$\frac{1}{\bar{X}_{n}} = \frac{\left(1 + \frac{k_{td}}{k_{t}}\right)k_{t}[P\bullet]}{k_{p}[M]} + \frac{k_{tr,T}}{k_{p}}\frac{[T]}{[M]} + \frac{k_{tr,I}}{k_{p}}\frac{[I]}{[M]} + \frac{k_{tr,M}}{k_{p}}$$
[59]

The ratio k_{tr}/k_p is called the transfer constant (C_{tr}) and C_{T} , C_{L} , and C_{M} are the transfer constants for transfer to transfer agent, initiator, and monomer, respectively. Appropriate substitution gives eqn [60]:

$$\frac{1}{\bar{X}_{n}} = \frac{\left(1 + \frac{k_{td}}{k_{t}}\right)k_{t}[P^{\bullet}]}{k_{p}[M]} + C_{T}\frac{[T]}{[M]} + C_{I}\frac{[I]}{[M]} + C_{M}$$
 [60]

The degree of polymerization in the absence of a chain transfer agent is given by eqn [61]:

$$\frac{1}{\bar{X}_{n0}} = \frac{\left(1 + \frac{k_{td}}{k_t}\right)k_t[\mathbf{P}\bullet]}{k_p[\mathbf{M}]} + C_I\frac{[\mathbf{I}]}{[\mathbf{M}]} + C_{\mathsf{M}}$$
[61]

Thus

$$\frac{1}{\bar{X}_{n}} = \frac{1}{\bar{X}_{n0}} + C_{\rm T} \frac{[{\rm T}]}{[{\rm M}]}$$
[62]

This equation (eqn [62]) is commonly known as the Mayo equation.³⁴⁵ The equation is applicable at low (zero) conversion and is invalidated if the rate constants are chain length dependent.

The magnitude of a transfer constant depends on structural features of both the attacking radical and the transfer agent. A $C_{\rm tr}$ of unity has been called ideal. In these circumstances, the transfer agent:monomer ratio ([T]:[M]) will remain constant throughout the polymerization.³⁴⁴ This means that \bar{X}_n remains constant with conversion and the dispersity of the molecular weight distribution is thus minimized (\bar{X}_W/\bar{X}_n close to 2.0). If $C_{\rm tr}$ is high ($\gg 1$), the transfer agent will be consumed rapidly during the early stages of polymerization and the polymerization will be unregulated at higher conversion. If, on the other hand, C_{tr} is low ($\ll 1$), [T]:[M] will increase as the polymerization progresses and there will be a corresponding decrease in \bar{X}_n with conversion. In both circumstances, a broad molecular weight distribution will result from a high-conversion batch polymerization. It is often possible to overcome these problems by establishing an incremental protocol for monomer and/or transfer agent addition such that [T]:[M] is maintained at a constant value throughout the polymerization.

The rate constants for chain transfer and propagation may well have a different dependence on temperature (i.e., the two reactions may have different activation parameters) and, as a consequence, transfer constants are temperature dependent. The temperature dependence of $C_{\rm tr}$ has not been determined for most transfer agents. Care must therefore be taken when using literature values of $C_{\rm tr}$ if the reaction conditions are different from those employed for the measurement of $C_{\rm tr}$. For cases where the transfer constant is close to 1.0, it is sometimes possible to choose a reaction temperature such that the transfer constant is 1.0 and thus obtain ideal behavior.³⁴⁶

The value of C_{tr} in homopolymerization can show significant chain length dependence for chain lengths $\leq 5^{.227}$ The variation in C_{tr} with chain length can reflect variations in $k_{\rm p}$ or $k_{\rm tr}$ or (most likely) both. The data provided in Section 3.04.3.4.3 show that $k_{\rm p}$ can be dependent on chain length for at least the first few propagation steps. The magnitude of the effect on $C_{\rm tr}$ for a given monomer varies according to the particular transfer agent. This indicates the sensitivity of $k_{\rm p}$ and $k_{\rm tr}$ to the penultimate unit is different. Chain transfer constants in addition–fragmentation and catalytic chain transfer have also been shown to be chain length dependent (Section 3.04.5.1.5).

Bamford³⁴⁷ has provided evidence that, in copolymerization, penultimate unit effects can be important in determining the reactivity of propagating radicals toward transfer agents. The magnitude of this effect also depends on the particular monomers and the transfer agent involved. The finding that the most pronounced remote unit effects are observed for the most bulky transfer agents has been taken as evidence that the magnitude of the remote unit effect is determined at least in part by steric factors. However, this view has been questioned.³⁴⁸

3.04.5.1.1 Measurement of transfer constants

Various methods for estimating transfer constants in radical polymerization have been devised. The methods are applicable irrespective of whether the mechanism involves homolytic substitution or addition–fragmentation.

The most used method is based on application of the Mayo equation (eqn [62]). For low (zero)-conversion polymerizations carried out in the presence of added transfer agent T, it follows from eqn [62] that a plot of $1/\bar{X}_n$ versus $[T]_0/[M]_0$ should yield a straight line with slope C_{tr} .³⁴⁵ Thus, a typical experimental procedure involves evaluation of the degree of polymerization for low-conversion polymerizations carried out in the presence of several concentrations of added transfer agent. The usual way of obtaining \bar{X}_n values is by GPC analysis of the entire molecular weight distribution.

GPC-derived weight average molecular weights are often less prone to error than number average molecular weights. When termination is wholly by disproportionation or chain transfer and chains are long (> 10 units), classical kinetics predicts $\bar{X}_n = \bar{X}_W/2$ (Section 3.04.4.1). It follows that $C_{\rm tr}$ can be obtained from the slope of a plot of $2/\bar{X}_w$ versus $[T]_0/[M]_0.^{326,349}$ The errors introduced even when the dominant process for radical–radical termination is combination (e.g., S polymerization) are small as long as \bar{X}_n is small in relation to \bar{X}_{n0} .

It has been shown that equivalent information can be obtained by analysis of log (number CLD) plots (the log CLD method).^{326,349–351} For the case where termination is wholly

by disproportionation or chain transfer, it is possible to show that eqn [63] applies:

$$\frac{\mathrm{dln}(n_i)}{\mathrm{d}i} = \frac{\mathrm{dln}[\phi^{i-1}(1-\phi)]}{\mathrm{d}i} = \mathrm{ln}(\phi)$$
[63]

For long chains ($\bar{X}_n > 50$ for < 1% error)

$$\ln(\phi) \approx 1 - \frac{1}{\phi} = \frac{1}{(\bar{X}_n - 1)}$$
 [64]

it is possible to write eqn [65] that is equivalent to the Mayo equation:

$$-\frac{\mathrm{dln}(n_i)}{\mathrm{d}i} \approx \frac{\left(1 + \frac{k_{\mathrm{td}}}{k_{\mathrm{t}}}\right)k_{\mathrm{t}}[\mathrm{P}^{\bullet}]}{k_{\mathrm{p}}[\mathrm{M}]} + \frac{k_{\mathrm{tr},\mathrm{T}}}{k_{\mathrm{p}}}\frac{[\mathrm{T}]}{[\mathrm{M}]} + \frac{k_{\mathrm{tr},\mathrm{I}}}{k_{\mathrm{p}}}\frac{[\mathrm{I}]}{[\mathrm{M}]} + \frac{k_{\mathrm{tr},\mathrm{M}}}{k_{\mathrm{p}}} \quad [65]$$

$$=\frac{1}{\bar{X}_{n0}} + \frac{k_{\rm tr,T}[{\rm T}]}{k_{\rm p}[{\rm M}]}$$
[66]

It follows that a plot of the slopes of the log CLD plots versus $[T]_0/[M]_0$ should yield a straight line with slope $-C_{tr}$.

In the more general case, where some termination is by combination, it can be shown that for sufficiently large chain length (i):

$$\lim_{i \to \infty} \frac{\mathrm{dln}(n_i)}{\mathrm{d}i} = \mathrm{ln}(\phi)$$
[67]

While it is, in principle, desirable to take the limiting slope of the log CLD plot, in practice the limiting slopes are very susceptible to experimental noise and baseline choice issues. Moad and Moad³²⁶ have shown that very little error is introduced by systematically taking the slope over the top 10% or the top 20% of the CLD. The values for the slopes will overestimate ln(ϕ). However, because the discrepancy is systematic, the 'Mayo' analysis still provides a good estimate for $C_{\rm tr}$ (~ 6% error for the example in Figure 19).

The log CLD method can sometimes provide better quality data than the conventional Mayo method. It is less sensitive to experimental noise and has application in measuring the



Figure 19 'Mayo plots' in which the calculated limiting slopes (triangles, _____, C_{tr} (app) = 0.184), 'last 10% slopes' (circles, ____, C_{tr} (app) = 0.180), and 'top 20% slopes' (squares, ----, C_{tr} (app) = 0.169) are graphed as a function of [T]/[M]. Data are for system with $\overline{X}_n = 5155$, $k'_{tr}/(k_{tc} + k'_{to}) = 1.0$ and $C_{tr} = 0.184$.³²⁶ C_{tr} (app) is the apparent C_{tr} from the slope of the 'Mayo plot'.

transfer constant to polymeric species where the distributions of the transfer agent and the polymer product partially overlap.³²⁶

Problems arise with any of the above-mentioned methods in the measurement of transfer constants for very active transfer agents. Bamford³⁵² proposed the technique of moderated copolymerization. In these experiments, the monomer of interest is copolymerized with an excess of a moderating monomer that has a much lower (preferably negligible) transfer constant. The method has also been applied to evaluate penultimate unit effects on the transfer constant.³⁵²⁻³⁵⁴

Another classical method for evaluating transfer constants involves evaluation of the usage of transfer agent (or better the incorporation of transfer agent fragments into the polymer) and the monomer conversion:³⁵⁵

$$\frac{\mathbf{d}[\mathbf{T}]}{\mathbf{d}[\mathbf{M}]} = \frac{k_{\mathrm{trT}}[\mathbf{P}\bullet][\mathbf{T}] + k_{\mathrm{iT}}[\mathbf{T}\bullet][\mathbf{M}]}{k_{\mathrm{p}}[\mathbf{P}\bullet][\mathbf{M}]}$$
[68]

For long chains, consumption of the monomer in the reinitiation step can be neglected and eqn [68] simplifies to eqn [69]:

$$\frac{\mathrm{d}[\mathrm{T}]}{\mathrm{d}[\mathrm{M}]} = \frac{k_{\mathrm{tr}}[\mathrm{T}]}{k_{\mathrm{p}}[\mathrm{M}]} = C_{\mathrm{tr}} \frac{[\mathrm{T}]}{[\mathrm{M}]}$$

$$[69]$$

from which eqn [70] follows:

$$\frac{d \ln[T]}{d \ln[M]} = C_{\rm tr}$$
^[70]

Thus, the slope of a plot of ln[T] versus ln[M] will yield the transfer constant. This method does not rely on molecular weight measurements.

For the situation where short chains cannot be ignored, eqn [68] can be transformed to eqn [71]:

$$\frac{d[M]}{d[T]} = \frac{[M]}{C_{tr}[T]} + 1$$
[71]

A number of authors have provided integrated forms of the Mayo equation^{314,318,356-358} which have application when the conversion of monomer to polymer is nonzero. Integration of eqn [69] provides eqn [72]:

$$\frac{[\mathrm{T}]}{[\mathrm{T}]_0} = \left(\frac{[\mathrm{M}]}{[\mathrm{M}]_0}\right)^{\mathrm{C}_{\mathrm{tr}}}$$
[72]

This enables substitution for [T] in eqn [73] to give eqn [74]:^{314,357}

$$\frac{1}{\bar{X}_{n}} = \frac{1}{\bar{X}_{n0}} + \frac{[T] - [T]_{0}}{[M] - [M]_{0}}$$
[73]

$$\frac{1}{\bar{X}_{n}} = \frac{1}{\bar{X}_{n0}} + \frac{\left[T\right]_{0} \left[1 - \left(\frac{[M]}{[M]_{0}}\right)^{C_{tr}}\right]}{\left[M\right]_{0} \left[1 - \left(\frac{[M]}{[M]_{0}}\right)\right]}$$
[74

Rearrangement and substitution of 1 - x for [M]/[M]₀ provides eqn [75]:

$$\ln\left[1 - \frac{[\mathbf{M}]_0 x}{[\mathbf{T}]_0} \left(\frac{1}{\bar{X}_n} - \frac{1}{\bar{X}_{n0}}\right)\right] = C_{\mathrm{tr}} \ln(1 - x)$$

$$[75]$$

where *x* is the fractional conversion of monomer into polymer. Thus, a plot of

$$\ln\left[1 - \frac{[M]_0 x}{[T]_0} \left(\frac{1}{\bar{X}_n} - \frac{1}{\bar{X}_{n0}}\right)\right] \text{ versus } \ln(1-x)$$

should provide a straight line passing through the origin with slope C_{tr} . Bamford and Basahel^{352–354} have reported the derivation of a similar equation for copolymerization. This method is highly dependent on the precision of the conversion measurements since errors in conversions are magnified in C_{tr} .

Cardenas and O'Driscoll³⁵⁶ and Stickler³¹⁸ have shown that, provided that the consumption of transfer agent is negligible with respect to monomer, a plot of

$$\frac{1}{\bar{X}_{n}} \text{ versus} - \frac{[T]_{0}}{[M]_{0}} \frac{\ln(1-x)}{x}$$

should also yield a straight line with slope C_{tr} . ^{318,356}

Nair *et al.*³⁵⁹ have proposed a modified Mayo equation for use when retardation through primary radical termination with transfer agent-derived radicals is significant.

Chain transfer is kinetically equivalent to copolymerization. The Q-e and 'patterns of reactivity' schemes used to predict reactivity ratios in copolymerization can also be used to predict reactivities (chain transfer constants) in chain transfer and the same limitations apply. Tabulations of the appropriate parameters can be found in the *Polymer Handbook*.^{360,361}

3.04.5.1.1(i) Addition-fragmentation

Some transfer agents react by addition-fragmentation (Section 3.04.5.1.3) or abstraction-fragmentation mechanisms. Both of these processes involve the formation of a short-lived intermediate. The reaction scheme for addition-fragmentation can be summarized schematically as follows (Scheme 52).

The reactivity of the transfer agent (T) toward the propagating species and the properties of the adduct ($P_nT\bullet$) are both important in determining the effectiveness of the transfer agent: if the lifetime of the intermediate ($P_nT\bullet$) is significant, it may react by other pathways than β -scission; if it ($P_iT\bullet$) undergoes coupling or disproportionation with another radical species, the rate of polymerization will be retarded; if it adds to monomer (T copolymerizes), it will be an inefficient transfer agent.

If both addition and fragmentation are irreversible, the kinetics differ little from conventional chain transfer. In the more general case, the rate constant for chain transfer is defined in terms of the rate constant for addition (k_{add}) and a partition coefficient that defines how the adduct is partitioned between products and starting materials (eqn [76]).

$$k_{\rm tr} = k_{\rm add} \frac{k_{\beta}}{k_{\rm -add} + k_{\beta}}$$
[76]

Methods used for evaluating transfer constants are the same as for conventional chain transfer.

Scheme 52

3.04.5.1.1(ii) Reversible chain transfer

In some cases, the product of chain transfer (P_n^T) is itself a transfer agent and chain transfer is reversible. Examples include alkyl iodides (Scheme 53) and certain addition–fragmentation transfer agents (e.g., macromonomers and thiocarbonylthio compounds) (Scheme 54).

For very active transfer agents, the transfer agent-derived radical (T•) may partition between adding to monomer and reacting with the polymeric transfer agent (P_n^T) even at low conversions. The transfer constant measured according to the Mayo or related methods will appear to be dependent on the transfer agent concentration (and on the monomer conversion).³⁶²⁻³⁶⁴ A reverse transfer constant can be defined as follows (eqn [77]):

$$C_{-\rm tr} = \frac{k_{-\rm tr}}{k_{\rm iT}}$$
[77]

and the rate of transfer agent consumption is then given by eqn [78]:

$$\frac{d[T]}{d[M]} \approx C_{tr} \frac{[T]}{[M] + C_{tr}[T] + C_{-tr}[P_n^T]} = C_{tr} \frac{[T]}{[M] + C_{tr}[T] + C_{-tr}([T]_0 - [T])}$$
[78]

This equation can be solved numerically to give values of $C_{\rm tr}$ and $C_{-\rm tr}$.^{362,363} For RAFT (Scheme 54), the rate constant for the reverse reaction is defined as shown in en. [79]:

$$k_{\rm -tr} = k_{-\beta} \frac{k_{\rm -add}}{k_{\rm -add} + k_{\beta}}$$
^[79]

Systems that give reversible chain transfer can display the characteristics of living polymerization. Such systems are discussed in Section 3.04.6.6.

3.04.5.1.2 Homolytic substitution chain transfer

Chain transfer most commonly involves transfer of an atom or group from the transfer agent to the propagating radical by a homolytic substitution (S_H^2) mechanism. Rate constants are determined by a combination of bond strength, steric, and polar factors. Transfer agents that react by addition-fragmentation are dealt with in Section 3.04.5.1.3. Organometallic species that give catalytic chain transfer are discussed in Section 3.04.5.1.5.

The moiety transferred will most often be a hydrogen atom, for example, when the transfer agent is a thiol (e.g., *n*-butanethiol – **Scheme 55**), a hydroperoxide, the solvent, and so on.

It is also possible to transfer a heteroatom (e.g., a halogen atom from bromotrichloromethane – Scheme 56), or a group of atoms (e.g., from diphenyl disulfide – Scheme 57).

Group transfer processes are of particular importance in the production of telechelic or di-end-functional polymers.

3.04.5.1.3 Addition–fragmentation chain transfer

Addition–fragmentation chain transfer has been reviewed by Rizzardo *et al.*,³⁶⁵ Colombani and Chaumont,³⁶⁶ Colombani,¹³⁸ Yagci and Reetz,³⁶⁷ Chiefari and Rizzardo,³³⁸ and Moad *et al.*³¹⁵ Certain unsaturated compounds may act as transfer agents by a two-step addition–fragmentation mechanism. All of the compounds discussed in this section have the general structure **48** or **49** where C=X is a reactive double bond (X is most often carbon or sulfur); Z is a group chosen to give the transfer agent an appropriate reactivity with respect to the monomer(s); A is typically CH₂, O, or S; B is typically O; and R is a radical leaving group. Chain transfer to monomer in VC polymerization and transfer to benzene can also be considered as examples of addition–fragmentation chain transfer.





Transfer

$$P_n \bullet + T \implies P_n^T + T \bullet \quad R_{tr} = k_{tr} [P \bullet][T]; R_{-tr} = k_{-tr} [T \bullet][P^T]$$

Reinitiation
 $T \bullet + M \rightarrow P_1 \bullet \qquad R_{iT} = k_{iT} [T \bullet][M]; k_{iT} >> k_p$

Radical addition-fragmentation processes have been

$$P_n^{\bullet}$$
 + H-S(CH₂)₃CH₃ \longrightarrow P_n -H + •S(CH₂)₃CH₃

Scheme 55

$$P_n^{\bullet} + Br - CCl_3 \longrightarrow P_n - Br + \bullet CCl_3$$

Scheme 56

$$P_n + PhS - SPh \longrightarrow P_n - SPh + SPh$$

Scheme 57

Transfer

Scheme 54

Addition $\begin{array}{rcl}
P_{n}\bullet+T & \longleftarrow & [P_{n}T\bullet] \ R_{add} = k_{add} \ [T][P\bullet]; \ R_{-add} = k_{-add} \ [PT\bullet] \\
Fragmentation \\
[P_{n}T\bullet] & \bigoplus & P_{n}^{-T} + T\bullet & R_{\beta} = k_{\beta} \ [PT\bullet]; \ R_{-\beta} = k_{-\beta} \ [T\bullet][P^{T}] \\
Reinitiation \\
T\bullet+M & \rightarrow & P_{1}\bullet & R_{iT} = k_{iT} \ [T\bullet][M]; \ k_{iT} >> k_{p} \end{array}$ Chain transfer



$$R \cdot \longrightarrow R - P_n$$

Scheme 58



Scheme 59

the Barton-McCombie deoxygenation process with xanthates are two examples of reactions known to involve an S_H2' mechanism. However, the first reports of additionfragmentation transfer agents in polymerization appeared in the late 1980s.^{313,371,372} Mechanisms for additionfragmentation chain transfer are shown in Schemes 58 and 59. Since functionality can be introduced to the products 51 or 53 in either or both the transfer (from Z, X, A, or B) and reinitiation (from R) steps, these reagents offer a route to a variety of end-functional polymers including telechelics.

Rates of addition to transfer agents 50 and 51 are determined by the same factors that determine rates of addition to monomers. Substituents on the remote terminus of a double bond typically have only a minor influence. Thus, in most cases, the double bonds of the transfer agents have a reactivity toward propagating radicals that is comparable with that of the common monomers they resemble. With efficient fragmentation, transfer constants can be close to unity. The radicals formed by addition typically have low reactivity toward further propagation and other intermolecular reactions because of steric crowding about the radical center.

Efficient transfer requires that radicals formed by addition undergo facile β -scission (for 52) or rearrangement (for 54) to form a new radical that can reinitiate polymerization. The driving force for fragmentation of the intermediate radical is provided by cleavage of a weak A-R bond and/or formation of a strong C=X bond (for 50). If fragmentation leads preferentially back to starting materials, the transfer constant will be low. If the overall rate of β-scission is slow relative to propagation, then retardation may result. Adducts 52 and 54 then have the potential to undergo side reactions by addition (e.g., copolymerization of the transfer

agent) or radical-radical termination. Retardation is an issue particularly for high k_p monomers such as VAc and MA. In designing transfer agents and choosing an R group (see 50, 51), a balance must be achieved between the leaving group ability of R and the reinitiation efficiency by R•.

When the product of the reaction is itself a potential transfer agent or macromonomer (50, X=A=CH₂, X=A=S) block, graft or hyperbranched copolymer formation may be an issue particularly at high conversions.^{313,373} The design of transfer agents that give RAFT has provided one of the more successful approaches to RDRP. The pathway can be blocked by choice of A (see 50). For example, when A is oxygen (vinyl ethers) or bears an alkyl substituent (e.g., A=CH-CH₃), the product is unreactive to radical addition.

If R and Z, A, or X are connected to form a ring structure, the result is a potential ring-opening monomer. For many of the transfer agents in this section, there are analogous ring-opening monomers.315

3.04.5.1.4 Abstraction–fragmentation chain transfer

Other multistep mechanisms for chain transfer are possible. An example is abstraction-fragmentation chain transfer shown by silylcyclohexadienes (54, Scheme 60).374

The cyclohexadiene 56 is a good H donor, but the cyclohexadienyl radical 57 is slow to react and fragments to provide the silvl radical 58 that initiates polymerization. The reported transfer constant for 56 in S polymerization at 80 °C is very low (0.00045).³⁷⁴

3.04.5.1.5 Catalytic chain transfer

Enikolopyan et al.³⁷⁵ found that certain Co^{II} porphyrin complexes (e.g., 57) function as catalytic chain transfer agents. Later work has established that various square planar cobalt complexes (e.g., the cobaloximes 58-62) are effective transfer agents.^{376,377} The scope and utility of the process has been reviewed several times, 378-383 most recently by Heuts et al,³⁸¹ Gridnev,³⁸² and Gridnev and Ittel.³⁸³ The latter two references^{382,383} provide a historical perspective of the development of the technique.

The major applications of catalytic chain transfer are in molecular weight control and in synthesis of macromonomers based on methacrylate esters. However, they have also been shown effective in polymerizations and copolymerizations of MAA, MAM, MAN, AMS, S, and some other monomers.

A major advantage of catalytic transfer agents over conventional agents is that they have very high transfer constants. The value of $C_{\rm tr}$ in MMA polymerization is in the range $10^3 - 10^5$; thus only very small amounts are required to bring about a large reduction in molecular weight. Exact values for Ctr are dependent on the reaction conditions^{375,376,384,385} and, for chain lengths \leq 12, on the molecular weight of the propagating species.^{384,385} Ideally, they are not used up during polymerization.





3.04.5.1.6 Transfer to monomer

Nonzero transfer constants (C_M) can be found in the literature for most monomers. Values of C_M for some common monomers are given in **Table 8**. for S and the (meth)acrylates, the value is small, in the range 10^{-5} – 10^{-4} . Transfer to monomer is usually described as a process involving hydrogen atom transfer. While this mechanism is reasonable for those monomers possessing aliphatic hydrogens (e.g., MMA, VAc, allyl monomers), it is less acceptable for monomers possessing only vinylic or aromatic hydrogens (e.g., VC, S). The details of the mechanisms by which transfer occurs are, in most cases, not proven. Mechanisms for transfer to monomer that involve loss of vinylic hydrogens seem unlikely given the high strength of the bonds involved.

Irrespective of the mechanism by which transfer to monomer occurs, the process will usually produce an unsaturated radical as a by-product. This species initiates polymerization to afford a macromonomer that may be reactive under typical polymerization conditions.

3.04.5.1.7 Transfer to polymer

Two forms of transfer to polymer should be distinguished:

- 1. Intramolecular reaction or backbiting, which gives rise to short chain branches (length \leq 5 carbons).
- Intermolecular reaction, which generally results in the formation of long chain branches.

The intramolecular process does not give rise to a new polymer chain and is considered in Section 3.04.3.3.3. It will not be considered further in this section.

 Table 8
 Selected values for transfer constants to monomer

Monomer	Temperature (°C)	$\textit{C}_{M}\times 10^{4}$	References
S	60	0.6	386
MMA	60	0.1	387
MA	60	0.4	388
AN	60	0.3	389
VAc	60	1.8	390
VC	100	50	391.392
Allyl acetate	80	1600	393
Allyl chloride	80	700	393

Values rounded to one significant figure and are taken from the references shown. There is considerable scatter in literature values for many monomers.³⁹⁴ S, styrene; MMA, methyl methacrylate; MA, methyl acrylate; AN, acrylonitrile; VAc, vinyl acetate; VC, vinyl chloride

Available evidence suggests that the main reaction accounting for transfer to vinyl polymers (e.g., PMA, PVAc, PVC, PVF) usually involves abstraction of a methine hydrogen (Scheme 61). However, definitive evidence for the mechanism is currently only available for a few polymers (e.g., PVAc, PVF).







Monomer	Temperature (°C)	$\mathcal{C}_{P} imes 10$
S	60	1.9–16
MMA	60	0.1–360
MA	60	0.5-1.0
AN	60	3.5
VAc	60	1.4–47
VC	50	5
E	175	110

Table 9	Transfer constants to polymer
---------	-------------------------------

S, styrene; MMA, methyl methacrylate; MA, methyl acrylate; AN, acrylonitrile; VAc, vinyl acetate; VC, vinyl chloride; E, ethylene

Numbers are taken from Ueda, A.; Nagai, S. In *Polymer Handbook*, Brandup, J., Immergut, E. H., Grulke, E. A., Eds; 4th ed.; John Wiley & Sons: New York, 1999; pp II/97–168³⁹⁴ and have been rounded to two significant figures.

Transfer constants to polymer (C_P) are not as readily determined as other transfer constants because the process need not lead to an overall lowering of molecular weight. If transfer occurs by hydrogen–atom abstraction from the polymer backbone, then, for every polymer chain terminated by transfer, another branched chain is formed. In these circumstances, the overall molecular weight remains constant. The extent of chain transfer can then be estimated by measuring the number of long chain branches or by analyzing the molecular weight distribution. As NMR measurement of long-chain branching relies on determining the branch points, a major analytical problem is distinguishing the long-chain branches from the short chain branches formed by backbiting.

The values of C_P to added polymer are measurable in circumstances where the added material is readily distinguishable from that being formed *in situ*, for example, if it is of significantly different molecular weight or if it is uniquely labeled.³⁹⁵ Studies with model compounds suggest that oligomers of chain length ≥ 3 can be used to provide a good estimate of the transfer constant.^{396,397}

For some polymers, the value of C_P depends on the polymer molecular weight. This may help account for the wide range of values for C_P in the literature (Table 9).

3.04.5.1.8 Transfer to initiator

The mechanism and incidence of transfer to initiator is discussed in Section 3.04.2.1.10.

3.04.6 Reversible Deactivation Radical Polymerization

The first demonstration of living polymerization and the current definition of the process can be attributed to Swarc.^{398,399} Living polymerization mechanisms offer polymers of controlled composition, architecture, and molecular weight distribution. They provide routes to low-dispersity end-functional polymers, to high-purity block copolymers, and to stars and other more complex architectures. Traditional methods of living polymerization are based on ionic, coordination, or group transfer mechanisms.

Ideally, the mechanism of living polymerization involves only initiation and propagation steps. All chains are initiated at the commencement of polymerization and propagation continues until all monomer is consumed. The combination of a living mechanism with the scope and versatility of the radical process should allow a wider selection of monomers and monomer combinations and more freedom in choosing reaction conditions. This potential and the applications that follow have provided the impetus for the very significant research efforts that have been devoted to this area over the last decade. In this chapter, we discuss the various approaches that have been developed in moving toward a living radical polymerization paying particular attention to the mechanism and the scope of each method.

At the time of the first edition of this book (1995),⁴⁰⁰ this field was still very much in its infancy. NMP was described, though little had been published in the open literature, and methods such as ATRP and RAFT had not been reported. Since 1995, the area has expanded dramatically and by themselves RDRP processes now account for a very substantial fraction of all research on radical polymerization (Chapter **3.01**). The development of this field over this period can be followed in the publications following successful ACS symposia held in 1997,⁴⁰¹ 2000,⁴⁰² and 2002⁴⁰³ and SML meetings held in 1996⁴⁰⁴ and 2001.⁴⁰⁵ Publications continue to appear at a rapid rate. Matyjaszewski⁴⁰⁶ has provided an overview of the history and development of RDRP through 2001 in the *Handbook of Radical Polymerization*.⁴⁰⁶

3.04.6.1 Living? Controlled? Mediated?

The terminology used in this chapter deserves some mention. There has been some controversy over the use of the terms 'living' and 'controlled' in the context of describing a radical polymerization.407-411 The current IUPAC recommendation, that a living polymerization is "a chain polymerization from which irreversible chain transfer and irreversible chain termination (deactivation) are absent," would preclude use of the term 'living' in the context of a radical process.^{29,413} The use of the adjective 'controlled' by itself to designate these polymerizations is also contrary to IUPAC recommendations.^{29,412} The adjective 'controlled' should only be used when the particular aspect of polymerization that is being controlled is specified. It is not recommended that 'controlled' be used in an exclusive sense to mean a particular form of polymerization since the word has an established, much wider, usage. The construct 'controlled living polymerization' would seem acceptable when used to refer to those living polymerizations whose outcomes are defined by controlling the reaction conditions or other features. The word 'controlled' should not be used to indicate that systems have a lower degree of livingness. Other terms such as 'pseudo-living' and 'quasi-living' are also discouraged.^{29,412} It has been stated that the definition of living polymerization "tolerates no restrictive adjectives implying something close to but not strictly living".407

For this section we use the IUPAC recommended term 'reversible deactivation radical polymerization' (RDRP). Termination is present in all of the polymerizations described, even though many polymerizations display many of the observable characteristics normally associated with living polymerization.

3.04.6.2 Tests for Living (Radical) Polymerization

Following on from the above, various methods have been described to test and/or rank the 'livingness' of polymerization processes.^{407,408,413–416} All of these tests have limitations. The following list paraphrases a set of criteria for living polymerization set out by Quirk and Lee⁴⁰⁷ who also critically assessed their applicability primarily in the context of living anionic polymerization.

- "Living polymerizations proceed until all monomer is consumed and may continue growth if further monomer is added." This criterion paraphrases one of Szwarc's definitions of living polymerization.^{398,399} It becomes a rigorous criterion if we add "and the number of living chains remains constant."
- "In a living polymerization the molecular weight increases linearly with conversion." This contrasts with observations for conventional radical polymerizations where molecular weights are initially high and decrease with conversion due to monomer depletion (Figure 20). However, molecular



Figure 20 Predicted evolution of molecular weight (arbitrary units) with monomer conversion for a conventional radical polymerization with a constant rate of initiation (---) and a living polymerization (---).

weights obtained in radical polymerizations with conventional transfer agents with $C_{tr} > 1$ will increase with conversion and may meet this test. Expressions for the dependence of molecular weight on conversion for NMP (and similar polymerizations), ATRP, and RAFT appear in Sections 3.04.6.4.1(ii), 3.04.6.5.1, and 3.04.6.6.1, respectively. A plot of \overline{M}_n versus conversion will remain linear even in circumstances where there is a loss of a substantial fraction of the living chains, although in that case there will be a broadening of the molecular weight distribution.

- 3. "In a living polymerization the concentration of active species remains constant." A plot of ln([M]₀/[M]_t) versus time should be linear. In many conventional radical polymerizations, a steady state is established such that, over a wide conversion range, the concentration of active chains remains approximately constant. Thus, these polymerizations will meet this test. Conversely, some living polymerizations with reversible deactivation will not meet this test (Section 3.04.6.4.1(iii)). A rigorous criterion that also covers these cases is that the total concentration of active and dormant chains should remain constant. However, this is more difficult to establish from kinetic measurements alone.
- 4. "Living polymerizations provide narrow molecular weight distributions." This is a more qualitative test. What constitutes low dispersity? Theoretically, a dispersity (\bar{X}_w/\bar{X}_n) of 1.5 is the narrowest achievable in a conventional radical polymerization with termination by combination for long chains (Section 3.04.4.1.1(iii)). An ideal living polymerization can provide a Poisson molecular weight distribution and $\bar{X}_w/\bar{X}_n = 1 + 1/\bar{X}_n$; $\bar{X}_w/\bar{X}_n = 1.01$ for $\bar{X}_n = 100$ (Figure 21). The better RDRP systems produce \bar{X}_w/\bar{X}_n in the range 1.05–1.2. Errors associated with measuring the dispersity can be significant and most cause an underestimate of the actual value. A low dispersity alone does not imply the absence of side reactions.
- 5. "Block copolymers can be prepared by sequential addition of monomers." This is a special case of (1) above.
- 6. "End groups are retained allowing end-functional polymers to be obtained in quantitative yield." Assessment of the



Figure 21 Calculated (a) number and (b) GPC distributions for three polymers each with $\bar{X}_n = 100$. The number distributions of chains formed by conventional radical polymerization with termination by disproportionation or chain transfer (- -, $\Sigma n_i = 1.0$, $\bar{X}_w/\bar{X}_n = 2.0$) or termination by combination (-----, $\Sigma n_i = 1.0$, $\bar{X}_w/\bar{X}_n = 1.5$) were calculated as discussed in Section 3.04.4.1.1(iii). The number distribution of chains formed in an ideal living polymerization (----, $\Sigma n_i = 1.0$, $\bar{X}_w/\bar{X}_n = 1.0$) was calculated using a Poisson distribution function.

fraction of living chains can provide a quantitative measure of the quality of a living polymerization. Currently, the most used methods for end-group determination are NMR and mass spectrometry.

Quirk and Lee concluded "there is no single criterion which is satisfactory for determination of whether a given polymerization is living or not".⁴⁰⁷ Most of the radical polymerizations discussed in this chapter meet one or more of these criteria. None meet all of the criteria.

3.04.6.3 Agents Providing Reversible Deactivation

The kinetics and mechanism of RDRP have been reviewed by Fischer,⁴¹⁷ Fukuda *et al.*,⁴¹⁸ and Goto and Fukuda.⁴¹⁹ In conventional radical polymerization, new chains are continually formed through initiation while existing chains are destroyed by radical-radical termination. The steady-state concentration of propagating radicals is $\sim 10^{-7}$ M and an individual chain will have a lifetime of only 1-10s before termination within a total reaction time that is typically greater than 10000s. A consequence is that long chains are formed early in the process and (in the absence of other influences) molecular weights decrease with monomer conversion due to the depletion of monomer (Figure 20). In conventional (classical anionic^{398,399}) living polymerization, all chains are initiated at the beginning of the reaction and grow until all monomer is consumed. As a consequence, molecular weight increases linearly with conversion and the molecular weight distribution is narrow.

The propensity of radicals to undergo self-reaction thus precludes the use of the simple strategy applied in anionic polymerization in developing a living radical polymerization. Radical polymerizations can display the characteristics normally associated with living polymerization in the presence of species that reversibly deactivate or terminate chains. These reagents control the concentration of active propagating species by maintaining a majority of chains in a dormant form. In homogeneous radical polymerization, the rate of radical-radical termination is proportional to the square of the radical concentration ($R_t \propto [P_n \bullet.]^2$) Thus, the incidence of termination can be reduced relative to propagation ($R_p \propto [P_n \bullet]$) by reducing the radical concentration.

In RDRP, the concentration of propagating radicals is usually similar to or lower than that in conventional radical polymerization (i.e., $\leq 10^{-7}$ M). For control, and to retain a high fraction of living chains, the lifetime of chains in their active state must be significantly less than in the conventional process ($\ll 1-10$ s). A rapid equilibration between active and dormant forms then ensures that all propagating species have equal opportunity for chain growth. All chains grow intermittently.

It is not necessary that RDRP be slow with respect to conventional radical polymerization. However, it follows from the above discussion that, for a high fraction of living chains, either the final degree of polymerization must be significantly lower than that in an otherwise similar conventional process or conditions must be chosen such that the rate of polymerization is substantially lower.

Heterogeneous polymerization processes (emulsion, miniemulsion, nonaqueous dispersion) offer another possibility for reducing the rate of termination through what are known as compartmentalization effects. In emulsion polymerization, it is



Scheme 62



Scheme 63



believed that the mechanism for chain stoppage within the particles is not radical-radical termination but transfer to monomer (Section 3.04.5.1.6). These possibilities have provided impetus for the development of heterogeneous RDRP.

We can distinguish several subclasses of activationdeactivation processes according to their mechanism. These are shown in Schemes 62–64.

- 1. Those giving deactivation by reversible coupling and involving a unimolecular activation process as shown in **Scheme 62**. $P_n \bullet$ is a propagating radical (an active chain). The deactivator (X) is usually, though not always, a stable radical. However, X may also be an even electron (diamagnetic) species, for example, diphenylethylene. In this case P_n -X would be a persistent radical, or a transition metal complex, for example, a low-spin cobalt (II) complex. These systems are discussed in Section 3.04.6.4. Possibly the best-known process is NMP (Section 3.04.6.4.2).
- 2. Those giving deactivation by reversible atom or group transfer and involving a bimolecular activation process (Scheme 63). For the systems described, the deactivator (X–Y) is a transition metal complex where Y is the metal in a higher oxidation state. Y• is then the metal in a lower oxidation state. Y• is inert with respect to monomer. Y• can be considered as a catalyst for the process shown in Scheme 62 and many aspects of the kinetics are similar. The best-known example is ATRP (Section 3.04.6.5) where the deactivator X–Y is, for example, a copper(II) halide.
- 3. Those giving simultaneous deactivation and activation by reversible (degenerate) chain transfer (Scheme 64). These systems are discussed in Section 3.04.6.6. The best known of this class is RAFT with thiocarbonylthio compounds

(Section 3.04.6.6.2). In this case, the chain transfer step involves formation of an intermediate adduct. Other examples believed to involve a transfer by homolytic substitution are iodine transfer polymerization (ITP) and telluride-mediated polymerization (TERP).⁴²⁰

The polymerizations (1) and (2) owe their success to what has become known as the persistent radical effect.⁴¹⁷ Simply stated, when a transient radical and a persistent radical are simultaneously generated, the cross-reaction between the transient and persistent radicals will be favored over self-reaction of the transient radical. Self-reaction of the transient radicals leads to a buildup in the concentration of the persistent species that favors cross-termination with the persistent radical over homotermination. The homotermination reaction is thus self-suppressing. The effect can be generalized to a persistent species effect to embrace ATRP and other mechanisms mentioned in Sections 3.04.6.4 and 3.04.6.5. Many aspects of the kinetics of the processes discussed under (1) and (2) are similar,⁴¹⁷ the difference being that (2) involves a bimolecular activation process.

The reversible chain transfer process (3) is different in that ideally radicals are neither destroyed nor formed in the activation-deactivation equilibrium. This is simply a process for equilibrating living and dormant species. Radicals to maintain the process must be generated by an added initiator.

Though there is still debate about detailed mechanism, in each of the processes (1–3) the propagating species is believed to be a conventional propagating radical. Thus, termination by radical–radical reaction is not eliminated, though, as we shall see, with appropriate choice of reaction conditions, the significance of this process can be markedly reduced.

3.04.6.4 Deactivation by Reversible Coupling and Unimolecular Activation

Most polymerizations in this section can be categorized as stable (free) radical-mediated polymerizations (sometimes abbreviated as SFRMP). In the following discussion, systems have been classed according to the type of stable radical involved, which usually correlates with the type of bond homolyzed in the activation process. Those described include systems where the stable radical is a sulfur-centered radical, a selenium-centered radical, a carbon-centered radical, an oxygen-centered radical, or a nitrogen-centered radical.

3.04.6.4.1 Kinetics and mechanism

3.04.6.4.1(i) Initiators, iniferters, initers

In each of the sections below, we will consider the initiation process separately. For each system, various initiation methods have been applied. In some cases, the initiator is a low-molecular-weight analog of the propagating species; in other cases, it is a method of generating such a species. The initiator-transfer agent-chain terminator) or initers (*initiator-chain terminator*). These terms were coined by Otsu and Yoshida³⁰ based on the similar terminology introduced by Kennedy⁴²¹ to cover analogous cationic systems. Except for the case of the dithiuram disulfides and related species, these expressions have now fallen from favor and are no longer used as a generic terminology. In this chapter, we use the term initiator to denote

alkoxyamines in NMP and halo compounds in ATRP despite the confusion this can create, especially when the process also involves added conventional initiators.

In order for the characteristics of living polymerization to be displayed, initiators should possess the following attributes:

- 1. One (in some cases, both) of the radicals formed on initiator decomposition is persistent or long-lived and unable (or slow) to initiate polymerization.
- 2. Primary radical termination (or transfer to initiator) should be the only significant mechanism for the interruption of chain growth. Primary radical termination should occur exclusively by combination. Transfer to initiator, when involved, should occur exclusively by group transfer to give a product analogous to that formed by termination by combination.
- 3. The bond to the end group (X) formed by these mechanisms must be thermally or photochemically labile under the reaction conditions such that reversible homolysis regenerates the propagating radical.
- 4. The initiator must be consumed rapidly with respect to the rate of polymerization.

3.04.6.4.1(ii) Molecular weights and distributions

The initiator or iniferter determines the number of growing chains. Several methods of initiation are used. Only three will be considered here. The first involves direct use of a species I–X (e.g., an alkoxyamine – Section 3.04.6.4.2) as shown in **Scheme 65**. Ideally, the degree of polymerization is given by eqn [80] and the molecular weight by eqn [81].

$$\bar{X}_{n} = \frac{([M]_{0} - [M]_{t})}{[IX]_{0}} = \frac{[M]_{0}}{[IX]_{0}}c$$
[80]

$$\bar{M}_{n} = \frac{([M]_{0} - [M]_{t})}{[IX]_{0}} m_{M} + m_{IX}$$
[81]

where $([M]_0-[M]_t)$ is the amount of monomer consumed, m_M and m_{IX} are the molecular weights of the monomer and the initiator (IX), respectively, and *c* is the monomer conversion. For a slow decomposing initiator, the term in the denominator should be $([IX]_0-[IX]_t) = [IX](1-\exp(-k_{act}t))$, that is, the amount of initiator consumed. An efficiency term f that has the usual definition (eqn [82]) can be introduced which allows for side reactions during the decomposition of IX or in the formation of P₁•. The species I• often has different reactivity and specificity for reaction with monomer than the propagating species (P_n•). Side reactions involving I• cause the molecular weight to be higher than expected.

$$I - X \xrightarrow{k'_{act}} I^{\bullet} + X$$

$$k'_{deact}$$

$$k_{i} \downarrow Monomer$$

$$P_{1} - X \xrightarrow{k_{act}} P_{1}^{\bullet} + X$$

$$\downarrow Monomer$$

Scheme 65



$$f' = \frac{[\text{Chains initiated}]}{[\text{IX}]_0}$$
[82]

For a polymerization with initiation by the process shown in Scheme 65 with $k'_{act} = k_{act}$ and $k'_{deact} = k_{deact}$, the dispersity is given by eqn [83]:

$$\frac{\bar{X}_{w}}{\bar{X}_{n}} = 1 + \frac{1}{\bar{X}_{n}} + \left(\frac{2-c}{c}\right) \frac{k_{p}[IX]}{k_{deact}}$$
[83]

where *c* is the monomer conversion. The dispersity depends on the molecular weight, the monomer conversion, and the ratio k_p/k_{deact} . This ratio governs the number of propagation steps per activation cycle and should be large for a narrow molecular weight distribution.

A second process involves use of a conventional initiator (I_2 ; e.g., AIBN, BPO) in the presence of X (e.g., a nitroxide) to generate a species IX *in situ* as shown in Scheme 66.

The degree of polymerization will usually be determined by the concentration of X. Some X may be lost in side reactions during the formation of IX. In some cases, I• must undergo at least one propagation step before combination with X is likely (e.g., in NMP with BPO as initiator). Any processes that irreversibly consume X will raise the molecular weight. Any process that provides additional chains will lower the molecular weight (e.g., thermal initiation in S polymerizations or an additional thermal initiator).

A third process involves use of the species (X–X) to generate the 'stable radical' in pairs and relies on the stable radical being able to react with monomer, albeit slowly, to generate P_1X (Scheme 67). Polymerizations with dithiuram and other disulfides and hexasubstituted ethanes belong to this class.

Other variations and combinations of these processes are also possible and are described in the following sections.

3.04.6.4.1(iii) Polymerization kinetics

General features of the polymerization kinetics for polymerizations with deactivation by reversible coupling have already been mentioned. Detailed treatments appear in reviews by Fischer,⁴¹⁷ Fukuda *et al.*,⁴¹⁸ and Goto and Fukuda⁴¹⁹ and will not be repeated here.

In conventional radical polymerization, the rate of polymerization is described by eqn [84]. As long as the rate of initiation remains constant, a plot of $\ln([M]_0/[M]_t)$ versus time should provide a straight line.

$$\ln\frac{[\mathsf{M}]_{0}}{[\mathsf{M}]_{t}} = k_{\mathrm{p}} \left(\frac{R_{\mathrm{i}}}{k_{\mathrm{t}}}\right)^{1/2} t \qquad [84]$$

For polymerizations where initiation is described by **Scheme 65**, the rate of polymerization is given by eqn [85]:⁴¹⁷

$$\ln\frac{[M]_0}{[M]_t} = \frac{3}{2}k_p \left(\frac{K[IX]_0}{3k_t}\right)^{1/3} t^{2/3}$$
[85]

where $K = k_{act}/k_{deact}$. The derivation of this equation requires that $[X]_0$ is zero and that there is no initiation source other than IX. Note that the relationship between $ln([M]_0/[M]_t)$ and time is *not* anticipated to be linear. Under these circumstances, the rate of polymerization is controlled by the value of the activation–deactivation equilibrium constant *K*.

If there is an external source of free radicals (e.g., from thermal initiation in S polymerization or from an added conventional initiator), eqn [84] may again apply. The rate of polymerization becomes independent of the concentration of IX and, as long as the number of radicals generated remains small with respect to [IX]₀, a high fraction of living chains and low dispersities is still possible. The validity of these equations has been confirmed for NMP and with appropriate modification has also been shown to apply in the case of ATRP.⁴¹⁸

3.04.6.4.2 Nitroxide-mediated polymerization

The literature on NMP through 2001 was reviewed by Hawker *et al.*^{34,422} More recently, the subject has been reviewed by Studer and Schulte⁴²³ and Solomon.⁴²⁴ NMP is also discussed by Fischer²²⁸ and Goto and Fukuda⁴¹⁹ in their reviews of polymerization kinetics and is mentioned in most reviews on RDRP. A simplified mechanism for NMP is shown in **Scheme 68**.

Prior to the development of NMP, nitroxides were well known as inhibitors of polymerization (Section 3.04.4.2). They and various derivatives were (and still are) widely used in polymer stabilization. Both applications are based on the property of nitroxides to efficiently scavenge carbon-centered radicals by combining with them at near diffusion-controlled rates to form alkoxyamines. This property also saw nitroxides exploited as trapping agents to define initiation mechanisms.

The exploitation of alkoxyamines as polymerization initiators and the use of NMP for producing block and end-functional polymers was first described in a patent





application by Solomon *et al.* in 1985.³² In this work, NMP was described as a method of living radical polymerization. This work was mentioned in a communication⁴²⁵ in 1987 and a conference paper⁴²⁶ in 1991. In 1990, Johnson *et al.*⁴²⁷ described what is now known as the persistent radical effect⁴²⁸ and showed that NMP, with appropriate selection of alkoxyamine and control of reaction conditions, could, in principle, provide low-dispersity polymers. These early papers focused on NMP of acrylates. However, the method only received significant attention in the wider literature following the demonstration by Georges *et al.*³³ in 1993 that NMP could be used to prepare PS with a narrow molecular weight distribution. Since that time the literature on NMP has expanded greatly and, along with ATRP and RAFT, NMP is now one of the more cited methods for RDRP.

3.04.6.5 Atom Transfer Radical Polymerization

The addition of halocarbons (RX) across alkene double bonds in a radical chain process, the Kharasch reaction (**Scheme 69**),⁴²⁹ has been known to organic chemistry since 1932. The overall process can be catalyzed by transition metal complexes (Mtⁿ–X); it is then called atom transfer radical addition (ATRA) (**Scheme 70**).^{430,431}

Polymer formation during the Kharasch reaction (Scheme 69) or ATRA (Scheme 70) can occur if trapping of the radical (63), by halocarbon or metal complex respectively, is sufficiently slow such that multiple monomer additions can occur. Efficient polymer synthesis additionally requires that the trapping reaction is reversible and that both the activation and deactivation steps are facile.

The first purposeful use of ATRA in polymer synthesis was in the production of telomers.⁴³² In this early work, comparatively poor control over the polymerization was achieved and little attempt was made to explore the wider utility of the process. Some analogies may also be drawn with the work of



Scheme 69





Bamford *et al.* and others on transition metal/organic halide redox initiation.⁴³³

The first reports of ATRP, which clearly displayed the characteristics of living polymerization, appeared in 1995 from the laboratories of Sawamoto,⁴³⁴ Matyjaszewski,^{430,435} and Percec.⁴³⁶ The literature on ATRP is now so vast that a comprehensive review cannot be presented here. A number of reviews on ATRP have appeared. Most informative on the scope of the process are those by Matyjaszewski and Xia,^{35,437} Kajimoto *et al.*,^{36,438} and Ouchi *et al.*⁴³⁹ The kinetics of ATRP are considered in reviews by Fischer²²⁸ and Goto and Fukuda.⁴¹⁹ ATRP is sometimes also called transition metal-mediated radical polymerization. We use this latter term for radical polymerizations where control is achieved by a reversible coupling mechanism.

A much-simplified mechanism for reversible activationdeactivation of polymer chains during ATRP is shown in **Scheme 71**. In the deactivation process, propagating radicals are trapped by atom or group transfer (most commonly a halogen (Cl, Br, I) although other groups (e.g., SCN) are known) from a metal complex in its higher oxidation state. The activation process involves a redox reaction between the polymer end group and the metal complex in its reduced form.

The atom transfer reaction is generally thought to involve inner sphere electron transfer (ISET) with concerted transfer of the halogen from initiator to the metal complex and various kinetic and other data support this view for most of the common initiator/catalyst/monomer combinations. However, it is possible to write the process as two steps, the first being an outer sphere electron transfer (OSET) process to provide an intermediate radical anion (Scheme 72).^{35,440} The living polymerization of vinyl chloride with alkyl iodide initiators and nascent Cu(0) catalyst is considered to involve an OSET process.^{442,443} OSET does not require a transition metal catalyst and can involve other single electron reducing agents such as dithionite.⁴⁴³ For this case it is also possible that the chain equilibration step is, in part, similar to that discussed under iodine transfer polymerization.⁴⁴³

Ideally, the metal complex is a catalyst and, in principle, is only required in very small quantities. However, the kinetics of initiation for the systems described to date dictate that relatively large amounts are used and catalyst:initiator ratios are typically in the range 1:1 to 1:10. The most commonly used catalysts are metal complexes based on Cu and Ru. However, a wide range of metals and ligands has been used. Conditions and catalysts have been found such that most monomers polymerizable by a radical mechanism can be used in ATRP. Difficult monomers are vinyl acetate and simple olefins (in homopolymerization) and monomers that coordinate strongly





$$P_n^{\bullet} + X - Mt^{n+1} \longrightarrow P_n - \overline{X}^{\bullet} + Mt^{n+1} \longrightarrow P_n - X + Mt^n$$

with metal centers. It is extremely important to select the initiator, catalyst, and reaction conditions for the particular monomer.

There has been some discussion on whether ATRP is a 'free' radical polymerization.444,445 Are the reactions of initiating and propagating species produced in ATRP influenced by the presence of the metal complex? Reports^{444,445} that reactivity ratios in copolymerization by ATRP differ from those observed in conventional radical polymerization appear to be an effect of chain length. There is no doubt that the rate of polymerization in ATRP can be dramatically affected by the reaction medium, but this can in large part be attributed to changes in the activation/deactivation equilibrium. The current general consensus is that the common forms of ATRP are radical processes and the propagating radicals behave as 'free' propagating radicals under the reaction conditions. The polymerization kinetics can be interpreted on this basis and radical-radical termination occurs to the extent expected given the radical concentration.

Notwithstanding the occurrence of any side reactions, a successful ATRP experiment will generally yield a polymer with halogen end groups. These end groups are potentially labile and may impair polymer stability. Moreover, corrosive by-products (hydrohalic acids) can be formed by thermal elimination. However, the end groups are also precursors to a wide range of other functionality. It is possible to transform them into groups that are chemically inert or to useful functionalities. They also render the polymers useful as precursors to block, star, comb, and more complex architectures.

3.04.6.5.1 Molecular weights and distributions

In ATRP, the initiator (RX) determines the number of growing chains. Ideally, the degree of polymerization is given by eqn [86] and the molecular weight by eqn [87]. Note the appearance of the initiator efficiency (f') in the numerator of these expressions. In practice, the molecular weight is often higher than anticipated because the initiator efficiency is decreased by side reactions. In some cases, these take the form of heterolytic decomposition or elimination reactions. Further redox chemistry of the initially formed radicals is also known. The initiator efficiencies are dependent on the particular catalyst employed.

$$\bar{X}_{n} = \frac{([M]_{0} - [M]_{t})f'}{[RX]_{0}} = \frac{[M]_{0}f'}{[RX]_{0}}c$$
[86]

$$\bar{M}_{\rm n} = \frac{([{\rm M}]_0 - [{\rm M}]_{\rm t})f'}{[{\rm RX}]_0} m_{\rm M} + m_{\rm RX}$$
[87]

where $([M]_0-[M]_t)$ is the concentration of monomer consumed m_M and m_{RX} are the molecular weights of the monomer and the initiator (RX), respectively, and *c* is the monomer conversion.

It is assumed in the derivation of eqn [86] that RX is completely consumed. In order to obtain good control (low dispersities, molecular weights according to eqn [86]), it is critical that initiation is rapid with respect to propagation such that RX is consumed before there is any substantial conversion of monomer. Slow usage of RX will give a posttailing or bimodal molecular weight distribution.

In S polymerization, thermal initiation will be a source of extra chains. Additional chain formation processes will cause the molecular weight to be lower than anticipated by eqn [86]. Sometimes conventional thermal initiators are added with similar effect. A pretailing molecular weight distribution may result.

In ideal circumstances, with polymerization described by Scheme 71 and rate of activation of RX equal to that of P_nX , the dispersity is given by eqn [88]:⁴¹⁹

$$\frac{\bar{X}_{w}}{\bar{X}_{n}} = 1 + \frac{1}{\bar{X}_{n}} + \left(\frac{2-c}{c}\right) \frac{k_{p}[\text{RX}]}{k_{\text{deact}}[\text{Mt}^{n+1}\text{X}]}$$
[88]

where c is the monomer conversion.

The rate of polymerization is given by eqn [89]:

$$R_{\rm p} = k_{\rm p} K \frac{[\rm RX][\rm Mt^{n}]}{[\rm Mt^{n+1}X]} [\rm M]$$
[89]

The ATRP experiment is usually commenced with all of the catalyst in its lower oxidation state. The number of propagation events per activation cycle is dependent on the concentration of catalyst in its higher oxidation state. For low dispersities, it is important that this number is small. As indicated by eqn [88], dispersity is inversely proportional to the concentration of the deactivator ($Mt^{n+1}X$). Thus, just as in NMP, where it is desirable to have a very low concentration of free nitroxide in the polymerization medium, in ATRP it can be important to have a proportion of the catalyst in its higher oxidation state. However, as implied by eqn [89], a concentration of deactivator that is too high can cause retardation or even inhibition of polymerization.

3.04.6.6 Reversible Chain Transfer

Radical polymerizations that involve a reversible chain transfer step for chain equilibration and that displayed the characteristics of living polymerizations were first reported in 1995.^{304,446} The mechanism of the reversible chain transfer step may involve homolytic substitution (Scheme 73) or addition–fragmentation (RAFT) (Scheme 74). An essential feature is that the product of chain transfer is also a chain transfer agent with similar activity to the precursor transfer agent. The process has also been termed degenerate or degenerative chain transfer







since the polymeric starting materials and products have equivalent properties and differ only in molecular weight.

Polymerization of S and certain fluoro-monomers in the presence of alkyl iodides provided the first example of the reversible homolytic substitution process (Scheme 73). This process is also known as iodine transfer polymerization.^{446,447} Other examples of reversible homolytic substitution are polymerizations conducted in the presence of certain alkyl tellurides (TERP) or stibines.⁴²⁰

Polymerizations of methacrylic monomers in the presence of methacrylic macromonomers under monomer-starved conditions display many of the characteristics of living polymerization (Scheme 74). These systems involve RAFT. However, RAFT with appropriate thiocarbonylthio compounds is the most well-known process of this class (Section 3.04.6.6.2). It is also the most versatile having been shown to be compatible with most monomer types and a very wide range of reaction conditions.^{37,315}

3.04.6.6.1 Molecular weights and distributions

As with other forms of RDRP, the degree of polymerization and the molecular weight can be estimated from the concentration of monomer and reagents as shown in eqns [90] and [91], respectively.⁴⁴⁸

$$\bar{X}_{n} = \frac{[M]_{0} - [M]_{t}}{[T]_{0} + df([I_{2}]_{0} - [I_{2}])_{t}}$$
[90]

$$\bar{M}_{n} = \frac{[M]_{0} - [M]_{t}}{[T]_{0} + df([I_{2}]_{0} - [I_{2}])_{t}} m_{M} + m_{T}$$
[91]

where $m_{\rm M}$ and $m_{\rm T}$ are the molecular weights of the monomer (M) and the transfer agent (T), respectively, *d* is the number of chains produced in a radical-radical termination event ($d \sim 1.67$ for MMA polymerization and ~ 1.0 for S polymerization), and *f* is the initiator efficiency. The form of this term in the denominator is suitable for initiators such as AIBN that produce radicals in pairs but will change for other types of initiator.

Reaction conditions should usually be chosen such that the fraction of initiator-derived chains (should be greater than or equal to the number of chains formed by radical-radical termination) is negligible. The expressions for number average degree of polymerization and molecular weight (eqn [90] and [91]) then simplify to eqns [92] and [93]:

$$\bar{X}_n = \frac{[M]_0 - [M]_t}{[T]_0}$$
 [92]

$$\bar{M}_{\rm n} = \frac{[M]_0 - [M]_{\rm t}}{[T]_0} m_{\rm M} + m_{\rm T}$$
 [93]

These equations suggest that a plot of \overline{M}_n versus conversion should be linear. A positive deviation from the line predicted by eqn [93] indicates incomplete usage of transfer agent (*T*), while a negative deviation indicates that other sources of polymer chains are significant (e.g., the initiator).

Analytical expressions have been derived for calculating dispersities of polymers formed by polymerization with reversible chain transfer. The expression (eqn [94]) applies in circumstances where the contributions to the molecular weight distribution by termination between propagating radicals, external initiation, and differential activity of the initial transfer agent are negligible.^{363,420}

$$\frac{\bar{X}_{w}}{\bar{X}_{n}} = 1 + \frac{1}{\bar{X}_{n}} + \left(\frac{2-c}{c}\right)\frac{1}{C_{tr}}$$
[94]

where c is the fractional conversion of monomer.

The transfer constant governs the number of propagation steps per activation cycle and should be small for a narrow molecular weight distribution. Rearrangement of eqns [94]–[95] suggests a method of estimating transfer constants on the basis of measurements of the conversion, molecular weight, and dispersity.⁴²⁰

$$\left(\frac{\bar{X}_{w}}{\bar{X}_{n}} - 1 - \frac{1}{\bar{X}_{n}}\right)^{-1} = C_{tr}\left(\frac{c}{2-c}\right)$$
[95]

In more complex cases, kinetic simulation has been used to predict the time/conversion dependence of the dispersity. Much of the research in this area has been carried out with a view to understanding the factors that influence retardation. The main difficulty in modeling RAFT lies in choosing values for the various rate constants.

3.04.6.6.2 Thiocarbonylthio RAFT

Although the term RAFT (an acronym for reversible addition-fragmentation chain transfer)³⁷ is sometimes used in a more general sense, it was coined to describe, and is most closely associated with, the reaction when it involves thiocarbonylthio compounds. RAFT polymerization, involving the use of xanthates, is also sometimes called MADIX (macromolecular design by interchange of zanthate).⁴⁴⁹ The process has been reviewed by Rizzardo *et al.*,⁴⁵⁰ Chiefari and Rizzardo,³³⁸ Barner-Kowollik *et al.*,⁴⁵¹ McCormick *et al.*,⁴⁵² and Moad *et al.*,⁴⁵³

Organic chemists have been aware of reversible additionfragmentation involving xanthate esters in organic chemistry for some time. It is the basis of the Barton–McCombie process for deoxygenation of alcohols (Scheme 75).^{456–458}



In 1988 a paper by Zard and coworkers⁴⁵⁹ reported that xanthates were a convenient source of alkyl radicals by reversible addition–fragmentation and used the chemistry for the synthesis of a monoadduct to monomer (a maleimide). Many applications of the chemistry in organic synthesis have now been described in papers and reviews by the Zard group.^{460,461}

RDRP using thiocarbonylthio RAFT agents (including dithioesters, trithiocarbonates, and xanthates) was first described in a patent published in 1998.⁴⁶² The first paper describing the process also appeared in 1998.³⁷ Other patents and papers soon followed. Papers on this method, along with NMP and ATRP, now dominate the literature on radical polymerization.

A key feature of the mechanism of RAFT polymerization is the sequence of addition–fragmentation equilibria shown in **Scheme 76**.³⁷ Initiation and radical–radical termination occur as in conventional radical polymerization. In the early stages of the polymerization, addition of a propagating radical (P_n^{\bullet}) to the thiocarbonylthic compound (64) followed by fragmentation of the intermediate radical (65) gives rise to a polymeric thiocarbonylthic compound (66) and a new radical (R^{\bullet}). Reaction of the radical (R^{\bullet}) with monomer forms a new propagating radical (P_m^{\bullet}). A rapid equilibrium between the active propagating radicals (P_n^{\bullet} and P_m^{\bullet}) and the dormant polymeric

Initiation $\xrightarrow{}$ I \xrightarrow{M} \xrightarrow{M}

Reversible chain transfer/propagation

$$\begin{array}{c} P_n^{\bullet} + S \\ M \\ k_p \\ z \\ 66 \\ 67 \\ 68a \end{array} \begin{array}{c} P_n^{-S} \\ R_{-\beta} \\ R_{-\beta}$$

 P_n^{\bullet}

Reinitiation

$$R^{\bullet} \xrightarrow{M}_{k_{\mathrm{IT}}} R^{\bullet} R^{\bullet} \xrightarrow{M} P_{m}^{\bullet}$$

Reversible (degenerate) chain transfer/propagation

$$\begin{array}{c} P_{m}^{\bullet} + S \\ (M) \\ (M) \\ k_{p} \\ z \\ 68a \\ 69 \\ 68b \end{array}$$

Termination

$$P_n^{\bullet} + P_m^{\bullet} \xrightarrow{k_t} dead polymer$$

Scheme 76

thiocarbonylthio compounds (66) provides equal probability for all chains to grow and allows for the production of low-dispersity polymers. With appropriate attention to the reaction conditions, the vast majority of chains will retain the thiocarbonylthio end group when the polymerization is complete (or stopped). Radicals are neither formed nor destroyed in the chain equilibration process. Thus once the equilibria are established, rates of polymerization should be similar to those in conventional radical polymerization. This is borne out by experimental data, which show that, with some RAFT agents, RAFT polymerization is half order in initiator and zero order in the RAFT agent over a wide range of initiator and RAFT agent concentrations.

For very active RAFT agents, the RAFT agent derived radical (\mathbb{R}^{\bullet}) may partition between adding to monomer and reacting with the transfer agent (polymeric or initial). In these circumstances, the transfer constant measured according to the Mayo or related methods will appear to be dependent on the transfer agent concentration and on the monomer conversion. A reverse transfer constant can be defined as follows (eqn [77]):

$$C_{-\rm tr} = \frac{k_{-\rm tr}}{k_{\rm IT}}$$
[96]

and the rate of RAFT agent consumption is then given by eqn [78]:³⁶⁴

$$-\frac{d[66]}{d[M]} \approx C_{tr} \frac{[66]}{[M] + C_{tr}[66] + C_{-tr}[68]}$$
[97]

For addition-fragmentation chain transfer, the rate constants for the forward and reverse reactions are defined as shown in eqns [98] and [99], respectively:

$$k_{\rm tr} = k_{\rm add} \frac{k_{\beta}}{k_{\rm -add} + k_{\beta}}$$
[98]

$$k_{-\rm tr} = k_{-\beta} \frac{k_{-\rm add}}{k_{-\rm add} + k_{\beta}}$$
[99]

RAFT polymerization provides the characteristics usually associated with living polymerization. The overall process results in monomer units being inserted into the RAFT agent structure as shown in **Scheme 6**. Expressions (eqns [90]–[93]) for estimating number average degree of polymerization and molecular weight in RAFT polymerization are provided in Section 3.04.6.6.1. Dispersities will depend on the chain transfer constants associated with both the initial and polymeric RAFT agents. The reaction conditions should be chosen such that the initial RAFT agent is rapidly consumed during the initial stages of the polymerization.

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385

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3.05 Controlled and Living Radical Polymerization – Principles and Fundamentals

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2 05 1	Introduction	100
3.00.1	Introduction	120
3.05.2	Principles and Classification of LRP Techniques	120
3.05.2.1	General Polymerization Behavior	120
3.05.2.2	Activation–Deactivation Quasi-Equilibrium	121
3.05.2.3	Examples of Capping Agent X	121
3.05.2.4	Mechanistic Classification of Reversible Activation Processes	121
3.05.2.4.1	Dissociation-combination	121
3.05.2.4.2	Atom transfer	122
3.05.2.4.3	Degenerative chain transfer and reversible addition-fragmentation chain transfer	122
3.05.2.4.4	Reversible chain transfer	123
3.05.3	Kinetic Theory of LRP: Polymerization Rates	123
3.05.3.1	Systems of DC Type	123
3 05 3 1 1	Persistent radical effect	123
3 05 3 1 2	General equations	124
3 05 3 1 3	Steady-state systems	124
3 05 3 1 1	Power-law and related systems	124
3 05 3 1 5	Comparison of general nower-law and steady-state equations	124
2.05.2.1.5	Crossover between newer law and steady state kinetice	120
3.03.3.1.0 2.0F.2.1.7	Additional commante	120
3.03.3.1.7		120
3.05.3.2	Systems of AT Type	120
3.05.3.3	Systems of DT Type	126
3.05.3.4	Systems of RT Type	126
3.05.4	Kinetic Theory of LRP: Polydispersities	126
3.05.4.1	Steady-State Systems	126
3.05.4.1.1	Systems with constant [P [•]] and constant [M]	126
3.05.4.1.2	Batch systems with constant [P [*]]	127
3.05.4.2	Power-Law Systems	127
3.05.4.3	Deviations from Ideality	127
3.05.4.4	Correction for Initiator Mass (Block Copolymerization)	127
3.05.5	Nitroxide-Mediated Polymerization	128
3.05.5.1	TEMPO-Mediated Polymerization of Styrene	128
3.05.5.1.1	Polymerization rates	128
3.05.5.1.2	Activation-deactivation equilibrium	128
3.05.5.1.3	Activation process: curve-resolution method	134
3.05.5.1.4	Activation process: PDI method	135
3.05.5.1.5	Side reactions	136
3.05.5.2	DEPN-Mediated Polymerization of Styrene	136
3.05.5.2.1	Activation and deactivation processes	136
305522	Polymerization rates	137
3 05 5 2 3	Polydisnersities	137
3 05 5 3	NMP of Acrylates	138
3 05 5 4	NMP of Methachylates	139
3 05 6	Atom Transfer Badical Polymerization	130
3 05 6 1	Conner-Mediated ATRP of Styrene	130
2 05 6 1 1	Activation and deactivation processor	120
2.05.6.1.2	Polymerization rates and polydionersities	140
3.00.0.1.2 2.05.6.1.2	FulyInenzation rates and polyuispersities	140
3.03.0.1.3	Liyanus anu suivenis	140
3.05.0.1.4	Stud reactions	141
3.05.0.2	ATMY OF INTERNATION ACTIVIATES	141
3.05.6.3	Some Uner Notes on ATRP	141
3.05.7	Degenerative chain Transfer-Mediated Polymerization	141
3.05.7.1	Iodide-Mediated Polymerization of Styrene	141
3.05.7.1.1	Polymerization rates	141
3.05.7.1.2	Activation process	141

Keterences		154
3.05.10	Conclusions	154
3.05.9.2.2	Deactivation rate constants for polymer adducts	153
3.05.9.2.1	Activation rate constants for polymer adducts	148
3.05.9.2	Polymer Adducts	148
3.05.9.1.2	Deactivation rate constants for low-mass adduct	148
3.05.9.1.1	Activation rate constants for low-mass adducts	147
3.05.9.1	Low-Mass Model Adducts	147
3.05.9	Summary on Activation and Deactivation Rate Constants	147
3.05.8.2	Reversible Chain Transfer-Catalyzed Polymerization	146
3.05.8.1	Organotellurium-Mediated LRP and Others	145
3.05.8	Experiments on Some Newer Systems	145
3.05.7.2.4	Retardation in polymerization rates	144
3.05.7.2.3	Comments on the intermediate radical concentrations	144
3.05.7.2.2	Activation process in copolymerizations	144
3.05.7.2.1	Activation process in homopolymerizations	142
3.05.7.2	RAFT Polymerization	142
3.05.7.1.3	Polydispersities	142

3.05.1 Introduction

Controlled/living radical polymerization, abbreviated here as LRP, has attracted enormous attention over the past two decades or so for providing simple and robust routes to the synthesis of well-defined, low-polydispersity polymers and the fabrication of novel functional materials.^{1–27} LRP includes a group of radical polymerization (RP) techniques which are based on a common mechanistic principle by which it is distinguished from free RP or conventional RP. It is a reversible activation process (Scheme 1), in which the dormant (end-capped) chain P-X is supposed to be activated (uncapped) to the polymer radical P[•] by thermal, photochemical, and/or chemical stimuli. In the presence of a monomer M, P[•] will undergo propagation until it is deactivated (capped) back to P-X. In practically important systems, it usually holds that $[P^{\bullet}]/[P-X] \leq 10^{-5}$, meaning that a living chain spends most of its polymerization time in the dormant state. Here we have implicitly defined 'living chains' as the sum of the active and dormant chains. Accordingly we define LRP as the RP that is structurally and kinetically controlled by the work of living chains. If each living chain experiences activation-deactivation cycles many times during the polymerization run, all of them will have a nearly equal chance to grow, giving a low-polydispersity product. Many of the fundamental issues to be addressed in LRP are, therefore, associated with the reversible activation process. How can we realize this process experimentally? How is the frequency of activation (or deactivation) correlated with the chain length and chain length distribution of the product polymer? How is it possible to





experimentally determine this frequency? And how does this frequency depend on the chemical structure of the dormant chain and the thermal, photochemical, and/or chemical stimuli applied to the system? Answers to these questions are essential for systematically understanding LRP, evaluating the performance of individual LRP systems, making the most effective use of them, and designing new systems of higher performance.

LRP is distinguished also from termination-free polymerizations like living anionic polymerization (in its ideal form) by the existence of bimolecular termination, chain transfer, and all other elementary reactions involved in conventional RP. While it clearly limits the degree of structural control attainable by LRP, it provides the systems with a variety of kinetically unique and interesting characteristics. Given the rate constants of all the elementary reactions and experimental conditions such as the original concentrations of reactants and temperature, one will be able to simulate the whole process of an LRP run and predict the characteristics of the product polymer, quite accurately in principle. This, in turn, indicates the feasibility of optimizing experimental conditions for the highest possible performance. The demerit of termination and other 'side reactions' would thus be minimized in a well-designed LRP run.

This chapter is intended to describe the principles and fundamentals of LRP. It covers a brief survey of LRP in Section 3.05.2, the theories of polymerization rate R_p and polydispersity index (PDI) in Sections 3.05.3 and 3.05.4, respectively, and the experimental investigations into several typical LRP systems in Sections 3.05.5 through 3.05.8. The kinetic parameters related to reversible activation reactions are briefly summarized in Section 3.05.9. The readers are referred also to our previous reviews.^{25–31}

3.05.2 Principles and Classification of LRP Techniques

3.05.2.1 General Polymerization Behavior

In conventional RP, the lifetime of a polymer radical P^{\bullet} is typically in the order of a second, during which initiation, propagation, and termination take place, yielding a dead
chain with a degree of polymerization (DP) of, say, $10^3 - 10^4$ in the absence of a chain transfer agent. Such dead chains are formed at every instant and accumulated throughout the course of polymerization that may last for several hours in many cases. In LRP, polymerization is usually started with an initiating adduct P₀-X, which is, in many cases, a low-mass homologue of the dormant polymer P-X and is sometimes produced in situ at an early stage of polymerization. As mentioned in Section 3.05.1, every living chain repeatedly experiences the activation-deactivation cycle and thus grows in an intermittent fashion or, viewed in a long timescale, grows 'slowly'. The transient lifetime of the activated chain P[•], namely, the time interval between the activation and subsequent deactivation events occurring on the same chain, is typically in the order of a millisecond, which is followed by the dormant state P-X lasting for minutes, typically. Obviously, the sum of transient lifetimes of a chain over the whole polymerization run determines the DP finally achieved.

Now let us compare an LRP and a conventional RP with the same $[P^{\bullet}]$ (and hence the same rate of polymerization R_{p}) and assume, for the sake of simplicity, [M] and [P[•]] to be independent of time. The chance of radical-radical termination is obviously the same for the two systems. If the radical lifetime in the conventional system is 1s, for example, the sum of transient lifetimes in the corresponding LRP system has to be set sufficiently smaller than 1 s, since otherwise a greater portion of living chains (the sum of activated and dormant chains) will be dead at the end of the run. In other words, if the number-average DP (DPn) achieved in the conventional RP run is 10⁴, for example, that in the LRP run has to be set sufficiently smaller than 10⁴. If it is set to 10³, we may expect that about 10% of the living chains will be dead, and if it is set to 10², dead chains in the LRP system will be only about 1% in fraction at the end of the run. A high fraction of living chains is an obvious requisite for preparing well-defined polymers. Hence the target DPn in an LRP run, which may be approximated by eqn [1], should be relatively low, say, less than several hundreds in typical cases:

$$DP_{n} = \frac{c[M]_{0}}{[P_{0} - X]_{0}}$$
[1]

In eqn [1], *c* is the fractional conversion and the subscript '0', denotes the initial state. Of course such an estimate heavily depends on monomers and experimental conditions. One can relax the limitation imposed on DP_n by carrying out experiments at, for example, an unusually low [P[•]] or an unusually high pressure.^{32,33} In these conditions, one can expect unusually large DP_n for both conventional and LRP systems, but, of course, at the cost of a long polymerization time or a complicated and costly experimental setup, respectively.

3.05.2.2 Activation–Deactivation Quasi-Equilibrium

The rate constants of activation k_{act} and deactivation k_{deact} given in the general scheme (Scheme 1) are defined as a pseudofirst-order constant in the unit of s⁻¹. Every dormant chain is activated once every k_{act}^{-1} s and deactivated back to the dormant state after a transient lifetime of k_{deact}^{-1} s, on average. In typical successful LRPs, $k_{act}^{-1} = 10-10^3$ s and $k_{\text{deact}}^{-1} = 0.1-10$ ms. The steadiness of polymerization requires the following equilibrium to hold:

$$k_{\rm act}[P-X] = k_{\rm deact}[P^{\bullet}]$$
^[2]

Actually, this equilibrium is never realized rigorously because of the presence of termination (and other 'side' reactions that can affect the active chain concentration $[P^{\bullet}]$). It is a 'quasiequilibrium' state in which eqn [2] only approximately holds when the rates of activation and deactivation are much larger than those of termination (and other side reactions).

The rate constant k_{act} denotes the activation frequency per chain, that is, the number of activation events occurring on a chain per unit time, which, in the quasi-equilibrium state, is approximately equal to the deactivation frequency per chain. This frequency determines the polydispersity of the product. In the ideal case with constant concentrations of monomer and all other components along with negligible fractions of dead and conventionally initiated chains, the PDI of the LRP product may be given by (see Section 3.05.4.1.1)

$$PDI = 1 + \frac{1}{DP_n} + \frac{2}{k_{act}t}$$
[3]

The PDIs of actual systems become more or less larger than suggested by this equation for various nonidealities. Nevertheless it will work as a rough measure for what we can expect for the given LRP system.

3.05.2.3 Examples of Capping Agent X

Miscellaneous capping agents X are used for LRP. Examples are listed in Scheme 2. They include sulfur compounds $2(a)^{9,34}$ $2(e)^{16,35}$; (Schemes and stable nitroxides 2(b));^{10,11,36,37} (Scheme transition metal complexes (Scheme 2(c));^{38,39} iodine (Scheme 2(d));^{15,40-42} halogens with transition metal catalysts (Scheme 2(f));^{12-14,43,44} organotellurium, stibine, and bismuth compounds (Scheme 2(g));^{17,45–48} and iodine with nontransition metal catalysts (Scheme 2(h)).^{18,49}

3.05.2.4 Mechanistic Classification of Reversible Activation Processes

The reversible activation reactions in the most successful LRPs currently known may be classified into four main mechanisms, which are (1) the dissociation-combination (DC), (2) the atom transfer (AT), (3) the degenerative chain transfer (DT), and (4) the reversible chain transfer (RT) mechanisms (Scheme 3), which will be briefly described below. For more details, see the relevant sections.

3.05.2.4.1 Dissociation-combination

In this mechanism, P-X is thermally or photochemically dissociated into P^{\bullet} and X^{\bullet} , where a stable (persistent) radical X^{\bullet} is assumed to be stable enough to undergo no reaction other than the combination with P^{\bullet} (and other alkyl radicals, if any present), namely, an 'ideal' stable free radical (SFR) does not react among themselves, does not initiate polymerization, and does not undergo disproportionation with P^{\bullet} . The best known examples of SFR are nitroxides such as TEMPO (2,2,6,6- tetramethylpiperidinyl-1-oxy) (Figure 1), even though they are not perfectly ideal in the mentioned sense. The rate constants of (a) Dithiocarbamate (Iniferter polymerization)

$$X = -SC = S$$

(b) Nitroxides

$$X = -O - N$$
 etc.





(d) lodine

Х

X = -I

(e) Dithioesters (RAFT)

$$= -SC = S$$

$$Z$$
(z = Ph, CH₃, etc.)

(f) Halogens with metals (ATRP)

$$X = -Br, CI + Metal (e.g., CuIBr/2L)$$

(g) Organo-tellulium (TERP), stibine (SBRP), and bismuth (BIRP)

$$X = -TeR SbR_2 BiR_2$$
 (R = CH₃, etc.)

(f) lodine with non-metals (RTCP)

X = -I + Non-metal (e.g., Ge, P, N, O and C compounds) Scheme 2 Examples of X.

dissociation $k_{\rm d}$ and combination $k_{\rm c}$ are related to $k_{\rm act}$ and $k_{\rm deact}$ by

$$k_{\rm act} = k_{\rm d} \quad (\rm DC) \qquad [4a]$$

$$k_{\text{deact}} = k_{\text{c}}[X^{\bullet}] \quad (\text{DC})$$
 [4b]

(a) Dissociation-Combination

$$P-X \xrightarrow{k_d} P^{\bullet} + X^{\bullet}$$

(b) Atom Transfer

$$P-X + A \xrightarrow{k_a} P^{\bullet} + AX^{\bullet}$$

(c) Degenerative Chain Transfer

$$P-X + P'^{\bullet} \xrightarrow{K_{ex}} P^{\bullet} + X-P'$$

(d) Reversible Chai Transfer

$$P-X + A^{\bullet} \xrightarrow{k_a} P^{\bullet} + AX$$

Scheme 3 Three main mechanisms (a, b, and c) of reversible activation.

Some transition metal complexes such as cobalt and chromium complexes are also used as SFRs. (In the cobalt and chromium systems, not only DC but also DT is suggested to be concurrently involved.^{50–52} Chromium was also used as a catalyst for the AT process with an alkyl halide as a dormant species, in which DC, DT, and AT are suggested to coexist.⁵²)

3.05.2.4.2 Atom transfer

In this mechanism, P–X is activated by the catalysis of activator A, and the capping agent is transferred to form a stable species AX[•]. All currently known successful LRPs in this category use a halogen like Cl and Br as a capping agent X and a halide complex of transition metal like Cu⁴⁴ and Ru⁴³ as an activator A. These LRPs are commonly termed atom transfer radical polymerization (ATRP).⁴⁴ The rate constants k_a and k_{da} defined in Scheme 3 are related to k_{act} and k_{deact} by

$$k_{\rm act} = k_{\rm a}[{\rm A}] \quad ({\rm AT})$$
[5a]

$$k_{\text{deact}} = k_{\text{da}}[AX^{\bullet}] \quad (AT)$$
[5b]

3.05.2.4.3 Degenerative chain transfer and reversible addition-fragmentation chain transfer

In the DT mechanism, P–X is attacked by the propagating radical P'^{\bullet} to form the active species P^{\bullet} and the dormant species



Figure 1 Examples of nitroxides.

(a) RAFT ($Z = CH_3$ or Ph)

$$P_{A}^{\bullet} + \frac{S}{Z} P_{B} \xrightarrow{k_{ad}BA}_{k_{fr}AB} P_{A}^{S} \xrightarrow{S}_{C} P_{B} \xrightarrow{k_{fr}BA}_{k_{ad}AB} P_{A}^{S} \xrightarrow{S}_{C} P_{B} \xrightarrow{k_{fr}BA}_{k_{ad}AB} P_{A}^{S} \xrightarrow{S}_{C} + P_{B}^{\bullet}$$

$$(X-P_{B}) \qquad (P_{A}-(X^{\bullet})-P_{B}) \qquad (P_{A}-X)$$

(b) Degenerative Chain Transfer

$$P_A^{\bullet} + X_P_B \xrightarrow{k_{ex}AB} P_A X + P_B^{\bullet}$$

Scheme 4 (a) RAFT and (b) general scheme of DT.

P'–X. This is an exchange reaction. If the radicals P[•] and P'[•] are kinetically identical, then $k_{ex} = k_{ex}'$, and we can write

$$k_{\rm act} = k_{\rm ex}[{\rm P}^{\bullet}] \quad ({\rm DT})$$
 [6a]

$$k_{\text{deact}} = k_{\text{ex}}[P - X]$$
 (DT) [6b]

Two types of LRPs belong to the DT category. In one type, X is an atom or a simple group. In this case, X is simply transferred from radical to radical without forming any kinetically important intermediate. A typical example is the iodide-mediated polymerization, where X is iodine. A group of LRPs mediated by organotellurium (TERP) (X = TeCH₃; Scheme 2g),⁴⁶ organostibine (SBRP) (X = Sb(CH₃)₂; Scheme 2g),⁴⁷ and organobismuth (BIRP) (X = Bi(CH₃)₂; Scheme 2g),⁴⁸ are also included in this mechanism, while the DC and other mechanisms may coexist in these LRPs (Section 3.05.8).

In the other type, X is a group with a double bond that is accessible to the addition of P[•] (Scheme 4a). The exchange reaction occurs via the addition of PA* to PB-X to form the intermediate radical P_A -(X[•])- P_B (rate constant k_{adAB}) followed by fragmentation of $P_A - (X^{\bullet}) - P_B$ into P_B^{\bullet} and $P_A - X$ (rate constant k_{frAB}). This process was named reversible addition-fragmentation chain transfer (RAFT).³⁵ Dithioester compounds are representative RAFT agents (Scheme 2e). Hence, RAFT polymerization as a high-performance LRP has the additional prerequisites that fragmentation should occur fast enough that the concentration of the intermediate radical remains at a low equilibrium level, and that the intermediate radical should not damagingly work as an initiator or a radical trap. If the radicals PA° and PB° are kinetically identical, and if the work of PA and PB moieties in the intermediate radical $P_A-(X^{\bullet})-P_B$ is also kinetically identical, we can write $k_{ad} = k_{adAB} = k_{adBA}$ and $k_{frAB} = k_{frBA}$ and therefore the RAFT process may be related to the DT process by

$$k_{\rm ex} = \left(\frac{1}{2}\right) k_{\rm ad} \quad ({\rm RAFT})$$
 [7]

3.05.2.4.4 Reversible chain transfer

In this mechanism, P–X is activated by a catalyst radical A^{\bullet} (activator) to form P[•] and AX (deactivator). Mechanistically, this is a RT between P–X and A[•]. The A[•] is supplied *in situ* in the polymerization via a reaction of AX and P[•] (deactivation), for which AX and a conventional radical initiator (a source of P[•]) are added as starting compounds or, alternatively, via that of AH (with a hydrogen) and P[•], for which AH and a conventional radical initiator are used as starting compounds. The currently

reported systems use iodine as an X and a nontransition metal compound (e.g., Ge,^{49,53} P,⁵³ N,⁵⁴ O,⁵⁵ or C⁵⁵-centered organic molecule) as a catalyst (AX or AH). The LRP in this category was termed RT-catalyzed polymerization (RTCP).⁵³ The rate constants k_a and k_{da} defined in **Scheme 3** are related to k_{act} and k_{deact} by

$$k_{\rm act} = k_{\rm a} \left[{\rm A}^{\bullet} \right] \quad ({\rm RT}) \tag{8a}$$

$$k_{\text{deact}} = k_{\text{da}} [\text{AX}] \quad (\text{RT})$$
 [8b]

3.05.3 Kinetic Theory of LRP: Polymerization Rates

The existence of termination (and conventional initiation) provides the rate equations of LRP with several unique features depending on activation-deactivation mechanisms and experimental conditions, as will be theoretically surveyed in this section.

3.05.3.1 Systems of DC Type

3.05.3.1.1 Persistent radical effect

Here we consider a system including only an initiating adduct P_0 -X and a monomer at time t = 0. When a polymerization run is started by allowing Po-X to dissociate, the same number of P_0^{\bullet} and X^{\bullet} will be produced in a unit time, and $[P_0^{\bullet}]$ and $[X^{\bullet}]$ will linearly increase with t. The radical P_0^{\bullet} may add to the monomer to give a polymer radical P^{\bullet} , but for a moment, P_0^{\bullet} and P[•] are assumed to be kinetically identical and both of them will be written as P[•]. As [P[•]] and [X[•]] increase to a certain level, the reaction between P's and that between P and X will become significant. While the self-termination of P[•] results in a decrease of [P[•]] relative to [X[•]], [X[•]] will steadily increase, and the reaction between P* and X* will become more and more important. This eventually leads to a balance of the rate of deactivation, $k_{\rm c}[{\rm P}^{\bullet}][{\rm X}^{\bullet}]$, with that of activation, $k_{\rm d}[{\rm P}-{\rm X}]$, namely, quasi-equilibrium eqn [2] will hold there and thereafter. On the other hand, while the quasi-equilibrium holds, $[P^{\bullet}]$ must be a decreasing function of *t*, since self-termination continues to occur. This means that [P[•]], which linearly increases with t at the onset of polymerization, will turn to decrease, going through a maximum. Actually, [P[•]] decays in a power law in the quasi-equilibrium regime (see below). After a long time, [P[•]] and hence the rate of polymerization will therefore become impractically too low. The role of conventional initiation, whose rate R_i is usually much smaller than k_d [P–X],

is unimportant during an early stage of polymerization, but becomes crucially important when $[P^*]$ comes down to the level at which the equality of the initiation and termination rates holds:

$$R_{\rm i} = k_{\rm t} [\mathrm{P}^{\bullet}]^2 \tag{9}$$

where k_t is the termination rate constant. (In eqn [9], the termination rate constant k_t is implicitly defined by $R_t = k_t [P^\bullet]^2$, where R_t is the number of radicals lost by termination per unit time and unit volume. This definition differs from the IUPAC recommendation, ^{56,57} $R_t = 2k_t [P^\bullet]^2$, but is simpler and better consistent to the general physicochemical notations.) Equation [9] brings about a steady (stationary) concentration of P[•] and hence a steady rate of polymerization in LRP as well as in conventional RP. If a small amount of X[•] is present at t = 0, it obviously shortens the time to reach quasi-equilibrium. On the other hand, too much of X[•] present at t = 0 will make the equilibrium value of [P[•]] too low or the polymerization rate impractically too low.

The mentioned work of SFR to adjust the radical concentrations for a high preference of cross-combination was originally recognized in the chemistry of low-mass compounds and termed the persistent radical effect (PRE).^{58–61} In the field of polymerization, such a work of X[•] was clearly recognized by Johnson *et al.*⁶² in their computer simulation work, and subsequently by Fukuda *et al.*⁶³ and Greszta and Matyjaszewski,⁶⁴ and clear experimental evidence for the inequality [X[•]] » [P[•]] and the quasi-equilibrium in eqn [2] was first presented for a nitroxide-mediated LRP of styrene by Fukuda *et al.*⁶³ Subsequently, Fischer^{65,66} made a detailed theoretical analysis of the PRE in polymerization. For more details about PRE, the readers are referred to the review by Fischer.²⁴

In the following, we consider systems where (1) the quasi-equilibrium is reached so fast that the main body of polymerization occurs in the time range of quasi-equilibrium and that the preequilibrium stage has no significant effect on the polymerization kinetics and (2) the cumulative numbers of dead chains (by termination) and initiated chains (by conventional initiation) are sufficiently small compared with the number of dormant chains, that is, the equations $[P-X] = [P-X]_0 = [P_0-X]_0$ approximately hold throughout the polymerization. The conditions for the existence of the quasi-equilibrium were rigorously discussed.^{65–67} The results showed that, in most successful and hence practically important systems, the quasi-equilibrium exists, and the time needed to reach the quasi-equilibrium is much less than 1 s, typically 1–100 ms.

3.05.3.1.2 General equations

Setting the above statements into equations, we have the following two differential equations:

$$\frac{\mathbf{d}[\mathbf{X}^{\bullet}]}{\mathbf{d}t} = k_{\mathbf{d}}[\mathbf{P} - \mathbf{X}] - k_{\mathbf{c}}[\mathbf{P}^{\bullet}][\mathbf{X}^{\bullet}]$$
[10]

$$\frac{\mathrm{d}[\mathbf{P}^{\bullet}]}{\mathrm{d}t} = k_{\mathrm{d}}[\mathbf{P} - \mathbf{X}] - k_{\mathrm{c}}[\mathbf{P}^{\bullet}][\mathbf{X}^{\bullet}] + R_{\mathrm{i}} - k_{\mathrm{t}}[\mathbf{P}^{\bullet}]^2$$
[11]

Here we assume that R_i is constant. All possible reactions other than those indicated in eqns [10] and [11] have been neglected, and all the rate constants are assumed to be independent of chain length. These equations can be approximately solved

analytically by the method of Fukuda,^{27,29,68} namely, the sum of eqns [10] and [11] gives

$$\frac{\mathrm{d}[\mathrm{P}^{\bullet}]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{X}^{\bullet}]}{\mathrm{d}t} + R_{\mathrm{i}} - k_{\mathrm{t}}[\mathrm{P}^{\bullet}]^{2}$$
[12]

The quasi-equilibrium (eqns [2] or [10] with $d[X^{\bullet}]/dt \cong 0$) with negligible fraction of dead chains is represented by

$$[P^{\bullet}][X^{\bullet}] = K[P - X] = KI_0$$
[13]

$$K = \frac{k_{\rm d}}{k_{\rm c}}$$
[14]

where $I_0 = [P-X]_0 = [P_0-X]_0$. Since it usually holds that $[P^\bullet] \ll [X^\bullet]$, we may neglect $d[P^\bullet]/dt$ as compared with $d[X^\bullet]/dt$ in eqn [12], which, with eqn [13], gives

$$\frac{\mathbf{d}[\mathbf{X}^{\bullet}]}{\mathbf{d}t} = \frac{k_t K^2 I_0^2 - R_i [\mathbf{X}^{\bullet}]^2}{[\mathbf{X}^{\bullet}]^2}$$
[15]

This can be easily solved to yield^{29,68}

$$\ln\frac{(1+z)(1-z_0)}{(1-z)(1+z_0)} - 2(z-z_0) = bt$$
 [16]

$$z = \left(\frac{R_{\rm i}}{k_{\rm t} K^2 {I_0}^2}\right)^{1/2} [X^{\bullet}]$$
 [17]

$$b = \frac{2R_{\rm i}^{3/2}}{\left(k_{\rm t}K^2I_0^2\right)^{1/2}}$$
[18]

where z_0 is the value of z at t = 0 ($[X^\bullet] = [X^\bullet]_0$). The polymerization rate R_p is obtained from $R_p = k_p [P^\bullet][M]$, where k_p is the propagation rate constant and $[P^\bullet]$ can be calculated from $[P^\bullet] = (KI_0/[X^\bullet])$ (eqn [13]) with $[X^\bullet]$ obtained from eqns [16]–[18]. In the following, some special cases will be discussed.

3.05.3.1.3 Steady-state systems

The first one is the case with $R_i > 0$, $[X^\bullet]_0 = 0$, and $bt \gg 1$. In this limit, eqn [16] reduces to z = 1, which is equivalent to eqn [9] with eqn [13] and corresponds to the steady state:⁶³

$$[X^{\bullet}] = K I_0 \left(\frac{k_t}{R_i}\right)^{1/2} \quad (\text{steady state})$$
 [19]

$$[\mathbf{P}^{\bullet}] = \left(\frac{R_{\rm i}}{k_{\rm t}}\right)^{1/2} \quad (\text{steady state})$$
 [20]

In this limit, R_p is independent of the reversible activation and identical with that for the conventional RP, as mentioned above. The conversion index $\ln([M]_0/[M])$ is first order in *t*:

$$\ln\left(\frac{[M]_0}{[M]}\right) = k_p \left(\frac{R_i}{k_t}\right)^{1/2} t \quad (\text{steady state})$$
[21]

The steady-state concentration of X^{\bullet} depends on the reversible activation, initiation, and termination (eqn [19]).

3.05.3.1.4 Power-law and related systems

Another special case is the one without conventional initiation $(R_i = 0 \text{ or } b = 0)$. Expansion of eqn [16] around $z = z_0 = 0$ or, more straightforwardly, direct solution of eqn [15] with $R_i = 0$ gives²⁵

$$[X^{\bullet}]^{3} - [X^{\bullet}]_{0}^{3} = 3k_{t}K^{2}I_{0}^{2}t \quad (R_{i} = 0)$$
[22]

Along with eqn [13], this yields

$$[\mathbf{P}^{\bullet}] = \frac{KI_0}{\left(3k_t K^2 I_0^2 t + [X^{\bullet}]_0^3\right)^{1/3}} \quad (R_i = 0)$$
 [23]

 $\ln([M]_0/[M])$ is given by

$$\ln\left(\frac{[M]_{0}}{[M]}\right) = \left(\frac{k_{p}}{2k_{t}KI_{0}}\right) \left\{ \left(3k_{t}K^{2}I_{0}^{2}t + [X^{\bullet}]_{0}^{3}\right)^{2/3} - [X^{\bullet}]_{0}^{2} \right\} \quad (R_{i} = 0)$$
[24]

It is illuminating to consider two limiting cases. When $[X^{\bullet}]_0 = 0$, eqn [24] gives the now familiar power law (eqn [25]), which was first derived by Fischer^{65,66} from a dimensional analysis approach and subsequently modified to the present k_t -including form by Ohno *et al.*⁶⁷ using this approach.

$$\ln\left(\frac{[M]_{0}}{[M]}\right) = \frac{3}{2}k_{p}\left(\frac{KI_{0}}{3k_{t}}\right)^{1/3}t^{2/3} \quad (R_{i} = 0; [X^{\bullet}]_{0} = 0) \qquad [25]$$

In the other limit of large $[X^{\bullet}]_0 \left([X^{\bullet}]_0 \gg (3k_t K^2 I_0^2 t)^{1/3} \right)$, eqn [24] reduces to²⁵

$$\ln\left(\frac{[M]_0}{[M]}\right) = \left(\frac{k_p K I_0}{[X^\bullet]_0}\right) t \quad (R_i = 0; \text{large} [X^\bullet]_0) \qquad [26]$$

In this limit, the conversion index is first order in *t* as in the steady-state system (eqn [21]). Therefore, when $[X^{\bullet}]_0 > 0$, the

conversion index will depend on *t* with any power between 2/3 and 1, depending on $[X^*]_0$ and *t*. Equation [26] is often used to determine the equilibrium constant *K* with an excess of X^* at t = 0.

3.05.3.1.5 Comparison of general, power-law, and steady-state equations

Figure 2 compares the dependence of *z* on *bt* for $R_i > 0$ and $R_i = 0$, where *z* is the reduced [X[•]] defined by eqn [17] and *bt* is the reduced time with *b* defined by eqn [18]. The solid curves represent eqn [16] with $R_i > 0$, while the broken lines represent eqn [22] (or eqn [16] with $R_i = 0$), where eqn [22] is rewritten as⁶⁸

$$z^{3} = z_{0}^{3} + \frac{3}{2}bt \quad (R_{i} = 0)$$
 [27]

For $z_0 = [X^\bullet]_0 = 0$ (Figure 2(a)), eqn [16] with $R_i > 0$ is approximated by the power-law equation (eqn [27]) for small *bt*, while for large *bt*, it becomes asymptotic to the steady state given by z = 1 (dotted line). For $z_0 = 1.3$ (Figure 2(b)), which shows the case with a small excess of $[X^\bullet]_0$ over the steady-state concentration, *z* continuously increases with *bt* for $R_i = 0$ (eqn [27]) due to continuous termination, while for $R_i > 0$, *z* decreases with increasing *bt*, approaching z = 1 due to the consumption of the excess X^\bullet by conventional initiation. For a very large z_0



Figure 2 Plot of *z* vs. *bt*. (a) $z_0 = 0$, (b) 1.3, and (c) 50. The solid lines show eqn [16] and the broken lines show eqn [27]. The dotted line represents the stationary state (*z* = 1). Reproduced from Goto, A.; Fukuda, T. *Prog. Polym. Sci.* **2004**, *29*, 329–385,²⁶ with permission from Elsevier.

($z_0 = 50$; Figure 2(c)), z is approximated by $z = z_0$ throughout the range of the reduced time shown in the figure irrespective of $R_i = 0$ or $R_i > 0$.

3.05.3.1.6 Crossover between power-law and steady-state kinetics

As shown in **Figure 2(a)**, the system with $R_i > 0$ and $z_0 = [X^*]_0 = 0$ obeys the power-law kinetics for sufficiently small *bt* and the steady-state kinetics for sufficiently large *bt*. The crossover time t_{cross} between the two types of kinetics can be estimated by equating eqn [27] and z = 1 (see also **Figure 2(a)**):^{30,69}

$$t_{\rm cross} = \frac{(k_{\rm t} K^2 {\rm I}_0{}^2)^{1/2}}{3 R_{\rm i}{}^{3/2}} = \frac{2}{3b}$$
[28]

More quantitatively, the power-law kinetics $(z^3 = (3/2)bt)$ and the steady-state kinetics (z=1) hold for bt < 0.2 and bt > 2, respectively, within a few percent of error.

3.05.3.1.7 Additional comments

Given all the rate constants and the initial conditions, eqns [10] and [11] can be numerically solved without introducing any assumptions and approximations.^{26,39} Comparison of the analytical results with numerical solutions indicates that the analytical solutions, eqn [16] and its derivatives, generally give good approximations. In some cases, deviations from the numerical results become evident, indicating the inadequacy of the assumptions on which eqn [16] is based. Several examples for comparing analytical values with numerical solutions with varying parameters have also been provided by Fischer *et al.*^{24,66,67,69–71} These indicate that the approximation of $[P-X] = I_0$ (constant) may be inadequate, especially in a later stage of polymerization in a power-law-type system, where [P-X] continuously decreases by termination.

The Fukuda²⁷ method was also applied to the case with variable [P-X] (= I_0 - $[X^{\bullet}]$) and with $[X^{\bullet}]_0 = 0$ to obtain an analytical solution with a higher degree of accuracy:⁷²

$$\frac{I_0^2}{I_0 - [\mathbf{X}^\bullet]} + 2I_0 \ln\left(\frac{I_0 - [\mathbf{X}^\bullet]}{I_0}\right) - (I_0 - [\mathbf{X}^\bullet]) = 2k_t K^2 t \qquad [29]$$

3.05.3.2 Systems of AT Type

All the equations derived for systems of DC type are basically applicable to systems of AT type, that is, ATRPs by the reinterpretations of

$$X^{\bullet} = AX^{\bullet}$$
 [30a]

$$k_{\rm d} = k_{\rm a}[{\rm A}] \qquad [30b]$$

$$k_{\rm c} = k_{\rm da} \qquad [30c]$$

Hence (cf. Scheme 3),

$$K = K_{\rm AT}[A]$$
[31a

$$K_{\rm AT} = \frac{k_{\rm a}}{k_{\rm da}}$$
[31b

In relation to eqn [29], the power-law system with variable [P-X] (= I_0 -[AX^{\bullet}]) and [A] (=[A]_0 - [AX^{\bullet}]) and with [AX^{\bullet}]_0 = 0 follows:⁷³

$$\begin{pmatrix} I_0[A]_0\\ \overline{[A]_0 - I_0} \end{pmatrix}^2 \left(\frac{1}{\left[A\right]_0^2 (I_0 - [AX^\bullet])} + \frac{2}{I_0[A]_0([A]_0 - I_0)} \right. \\ \left. \times \ln \left(\frac{I_0 - [AX^\bullet]}{[A]_0 - [AX^\bullet]} \right) + \frac{1}{I_0^2([A]_0 - [AX^\bullet])} \right) = 2k_t K_{AT}^2 t + c_s^2$$

where

$$c' = \left(\frac{I_0[A]_0}{[A]_0 - I_0}\right)^2 \left(\frac{1}{[A]_0^2 I_0} + \frac{2}{I_0[A]_0([A]_0 - I_0)} \ln\left(\frac{I_0}{[A]_0}\right) + \frac{1}{I_0^2[A]_0}\right)$$
[32]

Based on eqns [22], [29], and [32], a large number of *K* and K_{AT} values were determined by following the time evolution of [X[•]] or [AX[•]].^{72–75} Equations [29] and [32] were particularly useful for large *K* and K_{AT} systems where *I* and [A] significantly vary.^{72–74}

3.05.3.3 Systems of DT Type

In these systems, radicals must be generated by a conventional initiation to start and maintain polymerization. As in conventional RP, the radical concentration would be basically unchanged by a chain transfer reaction unless it is a retarding or degrading one. For this reason, the steady-state kinetics, eqn [21], should hold.

In certain RAFT systems, the intermediate radical (cf. **Scheme 4a**) can undergo reactions with other radicals, causing retardation from eqn [21] (see Section 3.05.7.2.4).

3.05.3.4 Systems of RT Type

Like the DT system, radicals must be generated by a conventional initiation to start and maintain polymerization in the RT system, too. The RT is a chain transfer reaction and does not basically change the radical concentration, and hence the steady-state kinetics, eqn [21], should hold. The catalyst radical (activator A^{\bullet}) can undergo reactions with other radicals, possibly causing retardation from eqn [21] (see Section 3.05.8.2).

3.05.4 Kinetic Theory of LRP: Polydispersities

3.05.4.1 Steady-State Systems

3.05.4.1.1 Systems with constant [P[•]] and constant [M]

It is informative to start with an 'ideal' system, in which reactions other than activation, deactivation, and propagation are absent and in which [P[•]] and [M] are constant. Actual LRP systems that are in a steady state and at an early stage of polymerization may be viewed as approximately ideal. A living species experiences an activated and a deactivated (dormant) state alternatingly, and in the activated state, the chain can be added by a monomer unit with a probability *p* or deactivated with a probability 1-p. The transition from the deactivated to activated state occurs with a probability density k_{act} (times per second), so that the parameter γ_n given by $\gamma_n = k_{act}t$ is the mean number of such transitions during polymerization time *t*. This model leads to the following expression for PDI = x_w/x_{nr} , where x_w and x_n are the weight- and number-average degrees of polymerization, respectively:⁷⁶

$$\frac{x_{\rm w}}{x_{\rm n}} = 1 + \frac{1}{x_{\rm n}} + \frac{2}{y_{\rm n}} \quad (y_{\rm n} = k_{\rm act}t)$$
[33]

Müller *et al.*⁷⁷ and Souaille and Fischer⁶⁹ also derived this equation by a different approach. In the limit of $y_n \rightarrow \infty$, PDI approaches that of the Poisson distribution, that is, PDI = 1 + (1/ x_n). When x_n is sufficiently large, PDI is determined only by y_n . In order for the PDI of a sufficiently long chain ($(x_n)^{-1} \cong 0$) to be smaller than 1.1, for example, y_n has to be larger than 20.

3.05.4.1.2 Batch systems with constant [P[•]]

In batch polymerization, [M] decreases with conversion, and so does the number of monomer units added per cycle. This makes PDI larger than that expected from eqn [33], modifying it to^{78,79}

$$\frac{x_{\rm w}}{x_{\rm n}} = 1 + \frac{1}{x_{\rm n}} + \frac{F(c)}{y_{\rm n}} \quad (y_{\rm n} = k_{\rm act}t)$$
 [34]

$$F(c) = \left(1 - \frac{2}{c}\right) \ln(1 - c)$$
[35]

where $c = ([M]_0 - [M])/[M]_0$ is the fractional conversion. The function F(c) is illustrated in Figure 3. It tends to 2 (the value for the constant-[M] system) for $c \rightarrow 0$.

Equation [34] with eqn [35] can be expressed as a function of either *t* or *c* only by using the first-order rate equation (eqn [21] or [26]).^{26,80–82} For systems of DT type, for example, we can write $k_{\text{act}} = k_{\text{ext}}[P^{\bullet}]$, with $[P^{\bullet}] = (R_i/k_t)^{1/2}$ and $k_{\text{deact}} = k_{\text{ext}}[P-X]$, and hence^{79,81–83}

$$\frac{x_{\rm w}}{x_{\rm n}} = 1 + \frac{1}{x_{\rm n}} + \left(\frac{2-c}{c}\right) \left(\frac{1}{C_{\rm ex}}\right) \quad \left(C_{\rm ex} = \frac{k_{\rm ex}}{k_{\rm p}}\right) \qquad [36]$$

The theoretical minimum PDI of DT systems is, therefore, $1 + (I_0/[M]_0) + C_{\text{ex}}^{-1}$, where $[M]_0/I_0$ is the value of x_n at c = 1.

3.05.4.2 Power-Law Systems

Here we still consider an idealized LRP in which termination exists, but the contribution of dead chains to the chain length and its distribution is negligible, and termination only affects



Figure 3 Plot of F(c) or G(c) vs. *c*. Reproduced from Fukuda, T.; Goto, A.; Tsujii, Y. In *Handbook of Radical Polymerization*; Matyjaszewski, K., Davis, T. P., Eds.; Wiley: New York, 2002; pp 407–462,³⁰ with permission from Wiley.

the time dependence of transient lifetime of the living chains in a quasi-equilibrium system. This model therefore applies to those systems under PRE with no conventional initiation. For simplicity, we consider a DC-mediated polymerization. $[X^*]$ increases with *t* because of termination, and $[P^*]$ decreases with *t*, as already noted. Since the activation frequency is essentially time independent, a decrease in $[P^*]$ means a decrease in the transient lifetime. For this reason, the number of monomer units added per cycle decreases with *t*. This brings about an increase of PDI over the ideal values given by eqns [33] (constant [M]) and [34] (batch). For a batch system with $[X^*]_0 = 0$, the following expression was derived by Fischer⁶⁶ using a kinetic approach and later by Fukuda²⁷ using a probability theory approach:

$$\frac{x_{\rm w}}{x_{\rm n}} = 1 + \frac{1}{x_{\rm n}} + \frac{G(c)}{y_{\rm n}} \quad (y_{\rm n} = k_{\rm act}t)$$
[37]

$$G(c) = \left(\frac{\pi^{1/2}}{3c^2}\right) u^3 \operatorname{erf}(u)$$
[38]

$$u = [-2\ln(1-c)]^{1/2}$$
 [39]

where erf is the error function. The function G(c) is illustrated in **Figure 3**. It tends to 8/3 for $c \rightarrow 0$ ($t \rightarrow 0$) and monotonously increases with increasing *c*.

$$\frac{x_{\rm w}}{x_{\rm n}} = 1 + \frac{1}{x_{\rm n}} + \frac{8/3}{y_{\rm n}} \quad (y_{\rm n} = k_{\rm act}t; t \to 0)$$
 [40]

Equation [40] differs from eqn [33] or eqn [34] with $t \rightarrow 0$ in the numerical factor (8/3 vs. 2). The larger numerical factor 8/3 arises from the $t^{-1/3}$ dependent [P[•]]. In this regard, the existence of X[•] at t = 0 makes the time dependence of [P[•]] less significant (eqn [23]) and hence lowers PDI. In the limit of high [X[•]]₀, [P[•]] becomes time independent and PDI approaches the 'ideal' value represented by eqn [34]. This, of course, is achieved at the expense of slow polymerization. The addition of a conventional initiator can also give a constant [P[•]] or a steady state and simultaneously increase R_{pr} , as already discussed. This discussion also holds for ATRP by the suitable reinterpretations of k_d and k_c .

3.05.4.3 Deviations from Ideality

In actual systems, PDIs will be more or less deviated from the mentioned theoretical values for several reasons. First and most importantly, dead chains, (conventionally) initiated chains, and side reactions that are not taken into account in the theory will contribute to PDI. These contributions, while negligibly small at an early stage of polymerization, will become more and more important with increasing *t* and *c*. Second, chain length dependence (CLD) of the rate constants of elementary reactions can affect PDI as well as the polymerization rate. Third, the contribution of the preequilibrium or prestationary-state time regime of polymerization that is neglected in the theory can be important in some cases. These effects have been treated theoretically in part^{70,71} and by computer simulations^{62,64,69–71,84–87} more comprehensively.

3.05.4.4 Correction for Initiator Mass (Block Copolymerization)

The product polymer initiated from a low-mass or a polymeric adduct P_0 -X may be viewed as an A-B block copolymer with the

subchains A and B referring to P_0 –X and the incremental (grown) portion of the chain, respectively. The theoretical equations for polydispersity given earlier are referred to as 'the hypothetical polymer grown from a zero-mass initiator', and therefore those equations can be rigorously applicable to the incremental portion of the chain or the B subchain. The polydispersity parameter *Y* of the whole polymer (product polymer) defined by

$$Y = \left(\frac{x_{\rm w}}{x_{\rm n}}\right) - 1 \qquad [41]$$

is given by^{27,78}

$$Y = w_A^2 Y_A + w_B^2 Y_B$$
 [42]

where $Y_{K} = (x_{w,K}/x_{n,K}) - 1$, $w_{A} = 1 - w_{B} = x_{n,A}/x_{n'}$ and $x_{n} = x_{n,A} + x_{n,B'}$ with K = A or B.

Since w_A and Y_A are usually known, one can estimate *Y* using the theoretical value of Y_B . Alternatively and experimentally, one can deduce, by using eqn [42], Y_B and $x_{n,B}$ by measuring the x_n and x_w of the product polymer along with the known $x_{n,A}$ and $x_{w,A}$.

The PDI expression, for example, eqn [34] for the steady-state or first-order-type system applied to the B subchain, can be given by a linear function of t:⁷⁸

$$\left[Y_{\rm B} - \left(\frac{1}{x_{\rm n,B}}\right)\right]^{-1} = \frac{k_{\rm act}t}{F(c)}$$
[43]

For small *c* (small *t*) or constant [M], eqn [43] reduces to

$$\left[Y_{\rm B} - \left(\frac{1}{x_{\rm n,B}}\right)\right]^{-1} = \left(\frac{1}{2}\right)k_{\rm act}t \qquad [44]$$

A similar relation holds for the power-law system with F(c) in eqn [43] replaced by G(c), which for small c (small t) reduces to

$$\left[Y_{\rm B} - \left(\frac{1}{x_{\rm n,B}}\right)\right]^{-1} = \left(\frac{3}{8}\right)k_{\rm act}t \qquad [45]$$

These equations form the basis for applying the PDI equations to experimental analysis.

3.05.5 Nitroxide-Mediated Polymerization

Alkoxyamines such as S-TEMPO and BS-TEMPO in Figure 4 work as an initiating dormant species in nitroxide-mediated polymerization (NMP). They are synthesized and purified independently from the NMP run or are prepared *in situ* in the NMP run. In the latter, for example, a mixture of the conventional initiator benzoyl peroxide (BPO), monomer, and TEMPO in a suitable ratio is heated to generate BS-TEMPO and its analogues with two or more monomer units, which will work as initiating alkoxyamines.³⁷ For kinetic studies, the use of a purified alkoxyamine is preferable to avoid unnecessary complexities.

3.05.5.1 TEMPO-Mediated Polymerization of Styrene

3.05.5.1.1 Polymerization rates

Since the time of the seminal work of Georges *et al.* in 1993,³⁷ the mechanisms and kinetics of this system had not been well

understood for some time, until Catala *et al.*⁸⁸ reported the experimental data showing that R_p was independent of the concentration of the alkoxyamine S-di-*tert*-butyl nitroxide (DBN) used as an initiating adduct. Styrene is known to undergo thermal (spontaneous) polymerization especially at high temperatures. This and the mentioned observations of Catala *et al.* led Fukuda *et al.*^{63,89} to the idea of steady-state kinetics described in Section 3.05.3.1.3. In accord with eqn [21], the R_p values at different temperatures all agreed with those of thermal polymerization of styrene.⁸⁹ Qualitatively similar results were also presented by Greszta and Matyjaszewski.⁹⁰

Equation [21] was further tested in two ways. First, the time-conversion relation was precisely followed by dilatometry.⁶³ Figure 5 compares the first-order plots of [M] for styrene polymerizations with and without a polystyrene (PS)-TEMPO or BS-TEMPO adduct. Clearly, the $R_{\rm p}$'s of the nitroxide-containing systems are identical with each other, and when conversion is small (c < 0.30), they are equal to that of the thermal (nitroxide-free) system. Equation [21] was thus evidenced. (The deviations at higher *c* are due to the changes in $k_{\rm t}$ arising from differences in chain length and viscosity, and the nonlinearity of the first-order plots comes from the [M]³dependent R_{i} .) Second, the conventional initiator t-butylhydroperoxide (BHP) was added to the PS-TEMPO (48 mM)/styrene/114 °C system.⁷⁶ As in a nitroxide-free system, R_p increased with increasing [BHP]. For example, the addition of 4 mM of BHP increased R_p by a factor of about 3. Nevertheless, the chain length and its distribution were well controlled at least in the studied ranges of R_p and t (or c). The plot of $M_{\rm p}$ versus conversion fell on a straight line, indicating that the number of polymer chains was approximately constant throughout the course of polymerization. Thus, the use of a proper amount of conventional initiator is an effective method to increase R_p without losing the control on PDI, at least when c is not too high.

A fundamentally important implication disclosed by these studies is that termination does exist in LRP, and the value of k_t in LRP is just the same as that in the conventional RP. For some time after the discovery of LRP, the excellent performance of LRP in controlling polymer structure had led a few people to the idea of its being a termination-free polymerization. Even now some people seem to believe so. The fact is that there has been reported no theoretical or experimental evidence to support this. All experiments on NMP and other branches of LRP show that k_t is no different between LRP and conventional RP (see also below).

3.05.5.1.2 Activation–deactivation equilibrium

The existence of the DC equilibrium can be evidenced by proving the constancy of $[P^{\bullet}][X^{\bullet}]/[P-X] = K$ (eqn [13]). For the PS-TEMPO/styrene/125 °C system in **Figure 5**, the time evolution of $[X^{\bullet}]$ was followed by electron spin resonance (ESR) (**Figure 6(a)**),⁶³ and $[P^{\bullet}]$ was estimated from the data in **Figure 5** with the known k_p^{-91} of $2300 \text{ M}^{-1} \text{ s}^{-1}$ (**Figure 6(b**)).⁶³ The value of $[P^{\bullet}][X^{\bullet}]/[P-X]$ thus estimated was independent of *t* (**Figure 6(c**)), confirming the equilibrium. The *K* value thus obtained was $2.1 \times 10^{-11} \text{ M}$. The large difference between $[P^{\bullet}] (\sim 10^{-8} \text{ M})$ and $[X^{\bullet}] (\sim 10^{-5} \text{ M})$











































16: S-DBN

EtÓ 17: S-DEPN

OEt

CH₃-CH-ON

18: S-TIPNO

Figure 4 (Continued)





















26: BS-TEMPO

















35

32: S-HTEMPO





Figure 4 (Continued)

CH3

















 CH_3 -C-Br C=0 $-O-CH_3$































 $CH_3 S \\ H_3 - C - SC - OCH_2CF_3 \\ CH_3 - C - SC - OCH_2CF_3 \\ C = O \\ C = O$

77

Ó−Et



71



76

Figure 4 (Continued)



Figure 4 (Continued)





was brought about by the PRE mentioned above. The ratio of the equilibrium value of $[X^{\bullet}]$ to $[P-X]_0$ is about 5×10^{-5} M/ 3.6×10^{-2} M = 1.4×10^{-3} , which suggests that the equilibrium in this system is reached after 0.14% of the living chains are terminated, namely, at a fairly early stage of polymerization, much earlier than the steady state of $[P^{\bullet}]$ is reached.²⁸

3.05.5.1.3 Activation process: curve-resolution method

The early stage of polymerization in the PS-TEMPO/styrene system was studied by gel permeation chromatography (GPC) (size exclusion chromatography, SEC) to determine k_{act} .^{92,93} For this purpose, a styrene solution of a constant amount of PS-TEMPO (23 mM; $M_{\text{n}} = 1700$ and



Figure 5 First-order plot for the polymerization of styrene at 125 °C. [PS-TEMPO]₀ = 36 mM (\Box); [BS-TEMPO]₀ = 20 mM (\triangle); no nitroxide (**•**): the dotted line shows the [M]³-dependent initiation with constant $k_{\rm f}$ (no nitroxide). Reproduced from Fukuda, T.; Terauchi, T.; Goto, A.; *et al. Macromolecules* **1996**, *29*, 6393–6398,⁶³ with permission from the American Chemical Society.



Figure 6 Plots of $[X^*]$ (a), $[P^*]$ (b), and *K* (c) vs. *t* for the polymerization of styrene at 125 °C with $[PS-TEMPO]_0 = 36$ mM. Reproduced from Fukuda, T.; Terauchi, T.; Goto, A.; *et al. Macromolecules* **1996**, *29*, 6393–6398, ⁶³ with permission from the American Chemical Society.

 $M_w/M_n = 1.11$) used as an initiating adduct P₀–X and a variable amount of the conventional initiator BHP were heated at 110 °C for a prescribed time *t*, quenched to room temperature, and directly analyzed by GPC with a 'constant' amount of the reaction mixture injected into the column system. **Figure 7** shows the GPC curves of the mixtures for *t* = 0 and 10 min.⁹³ (Note that these experimental conditions chosen to determine k_{act} accurately are different from those chosen to produce low-polydispersity polymers.) When [BHP]₀ = 0, the curve slightly moves to the higher-molecular-weight side, but it is difficult to determine the required fraction of the



Figure 7 GPC chromatograms for the styrene/PS-TEMPO(P_0 -X)/BHP systems at 110 °C for 10 min; $[P_0-X]_0 = 23$ mM. The number attached on each curve indicates $[BHP]_0$ in mM. The solid curve is for the original (*t*=0) solution containing only P_0 -X as polymer species. Reproduced from Goto, A.; Fukuda, T. *Macromolecules* **1997**, *30*, 5183–5186,⁹³ with permission from the American Chemical Society.

uninitiated P_0 -X from such an elusion curve. For $[BHP]_0 \ge 5 \text{ mM}$, the curves became bimodal, composed of two components: the first component comprising the uninitiated P_0 -X and the second one comprising the once-activated adduct (P_1 -X) and other minor species originating from, for example, a further activation of P_1 -X and the decomposition of BHP. Thus, BHP had an effect to lower the equilibrium concentration of X[•], thereby increasing the transient lifetime of the propagating radical or increasing the number of monomer units to be added per activation-deactivation cycle. The bimodal curves can be accurately curve-resolved into the two components to give the time evolution of the uninitiated fraction of I (=[P_0 -X]). The k_{act} may be determined by

$$\ln\left(\frac{I_0}{I}\right) = k_{\rm act}t \tag{46}$$

Figure 8 shows that all the experimental points for different *t* and different [BHP] fall on a single straight line passing through the origin. Thus, this method allows accurate determination of k_{act} with no regard to kinetic details of the polymerization.

In Section 3.05.5.1.2, we implicitly assumed that this system was of the DC type. However, the DT mechanism can also be operative. If both the DC and DT mechanisms are important, k_{act} will take the form

$$k_{\rm act} = k_{\rm d} + k_{\rm ex}[\mathbf{P}^\bullet]$$
[47]

The experiment showing the independence of k_{act} on [BHP], therefore, means that the term $k_{ex}[P^{\bullet}]$ is unimportant compared with k_d , namely, $k_{act} \cong k_d$ in this system.⁹³

3.05.5.1.4 Activation process: PDI method

Next we examine the PDI for the system in Figure 7. The analysis of the GPC curves shows that constancy of R_p (and hence $[P^*]$) and of the number density of chains



Figure 8 Plot of $\ln(I_0/I)$ vs. *t* for the styrene/PS-TEMPO(P₀-X)/BHP systems in **Figure 7** (110 °C); $[BHP]_0 = 5$ (•), 10 (□), 20 (▲), and 80 (×) mM. Reproduced from Goto, A.; Fukuda, T. *Macromolecules* **1997**, *30*, 5183–5186, ⁹³ with permission from the American Chemical Society.

(negligible side reactions) holds in the studied range of time $(t \le 60 \text{ min})$ for all BHP concentrations. Figure 9 shows the plot of $[Y_B-(1/x_{n,B})]^{-1}$ versus *t*. The straight line in the figure has a slope of $(1/2)k_d$ according to eqn [44], where the theoretical k_d value of $3.73 \times 10^{-4} \text{ s}^{-1}$ was obtained from the above-noted curve-resolution method. The data points closely agree with this prediction.⁷⁸

A comment may be due regarding the accuracy of the PDI analysis by GPC. As is well known, the PDI estimated by GPC is subject to errors arising from the effects of axial dispersion, finite sample volume, and so on. Due to these errors, we should be careful in the GPC analysis, if the polymer sample in question has a PDI smaller than, say, 1.1. However, in the PDI analysis of the incremental portion of the chain (the B subchain, see Section 3.05.4.4) produced at an early stage of polymerization, the PDI is usually very large, ranging from ∞



Figure 9 Plot of $[Y_{B-}(1/x_{n,B})]^{-1}$ vs. *t* for the styrene/PS-TEMPO(P₀-X)/ BHP systems in **Figures 7** and **8**: $[BHP]_0 = 0$ (\circ), 5 (\bullet), 10 (\Box), 20 (\blacktriangle), and 80 (\times) mM. The solid line corresponds to eqn [44] with the k_d value (3.73 \times 10⁻⁴ s⁻¹) deduced by the curve-resolution method. Reproduced from Goto, A.; Fukuda, T. *Prog. Polym. Sci.* **2004**, *29*, 329–385,²⁶ with permission from Elsevier.

(at t = 0) down to 3 or 2. In this range of PDI, GPC errors should be only minor. This is the reason why the PDI analysis for k_{act} usually provides as accurate a result as the curve-resolution method. Another advantage of the PDI method over the curve-resolution method is that it does not require the GPC curve to be resolved into two peaks: it is applicable to any GPC curve, bimodal or unimodal ones.

3.05.5.1.5 Side reactions

Equation [43] expects that the plot of $[Y_{\rm B}-(1/x_{\rm n,B})]^{-1}$ versus t/F(c) is linear even for large t or c. Actually, this is not necessarily the case, because the effects of side reactions that are neglected in the theory will accumulate and eventually cause downward deviations from the straight line.⁷⁶ Possible causes for the deviations generally include contributions of terminated and/or conventionally initiated chains, chain transfer reactions, and the decomposition of alkoxyamines. Termination is common to all LRPs. Hence it will be typically observed that when t is small, the plot of PDI versus t (or c) decreases with increasing t because of the increase of the activation-deactivation cycles according to $y_n = k_{act}t$. However, the accumulated effects of termination (and other side reactions) will cause upward deviations of the curve from the theory, and in some cases, the curve will even increase with increasing t for large *t*, going through a minimum.

Importantly in NMP, the decomposition of alkoxyamines can occur through the reaction in **Scheme** 5, in which the β -proton abstraction by a nitroxide is assumed to take place in the solvent cage in both dissociation and combination processes. In this scheme, the rate constant of decomposition k_{dec} (the rate = k_{dec} [P–X]) will be proportional to k_d under the DC equilibrium and will take the relation

$$k_{\rm dec} = p_{\rm dec} k_{\rm d} \tag{48}$$

where p_{dec} is the probability of decomposition. The validity of this scheme was experimentally confirmed for most alkoxyamines,^{94,95} and p_{dec} was determined for PS-TEMPO⁹⁶ and other polymeric and low-mass alkoxyamines.^{94–101} An acrylate/ TEMPO system was shown to include a unimolecular pathway (simultaneous bond cleavage and formation)⁹⁴ as well as the (main) bimolecular pathway discussed earlier. The effect of decomposition on the kinetics of LRP was theoretically examined.⁷⁰

3.05.5.2 DEPN-Mediated Polymerization of Styrene

Despite the presence of thermal initiation, the polymerization of styrene mediated by DEPN also shows power-law behavior. This is because the equilibrium constant K in this system is so large that it takes a long time to reach the steady state, and therefore, the main body of polymerization in this system takes place in a pre-steady-state regime. The rate and PDI equations for the power-law kinetics were quantitatively examined for this system.

3.05.5.2.1 Activation and deactivation processes

Benoit *et al.*¹⁰² determined *K* of this system to be 6.0×10^{-9} M at 120 °C, which is more than 100 times larger than that of the TEMPO system. These authors and Goto and Fukuda¹⁰³



Scheme 5 Decomposition of an alkoxyamine.

determined k_d of this system by the GPC curve-resolution method to be 3.4×10^{-3} and $1.1 \times 10^{-2} \text{ s}^{-1}$, respectively, at 120° C. These values, even though considerably different from each other, are larger than that of PS-TEMPO $(1.0 \times 10^{-3} \text{ s}^{-1})$ ⁹² Benoit *et al.* estimated the k_c of this system to be $5.7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ (120° C) with their K and k_d . This value is increased to $k_c = 1.8 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ by the use of the latter authors' k_d and the same K due to Benoit et al. In any case, these values of k_c are much smaller than that between PS[•] and TEMPO $(k_c = 7.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1})^{92}$ indicating that the bulkiness of nitroxides has a large effect on k_c as well as on k_d .

3.05.5.2.2 Polymerization rates

Contrarily to the styrene/TEMPO system, the $R_{\rm p}$ of the styrene/ DEPN system was observed to increase with an increase of I_0 (=[P-X]₀).¹⁰² This nonsteadiness is due to the large K of the DEPN system, as noted above. The crossover time t_{cross} from the power-law to stationary-state kinetics is given by eqn [28]. For the PS-TEMPO/styrene/120 °C system, for example, we may roughly set $(R_i/k_t)^{1/2} = 2 \times 10^{-8} \text{ M}, k_t = 10^8 \text{ M}^{-1} \text{ s}^{-1},$ $K = 2 \times 10^{-11}$ M, and $I_0 = 10^{-2}$ M to estimate $t_{\rm cross} \sim 10^2$ s. This value is small compared with the polymerization time typically on the order of 10⁴ s and explains why the PS-TEMPO system shows steady-state behavior from an early stage of polymerization. On the other hand, the PS-DEPN system has a K value¹⁰² of 6.0×10^{-9} M, with which $t_{\rm cross}$ can be estimated to be about 3×10^4 s under the same condition. This $t_{\rm cross}$ value exceeds the usual experimental times and explains the nonsteadiness of the PS-DEPN system. Later on, Lutz et al.¹⁰⁴ observed a power-law behavior of the conversion index (eqn [25]) with respect to both t and I_0 . On the basis of their experimental data, they estimated $K = 6.1 \times 10^{-9}$ M according to eqn [25] with the literature data of $k_{\rm p}$ and $k_{\rm t}$. The good agreement of this K value with the above-cited, more directly determined one is another support of the power-law kinetics.

An absolute comparison of theory and experiment was made for the power-law kinetics in the polymerization of styrene with PS-DEPN (25 mM) at 80 °C.68 All parameters necessary to compute the theoretical values were taken from independent experiments (Table 1). For example, the specific value of k_t to be used in this study was determined by

Table 1	Kinetic pa	arameters i	used in	Figures	10,	11 , and	14
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Parameter	Value	Reference
NMP (PS-DEPN)		
$k_{\rm ith} ({\rm M}^{-2} {\rm s}^{-1})^a$	4.5×10^{-12}	105
$k_{i,BPO} (s^{-1})^{a}$	$6.7 imes10^{-5}$	106
$k_{\rm p} ({\rm M}^{-1}{\rm s}^{-1})$	650	91
$k_{\rm t} ({\rm M}^{-1} {\rm s}^{-1})$	$3.0 imes10^{8}$	68
$k_{\rm d} ({\rm s}^{-1})$	$1.16 imes 10^{-4}$	103
$K = k_{\rm d}/k_{\rm c}$ (M)	$1.7 imes 10^{-10}$	68
ATRP		
$k_{i,th} (M^{-2} s^{-1})^{b}$	$9.6 imes 10^{-11}$	105
$k_{i,VR110} (s^{-1})^{b}$	$3.0 imes10^{-5}$	107
$k_{\rm p} ({\rm M}^{-1} {\rm s}^{-1})$	1560	91
$k_{\rm t} ({\rm M}^{-1}{\rm s}^{-1})$	$3.6 imes10^8$	107
$k_{\rm a} ({\rm M}^{-1}{\rm s}^{-1})$	0.45	108
$K/[A] = k_a/k_{da} (-)$	2.4×10^{-8}	107

 ${}^{a}R_{i} = k_{i,th}[M]_{0}^{3} + k_{i,BP0}[BP0]_{0}.$ ${}^{b}R_{i} = k_{i,th}[M]_{0}^{3} + k_{i,VR110}[VR110]_{0}.$

examining the same system with a suitable amount (4.7 mM) of the conventional initiator, BPO, added to bring the system to a steady state. As Figure 10(a) shows, the first-order plot of [M] is linear, and the slope of the straight line gave k_t according to eqn [21] with the known k_p and R_i . Figure 10(b) shows the comparison of the theory (eqn [25], solid curve) and the duplicated experiment (open and filled circles) in the absence of BPO ($t_{cross} \sim 10^5$ s). The experimental points are well reproduced by the $t^{2/3}$ -dependent linear line predicted by the theory with the independently determined rate constants. This was the first experimental justification of eqn [25] on an absolute scale. The experimental data presented by Lutz et al.¹⁰⁴ and by Fischer²⁴ gave additional qualitative support for the power-law kinetics even at larger conversions.

3.05.5.2.3 Polydispersities

The first experimental test of the PDI equation (eqn [45]) (or eqn [40]) was made for the same power-law system related to Figure 10.⁶⁸ Figure 11 shows the comparison of the theory



Figure 10 Plots of $\ln([M]_0/[M])$ vs. (a) *t* and (b) $t^{2/3}$ for the styrene/PS-DEPN(P₀-X)/(BPO) systems (80 °C): $[P_0-X]_0 = 25 \text{ mM}$; $[BPO]_0 = 0$ (• and °) and 4.7 mM (• and \Box). The experiments are duplicated. The dotted line is the best fit representation of the experiments (• and \Box) according to eqn [21]. The solid line shows eqn [25] with the independently determined rate constants (**Table 1**). Reproduced from Yoshikawa, C.; Goto, A.; Fukuda, T. *Macromolecules* **2002**, *35*, 5801–5807,⁶⁸ with permission from the American Chemical Society.



Figure 11 Plot of $[Y_B - (1/x_{n,B})]^{-1}$ vs. *t* for the styrene/PS-DEPN(P₀–X)/ (BPO) systems in **Figure 10** (80 °C): [BPO]₀ = 0 (• and •) and 4.7 mM (• and \Box). The solid and broken lines show eqns [44] and [45], respectively, with the independently determined k_d value (**Table 1**). Reproduced from Yoshikawa, C.; Goto, A.; Fukuda, T. *Macromolecules* **2002**, *35*, 5801–5807, ⁶⁸ with permission from the American Chemical Society.

(solid line) with the experiments (circles). The result quantitatively proves the validity of eqn [45]. In this test, the authors used the k_d determined by themselves.¹⁰³ Figure 11 also demonstrates that eqn [44] (or eqn [33]) holds in the presence of BPO (broken line and squares), confirming the theoretical prediction that a conventional initiator makes the polymerization rate larger and the polydispersity lower than in its absence (for a fixed polymerization time).

3.05.5.3 NMP of Acrylates

DBN was found to control the polymerization of *tert*-butyl acrylate (tBA) at lower temperatures⁹⁸ than does a TEMPO derivative.¹⁰⁹ This is in line with the fact that the k_d of PS-DBN is about 40 times larger than that of PS-TEMPO (see

Section 3.05.9). The k_d of poly(tBA)-DBN was determined to be $1.0 \times 10^{-3} \text{ s}^{-1}$ at 120 °C,⁹⁸ which is as large as that of PS-TEMPO at the same temperature.⁹² Since spontaneous polymerization is absent in this system, a conventional radical initiator, dicumyl peroxide (DCP), was added to overcome the low polymerization rate and bring it to a steady-state level. However, R_p markedly decreased at later stages of polymerization and PDI increased after an initial decrease to about 1.3. This was due to the decomposition of the alkoxyamine to a macromonomer and a hydroxyamine, the latter working as an inhibitor.¹¹⁰ The decomposition probability per activation–deactivation cycle, p_{dec} (eqn [48]), was estimated to be 0.011,⁹⁸ which is 4 times as large as that of PS-TEMPO at the same temperature.⁹⁶

On the other hand, the polymerization of *n*-butyl acrylate (BA) mediated by DEPN proceeded highly satisfactorily without accompanying appreciable degradation of the alkoxyamine.¹⁰² The $k_{\rm d}$ of a PBA-DEPN adduct was $7.1 \times 10^{-3} \, {\rm s}^{-1}$, by which $k_{\rm c}$ is calculated to be $4.2 \times 10^7 \, {\rm M}^{-1} \, {\rm s}^{-1}$ for the observed *K* value of $1.7 \times 10^{-10} \, {\rm M}$.

General requisites for high-performance NMP would be a large k_d (>10⁻³ s⁻¹), a reasonably small K (K<10⁻¹⁰ M), and the absence or unimportance of degradation and other side reactions. When K is large, a large concentration of free nitroxide is required to achieve equilibrium. For example, putting $K = 10^{-9} \text{ M}, [P^{\bullet}] = 10^{-8} \text{ M}, \text{ and } [P-X] = 10^{-2} \text{ M} \text{ into eqn } [13], \text{ we}$ have $[X^{\bullet}] = 10^{-3}$ M, meaning that to get an equilibrium, we have to wait for 10% of the living species ([P-X]) to be terminated to give as much nitroxyl radical. This approximates the PS-DEPN system. In this regard, the addition of an appropriate amount of X[•] to the system prior to polymerization would be useful.¹⁰² But this amount can only be deduced by the information from a set of kinetic studies. The PBA-DEPN system may be nearly ideal with regard to the fairly large $k_{d'}$ the relatively small K (or relatively large k_c), and the absence of appreciable degradation of the alkoxyamine. The nitroxide TIPNO has also been reported to be powerful in controlling the polymerization of a range of monomers including acrylates.¹¹¹ Kinetic studies on related polymerization systems would be interesting and important.

3.05.5.4 NMP of Methacrylates

The NMP of methacrylates has been found difficult to provide well-defined, low-polydispersity polymers. Studies on model compounds such as 20 (Figure 4) indicated that the k_{act} of methacrylates are much larger than those of styrene- and acrylate-based adducts due to the bulkiness of methacrylate monomers.¹¹² However, they suffer serious hydrogen abstraction at the α-methyl group.⁹⁹ Ananchenko and Fischer⁹⁴ and Goto et al.⁹⁵ independently made a model study on 20 and found a similarly large value of p_{dec} . Nicolas *et al.* added a small amount of styrene¹¹³ or acrylonitrile (AN)¹¹⁴ to DEPN-mediated methyl methacrylate (MMA) polymerization, obtaining low-polydispersity polymers. The polymer chain end on the DEPN side has a strong tendency to possess a styrene or AN terminal unit rather than an MMA terminal unit (the MMA terminal radical adds to styrene or AN monomer much faster than it combines with DEPN), suppressing the decomposition.

3.05.6 Atom Transfer Radical Polymerization

Transition metal-catalyzed polymerizations are supposed to involve an AT process. In a copper-catalyzed ATRP, for example, a complex Cu(I)X/L, where X is a halogen (Br or Cl) and L is a ligand, is used as an activator A, and the complex $Cu(II)X_2/L$ acts as a persistent (stable) radical AX^{\bullet} (Scheme 3b). The basic kinetic features of ATRP closely resemble those of NMP in theory.

3.05.6.1 Copper-Mediated ATRP of Styrene

3.05.6.1.1 Activation and deactivation processes

The activation process of the ATRP of styrene catalyzed by the Cu(I)Br/2dHbipy (Figure 12) complex was studied by the GPC curve-resolution method at 110 °C.¹⁰⁸ Under the usual conditions, k_{act} was too large to determine accurately, so that the Cu(I) concentration was about an order of magnitude lower



Figure 12 Examples of ligands.



Figure 13 Plot of k_{act} vs. $[Cu(I)Br/2L]_0$ for the styrene/PS-Br(P₀-X)/ BHP/Cu(I)Br/2L systems (110 °C): $[P_0-X]_0 = 12$ mM; $[BHP]_0 = 20$ mM; L = dHbipy. The slope of the straight line gives the k_a of 0.45 M⁻¹ s⁻¹. Reproduced from Ohno, K.; Goto, A.; Fukuda, T.; *et al. Macromolecules* **1998**, *31*, 2699–2701,¹¹¹ with permission from the American Chemical Society.

than usual. If the activation process of this system is AT, k_{act} will be represented by eqn [5a] (A = Cu(I) complex in this case). **Figure 13** shows the plot of k_{act} versus [Cu(I)]₀. The plot is represented by a linear line passing through the origin, meaning that the activation of this system is predominated by the AT mechanism. (More strictly, k_{act} might include the contribution of DT: $k_{act} = k_a[A] + k_{ex}[P^\bullet]$. In this case, the dependence of k_{act} on [A] is not simple, for [P[•]] depends on [A] (cf. eqn [23]). However, despite the initiator BHP being included in the system as well as the spontaneous initiation of the monomer giving a finite value of [P[•]] even for [A] = 0, we still experimentally observed the linear relation passing through the origin (**Figure 13**). This means that the k_{ex} term is minor in any case. The slope of the line gives $k_a = 0.45 \text{ M}^{-1} \text{ s}^{-1}$.

This value agrees well with that $(0.43 \text{ M}^{-1} \text{ s}^{-1})$ determined in xylene (without a monomer).¹¹⁵ In the latter experiment, the PS radical released from PS-Br was scavenged by a nitroxide and detected by HPLC. The k_a of the low-mass model adduct **39** (Figure 4) with the same catalyst in toluene was $0.42 \text{ M}^{-1} \text{ s}^{-1}$, indicating that the CLD of k_a is insignificant.¹¹⁶ According to eqn [26], Matyjaszewski *et al.*¹¹⁷ studied R_p with an excess amount of Cu(II) and determined K_{AT} (= k_a/k_{da}) to be 3.9×10^{-8} in the same catalytic system. With this K_{AT} and the above-noted k_a value ($0.45 \text{ M}^{-1} \text{ s}^{-1}$), we estimate $k_{da} = 1.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$.

3.05.6.1.2 Polymerization rates and polydispersities

Taking the typical Cu(I) concentration of 0.05 M, we can calculate the K (= K_{AT} [Cu(I)]) in this system to be 2 × 10⁻⁹ M. This value is comparable with that (6 × 10⁻⁹ M) in the styrene/ DEPN/120 °C system, indicating that this ATRP system will, despite the presence of spontaneous initiation of styrene, follow the power-law equation (eqn [25]), as the DEPN system does (see Section 3.05.5.2). However, until recently (see below), the power-law behavior was not observed in this¹¹⁷ and any other ATRP system for several reasons. An ESR study has shown that there is a finite concentration of Cu(II) at time zero in many cases,¹¹⁸ which conflicts with the basic assumption for eqn [25]. An important origin of Cu(II) may be the oxidation of Cu(I) in air,^{119,120} particularly when Cu(I) is mixed with other reagents under insufficient deoxygenation. The amount of Cu(II) species may be just a few percent of $[Cu(I)]_{0}$, but it is clearly important compared with the equilibrium concentrations, which are typically on the order of 10% of [Cu(I)] or less. The second factor that causes the deviations from eqn [25] is the CLD of k_t . As the reaction proceeds, the chain becomes longer, the viscosity of the medium increases, and hence k_t becomes smaller. The third factor may be a subtle change of the reaction medium caused by polymerization, which can alter, for example, the solubility and activity of the catalyst. Shipp and Matyjaszewski^{86,87} carried out computer simulations with all these factors taken into account, stressing the importance of recognizing these factors.

By circumventing these complexities, Klumperman *et al.* experimentally observed the power-law behavior in several ATRP systems including styrene,^{120,121} MMA,^{122,123} and BA^{120,121} systems (see also below). Subsequently, Pintauer *et al.*⁷⁵ and Shipp and Yu¹²⁴ made similar observations in some ATRP systems.

More recently, Yoshikawa *et al.*¹⁰⁷ experimentally verified the power-law equation (eqn [25]) on an absolute scale, as they did for the styrene/DEPN system described in Sections 3.05.5.2.2 and 3.05.5.2.3. Particular care was taken to avoid the contamination of Cu(II) species. To minimize possible changes in k_t and the reaction medium, they used a polymer adduct as a P₀–X and focused on an early stage of polymerization. Subsequently, they tested the PDI equations, eqn [44] (for the steady-state system) and eqn [45] (for the power-law system), against the experiments with and without a conventional initiator, respectively, to confirm the validity of those equations on an absolute scale.¹⁰⁷

A comment may be due regarding the magnitude of k_a in the styrene/Cu(I)Br/dHbipy/110 °C system. Taking the typical concentration of $[Cu(I)]_0 = 0.05 \text{ M}$, we can expect from eqn [33] (with the $x_{n,B}^{-1}$ term neglected) that PDI will be smaller than 1.1 in about 15 min in a steady-state polymerization. For a power-law-type polymerization, this polymerization time is estimated to be somewhat longer than 23 min (eqn [45]). These estimates explain why a low-polydispersity polymer can be obtained from an early stage of polymerization in this system.

3.05.6.1.3 Ligands and solvents

Ligands and solvents can significantly change electronic, steric, and solubility properties of copper catalyst, thus tuning the kinetic behaviors of the system. Effort has been made to disclose the effects of ligands and solvents on k_a and k_{da} using polymer and low-mass model systems, as will be summarized in Section 3.05.9. To investigate the electronic effect of ligands, Matyjaszewski *et al.*^{125–127} measured the redox potentials of copper complexes with various ligands by cyclic voltammetry (CV) and correlated them with the experimentally obtained k_a and k_{da} values: a lower redox potential generally led to a larger k_a and a smaller $k_{da'}$ hence a larger K_{AT} . The effects of solvents on the thermodynamic components of the AT equilibrium were quantitatively evaluated.¹²⁸ This allows the prediction of K_{AT} in a wide variety of solvents and suggests that the catalyst activity strongly depends on solvents, as it can differ in more than 7 orders of magnitude between water and organic solvents.

3.05.6.1.4 Side reactions

A specific side reaction in ATRP that has been noted is the elimination of HBr from alkyl bromide.^{129,130} The elimination occurs in the presence of Cu(II)Br₂ that reacts with both alkyl bromide and alkyl (propagating) radical to form HBr and unsaturated species (polymer with unsaturated end).¹²⁹ Another side reaction is the oxidation of Cu(I) by (contaminated) oxygen to form inactive Cu(II) (see above). For methacrylates, Acar *et al.*¹³¹ and Nanda *et al.*¹³² found that the produced oxidized Cu(II)XOO can react with a monomer to give a biradical °CH₂-C(CH₃)(COOR)-OO° which can initiate the polymerization. This air-induced radical formation was used as a radical source for reverse ATRP of methacrylates.^{131,132}

3.05.6.2 ATRP of Methacrylates and Acrylates

Zhang *et al.*¹²² studied the Cu(I)Br/dNbipy-mediated ATRP of MMA. Careful elimination of the Cu(II) contaminated at t = 0 enabled them to observe the $t^{2/3}$ dependence of polymerization rate (eqn [25]). Moreover, they found that the polymerization rate was 0.29 and 0.34 orders with respect to the alkyl halide concentration I_0 and [Cu(I)Br]₀, respectively, in close agreement with the theoretical value of 1/3. The $t^{2/3}$ -dependent polymerization rate was also observed in the BA system.^{120,121}

According to eqn [26], K_{AT} was determined in the MMA^{122,123,133} and acrylate^{121,134} systems in the presence of excess Cu(II). Matyjaszewski *et al.* systematically determined K_{AT} for MA (1.2×10^{-9} (Br)),¹³⁴ styrene (1×10^{-8} (Cl) and 2×10^{-8} (Br)),¹¹⁷ and MMA (7×10^{-7} (Cl))¹³³ with dNbipy at 90 °C, showing that K_{AT} strongly depends on monomers. The enthalpies for the AT equilibrium estimated from the temperature dependence of K_{AT} were 96 kJ mol⁻¹ (Br) for MA,¹³⁴ 56 (Cl) and 50 (Br) kJ mol⁻¹ for styrene,¹¹⁷ and 40 kJ mol⁻¹ (Cl) for MMA.¹³³ Chambard *et al.*¹²¹ reported K_{AT} for styrene (6.0×10^{-9}) and BA (6.3×10^{-10}) systems with CuBr/dHbipy at 110 °C.

As mentioned earlier, the solubility of copper species depends on ligands. In particular, Cu(II) species has a very limited solubility with certain ligands such as PMDETA.¹³⁵ In such a system, the Cu(II) concentration would quickly reach the limiting value [Cu(II)]_{crit}, and thereafter, the effective (soluble) Cu(II) concentration would be constant and equal to [Cu(II)]_{crit}. Such a system would exhibit the apparent ideality represented by eqn [26]. However, if [Cu(II)]_{crit} is too low, the polymerization rate as well as the termination rate would stay at a high level. Snijder *et al.*¹³⁶ have discussed the polymerization rate of such a system taking into consideration the decay of alkylhalide and Cu (I) concentrations due to termination.

3.05.6.3 Some Other Notes on ATRP

The activator Cu(I), for example, can be regenerated from Cu(II) continuously in the polymerization in the presence of a reducing agent^{137,138} such as ascorbic acid¹³⁸ and a conventional radical initiator.¹³⁹ The systems with these additives can significantly reduce the required Cu concentration, while keeping a sufficiently large R_{pr} and they are termed activators regenerated by electron transfer (ARGET)¹³⁷ and initiators for

continuous activator regeneration $(ICAR)^{139}$ systems, respectively. In the ARGET system, we may assume that the reducing agent has a role of making K_{AT} large, while keeping it constant. The ARGET and ICAR systems follow the mentioned theoretical equations, with the apparently large K_{AT} for the ARGET system.

As a capping agent, dithioesters can be used instead of halogens.^{140,141} In this case, the AT and RAFT processes coexist, and the contribution of each process depends on dithioesters and monomers. This technique is particularly useful for the dithiocarbamate system,¹⁴¹ in which the RAFT process is too slow to achieve low polydispersity, while the addition of copper leads to a sufficiently fast AT process and hence achieves low polydispersity.

3.05.7 Degenerative Chain Transfer-Mediated Polymerization

3.05.7.1 Iodide-Mediated Polymerization of Styrene

lodide-mediated polymerization is a simple and robust LRP that can be performed in experimental conditions close to those of conventional RP. However, it has, at this moment, limited applicability, since it does not give polymers with a very low polydispersity.¹⁴² This is due to generally small values of k_{act} achievable by this polymerization. Mechanistically, it includes a DT process. In what follows, we will describe the kinetic features of iodide-mediated polymerization of styrene⁸³ in some detail for its importance as a model degenerative chain transfer-mediated polymerization (DTMP).

3.05.7.1.1 Polymerization rates

A polystyryl iodide (PS-I; $M_n = 1500$ and $M_w/M_n = 1.26$) was used as an initiating adduct P_0 -X. The polymerization of styrene was carried out at 80° C with a fixed amount of P_0 -X (17 mM) and varying amounts of BPO (0–30 mM). The first-order plot of [M] was linear, indicating that the steady-state kinetics (eqn [21]) holds, in all examined cases.⁸³ The values of $(R_p/[M])^2$ obtained from the first-order plot of [M] were linear in [BPO]₀ (filled circles in Figure 14(a)) and equal to those of the conventional (iodide-free) system (open circles in Figure 14(a)). This means that the iodide had no detectable effect on the polymerization rate.

3.05.7.1.2 Activation process

The GPC curves obtained in the above-noted study were analyzed by the curve-resolution method to yield well-defined k_{act} values as a function of [BPO]₀.⁸³ The activation, that is, the cleavage of the C–I bond, possibly occurs by a DT process (Scheme 3c) and/or by thermal dissociation (Scheme 3a). When the two mechanisms are involved, k_{act} will be given by eqn [47]. Figure 14(b) shows the plot of k_{act} versus $R_p/[M]$ (= $k_p[P^\bullet]$). The plot gives a linear line approximately passing through the origin, meaning that the k_d term is trivial and the k_{act} of the system may be identified with $k_{ex}[P^\bullet]$. The slope of the line in Figure 14(b) gives the exchange constant $C_{ex} = k_{ex}/k_p = 3.6$. With the known value⁹¹ of k_{pr} we have $k_{ex} = 2400 \text{ M}^{-1} \text{ s}^{-1}$. Similar experiments carried out at varying temperatures allowed us to estimate the activation energy of k_{ex} to be⁸³ 27.8 kJ mol⁻¹.



Figure 14 Plots of (a) $(R_p/[M])^2$ vs. [BPO]₀ and (b) k_{act} vs. $(R_p/[M])$ for the styrene/PS-I(P₀–X)/BPO systems (80 °C): [P₀–X]₀ = 0 (open circles) and 17 mM (filled circles); [BPO]₀ as indicated on the abscissa in **Figure 14(a)**. Reproduced from Goto, A.; Ohno, K.; Fukuda, T. *Macromolecules* **1998**, *31*, 2809–2814,⁸³ with permission from the American Chemical Society

3.05.7.1.3 Polydispersities

The PDI in a batch DTMP can be tested on the basis of eqn [49] (cf. eqn [36]), which follows the PDI as a function of *c*:

$$\left[Y_{\rm B} - \left(\frac{1}{x_{\rm n,B}}\right)\right]^{-1} = C_{\rm ex}\left(\frac{c}{2-c}\right)$$
[49]

Figure 15 gives the plot indicated by eqn [49], showing that all data points form a single straight line passing through the origin. The slope gives $C_{ex} = 3.6$. The beautiful agreement of this C_{ex} value with that determined by the curve-resolution method confirms the validity of the steady-state theory (eqn [49]) on an absolute scale. Side reactions such as termination and (conventional) initiation have no important effect on the PDI of this system in the studied range of *c* (or *t*).

As discussed in Section 3.05.4.1.2, eqn [36] (or eqn [49]) suggests that the smallest possible value of M_w/M_n is expected



Figure 15 Plot of $[Y_B - (1/x_{n,B})]^{-1}$ vs. c/(2-c) for the styrene/PS-I(P₀-X)/ BPO systems in **Figure 14** (80 °C). Reproduced from Goto, A.; Ohno, K.; Fukuda, T. *Macromolecules* **1998**, *31*, 2809–2814,⁸³ with permission from the American Chemical Society.

for full conversion (c = 1) and is 1.28 for $C_{ex} = 3.6$. The iodide-mediated LRP of styrene has thus limited controllability over polydispersity.

3.05.7.2 RAFT Polymerization

A representative RAFT system uses a dithiocarbonate as a mediator (Scheme 4a: $Z = CH_3$, Ph, etc.). As this scheme shows, a RAFT process involves the addition of radical P_A^{\bullet} to the adduct P_B-X (rate constant = k_{adAB}) to form the intermediate radical, followed by the fragmentation of the intermediate to release either P_A^{\bullet} (rate constant = k_{frBA}) or P_B^{\bullet} (rate constant = k_{frAB}). This process, viewed as a DT or exchange process, is simplified to Scheme 4b, where the rate constant of the exchange reaction, k_{exAB} , is related to those in Scheme 4a by

with

$$k_{\text{exAB}} = P_{\text{rB}}k_{\text{adAB}}$$
 [50]

$$P_{\rm rB} = \frac{k_{\rm frAB}}{k_{\rm frAB} + k_{\rm frBA}}$$
[51]

Equation [50] assumes that the system is in a quasi-equilibrium state, where an approximate equality of the rates of addition and fragmentation holds, namely

$$[\mathbf{P}_{\mathrm{A}}-(\mathbf{X}^{\bullet})-\mathbf{P}_{\mathrm{B}}] = \frac{k_{\mathrm{adAB}}[\mathbf{P}_{\mathrm{B}}-\mathbf{X}][\mathbf{P}_{\mathrm{A}}^{\bullet}] + k_{\mathrm{adBA}}[\mathbf{P}_{\mathrm{A}}-\mathbf{X}][\mathbf{P}_{\mathrm{B}}^{\bullet}]}{k_{\mathrm{frAB}} + k_{\mathrm{frBA}}}$$
[52]

Equations [50–52] show specific features of RAFT polymerization kinetics.

3.05.7.2.1 Activation process in homopolymerizations

The polymerization of styrene including a fixed amount (0.45 mM) of polystyryl dithioacetate (PS-SCSCH₃: $M_n = 1.94 \times 10^3$ and $M_w/M_n = 1.17$) as a probe adduct P₀-X and variable amounts of BPO (0–10 mM) as a radical initiator was studied.¹⁴³ In order to follow the fast exchange process in this system, the concentrations of P₀-X and BPO had to be unusually low. **Figures 16(a)** and **16(b)** show the first-order plots of [M] and [P₀-X], respectively (note the exceptionally small ordinate scale in **Figure 16(a)**). The values of $R_p/[M]$



Figure 16 Plots of (a) $\ln([M]_0/[M])$ and (b) $\ln(I_0/I)$ vs. *t* for the styrene/PS-SCSCH₃(P₀-X)/BPO systems (80 °C): $[P_0-X]_0 = 0.45$ mM; [BPO]₀ as indicated in **Figure 16**(a). Reproduced from Goto, A.; Sato, K.; Tsujii, Y.; *et al. Macromolecules* **2001**, *34*, 402–408,¹⁴³ with permission from the American Chemical Society.

obtained from Figure 16(a) were consistent with the steady-state rate law (eqn [21]). (However, independent experiments carried out with much larger amounts of P_0 -X revealed a decrease of R_p with increasing [P_0 -X]₀: see Section 3.05.7.2.4.)

The k_{act} obtained from Figure 16(b) was proportional to $R_p/[M]$ (Figure 17(a)), meaning that the first term in eqn [47] is unimportant in this system, too, and suggesting that the main mechanism of activation is the RAFT process. (There is a small possibility of the DT occurring directly to the C–S bond, but this process, if any occurs, is difficult to kinetically distinguish from the RAFT process. On the other hand, the RAFT process is supported by ESR observations of the intermediate radicals.^{144,145}) The slope of the straight line in Figure 17(a) gives C_{ex} (= k_{ex}/k_p) = 180. For this homopolymerization system starting with the polymeric adduct, we may put A = B in eqns [50] and [51] to obtain eqn [7]. With the abovementioned value of C_{ex} and the literature value of k_p , the value of k_{ad} is estimated to be $1.2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ (60 °C).

The steadiness of the radical concentration was also confirmed for this system, and therefore the PDI of the produced polymer should obey eqn [49], as in fact confirmed in Figure 17(b) quantitatively.

The activation energy of k_{ex} for this system was estimated to be 21.0 kJ mol⁻¹, which is comparable with that for PS-I (27.8 kJ mol⁻¹).⁸³ The activation energy of k_p for styrene is 32.5 kJ mol^{-1,91} meaning that C_{ex} is weakly and negatively temperature dependent in these two systems. This indicates that lowering the temperature would somewhat benefit the polydispersity of the system, according to eqn [36]. This is in contrast to NMPs where the activation energies of k_d are large (e.g., 124 kJ mol⁻¹ for PS-TEMPO⁹²) and hence high temperatures are necessary to achieve low polydispersities. Of course, at lower temperatures, k_p is smaller and it takes more time to achieve a desired conversion. Optimization of R_p is thus important.

The $k_{\rm act}$ in the polymerization of styrene with a polystyryl dithiobenzoate (PS-SCSPh) was too large to be determined with a similar precision to that for PS-SCSCH₃, but the GPC curve-resolution and polydispersity analyses provided a crude estimate of $C_{\rm ex}$ of 6000 ± 2000 at 40 °C.¹⁴³ This value is more than 30 times larger than the acetate value given above,



Figure 17 Plots of (a) k_{act} vs. $(R_p/[M])$ and (b) $[Y_B - (1/x_{n,B})]^{-1}$ vs. c/(2-c) for the styrene/PS-SCSCH₃(P₀-X)/BPO systems in **Figure 17** (80 °C). For (b), the three points for [BPO]₀ = 0 show some deviation from the line, but the deviation is ascribed to the experimental error arising from the extremely small R_p for the BPO-free system. Reproduced from Goto, A.; Sato, K.; Tsujii, Y.; *et al. Macromolecules* **2001**, *34*, 402–408,¹⁴³ with permission from the American Chemical Society.

demonstrating a large effect of the ester group on the RAFT moiety. This $C_{\rm ex}$ value corresponds to a $k_{\rm ad}$ value of about $2 \times 10^6 \,{\rm M}^{-1} \,{\rm s}^{-1}$ (40 C), an extremely large value for an addition reaction, and is perhaps near the 'diffusion-controlled reaction' region.

The polymerization of MMA with a poly(methyl methacrylate) (PMMA)-SCSPh adduct was similarly studied to give $C_{ex} = 140$ at 60 °C.¹⁴³ Comparison with the styrene/PS-SCSPh system shows a large effect of the polymer (alkyl) moiety, as well as the carbonate moiety, on k_{act} . The effects of alkyl and carbonate moieties on k_{act} were comprehensively studied for low-mass model adducts, as will be noted in Section 3.05.9.1.1. It was also shown that the RAFT process is virtually the only mechanism of activation in the MMA system, too.

3.05.7.2.2 Activation process in copolymerizations

The exchange constant (the DT constant) C_{exAB} defined by $C_{exAB} = k_{exAB}/k_{pA}$, where k_{pA} is the k_p of the homopolymerization of monomer A, was determined for several systems related to styrene, MMA, and dithioacetate.¹⁴⁶ Now referring to eqns [7], [50], and [51], we find that

$$\frac{C_{\text{exAB}}}{C_{\text{exAA}}} = 2P_{\text{rB}} \left(\frac{k_{\text{adAB}}}{k_{\text{adAA}}}\right)$$
[53]

The experimental results (Table 8) show that $C_{exAB}/C_{exAA} = 1.9$, when A and B are styrene and MMA, respectively. Since the rate constant of addition should not strongly depend on the polymer (alkyl) moiety that is far apart from the C=S bond, we may assume that k_{adAB}/k_{adAA} is approximately 1. Hence, we estimate that $P_{rB} \sim 0.95$. This estimate is supported by the other set of experimental data showing that $C_{exBA}/C_{exBB} = 0.02$, from which we estimate that $P_{rB} \sim 0.01$ or $P_{rB} = 1-P_{rA} \sim 0.99$. In any case, fragmentation of the intermediate $P_A-(X^{\bullet})-P_B$ predominantly occurs by releasing P_B^{\bullet} (PMMA radical) rather than P_A^{\bullet} (PS radical). This explains why the polymerization (block copolymerization) of MMA with a PS-dithiocarbonate macroinitiator is not as satisfactory as the block copolymerization of styrene with a PMMA macroinitiator.¹⁵⁹ According to eqn [54]

$$\ln\left(\frac{I_0}{I}\right) = C_{\rm ex} \ln\left(\frac{1}{1-c}\right)$$
[54]

which is valid for a batch DTMP,⁸³ we can calculate the (remaining) macroinitiator concentration *I* at a given conversion *c*. With $C_{exAB} = 420$ and $C_{exBA} = 0.83$ (**Table 8**), we estimate that the PMMA macroinitiator in styrene is half consumed at the conversion of 0.16%, while the PS macroinitiator in MMA is half consumed much later, at a 57% conversion, for example.

The study on the random copolymerization of styrene and MMA¹⁴⁶ revealed that P_{BA}^{\bullet} undergoes a (*c*. 0.3 times) slower addition than P_{AA}^{\bullet} , while fragmentation occurs at almost the same rate for the two radicals, where P_{ij}^{\bullet} is the propagating radical with the terminal unit *j* and the penultimate unit *i* (*i*, *j* = styrene(A) or MMA(B)). This means that there is a significant penultimate unit effect on the RAFT process in the styrene/MMA system, which appears in the addition process but not in the fragmentation process.

3.05.7.2.3 Comments on the intermediate radical concentrations

Equation [52] reduces to eqn [55], when P_A and P_B are kinetically identical:

$$[\mathbf{P} - (\mathbf{X}^{\bullet}) - \mathbf{P}] = K_{\text{RAFT}}[\mathbf{P} - \mathbf{X}][\mathbf{P}^{\bullet}] \quad (K_{\text{RAFT}}) = \frac{k_{\text{ad}}}{k_{\text{fr}}} \qquad [55]$$

Comparison of the homopolymerization of styrene and MMA mediated by the dithiocarbonates reveals that k_{ad} (styrene) > k_{ad} (MMA). It was also indicated that k_{fr} (MMA) » k_{fr} (styrene) (see above). Hence we expect from eqn [55] that the inequality¹⁴³

$$[PS - (X^{\bullet}) - PS] \gg [PMMA - (X^{\bullet}) - PMMA]$$
[56]

holds when comparison is made with other conditions fixed. Consistently, the intermediate radical for a styrene system was clearly detected by ESR, while that for an *n*-butyl methacrylate system was undetectable.¹⁴⁴

3.05.7.2.4 Retardation in polymerization rates

Retardation in $R_{\rm p}$ has been noted in some RAFT systems. It was particularly significant in the dithiobenzoate (Z=Ph) systems with styrene,¹⁶⁰ BA,¹⁶⁰ and acrylamide.¹⁶¹ Among others,¹⁶⁰ two opposing explanations for this phenomenon have been proposed. One was slow fragmentation. Barner-Kowollik et al.¹⁶² assumed that the intermediate radical is stable enough to cause no termination with P[•] (no cross-termination) and, under this assumption, made a computer simulation with their experimental data on the rate and polydispersity to estimate $k_{\rm fr}$ to be typically on the order of 10^{-2} s⁻¹. On the other hand, Brouwer *et al.*¹⁶³ noted the production of a tripled molecular weight species in a monomer-free model experiment with a UV-irradiated polystyryl dithiobenzoate. These authors¹⁶⁴ then assumed that the intermediate radical undergoes cross-termination with a rate constant k_t' equal to k_t and also made a computer simulation with their rate data to deduce $k_{\rm fr}$ to be about $10^5 \,{\rm s}^{-1}$. Between the $k_{\rm fr}$ values estimated by the two groups is a difference of 6-7 orders of magnitude. Since the rate data for the styrene/dithiobenzoate system used by the two groups are more or less similar, the huge difference in $k_{\rm fr}$ stems solely from the difference in the assumption for the cross-termination rate constant, that is, $k_t' = 0$ (Barner-Kowollik *et al.*) versus $k_t' = k_t$ (Monteiro *et al.*). Obviously, computer simulations could bring no solution to this controversy. Both $k_{\rm fr}$ and $k'_{\rm t}$ should be determined experimentally.

To elucidate the cause for the rate retardation, Kwak et al.¹⁶⁵ followed the polymerization of styrene with PS-SCSPh $(M_n = 1100 \text{ and } M_w/M_n = 1.08)$ and azoisobutyronitrile (AIBN) at 60° C by both dilatometry and ESR. The first-order plot of [M] was linear in both the presence and absence of PS-SCSPh (Figure 18(a)), and the $[P^{\bullet}]$ estimated from Figure 18(a) was smaller in the presence of PS-SCSPh than in its absence (Figure 18(b)). The [P-(X[•])-P] determined by ESR stayed nearly constant from an early stage of polymerization (Figure 18(c)). These results show that the steady state of the radical concentrations and the addition-fragmentation quasi-equilibrium are quickly achieved. With the obtained $[P^{\bullet}]$ and $[P-(X^{\bullet})-P]$, the equilibrium constant $K_{RAFT} = [P-(X^{\bullet})-P]/([P^{\bullet}][P-X])$ was determined to be 55 M⁻¹ (Figure 18(d)), and $k_{\rm fr} = k_{\rm ad}/K_{\rm RAFT}$ was estimated to be about $7 \times 10^4 \,\mathrm{s}^{-1}$ with the known $k_{\rm ad}$ $(2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1})$, see above). These results show that the rate retardation in this system was caused by cross-termination. Calitz et al.¹⁶⁶ also experimentally obtained similar K_{RAFT} values $(\sim 10^{1} \text{ M}^{-1})$ in the same system at 70 and 90 °C.

The existence of the addition-fragmentation quasi-equilibrium and the steadiness of the radical concentrations led to the following rate equation:¹⁶⁷



Figure 18 Plots of (a) $\ln([M]_o/[M])$, (b) $[P^*]$, (c) $[P-(X^*)-P]$, and (d) K_{RAFT} vs. *t* for the styrene/AIBN/(PS-SCSPh) systems (60 °C): [AIBN] $_0 = 300 \text{ mM}$; [PS-SCSPh] $_0$ as indicated in the figure. Reproduced from Kwak, Y.; Goto, A.; Tsujii, Y.; *et al. Macromolecules* **2002**, *35*, 3026–3029.¹⁶⁵ with permission from the American Chemical Society.

$$R_{\rm p} = R_{\rm p,0} \left(\frac{1}{1 + 2K_{\rm RAFT} \left(\frac{k'_{\rm t}}{k_{\rm t}} \right) \left[{\rm P} - {\rm X} \right]_0} \right)^{1/2}$$
[57]

where $R_{\rm p,0}$ is the polymerization rate for the RAFT agent-free ([P–X]₀=0) system. Equation [57] means that a RAFT system suffers a retardation of $R_{\rm p}$ by a factor of $\{1 + 2K_{\rm RAFT}(k_t'/k_t)$ [P–X]₀ $\}^{-1/2}$. In fact, the $R_{\rm p}$ measured with a fixed amount of AIBN and varying amounts of PS-SCSPh conformed to eqn [57].¹⁶⁷ This analysis gave $k_t'/k_t = 0.5 \pm 0.1$. Namely, k_t' is similar to k_t in the order of magnitude.

If cross-termination is recombination rather than disproportionation, it will produce a three-arm star chain. The production of the three-arm star was confirmed in two model experiments. One was that of Brouwer *et al.*,¹⁶³ as already noted. The other was that of Kwak *et al.*,¹⁶⁷ in which a solution of PS-SCSPh and PS-Br of nearly the same chain length was heated at 60 °C in the presence of a Cu(I)Br/Me₆TREN complex used as an AT catalyst to produce a high concentration of PS radicals from PS-Br. The GPC chart of the product clearly demonstrated the existence of the three-arm chain produced by cross-termination as well as the linear chain of doubled chain length produced by conventional self-termination. The concentration of the three-arm chain relative to that of the linear chain gave an estimate of $k_t'/k_t = 0.4$, in good agreement with the above-noted value for the actual polymerization system.¹⁶⁷ Since the dithiobenzoate intermediate can have a series of resonance structures, the radical–radical reaction can occur at the aromatic ring as well as at the S–C[•]–S moiety.¹⁶⁸ This issue was also examined using a low-mass model system.¹⁶⁹

Equation [57], for example, clearly shows that the rate retardation phenomenon depends on many factors. Careful experiments are primarily important in approaching correct answer(s). Rate constants such as k_{ad} and k_{fr} (and hence K_{RAFT}) can largely differ for different systems. They can significantly depend also on chain length, especially for short chains, as a body of experimental evidence for other LRP systems suggests. We should be careful in generalizing the results obtained for particular systems over others. For more publications on this topic, see References 170–180.

3.05.8 Experiments on Some Newer Systems

3.05.8.1 Organotellurium-Mediated LRP and Others

TERP is applicable to a variety of monomers.⁴⁶ The polymerization run is usually conducted at 80–100 °C with monomer(s) and an alkyl methyltellanyl included at the onset of polymerization.^{46,181} The activation process was at first believed to be reversible thermolysis of the C–Te bond¹⁸² due to the similarity of bond dissociation energies for alkyl methyltellanyl and TEMPO compounds with the same alkyl group.⁴⁶ It was later found that TERP is mainly driven by a DT mechanism with some contribution of a thermal dissociation (DC) mechanism.¹⁵⁴

Figure 19 shows the correlation of k_{act} and $R_p/[M]$ for the styrene polymerization with a polystyrene methyltellanyl (PS-TeCH₃) and a conventional azo initiator at 60 and 100 °C. The k_{act} linearly increases with increasing R_p at both 60 and 100 °C. We obtained $k_d = 1.2 \times 10^{-5}$ and $1.4 \times 10^{-4} \text{ s}^{-1}$ by the extrapolation to $[P^\bullet] = 0$, and $C_{ex} = 17$ and 20 from the slope of the line, at 60 and 100 °C, respectively, clearly suggesting that TERP proceeds via both the DT and DC mechanisms. This is the first clear example of the LRP proceeding via two competing pathways. The k_d is similar to that of PS-TEMPO ($k_d = 1.3 \times 10^{-4} \text{ s}^{-1}$ at



Figure 19 Plot of k_{act} vs. $(R_p/[M])$ for the styrene/PS-TeCH₃(P_0 -X)/ (AIBN or VR110) systems (60 (•) and 100 °C (•)); $[P_0-X]_0 = 5.4$ mM; $[AIBN]_0 = 0-26$ mM (60° C); $[VR110]_0 = 0-100$ mM (100° C). Reproduced from Goto, A.; Kwak, Y.; Fukuda, T.; *et al. J. Am. Chem. Soc.* **2003**, *125*, 8720–8721, ¹⁵⁴ with permission from the American Chemical Society.

100° C),⁹² which is consistent with the similarity of bond dissociation energies.⁴⁶ The C_{ex} is c. 5 times higher than that for the iodide-mediated system $(C_{ex} = 3.6)^{83}$ and c. 10 times lower than that for the dithioacetate derivatives $(C_{ex} = 180)$.¹⁴³ Methacrylate and acrylate systems also include the two activation processes.¹⁵⁶ While the main activation mechanism is DT, thermal dissociation of the organotellurium compound is crucial to generate the carbon-centered radicals to initiate and maintain the polymerization in the absence of conventional initiation. The high temperature required for the reported TERP systems^{46,181} must be due to slow thermal dissociation at low temperatures. This conclusion in turn suggests that the polymerization can proceed at a much lower temperature if one could supply radical species. As expected, the polymerization of styrene with an organotellurium compound in the presence of AIBN (a radical source) was complete, for example, within 11 h at 60 °C to give PS with a low polydispersity $(M_w/M_p \sim 1.17)$, while the previous conditions required 16 h at 100 °C for completion.¹⁵⁴ This method is thus efficient to overcome the largest disadvantage of TERP, slow polymerization even at high temperatures. The Cex depends on the substituent (R) of the tellanyl group (-TeR).¹⁵⁵ The Cex increases in the order of R = n-butyl ($C_{ex} = 10$ at 60° C) < Me (17) < phenyl (28) < p-MeO-phenyl (35) < p-CF₃-phenyl (44). The C_{ex} also depends on the polymer $(monomer)^{156}$ (see Chapter 6.09).

For MMA polymerization with X = TeMe, Yamago *et al.*¹⁸¹ synthesized low-polydispersity polymers ($M_w/M_n \sim 1.15$) by the addition of a small amount of dimethyl ditelluride (MeTe)₂, without which M_w/M_n exceeded 1.35 due to a small C_{ex} (e.g., 3.6 at 60° C¹⁵⁶). This suggests an increase of k_{act} in the presence of (MeTe)₂. A kinetic study on the role of (MeTe)₂¹⁸³ demonstrated that (MeTe)₂ worked as an efficient deactivator of P[•] to *in situ* generate MeTe[•] (and P-TeMe), and MeTe[•] then worked as a highly reactive activator of the dormant species P-TeMe. Namely, there is a rapid reversible activation–deactivation process mediated by (MeTe)₂, that is, P-TeMe + MeTe[•] \neq P[•] + (MeTe)₂ as another activation improvement of the polydispersity controllability.

SBRP⁴⁷ and BIRP⁴⁸ exhibit better polydispersity controllability than TERP. For St at 60° C, C_{ex} increases in the order of X = I $(C_{ex} = 4.0)^{83} < \text{TeMe} (17)^{154} < \text{SbMe}_2 (33)^{47} < \text{BiMe}_2 (56).^{48}$ This shows a clear trend that C_{ex} increases in the order of X = group 17 <16 <15 elements in the same period and in the order of X = period 5 < 6 elements in the same group (Figure 20). This trend is consistent with the observed polydispersity controllability. For MMA at 60° C, Cex is 13 for SbMe2, 157 which is large enough to explain why a distibine (R₂Sb-SbR₂) is not required to achieve low polydispersity even for MMA in SBRP (in contrast to TERP). For St at 100 ° C, k_d is virtually zero for X = SbMe₂ and increases in the order of X = TeMe $(1.5 \times 10^{-4} \text{ s}^{-1}) < \text{BiMe}_2$ $(5 \times 10^{-4} \text{ s}^{-1})$. The large k_d for BIRP accounts for the observed fast polymerization of BIRP even without a conventional radical initiator at high temperatures. A large C_{exv} along with a fairly large $k_{d_{\ell}}$ is a notable kinetic feature of BIRP.

3.05.8.2 Reversible Chain Transfer-Catalyzed Polymerization

RTCP is a simple and robust polymerization including, like iodide-mediated polymerization, a monomer, an alkyl iodide as a dormant species (X = I), and a conventional radical initiator as a source of P^{\bullet} , along with a catalyst such as GeI₄ as a deactivator (AX). It is applicable to, for example, styrene, methacrylates, AN, and the relevant functional monomers.^{18,55} Mechanistically, it is based on RT with a minor contribution of DT.

The k_{act} in this system (Scheme 3) is generally given by

$$k_{\rm act} = k_{\rm ex}[\mathbf{P}^{\bullet}] + k_{\rm a}[\mathbf{A}^{\bullet}]$$
^[58]

In the quasi-equilibrium of the RT process (Scheme 3d), eqn [58] takes the form⁵³

$$k_{\rm act} = k_{\rm ex}[\mathbf{P}^{\bullet}] + k_{\rm da}[\mathbf{P}^{\bullet}] \left(\frac{[\rm XA]}{[\rm P-X]}\right)$$
[59]

Hence, k_{act} increases with the ratio [XA]/[P–X]. Figure 21 shows the plot of k_{act} versus [XA]₀/[P–X]₀ for styrene polymerizations



(b) Thermal dissociation (100 °C)



Figure 20 Comparisons of (a) k_{ex} (60° C) and (b) k_d (100° C) for St with X = -I, -TeMe, -SbMe₂, and -BiMe₂.



Figure 21 Plot of $k_{act}/[P^*]$ vs. [AX]/[P-X] for the styrene/PS-I/BPO/AX systems (80° C); $[PS-I]_0 = 10 \text{ mM}$; $[BPO]_0 = 1 \text{ mM}$ (60° C); $[XA]_0$ as indicated in the figure. Symbols as indicated in the figure. Reproduced from Goto, A.; Wakada, T.; Tsujii, Y.; Fukuda, T. *Macromol. Chem. Phys.* **2010**, *211*, 594–600,¹⁷⁴ with permission from Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

with PS-I as a P–X and GeI₄ (Ge-centered catalyst), *p*-tolyl-GeI₃ (Ge-centered one), SnI₄ (Sn-centered one), PI₃ (P-centered one), and *N*-iodosuccinimide (NIS) (N-centered one) as an XA at 80 °C.¹⁵⁸ In all cases, k_{act} linearly increases with the [XA]₀/[P–X]₀ ratio, as expected.

For GeI₄, for example, in a typical RTCP condition with $[GeI_4]/[PS-I] = 5 \text{ mM}/80 \text{ mM} = 0.0625$, k_{act} would be about 20 times larger than in the absence of GeI4 (iodide-mediated polymerization) (Figure 21). This explains whv low-polydispersity polymers are obtainable in the Gel₄ system from an early stage of polymerization. From the slope of the straight line in the plot, k_{da} is determined to be $9.0\times 10^5\,M^{-1}\,s^{-1}.$ This value is large and comparable to the k_{da} for the DEPN-mediated polymerization of styrene (see Section 3.05.5.2.1). By an independent experiment, ^{53,158} the equilibrium constant K ($=k_a/k_{da}$) is estimated to be about 10⁰. It follows that, for a typical RTCP condition of $[PS-I] = 10^{-2} M_{\odot}$ $[PS^{\bullet}] = 10^{-8} M$, and $[GeI_4] = 10^{-3} M$, $[GeI_3^{\bullet}]$ is $10^{-9} M$ (nanomolar). Namely, the observed large k_{act} is achieved by a nanomolar level concentration of the activator. Thus, the k_a is remarkably large, estimated to be about 10⁶ M⁻¹ s⁻¹ with the mentioned K and k_{da} . These k_{da} and k_a values confirm a high deactivating ability of GeI4 and a high activation ability of the in situ formed radical GeI3*

In the typical RTCP condition with [XA]/[P-X] = 0.0625, k_{act} is about 13, 10, 5, and 3 times larger than in their absence for $XA = SnI_{4}$, NIS, p-tolyl-GeI₃, and PI₃, respectively. In all cases, k_{act} is so large as to give low-polydispersity polymers from an early stage of polymerization. Also noticeably, k_{act} significantly differed among the catalysts. For the germanium catalysts GeI4 and tolyl-GeI₃, the substitution of a tolyl group decreased the catalyst activity by a factor of about 1/4. Regarding the catalyst elements, the comparison of GeI4, SnI4, and PI3, all of which have no substituents, suggests that the activity increases in the order of P < Sn < Ge. NIS (N catalyst) exhibited a higher activity than PI₃ (P catalyst), while the elemental comparison of NIS and PI₃ is not simple due to the different substituents. Qualitatively, the result indicates that N tends to be more active than P. As a whole, the group 14 catalysts (Sn and Ge), which are weak Lewis acids, were more active than the group 15 catalysts (P and N), which are weak Lewis bases, for St at 80 °C. In the same group, the activity tended to increase for a lower period for St at 80 °C. The k_{act} for MMA was about 120 times larger than that for St in the case of p-tolyl-GeI3,

suggesting that the catalytic activity strongly depends on monomer. The order of the catalyst activity among the catalysts may also be different between St and MMA.

In the presence of the catalysts, R_p is slightly smaller than in their absence.⁵³ This is because the catalyst radicals (A[•]) undergo irreversible cross-termination with P[•] and irreversible self-termination between A[•].^{53,183} This mechanism is analogous to the one causing the rate retardation in the RAFT polymerization (see Section 3.05.7.2.4).

3.05.9 Summary on Activation and Deactivation Rate Constants

3.05.9.1 Low-Mass Model Adducts

Low-mass compounds such as shown in **Figure 4** have been studied with their activation/deactivation processes as models for polymer adducts, and some of them are actually used as efficient initiating adducts of LRP. Examples are shown below.

3.05.9.1.1 Activation rate constants for low-mass adducts

Tables 2 and **3** list the activation rate constants for low-mass alkoxyamines $(k_{act} = k_d)$,^{95,101,112,147,150,184–203} **Table 4** lists those for copper-catalyzed ATRP $(k_{act} = k_a[A]$ with

Table 2 $k_{\rm act}$ of low-mass model alkoxyamines

Alkoxyamine	Solvent	$10^3 k_{act} s^{-1}$	Т (°С)	Reference
1	Hexane	0.30	110	184
1	Ethyl acetate	0.35	60	184
1	Methanol	0.68	110	184
2	Ethyl acetate	<0.012	110	184
3	Ethyl acetate	0.029	80	184
4	Ethyl acetate	0.17	60	184
6	Styrene (in bulk)	1.2-2.3	123	185
7	Styrene (in bulk)	0.077	123	185
8	Styrene (in bulk)	< 0.039	123	185
9	Benzene	0.0017	60	186
10	Methanol	0.0026	60	186
11	Methanol	0.27	60	186
12	<i>t</i> -Butylbenzene	0.7	120	150

Alkoxyamine	Solvent	A _{act} (S ⁻¹)	E _{act} (kJ mol⁻¹)	10 ³ k _{act} s ⁻¹ (120 °C) ^a	Reference
5	Cyclohexane	$1.0 imes 10^{14}$	114	70	187
5	<i>t</i> -Butylbenzene	$1.3 imes 10^{14}$	114.4	81	188
5	t-Butylbenzene	$2.0 imes 10^{14}$	115.7	84	112
6	Cvclohexane	$5.0 imes 10^{13}$	129	0.36	187
6	<i>t</i> -Butylbenzene	$2.5 imes 10^{14}$	133.0	0.52	112
6	Acetonitrile	1.2×10^{14}	128	1.2	95
7	Cyclohexane	4.0×10^{13}	137	0.025	187
7	<i>t</i> -Butylbenzene	$2.6 imes10^{14}$	145.7	0.011	112
7	t-Butylbenzene	7.1×10^{11}	99	49	189
13	Toluene	$1.1 imes 10^{14}$	133.2	0.22	147
13	Toluene	9.1×10^{14}	138.8	0.32	147
14	Chlorobenzene	6.3×10^{14}	102.6	14 500	190
15	Cyclohexane	$1.1 imes 10^{9}$	92.1	0.63	190
15	Methanol	1.2×10^{11}	96.3	19	190
16	t-Butylbenzene	2.2×10^{14}	121.8	14	112
17	t-Butylbenzene	$1.9 imes 10^{14}$	124.5	5.4	112
18	t-Butylbenzene	$5.6 imes 10^{14}$	129.6	3.3	112
19	t-Butylbenzene	$1.0 imes 10^{14}$	139.0	0.033	112
20	t-Butylbenzene	$1.8 imes 10^{14}$	119.8	22	112
21	t-Butylbenzene	(2.6×10^{14})	136.9 ^b	0.17	191
22	t-Butylbenzene	(2.6×10^{14})	125.1 ^{<i>b</i>}	6.1	191
23	t-Butylbenzene	(2.4×10^{14})	138 [°]	0.13	192
24	t-Butylbenzene	9.0×10^{13}	126	1.6	192
25	t-Butylbenzene	$9.0 imes 10^{13}$	121	8.1	192
26	Xylene	-	130	-	193
27	Xylene	-	113	-	193
28	t-Butylbenzene	$5.8 imes 10^{10}$	97	7.4	189
29	t-Butylbenzene	$2.5 imes 10^{10}$	99	1.7	189
30	t-Butylbenzene	1.1×10^{14}	133	0.23	194
31	Benzene	1.6×10^{13}	116	6.1	195
32	t-Butylbenzene	9.7×10^{14}	138	0.44	95
33	Toluene	2.3×10^{13}	118	4.8	196
34	Toluene	7.3×10^{12}	119	1.1	196
35	t-Butylbenzene	(2.6×10^{14})	137.6 ^b	0.13	101
36	t-Butylbenzene	(2.6×10^{14})	133.3 ^{<i>b</i>}	0.50	101
37	t-Butylbenzene	(2.6×10^{14})	133.8	0.43	101
38	t-Butylbenzene	(2.6×10^{14})	123.7	9.4	197
39	t-Butylbenzene	(2.6×10^{14})	128.1 [°]	2.4	197
40	t-Butylbenzene	(2.6×10^{14})	125.7	5.1	197
41	t-Butylbenzene	(2.6×10^{14})	124.2	8.1	198
42	t-Butylbenzene	(2.6×10^{14})	122.0 ^{<i>p</i>}	15.8	199
43	t-Butylbenzene	(2.6×10^{14})	112.3 [°]	280	200
44	t-Butylbenzene	(2.6×10^{14})	132.9 [°]	0.53	201
45	t-Butylbenzene	(2.6×10^{14})	149.1"	0.0036	202
46 47	<i>t</i> -Butylbenzene <i>t</i> -Butylbenzene	(2.6×10^{14}) (2.6×10^{14})	126.4 ^b 133.4 ^b	3.8 0.48	203 202

Table 3 Arrhenius parameters for k_{act} and estimated k_{act} (120 °C) of low-mass model alkoxyamines

^aCalculated with A_{act} and E_{act}.

^bEstimated with the assumption of $A_{act} = 2.6 \times 10^{14} \text{ s}^{-1}$.

^cEstimated with the assumption of $A_{act} = 2.4 \times 10^{14} \text{ s}^{-1}$.

A = Cu(I)X/L),^{75,116,126,204-212} and **Table 5** lists those for dithioester compounds ($k_{act} = k_{ex}[P^{\bullet}]$ and $C_{ex} = k_{ex}/k_p$).^{160,152,213-224}

Cu(II)Br₂ complexes with varying ligands are in **Table 7** $(k_{\text{deact}} = k_{\text{da}}[D]$, with $D = AX^{\bullet} = Cu(II)X_2/L$ and X = Br).^{75,126,205}

3.05.9.1.2 Deactivation rate constants for low-mass adduct The deactivation rate constants for low-mass alkyl radicals (Figure 22) by low-mass nitroxides are in Table 6 $(k_{deact} = k_c[X^{\bullet}])^{220-224}$ and those for 1-phenylethyl radical by

3.05.9.2 Polymer Adducts

3.05.9.2.1 Activation rate constants for polymer adducts Table 8 lists the values of k_{actr} , k_{ar} and C_{ex} (= k_{ex}/k_p) for polymer adducts^{47,48,83,92,98,102,103,108,115,120,143,146-149,150-158} (see also

Alkyl halide	CuX	Ligand	Solvent	$k_a (M^{-1} s^{-1})$	Т <i>(°С)</i>	Reference
48	CuCl	bipy	Styrene (in bulk)	0.020	110	204
48	CuCl	dHbipy	Toluene	0.018	110	116
48	CuCl	dNbipy	Acetonitrile	0.000056	35	205
48	CuCl	Me ₆ TREN	Acetonitrile	1.5	35	205
48	CuBr	dHbipy	Toluene	0.010	110	116
49	CuBr	dHbipy	Toluene	0.42 ^a	110	116
49	CuCl	dHbipy	Toluene	0.52	110	116
49	CuBr	Me ₆ TREN	Acetonitrile	1200	35	206
49	CuBr	TERPY	Acetonitrile	0.42	35	126
49	CuBr	PMDETA	Acetonitrile	0.17 ^b	35	207,208
49	CuBr	dNbipy	Acetonitrile	0.085	35	205
49	CuBr	DOIP	Acetonitrile	0.014	35	126
50	CuBr	dHbipy	Toluene	0.18	110	116
51	CuBr	bipy	Acetonitrile/water ^c	~ 1.0	35	209
51	CuBr	bipy	Acetonitrile	0.24	35	209
51	CuBr	bipy	Acetonitrile/CB ^d	0.098	35	209
51	CuBr	Cyclam-B	Acetonitrile	710	35	210
51	CuBr	Me ₆ TREN	Acetonitrile	450	35	210
51	CuBr	PMDETA	Acetonitrile	2.7 ^e	35	207,208
51	CuBr	Me ₄ Cyclam	Acetonitrile	0.67	35	210
51	CuBr	dNbipy	Acetonitrile	0.60	35	210
52	CuBr	bipy	Acetonitrile	0.018	35	209
52	CuBr	dNbipy	Acetonitrile	0.052	35	205
52	CuBr	dNbipy	Acetonitrile	0.026	22	75
52	CuBr	PMDETA	Acetonitrile	0.33 ^f	35	207,208
53	CuCl	dNbipy	Toluene	0.06	60	211
53	CuBr	bipy	Acetonitrile	0.017	35	209
54	CuBr	bipy	Acetonitrile	0.0054	35	209
54	CuBr	dNbipy	Acetonitrile	0.0094	22	75
55	CuBr	bipy	Acetonitrile	1.9	35	212
56	CuBr	bipy	Acetonitrile	0.38	35	212
57	CuBr	bipy	Acetonitrile	0.020	35	212
58	CuBr	bipy	Acetonitrile	0.091	35	212
59	CuBr	PMDETA	Acetonitrile	0.030	35	207
6 0	CuBr	PMDETA	Acetonitrile	0.015	35	207
61	CuBr	PMDETA	Acetonitrile	0.53	35	207
62	CuBr	PMDETA	Acetonitrile	23	35	207

Table 4	k _a of	low-mass	model	alkyl	halides in	copper	-catalyzed	ATRP
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 ${}^{a}k_{a}$ (M⁻¹ s⁻¹) = 2.2 × 10⁵ exp(-42.1 kJ mol⁻¹ (RT)⁻¹).

 ${}^{b}k_{a}$ (M⁻¹ s⁻¹) = 3.0 × 10⁵exp(-36.4 kJ mol⁻¹ (RT)⁻¹). ^cAcetonitrile (44 wt.%)/water (56 wt.%).

ACELUTITITIE (44 WL. %)/Water (50 WL. %)

^dAcetonitrile (41.5 wt.%)/chlorobenzene (58.5 wt.%). ${}^{e}k_{a} (M^{-1} s^{-1}) = 1.7 \times 10^{5} exp(-27.5 kJ mol^{-1} (RT)^{-1}).$

 ${}^{f}k_{a}$ (M⁻¹ s⁻¹) = 1.2 × 10⁵ exp(-33.2 kJ mol⁻¹ (RT)⁻¹).

Table 9). Since the k_{act} for systems 12–46 is proportional to $R_{p'}$ the listed values for those systems are referred to a standard value of $R_{p} = 4.8 \times 10^{-4} \text{ M s}^{-1}$, while the k_{act} for the other systems is independent of R_{p} .

Comparing the PS-nitroxide systems 1–7, the open-chain nitroxides DBN and DEPN give larger k_{act} than the less bulky ring-chain nitroxide TEMPO, meaning that steric factors are important. DEPN possesses a much bulkier side group than DBN but gives smaller k_{act} than DBN does. This implies that the electron-donating phosphonate group gives an important electronic effect. The observed order of k_{act} is consistent with that for low-mass models.

The comparison of absolute values of k_{act} between polymers and the low-mass models poses a question about the CLD of k_{act} . Bertin *et al.*¹⁴⁹ determined k_{act} for DEPN-based

model 17 by the O_2 capping method and polymer adducts with different chain lengths in *t*-butylbenzene and showed the absence of CLD. By the same method, Huang *et al.*¹⁹⁴ also observed no CLD for a TEMPO-based system. On the other hand, the k_{act} values for polymer adducts 82–84 determined in monomer by the GPC curve-resolution method by Goto *et al.* are systematically 2–3 times larger than those of the low-mass analogues 6, 16, and 17 determined in *t*-butylbenzene by the O₂ method. Guerret *et al.*¹⁵⁰ observed a clear CLD for the BA/DEPN system by the O₂ method: the k_{act} for PBA-DEPN 86 is about 3 times larger than that for the low-mass analogue 12. For the CuBr/dHbipy-catalyzed ATRP of styrene, the k_a of polymer adduct 97 (0.45 M⁻¹ s⁻¹) is close to that of the corresponding low-mass adduct 49 (0.42 M⁻¹ s⁻¹), suggesting that k_a is nearly independent of

Dithioester compound	Monomer ^a	C _{ex}	т <i>(°С)</i>	Reference
· · ·		0,1	()	
63	MA	105	60	213
63	Styrene	${\sim}50$	60	213
63	Styrene	26	110	160
63	MMA	0.03	60	160
64	Styrene	11	110	214
65	Styrene	10	110	160
66	Styrene	2.3	110	160
67	Styrene	0.72	110	160
68	Styrene	0.11	110	214
69	Styrene	0.01	80	160
70	MMA	0.15	60	213
71	Styrene	>150	60	213
71	MMA	56	60	213
72	MMA	25	60	213
73	Styrene	>150	60	213
73	MMA	1.7	60	213
74	MMA	0.03	60	213
75	BA	1.5	70	215
75	Styrene	0.69 ^b	60	216
76	Styrene	0.65 ^c	60	216
77	Styrene	3.9 ^d	60	216
78	Styrene	6	110	217
79	MÁ	110	60	218
80	BA	190	40	152
80	Styrene	53	80	152
81	Styrene	>100	80	219

 Table 5
 C_{ex} of low-mass model dithioester compounds

^aMA is methyl acrylate, MMA is methyl methacrylate, and BA is *n*-butyl acrylate.

 ${}^{b}k_{ex}$ (M⁻¹ s⁻¹) = 1.0 × 10⁸ exp(-36.2 kJ mol⁻¹ (RT)⁻¹).

 $^{c}k_{ex}$ (M⁻¹ s⁻¹) = 8.8 × 10⁷ exp(-35.6 kJ mol⁻¹ (RT)⁻¹).

 ${}^{d}k_{ex}$ (M⁻¹ s⁻¹) = 7.5 × 10⁷ exp(-30.4 kJ mol⁻¹ (RT)⁻¹).

chain length. For ATRP of methacrylates and acrylates, studies on model dimer and unimer suggested that CLD is important for methacrylates and unimportant for acrylates.²¹² For the RAFT polymerization of MMA, CLD dramatically appeared, where the C_{ex} (=140) of the polymer adduct 93 is 80 times larger than that (1.7) of the low-mass homolog 73 for the same radical (PMMA[•]). Since the addition rate of PMMA[•] to the polymer 93 would not exceed that to the low-mass 73, the observed CLD would be due to the higher fragmentation ability of the polymer than the low-mass alkyl group. In this way, the importance of CLD varies from system to system. CLD, if present, should be the strongest between unimer and dimer and become less significant as the chain becomes longer. Most generally, CLD may depend on monomers and capping agents as well as activation mechanisms.

According to **Table 8**, the DBN-mediated polymerization of tBA may be as well controlled as the TEMPO-mediated polymerization of styrene. Actually, however, the thermal degradation of the active chain end of PtBA-DBN occurs rather seriously at high temperatures, not allowing the polydispersity to be lowered as in the TEMPO/styrene system.⁹⁸ Clearly, a large k_{act} is a necessary but not a sufficient condition for a high-performance LRP.

The k_{act} for the RAFT-based system 20 with PS-SCSPh is surprisingly large (see Section 3.05.7.2.1), about 30 times as large as those for system 13 with PS-SCSCH₃ and system 20 with PMMA-SCSPh, showing that the RAFT velocity is strongly dependent on the structures of the dithiocarbonate group and the alkyl (polymer) moiety. Block and random copolymerization of styrene and MMA showed interesting features, as already noted in Section 3.05.7.2.2.

The k_{act} value for the ATRP system 25 is also large enough to account for the experimental observations that the system provides low-polydispersity polymers even from an early stage of polymerization.¹¹⁷ The results for systems 25–28 suggest that the polarity of solvents and the kind of polymers have important effects on k_{a} , which is consistent with the observation for low-mass alkyl halides.

The k_{act} values for TERP, SBRP, and BIRP systems 29–40 are also large enough to obtain low-polydispersity polymers. The k_{act} largely depends on the central atoms (Te, Sb, and Bi) and substituents of the capping group and polymers, as noted in Section 3.05.8.1. The k_{act} values for the RTCP systems 41–46 are also sufficiently large and depend on the catalysts and polymers, as noted in Section 3.05.8.2.



	Alkyl radical	Deactivator	Solvent	$10^{-7} \mathrm{k}_c \ (M^{-1} \mathrm{s}^{-1})$	т <i>(°С)</i>	Reference
1.	Ben	TEMPO	Isooctane	48 ± 8	18	220
2.	Ben	TEMPO	THF	23 ± 3	18	221
3.	Ben	TEMPO	THF	21	r.t. ^a	222
4.	Ben	TEMPO	Methanol	13 ± 1	18	221
5.	Ben	TEMPO	t-Butylbenzene	35	120	223
6.	PhEt	TEMPO	Isooctane	16 ± 4	18	220
7.	PhEt	TEMPO	Acetonitrile	13	r.t. ^a	224
8.	PhEt	TEMPO	t-Butylbenzene	25	120	223
9.	Cum	TEMPO	Isooctane	11.8 ± 0.1	18	220
10.	Cum	TEMPO	t-Butylbenzene	5.5	120	223
11.	DPhE	TEMPO	Isooctane	4.63 ± 0.02	18	220
12.	(Me)Pr	TEMPO	Acetonitrile	200	r.t. ^a	224
13.	(Me)iBu	TEMPO	Acetonitrile	25	120	223
14.	Ben	DBN	Isooctane	46 ± 2	18	220
15.	Ben	DBN	t-Butylbenzene	21	120	223
16.	PhEt	TIPNO	t-Butylbenzene	0.82	120	223
17.	PhEt	DEPN	t-Butylbenzene	0.46	120	223

Table 6 K _c for low-mass model	alkoxvamines
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^aRoom temperature.

Table 7 k_{da} for low-mass model adducts in ATRP

	Alkyl radical	Deactivator	Solvent	10 ⁻⁷ k _{da} (M ⁻¹ s ⁻¹)	т <i>(°С)</i>	Reference
1.	PhEt	CuBr ₂ /TERPY	Acetonitrile	0.041	75	126
2.	PhEt	CuBr ₂ /DOIP	Acetonitrile	0.31	75	126
3.	PhEt	CuBr ₂ /PMDETA	Acetonitrile	0.61	75	205
4.	PhEt	CuBr ₂ /Me ₆ TREN	Acetonitrile	1.4	75	205
5.	PhEt	CuBr ₂ /dNbipy	Acetonitrile	2.5	75	205
6.	PhEt	CuCl ₂ /dNbipy	Acetonitrile	0.43	75	205
7.	PhEt	CuBr ₂ /dNbipy	Ethyl acetate	24	75	205
8.	(Me)Pr	CuBr ₂ /dNbipy	Acetonitrile	2.9	22	75
9.	(tBu)Pr	CuBr ₂ /dNbipy	Acetonitrile	0.85	22	75

Table 8 $k_{\rm act}$ of polymer adducts

			10 ³	Т	
	P-X	Monomer (solvent) ^a	$k_{act} (s^{-1})$	(°C)	Reference
1	PS-TEMPO (82)	Styrene	1.0	120	92
2	PS-TEMPO (82)	Toluene	1.9	120	147
3	PS-TEMPO (82)	Chlorobenzene	0.32	120	148
4	PS-DBN (83)	Styrene	42	120	103
5	PS-DEPN (84)	Styrene	11	120	103
6	PS-DEPN (84)	Styrene	3.4	120	102
7	PS-DEPN (84)	t-Butylbenzene	5.6	120	149
8	PtBA-DBN (85)	tBA	1.0	120	98
9	PBA-DEPN (86)	BA	7.1	120	102
10	PBA-DEPN (86)	t-Butylbenzene	1.4–4.0 ^b	120	150
11	PMA- <i>co</i> /Porphyrin (87)	MA	4.0 ± 2.0	25	151
12	PS-I (88)	Styrene	$0.22^{c} (C_{ex} = 3.6)$	80	83
13	PS-SCSCH ₃ (89)	Styrene	13^{c} ($C_{ex} = 220$)	40	143
14	PS-SCSCH ₃ (89)	MMA	$0.050^c (C_{ex} = 0.83)$	40	146
15	PS-SCSCH ₃ (89)	Styrene/MMA ^d	4.5^{c} ($C_{ex} = 75$)	40	146
16	PS-SCSS-PS (90)	Styrene	>60 ^c (C _{ex} > 1000)	110	152
17	PMMA-SCSCH ₃ (91)	Styrene	25^{c} ($C_{ex} = 420$)	40	146
18	PMMA-SCSCH ₃ (91)	MMA	2.4^{c} ($C_{ex} = 40$)	40	146
19	PMMA-SCSCH ₃ (91)	Styrene/MMA ^d	9.0^{c} ($C_{ex} = 150$)	40	146
20	PS-SCSPh (92)	Styrene	360 ± 120^{c} ($C_{ex} = 6000 \pm 2000$)	40	143

	P–X	Monomer (solvent) ^a	10 ³ k _{act} (s ⁻¹)	т <i>(°С)</i>	Reference
21	PMMA-SCSPh (93)	MMA	8.4^{c} ($C_{ev} = 140$)	60	143
22	$PS-co-PMMA-SCSPh (94)^e$	Styrene/MMA ^d	48^{c} ($G_{ex} = 800$)	60	146
23	PBA-SCSS-PBA (95)	BA	13^{c} ($C_{0x} = 220$)	40	152
24	PMMA-macromonomer (96)	MMA	0.013^{c} ($C_{ex} = 0.22$)	80	153
25	PS-Br (97)/CuBr/dHbipy	Styrene	23^{c} ($k_{2} = 0.45 \text{ M}^{-1} \text{ s}^{-1}$)	110	108
26	PS-Br (97)/CuBr/dHbipy	Xvlene	$22^{c,f}$ ($k_a = 0.43 \text{ M}^{-1} \text{ s}^{-1}$)	110	115
27	PS-Br (97)/CuBr/dHbipy	MMA	15^{c} ($k_{a} = 0.30 \text{ M}^{-1} \text{ s}^{-1}$)	110	120
28	PBA-Br (98)/CuBr/dHbipy	Xylene	$3.6^{c,f}$ ($k_a = 0.071 \text{ M}^{-1} \text{ s}^{-1}$)	110	115
29	PS-TeCH ₃ (99)	Styrene	$1.0^{c,g} (\tilde{C}_{ex} = 17)$	60	154
30	PS-TeC ₄ H ₉ (100)	Styrene	0.60^{c} ($C_{ex} = 10$)	60	155
31	PS-TePh (101)	Styrene	1.6^{c} ($C_{ex} = 28$)	60	155
32	PS-Te-(p-MeO-Ph) (102)	Styrene	2.1^{c} ($C_{ex} = 35$)	60	155
33	PS-Te-(<i>p</i> -CF ₃ -Ph) (103)	Styrene	$2.6^{c} (C_{ex} = 44)$	60	155
34	PMMA-TeCH ₃ (104)	MMA	0.22^{c} ($C_{ex} = 3.6$)	60	156
35	PMA-TeCH ₃ (105)	MA	1.1^{c} ($C_{ex} = 19$)	60	156
36	PVAc-TeCH ₃ (secondary) (106)	VAc	6.6 ± 1.8^{c} ($C_{ex} = 110 \pm 30$)	60	156
37	PVAc-TeCH ₃ (primary) (107)	VAc	0.072^{c} ($C_{ex} = 1.2$)	60	156
38	PS-Sb(CH ₃) ₂ (108)	Styrene	$2.0^{c} (C_{ex} = 33)$	60	47
39	PMMA-Sb(CH ₃) ₂ (109)	MMA	$0.78^{c} (C_{ex} = 13)$	60	157
40	PS-Bi(CH ₃) ₂ (110)	Styrene	$3.4^{c,g}$ ($C_{ex} = 56$)	60	48
41	PS-I (88)/Gel ₄	Styrene	5.3^{h} ($k_{da} = 9.0 \times 10^{5} \text{ M}^{-1} \text{ s}^{-1}$)	80	158
42	PS-I (88)/SnI ₄	Styrene	3.5^{h} ($k_{da} = 5.7 \times 10^{5} \text{ M}^{-1} \text{ s}^{-1}$)	80	158
43	PS-I (88)/PI ₃	Styrene	$0.90^{h} (k_{da} = 1.2 \times 10^{5} \text{ M}^{-1} \text{ s}^{-1})$	80	158
44	PS-I (88)/NIS ⁱ	Styrene	2.7^{h} ($k_{da} = 4.3 \times 10^{5} \mathrm{M}^{-1} \mathrm{s}^{-1}$)	80	158
45	PS-I (88)/p-tolyl-Gel ₃	Styrene	1.6^{h} ($k_{da} = 2.5 \times 10^{5} \mathrm{M^{-1} s^{-1}}$)	80	158
46	PMMA-I (111)/p-tolyl-Gel ₃	MMA	$110^{h} (k_{da} = 3.1 \times 10^{3} \mathrm{M^{-1} s^{-1}})$	70	158

^atBA is *t*-butyl acrylate, BA is *n*-butyl acrylate, MA is methyl acrylate, MMA is methyl methacrylate, and VAc is vinyl acetate.

^b Chain length-dependent k_{act} (10³ k_{act} =1.4, 1.9, 2.4, and 4.9 s⁻¹ for M_n = 3000, 20 800, 30 700, and 37 000, respectively).

^cValue approximately estimated for $R_{\rm p} = 4.8 \times 10^{-4} \,\mathrm{M \, s^{-1}}$. (Systems 1–11 are independent of $R_{\rm p}$.)

^dMole fraction of styrene is 0.53 (azeotropic composition).

^eRandom copolymer of styrene and MMA with mole fraction of styrene unit of 0.53 (azeotropic composition).

^fStrong solvent dependence was observed.¹¹⁵

^{*g*} Not only DT but also thermal dissociation is involved at high temperatures, with the main mechanism being DT. The k_d at 100 °C is 1.5×10^{-4} s⁻¹ for entry 29 and 5×10^{-4} s⁻¹ for entry 40.

^h Values approximately estimated for $R_0 = 4.8 \times 10^{-4}$ M s⁻¹ and [XA]/[P–X] = 0.0625. The k_{da} values are also listed in **Table 10**.

Table 9 Arrhenius parameters for k_d and k_{ex} of polymer adducts^{*a*}

	P–X	Monomer (solvent)	$A_d (A_{ex})^b$	E _d (E _{ex}) (kJ mol ^{−1})	Reference
1.	PS-TEMPO (82)	Styrene	3.0×10^{13}	124	92
2.	PS-TEMPO (82)	Toluene	$1.0 imes 10^{16}$	141	147
3.	PS-TEMPO (82)	Chlorobenzene	$2.0 imes 10^{13}$	126	148
4.	PS-DBN (83)	Styrene	$3.8 imes 10^{14}$	120	103
5.	PS-DEPN (84)	Styrene	$2.0 imes10^{15}$	130	103
6.	PS-DEPN (84)	Styrene	$1.0 imes 10^{14}$	121	102
7.	PBA-DEPN (86)	BA	$1.7 imes 10^{15}$	130	102
8.	PS-I (88)	Styrene	$3.1 imes 10^{7}$	27.8	83
9.	PS-SCSCH ₃ (89)	Styrene	$1.3 imes 10^{8}$	21.0	143
10.	PMMA-macromonomer (96)	MMA	$2.2 imes 10^6$	26.2	153
11.	PS-TeCH ₃ (99)	Styrene	$2.8 imes 10^8$	30.0	156
12.	PMMA-TeCH ₃ (104)	MMA	$4.0 imes10^{6}$	20.0	156
13.	PS-Sb(CH ₃) ₂ (108)	Styrene	$3.9 imes 10^7$	22.6	157
14.	PMMA-Sb(CH ₃) ₂ (109)	MMA	$4.4 imes 10^6$	16.7	157
15.	PS-Bi(CH ₃) ₂ (110)	Styrene	7.0×10^7	22.7	48

 ${}^{a}k_{d}$ for systems 1–7 and k_{ex} for systems 8–15.

 ${}^{b}A_{d}$ and A_{ex} are in the units of s⁻¹ and M⁻¹ s⁻¹, respectively.

3.05.9.2.2 Deactivation rate constants for polymer adducts The deactivation rate constants for some polymer adducts are listed in Table 10.^{68,92,102,103,107,108,121,225,226} They can be cal-

culated if k_{act} and K (or K_{AT}) are known.

In some nitroxide systems, *K* was estimated, for instance, by following the time evolution of the concentration of the nitroxide (by ESR) and $R_{\rm p}$.^{63,102,104,194,195,226–231} The $k_{\rm c}$ value thus obtained for the PS-TEMPO combination is $7.6 \times 10^7 \,{\rm M}^{-1} \,{\rm s}^{-1}$ at 125 °C.⁸⁸ This value is about one-third of that for the low-mass counterpart (16 ± 4 or 25), while it reasonably compares with those between TEMPO and radicals such as diphenylmethyl (4.63±0.02) and 2-naphthylmethyl (5.7±1.8),²²⁰ where the values in parentheses are $k_{\rm c}$ in units of $10^7 \,{\rm M}^{-1} \,{\rm s}^{-1}$. This clearly shows

that the CLD in k_c originates in the steric effect of a polystyryl radical. Such a polymer effect on k_c is more apparent for the PS-DEPN combination due to the bulkiness of DEPN.¹⁰²

The equilibrium constants $K_{AT}^{107,108,121-124,133,134,232}$ and $k_{da}^{107,108,121,232}$ were determined for ATRP systems. Gromada and Matyjaszewski²²⁶ showed that k_{da} increases in the order of MMA < styrene < BA systems for the same Cu(II) complex. The most nucleophilic styryl radical has the highest affinity for halogen abstraction, whereas the most electrophilic PBA radical has the lowest affinity. Zhu and Wang²³³ observed a significant increase of K_{AT} in high-viscosity (gelled) systems, suggesting that deactivation is diffusion controlled in such systems.

Table 10	Deactivation	rate	constants	for	polymer	adductsa
	Deactivation	Tato	00113101113	101	polymor	auduois

	P*	Deactivator	Monomer (solvent)	10 ⁻⁷ k _c (k _{da}) (M ⁻¹ s ⁻¹)	т <i>(°С)</i>	Reference
1.	PS*	TEMPO	Styrene	7.6 ^b	125	92
2.	PS*	DEPN	Styrene	0.057 ^c	120	102
3.	PS*	DEPN	Styrene	0.18 ^d	120	102,103
4.	PS*	DEPN	Styrene	0.068 ^e	80	68
5.	PBA*	DEPN	BA	4.2 ^{<i>f</i>}	120	102
6.	PBA*	DEPN	BA	2.8 ^{<i>g</i>}	120	225
7.	PS*	CuBr ₂ /dHbipy	Styrene	1.1 ^{<i>h</i>}	110	108
8.	PS*	CuBr ₂ /dHbipy	Styrene	1.9 ⁱ	110	107
9.	PS*	CuBr ₂ /dHbipy	<i>p</i> -Xylene	7.2 ^j	110	121
10.	PS*	CuBr ₂ /dHbipy	Butyl acetate	5.5 ^k	110	121
11.	PBA*	CuBr ₂ /dHbipy	<i>p</i> -Xylene	12′	110	121
12.	PBA*	CuBr ₂ /dHbipy	Butyl acetate	11 ^{<i>m</i>}	110	121
13.	PS*	CuBr ₂ /Cyclam	Styrene	0.0018	110	226
14.	PS*	CuBr ₂ /Me ₄ Cyclam	Styrene	0.020	110	226
15.	PS*	CuBr ₂ /TERPY	Styrene	0.10	110	226
16.	PS*	CuBr ₂ /TPB	Styrene	0.0043	110	226
17.	PS*	CuBr ₂ /TPB	Styrene	0.0030 ⁿ	90	226
18.	PMMA*	CuBr ₂ /TPB	MMA	0.0014 ⁰	90	226
19.	PBA*	CuBr ₂ /TPB	BA	0.035 ^p	90	226
20.	PBA*	CuBr ₂ /TERPY	BA	0.09	75	226
21.	PS*	Gel ₄	Styrene	0.09	80	158
22.	PS*	Snl ₄	Styrene	0.057	80	158
23.	PS*	Pl ₃	Styrene	0.012	80	158
24.	PS*	NIS	Styrene	0.043	80	158
25.	PS*	<i>p</i> -tolyl-Gel ₃	Styrene	0.025	80	158
26.	PMMA*	<i>p</i> -tolyl-Gel ₃	MMA	3.1	70	158

 ${}^{a}k_{c}$ for systems 1–6 and k_{da} for systems 7–26.

^bCalculated with $K = 2.1 \times 10^{-11}$ M and $k_{d} = 1.6 \times 10^{-3}$ s⁻¹.

^cCalculated with $K = 6.0 \times 10^{-9}$ M and $k_{d} = 3.4 \times 10^{-3}$ s⁻¹.

^dCalculated with $K = 6.0 \times 10^{-9}$ M (Benoit *et al.*¹⁰²) and $k_d = 1.1 \times 10^{-2}$ s⁻¹ (Goto and Fukuda¹⁰³).

^eCalculated with $K = 1.7 \times 10^{-10}$ M and $k_{d} = 1.16 \times 10^{-4} \text{ s}^{-1}$.

^{*t*}Calculated with $K = 1.7 \times 10^{-10}$ M and $k_d = 7.1 \times 10^{-3}$ s⁻¹.

 ${}^{g}k_{\rm c}/k_{\rm p} = 320.$

^hCalculated with $K_{AT} = 3.9 \times 10^{-8}$ (in 50/50 v/v styrene/diphenyl ether) and $k_a = 0.45 \text{ M}^{-1} \text{ s}^{-1}$ (in bulk styrene). ⁱCalculated with $K_{AT} = 2.4 \times 10^{-8}$ (in 50/50 v/v styrene/*t*-butylbenzene) and $k_a = 0.45 \text{ M}^{-1} \text{ s}^{-1}$ (in bulk styrene). ⁱCalculated with $K_{AT} = 6.0 \times 10^{-9}$ (in 50/50 v/v styrene/*p*-xylene) and $k_a = 0.43 \text{ M}^{-1} \text{ s}^{-1}$ (in *p*-xylene). ^kCalculated with $K_{AT} = 5.0 \times 10^{-9}$ (in 50/50 v/v styrene/*p*-xylene) and $k_a = 0.075 \text{ M}^{-1} \text{ s}^{-1}$ (in butyl acetate). ^kCalculated with $K_{AT} = 6.3 \times 10^{-10}$ (in 50/50 v/v styrene/*p*-xylene) and $k_a = 0.075 \text{ M}^{-1} \text{ s}^{-1}$ (in *p*-xylene). ^mCalculated with $K_{AT} = 7.8 \times 10^{-10}$ (in 50/50 v/v styrene/*p*-xylene) and $k_a = 0.086 \text{ M}^{-1} \text{ s}^{-1}$ (in *p*-xylene). ^mCalculated with $K_{AT} = 7.8 \times 10^{-10}$ (in 50/50 v/v styrene/*p*-xylene) and $k_a = 0.086 \text{ M}^{-1} \text{ s}^{-1}$ (in *p*-xylene).

 ${}^{o}k_{dg}/k_{p} = 8.8$ and $k_{dg}/k_{(ST)} = 4.4$, where $k_{(ST)}$ is the propagation rate constant of PMMA[•] to styrene. ${}^{\rho}k_{dg}/k_{p} = 6.2$ and $k_{dg}/k_{(ST)} = 1.2$, where $k_{(ST)}$ is the propagation rate constant of PBA[•] to styrene.

3.05.10 Conclusions

The heart of LRP is the reversible activation of the dormant species P-X (or the reversible deactivation of the active species P^{\bullet}). A prerequisite for LRP is therefore the establishment of the quasi-equilibrium

$$k_{\rm act}[P-X] = k_{\rm deact}[P^{\bullet}]$$
[60

in a major part of the polymerization run ('quasi'equilibrium, because the equality holds only approximately in the presence of termination and/or conventional initiation reactions). Another prerequisite for LRP to provide a low-polydispersity polymer is a fast exchange or a sufficiently large number of activation-deactivation cycles to be experienced by every chain during the polymerization time *t*. Since this number is given by $k_{act} \times t$, and *t* is limited in practical applications, the pseudo-first-order rate constant k_{act} has to be sufficiently large. Another practically important requirement is the achievement of a high conversion in a limited time range. In other words, [P[•]] has to be sufficiently large, but, of course, not so large as to produce an important fraction of dead chains. It follows that, given k_{act} and [P–X], the desirable range of k_{deact} is limited.

In SFR-mediated polymerization and ATRP with given values of k_{act} and $[P-X]_0$, the value of k_{deact} (or $[P^\bullet]$) is self-adjusted by the PRE, producing characteristic time-conversion curves depending on the magnitude of conventional initiation R_i and/or the initial concentration of deactivator $[D]_0$ (= $[X^\bullet]_0$ or $[AX^\bullet]_0$). Existing examples of successful LRPs were in fact found to be characterized by a sufficiently large k_{act} and a sufficiently large R_p . The steady-state kinetics expectable for systems with a relatively large R_i and the power-law kinetics expectable for systems with zero or very small R_i were experimentally confirmed with respect to both R_p and PDI.

Since k_{deact} is proportional to the deactivator concentration [D], it could be controlled by externally controlling [D]. For example, addition of a conventional initiator for NMP^{76,234,235} and ATRP,^{107,108} of an acid for NMP,^{236–238} and of metallic copper Cu(0) for ATRP²³⁹ were found to be effective to decrease the equilibrium concentration of D. The direct addition of D would be useful to adjust [D],^{102,111,117} if the amount to be added is known and controllable. For more elaborate ATRP methods devised to control the activator and/or deactivator concentrations, see Reference 23.

In DT-mediated polymerization, the equilibrium usually holds, and a sufficiently large C_{ex} (= $k_{\text{ex}}/k_{\text{p}}$) is the only requirement for yielding low-polydispersity polymers. This polymerization, initiated and maintained by a conventional initiation, was confirmed to follow the steady-state kinetics with respect to both R_{p} and PDI. Some RAFT systems suffer rate retardation. A typical cause for the retardation has been experimentally disclosed for a particular RAFT system.

The LRP field is still developing far more powerful and/or comprehensive techniques with wider and/or specific applicability, meeting new ideas such as TERP and RTCP. In this chapter, we have discussed the principles and fundamental aspects of LRP mainly on the basis of kinetic studies. This was because kinetic approaches have proved to provide precise, deep, and systematic understandings of LRP as well as conventional RP. The issues and references herein discussed and cited are by no means comprehensive. For more details on individual LRPs, see the relevant chapters in this volume.

Acknowledgments

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan (Grant-in-Aids 17002007).

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156 Controlled and Living Radical Polymerization – Principles and Fundamentals

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Biographical Sketches



Takeshi Fukuda was born and brought up in Kyoto, the old city that had been the metropolis of Japan for about a thousand years until 140 years ago, and graduated from Kyoto University. Ever since 1973, when he received his doctorate in polymer chemistry from the Graduate School of Kyoto University, except for the following year and a half that he spent as a postdoctoral fellow for Prof. G. Allen at the Physical Chemistry Department of the University of Manchester, UK, he has remained at the Institute for Chemical Research, Kyoto University, as assistant, associate, and full professor until 2007 and as specially appointed professor emeritus until 2010. In earlier times in his academic career, he made physicochemical studies of copolymers, polymer blends, liquid crystals, and gels until his research interest moved to the kinetics of radical polymerization in the early 1980s. His recent work has been exclusively concerned with living/controlled radical polymerization and its kinetics and applications. He is the author or coauthor of about 270 original papers, book chapters, and reviews.



Atsushi Goto was born in 1974 in Aichi, Japan. He received his BS (1996), MS (1998), and PhD (2001) degrees in polymer chemistry from Kyoto University. His doctoral study was on the kinetics of living radical polymerization (LRP) under the direction of Prof. Takeshi Fukuda. He was appointed as an instructor in 2001, an assistant professor in 2002, and an associate professor in 2010 at the Institute for Chemical Research, Kyoto University, in which he has worked with Prof. Takeshi Fukuda, Prof. Yoshinobu Tsujii, and Prof. Hironori Kaji. He was a visiting scientist at the University of Göttingen working with Prof. Michael Buback in 2003 and at the University of Ottawa working with Prof. Juan C. Scaiano in 2006. His research interests include kinetics of LRP, development of new classes of LRP, applications of LRP, and organic electronic devices. He is the author or coauthor of about 80 original papers, book chapters, and reviews.

3.06 Degenerative Transfer with Alkyl lodide

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3.06.1	Introduction	159
3.06.2	Alkyl lodide Transfer Agents Used in Degenerative Transfer Polymerization with Alkyl lodides	160
3.06.2.1	Structures and Synthesis of Alkyl Iodides	160
3.06.3	Mechanism and Kinetics of Degenerative Transfer Polymerization with Alkyl lodide	161
3.06.3.1	Mechanism	161
3.06.3.2	Kinetics	162
3.06.4	Other Related Methods	164
3.06.4.1	Reverse Iodine Transfer Polymerization	164
3.06.4.2	Reversible Chain Transfer Catalyzed Polymerization with Iodo-Compounds	165
3.06.4.3	Single Electron Transfer – Degenerative Transfer Living Radical Polymerization with Iodo-Compounds	165
3.06.4.4	Atom Transfer Radical Polymerization with Iodo-Initiators	166
3.06.5	Monomers Used in Degenerative Transfer Polymerization with Iodo-Compounds	166
3.06.5.1	Halogenated Monomers	166
3.06.5.2	(Meth)Acrylates	168
3.06.5.3	Styrenics	170
3.06.5.4	Vinyl Esters	171
3.06.5.5	Other Monomers	172
3.06.6	Processes	172
3.06.6.1	Bulk and/or Solution Polymerization	172
3.06.6.2	Dispersion Polymerization	172
3.06.6.3	Microemulsion Polymerization	173
3.06.6.4	Miniemulsion Polymerization	173
3.06.6.5	Emulsion Polymerization	173
3.06.6.6	Suspension Polymerization	174
3.06.7	Macromolecular Architectures Prepared by Degenerative Transfer with lodo-Compounds	174
3.06.7.1	Telechelics	174
3.06.7.2	Alternated Copolymers	174
3.06.7.3	Gradient Copolymers	174
3.06.7.4	Block Copolymers	175
3.06.7.5	Graft Copolymers	175
3.06.7.6	Brushes	176
3.06.7.7	Hyperbranched and Star (Co)Polymers	176
3.06.7.8	Stereospecific Reversible-Deactivation Radical Polymerization	176
3.06.8	Applications of Polymers Prepared by Degenerative Transfer with Iodo-Compounds	177
3.06.9	Prospects	177
3.06.10	Conclusions	177
References		177

3.06.1 Introduction

Controlled and living radical polymerization (C&LRP), or reversible-deactivation radical polymerization as recommended by IUPAC,¹ is an area of research that has been growing very fast in the last 15 years.² It is now becoming a basic of the polymer chemists' tool box, opening a new avenue toward the very exciting field of macromolecular engineering and nanotechnology. Among the different C&LRP techniques that have been developed so far, degenerative transfer (DT) with alkyl iodide is one of the very oldest ones. It was pioneered by Tatemoto³ in the late 1970s for the preparation of curable iodo functional fluoroelastomer as well as the preparation of fluorinated thermoplastic elastomers, under the name of iodine transfer polymerization (ITP). Besides Tatemoto's work, little attention was paid to the ITP process at this time and the other studies with halogenated monomers were presented more as a telomerization,⁴ that is, the emphasis was not put on the reversible-deactivation radical process. Nevertheless, stepwise telomerization, that is, the use of the produced telomer as a transfer agent by itself, was consistent with a reversible-deactivation process.⁵ The ITP was rationalized in more detail as DT with alkyl iodide by Gaynor *et al.*⁶ in 1995 in the case of polymerization of nonfluorinated monomers: styrene and butyl acrylate. Then, in 1998 Goto *et al.*⁷ shed light on the kinetics of iodide-mediated polymerization in the case of styrene. Since then, the DT with alkyl iodide and other related C&LRP techniques based on iodo-compounds have smoothly but continuously progressed in academia and also in industry.⁸

3.06.2 Alkyl lodide Transfer Agents Used in Degenerative Transfer Polymerization with Alkyl lodides

3.06.2.1 Structures and Synthesis of Alkyl lodides

The structure of the iodinated transfer agent R-I, that is, the nature of the substituents in $R^1R^2R^3C$ -I, is obviously important since it will determine its reactivity in radical polymerization. The weaker bond energy of the carbon–iodine bond (52 kcal mol⁻¹, 2.16 Å, in CH₃-I) compared to the carbon–bromine (65 kcal mol⁻¹, 1.97 Å) and carbon–chlorine (78 kcal mol⁻¹, 1.79 Å) is favorable for the formation of the active radical species.^{4,9–11}

The polar and steric effects on the bond dissociation energy have been investigated, and several reports can help chemists to select and/or design the proper structure for the iodinated transfer agent.^{2,12–15}

To ensure that the reactivity of R-I is well suited to the polymerization of a given monomer, one usual way is to use a transfer agent that mimics the propagation chain end (e.g., 1-phenyl ethyl iodide will be typically used for the polymerization of styrene). Homolytic bond dissociation energy has been computed for several model systems: $CH_3C(CN)(CH_3)$ -I (AN-I) (41.2 kcal mol⁻¹), $CH_3C(CH_3)(CO_2Me)$ -I (MMA-I) (39.9 kcal mol⁻¹), CH_3CHPh -I (S-I) (42.6 kcal mol⁻¹), $CH_3CH(CO_2Me)$ -I (MA-I) (49.2 kcal mol⁻¹), CH_3CHCI -I (VC-I) (49.2 kcal mol⁻¹),

and CH₃CH(OAc)-I (VAc-I) (51.4 kcal mol⁻¹).¹⁴ The R-I should be reactive enough in the transfer step; this implies a labile enough C-I bond and the stabilization of the resulting R[•] radical through inductive or resonance effects. The following decreasing order of reactivity can be proposed based on the Rⁱ substituents (in $R^1R^2R^3C$ -I): $CN \sim CO_2R > Br \sim Cl > F > CH_3 > H$.⁴ Moreover, the steric effect gives the following decreasing order of reactivity of the R-I transfer agent: tertiary > secondary > primary. Another important point is the ability of the expelled R[•] radical to reinitiate the polymerization. Thus, it may be necessary to find a compromise between the stabilization of R[•] (good leaving group) and its reactivity in radical addition (good ability to reinitiate the polymerization). Typical alkyl iodides that have been tested in DT are summarized in Scheme 1 (some of them are poorly effective due to too strong carbon-iodine bond strength and/or poor reactivity of the resulting radical). They have been synthesized by three main routes: the addition of hydroiodic acid (HI) onto vinyl monomers, the addition of iodine monochloride (ICl) onto fluoroalkenes, and nucleophilic substitutions.

The addition of HI onto vinyl monomers $CH_2=CR^1R^2$ has successfully led to the formation of the corresponding monoadduct $CH_3CR^1R^2I$. For instance, this was applied to styrene (Sty), methylmethacrylate (MMA), ethyl acrylate (EA), vinyl acetate (VAc), vinyl chloride (VC), and vinylidene fluoride (VDF). One typical reaction is given in Scheme 2.¹⁶



Fluorinated transfer agents

CF₃I *i*C₃F₇I C₆F₁₃I I(C₂F₄)_nI

Scheme 1 Some alkyl iodides tested in DT polymerization.





$$I-CI + F_2C = CF \longrightarrow IF_2C - CFCI (40\%) + IFC - CF_2CI (60\%)$$

$$CF_3 CF_3 CF_3 CF_3 CF_3$$

$$I-CI + F_2C = CH_2 \longrightarrow IF_2C - CH_2CI (0-1\%) + IH_2C - CF_2CI (99-100\%)$$

Scheme 3 Synthesis of iodofluoroalkyls by reaction of ICI with fluoroalkenes.

The reactivity of ICl with various fluoroalkenes has been studied, leading to several regioisomers of the monoadducts in the case of asymmetric alkenes. For instance, the addition of ICl led to a mixture of products in the case of hexafluoropropene (HFP), whereas almost one pure isomer ICH₂CF₂Cl was formed in the case of VDF (Scheme 3).^{17,18} The following order of reactivity of ICl with fluoroalkenes was suggested: chlorotrifluorotoluene (CTFE) > trifluoroethylene (TrFE) > VDF > CF₂=CCl₂ > HFP.

The nucleophilic substitution of chloroor bromo-precursors (Finkelstein reaction, i.e., bimolecular nucleophilic substitution reaction (SN₂)) has also been performed to prepare alkyl iodides such as methyl-2-iodopropionate, vinyl iodoacetate, and 1-phenyl ethyl iodide. For instance, the reaction of methvl-2-bromopropionate with sodium iodide (NaI) in acetone led to the targeted iodo-compound (Scheme 4).¹⁹ This route cannot be applied to $R_f X$ (X = Cl, Br, $R_f = R-CF_2$ -) due to the strong electron-withdrawing effect of the fluorine atom.²⁰ It might also be disfavored for tertiary R-X compounds bearing a labile atom in beta position due to the possible competition with the elimination reaction (e.g., HX elimination).

Finally, the synthesis of iodinated chain transfer agents (CTAs) through the reaction of radicals with molecular iodine as a radical scavenger will be presented in Section 3.06.4.1.

One difficulty in handling alkyl iodides is their instability upon storage due to their rather high sensitivity to rays (e.g., UV light), heat, moisture, nucleophiles, and bases. Thus, special attention must be paid to purify them prior to use.

3.06.3 Mechanism and Kinetics of Degenerative Transfer Polymerization with Alkyl lodide

3.06.3.1 Mechanism

The general principle of the methods reported so far relies on a reversible activation–deactivation process between dormant chains (or capped chains) and active chains (or propagating radicals), with rate constants k_{act} and k_{deact} respectively (Scheme 5).^{2,21} Two main mechanisms of activation–deactivation can be involved in C&LRP, sometimes concomitantly: reversible termination (i.e., dissociation–combination cycles) and reversible transfer. The overall reaction of DT polymerization with alkyl iodide (R-I) is depicted in Scheme 6. Written in this form, it is formally equivalent to telomerization.^{4,5} However, the mechanism of DT polymerization



Scheme 4 Synthesis of methyl-2-iodopropionate by nucleophilic substitution with Nal.



Scheme 5 General scheme of reversible-deactivation radical polymerization.



Scheme 6 Overall reaction of DT polymerization with alkyl iodide.

involves the new DT key reaction (Scheme 7d), which enables the control and the livingness of the polymerization (Scheme 7).

In Scheme 7, the radical A[•] produced by decomposition of the initiator in step (a) adds to monomer M and the resulting radical propagates (steps (b) and (f)). The transfer reaction between the propagating radical P_n^{\bullet} and the transfer agent R-I, in step (c), results in the formation of dormant chains P_n -I and the formation of a new initiating radical R[•]. The difference in the stability of reactants and products in the reversible step (c) will cause a shift of the equilibrium $(K_{(c)} = k_{tr1}/k_{-tr1})$ to the right if $K_{(c)} > 1$ or to the left if $K_{(c)} < 1$. When the structure of R[•] mimics that of the propagating radical P_n^{\bullet} , it results in a nearly thermodynamically neutral transfer step ($K_{(c)} = 1$). Activated transfer agents ($K_{(c)} > 1$) are preferred in order to create the dormant polymer chains early in the process. Poor transfer agents would cause a slow generation of new polymer chains all along the process, broadening the molecular weight distribution (i.e., a lower control of the molecular weight). The radical R[•] must be able to reinitiate the polymerization by adding to monomer M and the resulting radical propagates (steps (e) and (f)) (otherwise degradative chain transfer would occur resulting in retardation and so forth). The exchange process in step (d) is thermodynamically neutral since both reactants and products have the same structure (i.e., $k_{ex} = k_{-ex}$: it is the so-called DT reaction where $K_{(d)}$ = 1). Termination still occurs during the polymerization (step (g)); therefore, minimizing termination will be important to keep a good control of the polymerization. In DT, the concentration of the polymer chains is equal to the sum of the concentration of the consumed transfer agent and of the consumed initiator. Thus the contribution of the termination is lowered under appropriate conditions, that is, low concentration of consumed initiator.

In first approximation (assuming a complete consumption of the transfer agent), the theoretical targeted number-average degree of polymerization at 100% monomer conversion can be Initiator decomposition:

(a)
$$A_2 \longrightarrow 2A$$

Initiation:

(b)
$$A^* + nM \longrightarrow A^*M_n^* (P_n^*)$$

Transfer reactions:

(c)
$$P_n + R - I \longrightarrow P_n - I + R' + k_{tr1} >> k_{tr1} >$$

(d)
$$P_m + P_n = 1$$
 \longrightarrow $P_m = 1 + P_n \cdot k_{ex} = k_{-ex}$

Reinitiation:

(e)
$$R^{*} + nM \longrightarrow R - M_{n}^{*} (P_{n}^{*})$$

Propagation:

(f)
$$P_m + nM \longrightarrow P_{m+n}$$

Termination reactions:

(g)
$$P_m' + P_n' (\text{or } A' \text{ or } R') \longrightarrow P_{n+m} \text{ or } P_n = + P_m H$$

Dead chains

Scheme 7 Mechanism of DT polymerization with alkyl iodide.

determined by eqn [1], where $[M]_0$ is the initial monomer concentration, $[R-I]_0$ is the initial transfer agent concentration.⁸

$$DP_{n,targeted} = [M]_0 / [R-I]_0$$
[1]

In addition, in first approximation, the theoretical polydispersity index (PDI = M_w/M_n) at 100% monomer (2 can be determined by eqn [2], where $C_{ex} = k_{ex}/k_p$ is the exchange constant between active and dormant chains).²¹

$$PDI=1+1/DP_{n,targeted}+1/C_{ex}=1+[R-I]_0/[M]_0+1/C_{ex}$$
 [2]

Hence, provided that the dormant chains are formed early during the polymerization (i.e., chain transfer to R-I is faster than propagation, corresponding to a chain transfer constant $C_{tr1} = k_{tr1}/k_p$ higher than 1), the molecular weight of the polymer chains is controlled by the concentration of the transfer agent [R-I]₀, while the molecular weight distribution is controlled by the degenerative chain transfer constant C_{ex} between dormant and active chains (the higher the C_{ex} value, the smaller the kinetic chain length during each activation–deactivation cycle and the narrower the molecular weight distribution).

It is noteworthy that, this mechanism can be modified by using high temperature and/or irradiation (such as UV light), because in that case the labile C–I bond in R-I (respectively P-I) can be cleaved to give R[•] (respectively P[•]) and I[•] radicals. However, in that case, the polymerization would be quickly inhibited unless appropriate conditions are chosen to get rid of the molecular iodine (I₂) (formed by recombination of I[•] radicals, resembling in this respect the persistent radical effect).^{22,23}

3.06.3.2 Kinetics

In DT polymerization with alkyl iodides, the kinetics of the polymerization is the same as in conventional polymerization (stationary state given by eqn [3], where k_t refers to the IUPAC recommended notation (eqn [4])) because the concentration of the radical is not affected by the transfer reaction (except when degradative reaction occurs, i.e., when R[•] does not efficiently reinitiate the polymerization).

$$[\mathbf{P}^{\bullet}] = (R_{\rm i}/(2k_{\rm t}))^{1/2}$$
[3]

$$R_{\rm t} = 2k_{\rm t} \times \left[\mathrm{P}^{\bullet}\right]^2 \tag{4}$$

Thus, the rate of polymerization is given by eqn [5], leading to the first-order evolution of $\ln([M]_0/[M])$ versus time (eqn [6]). A more accurate equation (eqn [7]) as proposed by Van Hook and Tobolsky²⁴ can be used to take into account the time dependency of R_i .

$$R_{\rm p} = k_{\rm p}[{\rm M}][{\rm P}^{\bullet}] = k_{\rm p}[{\rm M}](R_{\rm i}/2k_{\rm t})^{1/2}$$
[5]

$$\ln([M]_0/[M]) = k_p (R_i/(2k_t))^{1/2} \times t$$
[6]

$$\ln([M]_0/[M]) = 2k_p((f[initiator]_0)/(k_d k_t))^{1/2} \\ \times (1 - \exp(-k_d \times t/2))$$
[7]

In first approximation, the consumption of the transfer agent R-I is basically determined by its transfer constant $C_{tr1} = k_{tr1}/k_{pr}$, as in conventional telomerization (assuming a low reverse rate reaction $R_{-tr1} = k_{-tr1}[P_n-I][R^{\bullet}]$ as well as a negligible rate of self-dissociation $R_{d,R-I} = k_{d,R-I}[R-I]$ upon heating or irradiation). Several methods have been used to assess C_{tr1} . The method of Mayo²⁵ is based on the determination of the number-average degree of polymerization DP_{n,0} (i.e., molecular weight analysis and/or chain-ends analysis) at low monomer conversion, assuming a low contribution of initiator-derived chains (i.e., $[A-(M)_n-I] << [R-(M)_n-I])$ (eqn [8]). It was used for instance by Lansalot *et al.*²⁶ to determine $C_{tr1} = 1.4$ for the transfer agent C_6F_{13} -I in the bulk polymerization of styrene at 70 °C with α,α -azobis (isobutyronitrile) (AIBN) initiator.

$$C_{\rm trl} = [M]_0 / (DP_{\rm n,0} \times [R-I]_0)$$
 [8]

The alternative method of Bauduin *et al.*²⁷ based on the evolution of DP_n with monomer conversion *p* has also been used (eqn [9]). (This method holds for low values of C_{tr1} , typically $C_{tr1} < 1$; for $C_{tr1} \gg 1$, the DP_n value approaches DP_n = [M]₀×*p*/[CTA]₀ from low monomer conversion and therefore this method is not suited to calculate C_{tr1} in this case.) For instance, Teodorescu²⁸ applied this method to determine $C_{tr1} = 0.46$ for the transfer agent vinyliodoacetate (CH₂=CHOC(O)CH₂-I) in the solution polymerization of styrene in benzene at 60 °C with AIBN initiator.

$$C_{\rm trl} = \ln(1 - (p[M]_0 / ([R-I]_0 DP_n)) / (\ln(1-p))$$
[9]

The method of O'Brien and Gornick²⁹ is based on the evolution of conversions, applying eqn [10] where *p* and *q* are the conversions of monomer and transfer agent, respectively. It was, for instance, used by Boyer *et al.*³⁰ to determine $C_{tr1} = 7.4$ for the transfer agent C₆F₁₃CH₂CF₂-I in the solution polymerization of VDF in 1,1,1,3,3-pentafluorobutane at 75 °C initiated by *tert*-butylperoxypivalate.

$$C_{ttl} = \ln([R-I]_0/[R-I])/\ln([M]_0/[M]) = \ln(1-q)/\ln(1-p)$$
[10]

The exchange constant between active and dormant chains is given by $C_{\text{ex}} = k_{\text{ex}}/k_{\text{p}}$. It determines the average lifetime τ of propagating radicals given by eqn [11], leading to the average number of monomer units (ν) added during each activation-deactivation cycle given by eqn [12] (characteristic time for activation of P-I is given by $\theta = 1/(k_{\text{ex}}[\mathbf{P}^{\bullet}])$).

$$\tau = [\mathbf{P}^{\bullet}]/R_{\text{deact}} = [\mathbf{P}^{\bullet}]/(k_{\text{ex}}[\mathbf{P}\text{-}\mathbf{I}][\mathbf{P}^{\bullet}] + k_{\text{t}}[\mathbf{P}^{\bullet}]^2) \cong 1/(k_{\text{ex}}[\mathbf{P}\text{-}\mathbf{I}]) \quad [11]$$

$$\mathbf{v} = k_{\rm p}[\mathbf{M}]\mathbf{\tau}$$
 [12

The experimental value of C_{ex} can be determined in the same way as C_{tr1} provided that a degenerative macromolecular transfer agent P₀-I is used instead of R-I.

Thus, by using eqn [13], Lacroix-Desmazes *et al.*³¹ assessed $C_{\text{ex}} = 2.2$ for poly(methyl acrylate)-I at 70 °C.

$$C_{\text{ex}} = [M]_{0} / (DP_{n,0} \times [P_{0} - I]_{0})$$
[13]

Goto *et al.*⁷ and Goto and Fukuda²¹ employed eqn [14], where *p* and *q* are the conversion of monomer and macrotransfer agent, respectively, to determine C_{ex} = 3.6 in the case of polystyrene-I (PS-I) at 80 °C.

$$C_{\text{ex}} = \ln([P_0 - I]_0 / [P_0 - I]) / \ln[M](_0 / [M]) = \ln(1 - q) / \ln(1 - p)$$
[14]

Goto and co-workers^{7,21,32} have also developed an alternative method based on the analysis of the evolution of polydispersities at an early stage of polymerization. The polymer is defined as an A-B diblock copolymer, A referring to P₀-I and B referring to the incremental part of the molecule. The procedure is based on eqns [15] and [16], where $Y = (x_w/x_n) - 1$, $Y_K = (x_{w/K}/x_{n/K}) - 1$, $w_A = 1 - w_B = x_{n,A}/x_n$, $x_n = x_{n,A} + x_{n,B}$, and x_n and x_w are the number- and weight-average degrees of polymerization with K = A or B:

$$Y = w_{\rm A}^2 Y_{\rm A} + W_{\rm B}^2 Y_{\rm B}$$
 [15]

$$[Y_{\rm B} - (1/x_{\rm n,B})]^{-1} = C_{\rm ex}[p/(2-p)]$$
[16]

The results of Goto *et al.* were similar when they used the peak resolution analysis to follow the consumption of macro-transfer agent (eqn [14]) or the polydispersity analysis (eqn [16]).

The values of C_{tr1} and C_{ex} have an influence on the evolution of the molecular weight and the PDI of the polymer chains.

The number-average molecular weight is given by eqn [17], where *p* is the fractional monomer conversion, $[M]_0$ is the initial monomer concentration, M_{monomer} is the molecular weight of the monomer, *q* is the transfer agent conversion, [CTA]₀ is the initial concentration of the transfer agent, *a* is the mode of termination (1 for termination by combination, 2 for termination by disproportionation), *f* is the initiator efficiency, $[In]_0$ is the initial initiator concentration, and $[In]_p$ is the initiator concentration at *p*:

$$M_{\rm n} = (p[M_0M_{\rm monomer})/((q[{\rm CTA}]_0) + af([{\rm In}]_0 - [{\rm In}]_p)) \quad [17]$$

Combining eqns [10] and [17] gives eqn [18], indicating the effect of C_{tr1} on the evolution of M_n (C_{ex} has no effect on M_n since degenerative chain transfer does not change the number of polymer chains).

$$M_{n} = (p[M]_{0}M_{monomer}/)(([CTA]_{0}(1-(1-p)^{C_{rd}})) + af([In]_{0}-[In]_{p}))$$
[18]

The latter equation can be simplified if the contribution of the initiator is neglected (eqn [19]):

$$M_{\rm n} = (p[{\rm M}]_0 M_{\rm monomer} / ([{\rm CTA}]_0 (1 - (1 - p)^{C_{\rm trl}}))$$
[19]

Figure 1 illustrates the effect of C_{tr1} on the evolution of the molecular weights with monomer conversion. For low $C_{tr1} < 1$, the continuous generation of polymer chains leads to a decrease of M_n with conversion. For $C_{tr1} > 1$, at low monomer conversion, the upward deviation of M_n in comparison to the ideal linear behavior vanishes when the value of C_{tr1} increases.

The evolution of the PDI $(=M_w/M_n)$ is more complicated since it would require to take into account all the events of the polymerization. This can be performed by using a numerical simulation (such as PREDICI).^{33,34} Nevertheless, some attempts have been made to obtain some analytical equations in simplified cases. These analytical equations are useful to show the trends. For instance, Müller *et al.*³⁵ studied the particular case of $C_{tr1} = C_{ex}$ and neglected radical termination to obtain eqn [20].

PDI =
$$(1 + ([M]_0/[CTA]_0)(2 + (2-p)(1-C_{ex})/C_{ex}))/(p[M]_0/([CTA]_0(1-(1-p)^{C_{ex}})))$$
 [20]



Figure 1 Evolution of molecular weight M_n with monomer conversion for different values of C_{tr1} according to the equation $M_n = (p[M]_0 M_{monomer})/([CTA]_0 (1-(1-p)^{Cr1}))$ (conditions: $[M]_0/[CTA]_0 = 200$, $M_{monomer} = 100$ g mol⁻¹).



Figure 2 Evolution of PDI with monomer conversion for different values of C_{ex} according to the equation PDI = $(1 + ([M]_0/[CTA]_0)(2 + (2 - p)(1 - C_{ex})/(C_{ex}))/(p[M]_0/([CTA]_0)(1 - (1 - p)^{C_{ex}})))$ (conditions: $[M]_0/[CTA]_0 = 200$).

Goto and Fukuda²¹ derived a similar relationship where the theoretical PDI can be assessed by eqn [21].

$$PDI=1 + 1/DP_n + (2-p)/(p \times C_{ex})$$
 [21]

Figure 2 illustrates the effect of C_{ex} on the evolution of PDI with monomer conversion. It shows that PDI lower than 1.4 can be attained at high conversion for $C_{ex} > 3$. This is in agreement with the values of polydispersity of PS samples obtained by ITP or reverse iodine transfer polymerization (RITP) (see Section 3.06.4.1).^{7,36}

3.06.4 Other Related Methods

3.06.4.1 Reverse Iodine Transfer Polymerization

One limitation of ITP is that it requires the use of molecular iodinated transfer agents, which are usually rather unstable due to the weak C–I bond and thus prone to alteration upon storage. To overcome this limitation, Lacroix-Desmazes *et al.*^{31,37,38} have proposed a new method called RITP. RITP relies on the use of molecular iodine I₂ to synthesize *in situ* the iodinated transfer agents. Molecular iodine I₂ is known to be a very powerful inhibitor of polymerization. Indeed, it reacts very quickly with the radicals produced by the initiator. Thus, the simplified mechanism of RITP can be distinguished into two periods (Scheme 8).

In the first induction or inhibition period, the radicals react with molecular iodine to form an A-I adduct or propagate with a few monomer units before reacting with iodine to form short A-M_n-I oligomers. The monomer conversion in this first induction period usually remains very low. This first period lasts until essentially all iodine has been consumed, the corresponding time being assessed by eqn [22] (where *f* is the efficiency of the initiator and k_d is its rate constant of dissociation). This induction period can be significantly shortened by increasing the temperature (i.e., higher k_d) and/or the initiator concentration.

$$t_{\text{inhibition, theo.}} = -\ln(1 - [I_2]_0 / (f \times [\text{initiator}]_0)) / k_d \qquad [22]$$

Once almost all iodine has been consumed, the second period takes place where the polymerization proceeds, governed by degenerative chain transfer. Since one molecule of I_2 is able to control two polymer chains, the targeted molecular weight is given by eqn [23].

$$M_{n,theoretical} = (mass of monomer) \times conversion/2(\times(moles of I_2)) + M_{A-1}$$
[23]

RITP of acrylates typically follows these trends.^{31,39} Other behaviors can be encountered: for instance, high monomer conversion can be reached during the induction period⁴⁰ and other reactions such as complexation with iodine can be involved in the process.⁴¹ RITP has been successfully applied



Scheme 8 Simplified mechanism of RITP. (A^{*}, radical from the initiator; I_2 , molecular iodine; M, monomer unit; *n*, mean number degree of polymerization; k_{ex} degenerative chain transfer rate constant; k_0 , propagation rate constant).

to a wide range of monomers including acrylates, ^{31,39} methacrylates (not controlled by regular ITP),⁴² styrenics, ^{37,41} α -fluoroacrylates, ³⁷ VAc, ^{43,44} and vinylidene halides. ^{37,45}

3.06.4.2 Reversible Chain Transfer Catalyzed Polymerization with Iodo-Compounds

Another limitation of ITP is that the rate of exchange between dormant and active chains is rather slow in comparison with other reversible-deactivation radical polymerization methods (for instance, $C_{ex} = 3.6$ for ITP of styrene, whereas $C_{ex} = 180$ for RAFT of styrene at 80 °C).²¹ According to eqn [21], it implies that the PDI of polymers obtained by ITP is rather high (it is actually typically in the range of 1.2-1.6 for PS, 1.2-1.6 for poly(MMA), and 1.7-2.1 for poly(butyl acrylate) obtained by RITP in bulk at 80 °C). To address this limitation, Goto et al.⁴⁶⁻⁵⁴ proposed a new technique of polymerization called reversible chain transfer catalyzed polymerization (RTCP) with iodo-compounds. This technique is based on the use of activators G[•] produced in situ by reaction of compounds G-Z with radicals (Scheme 9). The G-Z compounds that were investigated include PI₃ and alkyl phosphites (P catalysts), germanium tetraiodide (GeI₄) and *p*-tolyl germanium triiodide (tolyl-GeI₃) (Ge catalysts), N-iodosuccinimide and succinimide (NIS) (N catalysts), SnI4 (Sn catalysts), and thymol iodide and 2,4,6-trimethyl phenol (O catalysts). The G-I compound either formed in situ or was directly added in the medium (in the case where Z = I) acts as a deactivator.

By this way, the number of activation–deactivation cycles is increased, leading to a lower PDI given by eqn [24].^{54,55}

$$PDI = 1 + 1/DP_n + (2-p)/(p \times (C_{ex} + C_{da}(G[-I]/[P-I])))$$
[24]

PS, poly(MMA), poly(glycidyl methacrylate), and poly (2-hydroxyethylmethacrylate) were obtained with a low polydispersity (PDI in the range of 1.1-1.3) and a predicted molecular weight. The catalysts can be used in small amounts (1-10 mM) and are active under relatively mild conditions (60–100 °C). Kinetic studies reported high values of k_a and k_{da} . ^{54,55} For instance, in the polymerization of styrene initiated at 80 °C by benzoyl peroxide in the presence of PS-I macrotransfer agent and GeI₄ catalyst, $k_a \cong 10^6 \,\mathrm{M}^{-1} \,\mathrm{s}^{-1}$, $k_{\rm da} = 9 \times 10^5 \,{\rm M}^{-1} \,{\rm s}^{-1}$, and $k_{\rm ex} = 0.024 \times 10^5 \,{\rm M}^{-1} \,{\rm s}^{-1}$.⁵⁴ The catalyst activity depends on monomers and the elements and substituents of the catalysts. For styrene polymerization at 80 °C, the catalyst activity follows the order PI3 < tolyl-GeI₃ < NIS < SnI₄ < GeI₄. Rate retardation is noticed in all cases and has been ascribed to the cross-termination between P[•] and G[•]. To counterbalance the depletion of the catalyst during the polymerization due to cross-termination, guidelines for





obtaining high-molecular-weight material via repeated addition of catalyst were developed.⁵⁵

Interestingly, it is possible to combine RTCP with RITP to obtain polymers in a more practical manner. Thus, low-polydispersity poly(MMA) (PDI \cong 1.2–1.4) has been prepared by RITP in the presence of nitrogen and phosphorus catalysts, enhancing the utility of RTCP.⁵⁶ However, the real benefit of RTCP/RTIP is still to be clearly demonstrated since low-polydispersity PMMA polymers are already reached by RITP alone.

3.06.4.3 Single Electron Transfer – Degenerative Transfer Living Radical Polymerization with Iodo-Compounds

In their studies to control the polymerization of VC, a monomer that is difficult to polymerize in a controlled manner due to the predominance of chain transfer to monomer, Rosen and Percec⁵⁷ have developed a polymerization technique based on single electron transfer (SET). SET allows production of radicals by reaction between an electron acceptor R-X and an electron donor (reducing agent) (Scheme 10). 14,58 The case where X = I falls in the scope of this review since DT of alkyl iodides can then operate. CHI₃, CH₂I₂, and CH₃CHClI have been used as the source of radicals. Several reducing agents have been tested. Copper in its lower oxidation state, Cu⁰, has been used in most cases in combination with ligands such as tris(2-aminoethyl) amine (TREN). It can be produced *in situ*, together with Cu^{II}, by disproportionation of Cu^I in polar media (Scheme 11).¹⁴ Metal-free systems have also been proposed with sodium dithionite (Na₂S₂O₄) or thioureadioxide [(NH₂)₂C=SO₂] as electron donor (Scheme 12).⁵⁹⁻⁶¹ Electron transfer cocatalysts such as 1,1'-dialkyl-4,4'-bipyridinium dihalides or alkyl viologens are sometimes required and accelerate the polymerization.⁶² To favor the SET process, the polymerization is usually performed in polar media such as H₂O (often heterogeneous polymerization), protic solvents (MeOH, EtOH, ethylene glycol, diethylene glycol, triethylene glycol, 2-(2-ethoxyethoxy)ethanol, tetraethylene glycol, glycerin, 2-hydroxyethyl methacrylate (HEMA), phenols), dipolar aprotic solvents (dimethyl sulfoxide (DMSO), dimethylformamide (DMF), dimethylacetamide (DMAc), n-methylpyrrolidone (NMP), etc.), and ionic liquids, at room temperature.⁶³ The mechanism of single electron transfer - degenerative transfer living radical polymerization (SET-DTLRP) is complex since it involves many compounds that may react in competing reactions. In metal-based systems, the authors reported that under suitable conditions the DT part of the SET-DTLRP can be eliminated since activation and deactivation steps are expected to be faster than chain transfer to initiators R-I and/or dormant species P-I, and the newly elaborated living radical polymerization becomes SET-LRP.⁶³ Vana and Goto⁵⁵ reported the same in RTCP where the influence of degenerative chain transfer, which occurs without the involvement of catalyst, was found to have a significant impact on the process only in poorly controlled systems, but was only very small in the case of well-controlled RTCP.

$$R-I \xrightarrow{+ e^{-}} [R----I]^{\bullet-} \longrightarrow R^{\bullet} + I^{-}$$

Scheme 10 SET reaction.



Scheme 11 Mechanism of SET-DTLRP with copper-based catalysts and iodo-compounds.

$$\begin{array}{c|cccc} Water & 2Na^{+} + S_2O_4^{2-} \\ S_2O_4^{2-} & \underbrace{Interface} & 2SO_2^{-} \\ R-I + SO_2^{-} & \underbrace{SET} & R' + I^{-} + SO_2 \\ P-I + SO_2^{-} & \underbrace{SET} & P' + I^{-} + SO_2 \end{array}$$

Scheme 12 SET from iodo-compounds with sodium dithionite as electron donor.

3.06.4.4 Atom Transfer Radical Polymerization with lodo-Initiators

Atom transfer radical polymerization (ATRP) or transition metal-catalyzed controlled radical polymerization is one of the leading techniques of controlled radical polymerization.^{64,65} It is based on the use of initiators such as alkyl halides (R-X) in combination with organometallic complexes, and the kinetics of the polymerization relies on the persistent radical effect (Scheme 13).^{21,22,66} It has been shown that alkyl iodides can be used in copper-mediated ATRP of acrylates and that they lead to controlled polymerization of styrene in ruthenium- and rhenium-based ATRP.^{65,67} In those systems with R-I initiators, degenerative chain transfer also takes place. Matyjaszewski et al. usually avoided using iodides because they require special precautions: they are light sensitive, can form metal iodide complexes with unusual reactivity (such as the thermodynamically unstable CuI₂), the R-I bond may undergo heterolytic cleavage, and iodine-based systems may redox initiate polymerization.^{67,68} Nevertheless, these authors tested OsCl₂(PPh₃)₃ as an ATRP catalyst to be used with alkyl iodide initiators for the polymerization of styrene and (meth) acrylates, the iodophilicity of this complex being studied by proton nuclear magnetic resonance (¹H-NMR) exchange experiments.⁶⁹ In contrast, Percec et al. took advantage of the





rich reactivity of iodo-compounds to develop the SET-DTLRP process as shown above and Sawamoto *et al.*^{65,70} extensively used iodo-compounds in iron-, rhenium-, and ruthenium-based polymerization systems. Other interplay of different control mechanisms such as metal-stabilized stable free-radical polymerization (with Ti^{III}, Mo^{III}, Os^{II}, and Co^{II}) where a carbon-metal bond is formed may complicate the mechanism in some cases.⁷¹⁻⁷⁴

3.06.5 Monomers Used in Degenerative Transfer Polymerization with Iodo-Compounds

3.06.5.1 Halogenated Monomers

ITP of fluorinated olefins was pioneered by Tatemoto³ in the late 1970s and several other teams have been active on fluoromonomers.^{20,75–78} Most studies dealt with the copolymerization of tetrafluoroethylene or VDF and HFP in the presence of fluorinated alkyl iodides (C_nF_{2n+1} -I) as transfer agents. Fluorinated vinyl ethers have also been incorporated as comonomers in copolymerization with tetrafluoroethylene. A detailed review is available on these fluoropolymers.⁷⁹

The polymerization of VDF in the presence of alkyl iodides has been particularly studied. It has been shown that the defects in polyvinylidene fluoride (PVDF) chaining, due to reverse (head-to-head) addition, were prejudicial for the control of the polymerization. Indeed, a model study was performed with C₆F₁₃-I, C₆F₁₃CH₂CF₂-I, and HCF₂CF₂CH₂-I transfer agents. The Ctr1 values of C6F13-I and C6F13CH2CF2-I were close (i.e., 7.9 and 7.4 at 75 °C, respectively) whereas that of HCF₂CF₂CH₂-I was lower (0.3 at 75 °C). Thus, in the polymerization of VDF, head-to-head addition leads to -CH2CF2CF2CH2-I chain ends, which are poor transfer agents. Polymer chains with -CF2CH2-I chain ends consequently accumulate in the reaction medium along the course of the polymerization, and the molecular weight distribution broadens. A good agreement with a targeted degree of polymerization of DPn < 30 together with a PDI of about 1.3-1.5 could be obtained with either C6F13-I or C6F13CH2CF2-I (Scheme 14a). These results highlight that a proper selection of the transfer agent is necessary to obtain well-controlled PVDF oligomers and that, due to reverse addition of the monomer units, the control of the polymerization becomes tricky when the degree of polymerization increases.³⁰



Scheme 14 Typical examples of polymerization of halogenated monomers with iodo-compounds.

It must be noted here that, contrary to the general belief, ITP is not the only reversible-deactivation radical polymerization method to control the polymerization of fluorinated olefins. Indeed, it has been shown that poly(VDF-*co*-HFP) could be obtained with a good control of molecular weight by RAFT with α -(*O*-ethylxanthyl)methyl propionate as control agent.^{45,80}

The better understanding of the ITP of fluorinated olefins has allowed synthesis of terpolymers of VDF, HFP, and 1,1,2-trifluoro-2-pentafluorosulfanylethylene with a good control of molecular weight.⁸¹

The second class of halogenated monomers studied in DT with alkyl iodides deals with chlorinated monomers and especially VC (CH₂=CHCl) and vinylidene chloride (CH₂=CCl₂).

The aim of the preliminary studies was to reduce the molecular weight of poly(vinyl chloride) (PVC) and involved compounds such as iodoform (CHI₃) and 2-iodopropane ((CH₃)₂CHI) as traditional transfer agents without mentioning the potentially controlled nature of the polymerization.^{82,83} Later on, Bak et al.^{84,85} and Wang et al.⁸⁶ claimed the controlled polymerization of VC using compounds such as 1-chloro-1iodoethane (CH₃CHClI). However, the case of VC is particularly difficult because, in contrast to styrenics and (meth) acrylics, it is a nonactivated monomer and, additionally, its polymerization exhibits a high transfer to monomer. Recently, Percec et al. proposed a new catalyzed process to control the polymerization of VC. Systems based on the presence of metals in their zerovalent oxidation state, like I-CH₂-Ph-CH₂-I/Cu⁰/bpy (where bpy = 2,2'-bipyridyl) at 130 °C in ortho-dichlorobenzene, were first attempted to

control the polymerization of VC.87 However, because the persistent radical effect could not operate effectively due to the high chain transfer to monomer, the Cu⁰ catalyzed the radical polymerization of VC up to 40% at most. The method was then improved by using Cu^I (e.g., Cu₂O) complexes with TREN or poly(ethylenimine) as ligands in an aqueous reaction medium (Scheme 14b), allowing the *in situ* generation of Cu⁰ and Cu^{II} species by disproportionation of Cu^{I,88} Initiation from CHI3 as well as reactivation of dormant chains -CH₂CHClI takes place at low temperature by Cu⁰ donor, thanks to the SET mechanism depicted in Section 3.06.4.3.58 The SET-initiated polymerization of VC involving DT could also be achieved in the absence of transition metal, by using sodium dithionite or thiourea dioxide as catalyst, with iodoform as initiator and sodium hydrogenocarbonate as buffer.^{59,60} Iodoform acts as a difunctional initiator yielding a telechelic diiodo PVC whose chain ends can be further modified to introduce new functional end groups such as hydroxyls.⁸⁹ Electron transfer cocatalysts and phase transfer catalysts were tested to accelerate the SET-DTLRP of VC.60,62,90 Finally, PVC with molecular weight up to 200 000 g mol⁻¹ and PDI = 1.70 could be obtained by SET-DTLRP of VC with CHI₃ and sodium dithionite at 25 °C.91

There is less literature on the polymerization of vinylidene chloride. Lacroix-Desmazes *et al.*³³ have reported the successful controlled copolymerization of vinylidene chloride and methyl acrylate (80/20 feed molar ratio) with AIBN as initiator and 1-phenylethyliodide as transfer agent (Scheme 14c). Thus a copolymer of $M_{n,exp}$ = 8700 g mol⁻¹ ($M_{n,theoretical}$ = 7100 g mol⁻¹) and PDI = 2.06 was obtained.

Interestingly, the copolymerization was also controlled by RITP, using molecular iodine I₂ as control agent and AIBN as initiator at 70 °C, yielding a copolymer of $M_n = 8200 \,\mathrm{g \, mol^{-1}}$ and PDI = 1.70 (Scheme 14d). The evolution of molecular weight versus conversion showed that molecular weights were close to the targeted M_n (10 000 g mol⁻¹ at 100% conversion) soon from the beginning of the polymerization, with a PDI almost constant around 1.7, indicating an apparent transfer constant to dormant chains $C_{\rm ex}$ close to unity.^{37,45,80}

3.06.5.2 (Meth)Acrylates

The DT of acrylates (butyl acrylate and methyl acrylate) with alkyl iodides was reported by Gaynor *et al.*⁶ and Matyjaszewski *et al.*¹⁶ in 1995. For instance, solution polymerization of butyl acrylate in benzene initiated by AIBN at 50 °C in the presence of 1-phenylethyl iodide provided poly(butyl acrylate) with 97% monomer conversion in 7.5 h and $M_n = 19300 \text{ g mol}^{-1}$ (close to $M_{n,\text{theoretical}} = 18000 \text{ g mol}^{-1}$) (Scheme 15a). The PDI = 2.0 is large, indicating a rather low C_{ex} value. Later on, 2-ethylhexyl acrylate and *tert*-butyl acrylate were also polymerized by DT in the presence of bis(iodomethyl)benzene or PS-I, respectively.^{92,93}

To get rid of the synthesis of the transfer agent, Lacroix-Desmazes *et al.* introduced the new RITP process. RITP of methyl and butyl acrylate initiated by AIBN in the presence of molecular iodine I_2 was investigated in detail to

support the proposed mechanism (Scheme 15b).³¹ A good control of the molecular weight was achieved. For instance, poly(methyl acrylate) with $M_n = 21800 \text{ g mol}^{-1}$ ($M_{n,\text{theoretical}} = 20700 \text{ g mol}^{-1}$) was obtained with 98% monomer conversion and a PDI = 1.98. The degenerative chain transfer constant was assessed to be $C_{\text{ex}} = 2.2$ at 70 °C for the polymerization of methyl acrylate. A numerical simulation was successfully run to validate a model of RITP of acrylates.³⁹ RITP of *tert*-butyl acrylate and 1,1,2,2-tetrahydroperfluorodecylacrylate was also successfully performed.^{40,93}

Koumura *et al.* have reported a peculiar system based on the photo-induced polymerization of methyl acrylate in ethyl acetate in the presence of $Mn_2(CO)_{10}$ and ethyl-2-iodoisobutyrate at 40 °C (Scheme 15c). The manganese complex is thought to be effective for the activation of the C–I bond under photoirradiation, via the formation of a manganese radical complex, to generate the polymer chains with controlled molecular weights. For instance, poly(methyl acrylate) of $M_n = 19\,800 \,\mathrm{g}\,\mathrm{mol}^{-1}$ and PDI = 1.81 was obtained with a monomer conversion higher than 90%.⁹⁴ There is a possibility that DT and metal-catalyzed contribute to the control of the polymerization.⁶⁵

Percec *et al.* applied SET-DTLRP to control the polymerization of butyl acrylate,⁶¹ *t*-butyl acrylate,⁹⁵ and 2-ethyl hexyl acrylate.^{95,96} Sodium dithionite in NaHCO₃ aqueous buffer with the sodium salt of *para*-toluenesulfinic acid hydrate acted as an SET agent at low temperature (T=23–45 °C) to



Scheme 15 Typical examples of polymerization of acrylates with iodo-compounds.

initiate the polymerization of acrylates with iodoform (Scheme 15d).^{61,95,96} Iodoform behaves as a difunctional initiator leading to α, ω -di(iodo)poly(acrylates). For instance, a poly(*n*-butyl acrylate) (PBuA) with $M_{\rm p} = 31\,600\,{\rm g\,mol}^{-1}$ ($M_{\rm p}$ theoretical = 29300 g mol^{-1}) and PDI = 1.9 was obtained with a monomer conversion of 96% at 35 °C after 5 h of polymerization.⁶¹ In addition, ultrahigh-molecular-weight polymers were attainable: poly(tBuA) of $M_{\rm p} = 823 \, 150 \, {\rm g \, mol}^{-1}$ with a narrow molecular weight distribution (PDI=1.15) was produced in 71 h with a monomer conversion of 61%.95 The metal-catalyzed SET-LRP of methyl acrylate was also possible by using iodoform as initiator and Cu⁰/Me₆-TREN as organometallic catalyst in DMSO at 25 °C.^{63,97} Thus, for [MA]₀/[CHI₃]₀/[Cu⁰]₀/[Me₆-TREN]₀ = 1110/1/0.1/0.1, a very good control of the polymerization was obtained with an initiator efficiency of f_{eff} = 96% and a low PDI = 1.2 at high conversion (>80%). Nevertheless, the DT mechanism was thought to play a minor role in this case because the activation (by Cu⁰)-deactivation (by Cu^{II}) steps in SET-LRP are expected to be faster than chain transfer to initiator and/or dormant species.61,63,95-97

The polymerization of acrylates (methyl acrylate, *n*-butyl acrylate, *t*-butyl acrylate) was also investigated by Onishi *et al.*⁹⁸ by using a half-metallocene iron iodide complex [Fe(Cp)I(CO)₂] catalyst, Al(OiPr)₃ or Ti(OiPr)₄ as cocatalysts, and ethyl-2-iodoisobutyrate as initiator at T = 60-80 °C in toluene (Scheme 15e). For instance, poly(methyl acrylate) polymers of $M_n = 12\ 100 \text{ g mol}^{-1}$ with PDI = 1.19 were obtained with 93% monomer conversion. Methyl acrylate and *N*,*N*-dimethylacrylamide were also controlled by using a Fe₂Cp₂ (CO)₄/I₂ system for which a combination of metal-catalyzed, stable radical-mediated, and DT is expected to take place.⁹⁹

Another system was investigated by Stoffelbach *et al.*,⁷¹ using a transition metal-catalyzed polymerization based on a CpMoI₂(iPr₂dad) complex activated with Al(OiPr)₃ in the presence of ethyl-2-iodopropionate as initiator in toluene at 80 °C (molar ratio monomer/CpMoI₂(iPr₂dad)/Al(OiPr)₃/ethyl-2-iodopropionate 165/1/1/1) (Scheme 15f). A good control of the polymerization of methyl acrylate was achieved with M_n close to the theoretical values and PDI values lower than 1.3. In this case, the polymerization was thought to proceed mainly in ATRP conditions, possibly with interplay of organometallic radical polymerization (OMRP).⁷¹ The DT mechanism could also play a role in this fully iodinated system although to a minor extent according to the obtained low PDI values.

The case of methacrylates is profoundly different since MMA was not successfully controlled by DT in the first attempts with 1-phenyl ethyl iodide.⁶ The reason is that it requires a much more activated alkyl iodide since the PMMA-I bears a tertiary C-I bond. RITP efficiently fills this gap since very activated transfer agents such as (CH₃)₂CNC-I (and very short oligomers such as (CH₃)₂CNC-(MMA)_n-I) are synthesized in situ during the induction period.⁴² For instance, by RITP of MMA initiated by AIBN in the presence of molecular iodine I2 at 80 °C in toluene solution, PMMA of $M_n = 19200 \,\mathrm{g \, mol^{-1}}$ $(M_{n,theoretical} = 18400 \text{ g mol}^{-1})$ and PDI = 1.5 was obtained with a monomer conversion of 91% (Scheme 16a). Hence, RITP provides a very convenient way to control the polymerization of methacrylates by DT and the Cex value was assessed to be 2.6 at 80 °C for the polymerization of MMA. RITP of a phosphonated methacrylate (dimethyl(methacryloyloxy) methyl phosphonate) was also reported.¹⁰⁰



Scheme 16 Typical examples of polymerization of methacrylates with iodo-compounds.

Goto et al.⁴⁷ also investigated the polymerization of methacrylates and they reported an unexpectedly poor result for the polymerization of MMA initiated by AIBN at 70 °C in the presence of 2-cyanopropyl iodide, leading to $M_{\rm n} = 30\,300\,{\rm g\,mol^{-1}}$, significantly higher than $M_{\rm n,theoretical} = 20\,000\,{\rm g\,mol^{-1}}$, and a large PDI = 1.90 (monomer conversion = 99%). They improved the control by using the RTCP process, catalyzed by TGeI₃, GeI₄, PI₃, N-iodosuccinimide, diethylphosphite, and alcohols (such as 3,5-dibutyl-4-hydroxy anisole) with AIBN, benzoyl peroxide (BPO), or di(4-tert-butylcyclohexyl) peroxydicarbonate (Perkadox 16) as initiators. Thus, for instance, they could obtain PMMA with $M_n = 18400 \text{ g mol}^{-1}$ ($M_{n,\text{theoretical}} = 24000$ g mol⁻¹) and PDI=1.28 when using 2-cyanopropyl iodide, TGeI₃, and AIBN at 70 °C (monomer conversion = 60%) (Scheme 16b). They also applied RTCP to the polymerization of glycidyl methacrylate, hydroxyethylmethacrylate, benzyl methacrylate, poly(ethylene glycol) methacrylate, and copolycontaining dimethylaminoethylmethacrylate mers or methacrylic acid. 46,47,50-53 In addition, they applied RITP at T = 60-80 °C using azo-initiators (AIBN, V65, V70) and catalysts such as N-iodosuccinimide (i.e., combining RITP with RTCP) to prepare PMMA of controlled molecular weight with low polydispersity (PDI in the range of 1.2-1.4).⁵⁶

Percec *et al.*¹⁰¹ have investigated the metal-catalyzed radical polymerization of MMA with arenesulfonyl iodides as initiators. They found that the polymerization of MMA in diphenyl

ether at 70 °C initiated by tosyl iodide (CH₃PhSO₂-I) in the presence of CuI/ 2,2'-bipyridine was well controlled (Scheme 16c). For instance, an initiator efficiency of 94% was observed and a narrow poly(methyl methacrylate) (PMMA) was prepared with a PDI = 1.21 at 93% monomer conversion. Equally good results were obtained with Cu⁰, copper(I) oxide (Cu₂O), copper(I) sulfide (Cu₂S), copper(I) selenide (Cu₂Se), and copper(I) telluride (Cu₂Te)/2,2'-bipyridine catalysts. The polymerization is thought to benefit from multiple mechanistic pathways: SET-LRP, ATRP, and DT. It is worth mentioning that tosyl iodide is quite unstable in solution and under light,¹⁰¹ as anticipated by the low bond dissociation energy (BDE = 30.3 kcal mol⁻¹) for PhSO₂-I.¹⁴

Following the SET-DTLRP studies on VC, Percec et al. investigated the polymerization of MMA mediated by CuCl/ 2,2'-bipyridine as catalyst and a diiodo PVC as initiator in diphenyl ether or DMSO at 90 °C.¹⁰² A good control of the polymerization was observed with low polydispersity values down to 1.2. Various copper-based systems (CuCl, Cu2Te, Cu⁰), ligands (bpy, Me₆-TREN, 1,1,4,7,10,10-hexamethyltriethylene tetramine (HMTETA), polyethylenimine (PEI), permethyl(polyethylenimine) (MePEI)), and solvents (Ph₂O, DMSO, cyclohexanone, ethylenecarbonate) were tested.¹⁰³ It has been found that CuCl/Me6-TREN in DMSO at 90 °C provides an accelerated polymerization. An even faster polymerization was obtained with Cu⁰/Me₆-TREN in DMSO at 25 °C.¹⁰⁴ A model study was also performed with several initiators (CH₃CHClI, CHI₃, CH₂I₂, C₈F₁₇I), copper catalysts (CuCl, CuI, Cu₂O, Cu⁰), ligands (bipy, Me₆-TREN, PEI, HMTETA), and solvents (diphenyl ether, toluene, tetrahydrofuran (THF), DMSO, DMF, ethylene carbonate, DMAc, cyclohexanone) for the polymerization of MMA.¹⁰⁵ It was shown that Cu⁰/Me₆-TREN was an efficient catalyst to mediate the polymerization in DMSO at 25 °C, the higher initiator efficiency being observed with CH3CHClI initiator (Scheme 16d). The polymerization is thought to proceed mainly by an SET-LRP mechanism with a minimal contribution of DT.63

Matsubara and Matsumoto⁷³ also investigated the metal-catalyzed radical polymerization of MMA but they have chosen a cobalt derivative (CoI(PPh₃)₃) as catalyst. The polymerization was performed in THF at 60 °C for 24 h. It was shown that a fully iodine system using p-tosyl-I as initiator led to a low yield of polymerization (6% monomer conversion) with a strong deviation of the molecular weight $(M_{\rm n} = 26\,000\,{\rm g\,mol}^{-1} \gg M_{\rm n,theoretical} = 1900\,{\rm g\,mol}^{-1})$ although a narrow molecular weight distribution was obtained (PDI = 1.3). In contrast, when CCl_4 was used as initiator, the polymerization proceeded up to higher conversion (59%) with an improved initiator efficiency $(M_n = 49\,000\,\mathrm{g\,mol^{-1}})$, $M_{n,\text{theoretical}} = 19\,000\,\text{g}\,\text{mol}^{-1}$) and keeping a low PDI of 1.20. Importantly, the iodine ligand of CoI(PPh₃)₃ played an important role since the bromo- and chloro-analogues $(CoX(PPh_3)_{3})_{3}$ X = Br, Cl) led to uncontrolled polymerization (large PDI). The polymerization was thought to be mainly governed by the ATRP mechanism while DT would not be favored in those systems.

3.06.5.3 Styrenics

Gaynor *et al.*⁶ and Matyjaszewski *et al.*¹⁶ have shown that the polymerization of styrene can be controlled by alkyl iodides such as 1-phenylethyl iodide, iodoform (also investigated by

Barson et al.,¹⁰⁶ however, they did not look at the reversible-deactivation process), perfluorohexyl iodide, and iodoacetonitrile. For instance, the bulk polymerization of styrene initiated by AIBN at 70 °C in the presence of 1-phenylethyliodide yielded a rather narrow-molecularweight PS (PDI=1.5) with a good agreement between $M_{\rm n,SEC} = 7810 \,{\rm g \, mol}^{-1}$ $M_{\rm n,theoretical} = 6580 \,\mathrm{g \, mol}^{-1}$ and (Scheme 17a). Later on, Goto et al.⁷ investigated in detail the mechanism and kinetics of the bulk polymerization of styrene initiated by benzoyl peroxide at T = 50-80 °C in the presence of a PS-I macrotransfer agent (previously synthesized with 1-phenylethyliodide). DT was confirmed to be the only important mechanism of activation in this system. The degenerative chain transfer constant was determined by two methods giving C_{ex} = 3.6 at 80 °C in both cases. Other styrenic derivatives such as chloromethylstyrene and methoxysilylmethylstyrene were polymerized in the presence of alkyl iodide in a controlled manner.⁸

Teodorescu²⁸ investigated the polymerization of styrene in the presence of vinyl iodoacetate as CTA (Scheme 17b). Neither branching nor incorporation of VAc was noticed and the polymerization led to VAc-terminated PS macromonomers (VAc-PS-I). The iodine end groups were then replaced by $-N_3$ azido groups prior to copolymerization with VAc.

To get rid of the use of a transfer agent, the polymerization of styrene can be performed by RITP.37 Low-PDI PS of controlled molecular weight was obtained. It was shown that the mechanism of RITP for styrene presents a major difference from the one observed for acrylates and methacrylates. In RITP of styrene, the observed inhibition time is shorter than the theoretical value (eqn [22]), due to the reversible formation of styrene diiodide (and possibly a charge transfer complex), which is responsible for the disappearance of active free iodine before the expected end of the inhibition period. Nevertheless, since the whole iodine is eventually liberated during the polymerization, all iodine atoms are available to control the polymerization, leading to a good control of the molecular weights.⁴¹ For instance, bulk polymerization of styrene initiated by AIBN at 70 °C in the presence of iodine I2 led to PS with a good agreement between $M_{n,SEC} = 9200 \,\mathrm{g \, mol^{-1}}$ and $M_{\rm n,theoretical} = 8900 \,\mathrm{g \, mol^{-1}}$ and PDI = 1.3 (94% styrene conversion) (Scheme 17c).¹⁰⁷ The polymer chains were analyzed by mass spectroscopy techniques, with electrospray ionization time-of-flight (ESI-TOF) leading to a higher detection of chain-end groups than matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) (in particular, the dormant chains could be detected in ESI-TOF).³⁶ RITP of chloromethylstyrene was also successfully performed.93,108

Goto *et al.* then introduced the RTCP process and applied this catalytic process to the polymerization of styrene initiated by BPO at 80 °C (AIBN, dicumyl peroxide, 2,2'-azobis (2,4,4-trimethylpentane), and *tert*-butylperbenzoate were also used) in the presence of 1-phenylethyl iodide (iodoform and PMMA-I were also used) and catalyst GeI₄ (GeI₃, SnI₄, SnI₂, PI₃, dibutylphosphite, diethylphosphite, *N*-iodosuccinimide, phenol derivatives, and vitamin C were also used).^{46,47,50–53} For instance, they could obtain a PS of $M_{n,exp}$ = 8200 g mol⁻¹ ($M_{n,theoretical}$ = 8500 g mol⁻¹) with PDI = 1.24 by polymerizing styrene in bulk at 80 °C initiated by BPO with 1-penylethyliodide and GeI₄ (monomer conversion = 85%) (Scheme 17d).⁴⁷ A kinetic study was performed with a macro-transfer agent PS-I for various catalysts (GeI₄, SnI₄, SnI₄,



Scheme 17 Typical examples of polymerization of styrenics with iodo-compounds.

N-iodosuccinimide, tolyl-GeI₃, PI₃) to determine the values of the activation rate constant k_a and deactivation rate constant k_{da} , which were found to be very high: for instance, k_a and k_{da} are about 10⁶ M⁻¹ s⁻¹ at 80 °C with GeI₄ in the case of styrene, whereas $k_{ex} = 2.4 \times 10^3$ M⁻¹ s⁻¹.⁵⁴ Hence, for typical values of [G-I] = 10⁻³ M and [P-I] = 10⁻² M, $k_{act} = k_{ex}[P^\bullet] + k_{da}[P^\bullet][G-I]/$ [P-I] is mainly governed by the last term, that is, DT has a negligible effect in the case of the most active catalysts such as GeI₄. It was also shown that the polymerization rate was retarded in the presence of G-I due to the cross-termination occurring between P[•] and the *in situ* formed G[•]. The rate retardation was stronger for tolyl-GeI₃ and *N*-iodosuccinimide in comparison with SnI₄, GeI₄, and PI₃.⁵⁴

Styrene and other *para*-substituted styrenes were polymerized by Kotani *et al.*¹⁰⁹ with rhenium(V) ($\text{ReO}_2\text{I}(\text{PPh}_3)_2$) and iron(II) ($\text{FeCpI}(\text{CO})_2$) complexes in the presence of an iodoester and metal alkoxides. For instance, with ethyliodoisobutyrate initiator and $\text{FeCpI}(\text{CO})_2$ catalyst, a poly (*para*-chlorostyrene) could be obtained with a low PDI = 1.09 (**Scheme 17e**).¹⁰⁹

The system used above by Koumura *et al.* for methyl acrylate, based on the photo-induced polymerization in the presence of $Mn_2(CO)_{10}$ and ethyl-2-iodoisobutyrate at 40 °C, was also efficient for the bulk polymerization of styrene. For instance, PS of $M_n = 12200 \text{ g mol}^{-1}$ and PDI = 1.33 was

obtained with a monomer conversion higher than 95% (Scheme 17f).⁹⁴

3.06.5.4 Vinyl Esters

The controlled radical polymerization of vinyl esters is more difficult because they are nonconjugated monomers, so their propagating radical species are very reactive and tend to undergo side reactions such as high extent of transfer and irregular propagation (i.e., head-to-head and tail-to-tail addition).^{65,110} Furthermore, the C–I bond of vinyl esters is stronger than that of styrene and (meth)acrylates.^{14,15}

Ueda *et al.* have reported the polymerization of VAc in the presence of various alkyl iodides such as CHI₃, CH₂I₂, and C₆F₁₃-I and the adduct VAc + HI. For instance, bulk polymerization with initiator AIBN at 80 °C in the presence of CHI₃ led to poly(VAc) with PDI in the range of 1.2–1.5 and a good correspondence between experimental and theoretical molecular weights up to 30 000 g mol⁻¹.¹¹¹ Vinyl pivalate was also polymerized in this manner and random as well as block copolymers with VAc were prepared.¹¹² The photopolymerization of VAc in the presence of AIBN and IC₆F₁₂-I, C₆F₁₃-I, or ICH₂CN was also claimed to afford controlled polymers.¹¹³ Similar results were reported later by Mah *et al.*¹¹⁴ However, it was only in 2003 that the thermal polymerization of VAc



Scheme 18 Typical examples of polymerization of vinyl esters with iodo-compounds.

with alkyl iodides (methyl 2-iodopropionate, ethyl iodoacetate), initiated by AIBN (T = 60-80 °C) or α -cumyl peroxyneodecanoate (T = 50 °C), was discussed in detail (Scheme 18a).^{115,116} A careful ¹H-NMR analysis revealed that the iodo-terminated chain ends were unstable and decomposed to aldehyde moieties and to colored conjugated structures. The observed primary iodo end groups resulted from head-to-head addition. Similarly, a polydimethylsiloxane (PDMS) macrotransfer agent I-PDMS-I was successfully used for the bulk polymerization of VAc initiated by AIBN at 80 °C to prepare triblock copolymers PVAc-*b*-PDMS-*b*-PVAc.¹¹⁷ Copolymers of VAc with olefins and fluoro-olefins were synthesized by Borkar and Sen^{118,119} by using ethyl iodoacetate as CTA.

The use of iodine I₂ as inhibitor of the radical polymerization of VAc was reported many years ago.¹²⁰ However, the use of iodine I₂ to control the polymerization of VAc by RITP was described only recently in a few reports.^{43,44,121,122} It was found that a high excess of initiator over iodine, typically [AIBN]/[I₂] higher than 3, was required to obtain a quantitative monomer conversion together with a good level of control of the molecular weight and low PDI. For instance, the bulk polymerization of VAc in the presence of I₂ and initiated by AIBN at 75 °C ([AIBN]/[I₂] = 3.3) produced a polymer with 94% monomer conversion with a good agreement between $M_{n,theoretical} = 8300 \text{ g mol}^{-1}$ and $M_{n,SEC} = 9300 \text{ g mol}^{-1}$ and a low PDI ($M_w/M_n = 1.27$) (Scheme 18b).¹²² Nevertheless, as in ITP of VAc, it was noticed that the iodinated chain ends were prone to facile degradation (evidenced by a recoloration of the final reaction medium).⁴⁴

The polymerization of VAc was also controlled by an organometallic system composed of ethyl-2-iodoisobutyrate (or the HI adduct with VAc: $CH_3CH(OC(O)CH_3)I$), $[Fe(Cp)(CO)_2]_2$ as catalyst, and $Al(Oi-Pr)_3$ as cocatalyst in anisole at 60 °C (Scheme 18c).¹²³ Since the initiator is an iodinated alkyl iodide, ITP can occur competitively with metal-catalyzed radical polymerization, the latter being expected to be the dominant mechanism in this system.

The system of Koumura *et al.*⁹⁴ based on the photo-induced polymerization in the presence of $Mn_2(CO)_{10}$ and ethyl-2-iodoisobutyrate at 40 °C was tested for the bulk polymerization of VAc (Scheme 18d). The addition of *n*-Bu₃N accelerated the polymerization while maintaining a rather good control of the polymerization. For instance, poly(VAc) of $M_n = 18\,000$ and PDI = 1.75 was obtained with a monomer conversion of 95%. Again, the decomposition of chain ends and head-to-head addition were noticed.

3.06.5.5 Other Monomers

Oligomers of poly(butadiene) were prepared by telomerization of butadiene in the presence of 1-iodoperfluorohexane and 1-iodoperfluorooctane at 140–150 °C with di-*tert*-butyl peroxide as initiator and acetonitrile as solvent.¹²⁴ However, telomerization proceeded rather than ITP and the living properties were not achieved since 80% of the 1,4-adducts were found to lack a terminal iodine atom, yielding black final polymers. Better characteristics (less colored polymers) were obtained when potassium carbonate was added in the reaction medium to neutralize hydrogen iodide (HI) produced in the course of the reaction.¹²⁵

3.06.6 Processes

3.06.6.1 Bulk and/or Solution Polymerization

Most of the studies reported above were conducted in bulk or solution polymerization. The specific effect of the solvent has rarely been investigated in detail.¹²⁶ It was shown that RITP is compatible with several types of solvent (e.g., toluene, trifluor-otoluene, *tert*-butylbenzene, anisole, methylethyl ketone, butyl acetate, propylene carbonate, propionitrile, DMF).^{31,36} Bulk was sometimes found preferable in ITP and RITP to get rid of transfer reaction to solvent.^{107,117} Supercritical CO₂ was also used as solvent in ITP of VDF and the polymerization proceeded homogeneously when the reaction was carried out at 120 °C and 1500 bar with around 70 wt.% of CO₂.¹²⁷

3.06.6.2 Dispersion Polymerization

Dispersion polymerization of styrene in ethanol and ethanol/ water was performed at 70 °C with C_6F_{13} -I as reversible transfer agent, 2,2'-azobis(2-methylbutyronitrile) as radical initiator, poly(vinylpyrrolidone) as steric stabilizer, and Triton X-305 (octylphenol ethoxylate with average number of ethylene oxide units = 30) as costabilizer. A delayed addition of C_6F_{13} -I was required to avoid the disturbance of the nucleation period. In such a two-stage process, monodisperse micron-sized particles were produced and a rather good correlation between $M_{n,\text{theoretical}} = 8800 \text{ g mol}^{-1}$ and $M_{n,\text{exp}} = 11\,200 \text{ g mol}^{-1}$ $(M_w/M_n = 2.04)$ was obtained (monomer conversion = 95%).¹²⁸

3.06.6.3 Microemulsion Polymerization

Aqueous microemulsion has been used for the copolymerization of VDF and HFP in the presence of IC_6F_{12} -I as CTA. This technology, used in conjunction with the addition of diene as cross-linkers (e.g., CH_2 =CH-(CF_2)_n-CH=CF_2), allowed the preparation of fluorinated copolymers with improved performances.^{129,130}

3.06.6.4 Miniemulsion Polymerization

Aqueous miniemulsion polymerization of styrene was performed in the presence of C₆F₁₃-I as CTA, yielding particles with a good control of the molecular weights, in contrast to emulsion polymerization where the transfer agent efficiency was low due to a slow diffusion of the hydrophobic perfluorohexyl iodide from the monomer droplets to the active particles during polymerization.^{26,131} The chains were capped with iodine as evidenced by the successful chain extension upon addition of butyl acrylate.¹³² The miniemulsion process was also successfully applied to the preparation of triblock copolymers PS-b-PDMS-b-PS starting from a telechelic diiodopoly(dimethylsiloxane) macrotransfer agent.¹³³ A somewhat similar procedure was used to prepare PVAc-b-PDMS-b-PVAc triblock copolymers, but the polymerization was performed under UV irradiation (instead of thermal initiation) and in the absence of radical initiator. In this case, the aqueous dispersion medium was a key parameter to achieve a controlled polymerization (Scheme 19).23

To counterbalance the loss of iodine I_2 by disproportionation of iodine I_2 in water (formation of iodide (I^-) and iodate (IO_3^-)), RITP of styrene in miniemulsion was made possible by the addition of hydrogen peroxide as oxidant (Scheme 20).¹³⁴ Therefore, the polymerization of styrene was initiated by bis(4-*tert*-butylcyclohexyl) peroxydicarbonate



Scheme 19 Polymerization of VAc in the presence of an iodinated macrophotoiniferter in aqueous miniemulsion.

$$I_{2,aq} + H_2O$$
 \longrightarrow $I^- + H^+ + HOI$ (1)

$$3HOI = IO_3^- + 2I^- + 3H^+$$
 (2)

$$3I_{2,aq} + 3H_{2}O \implies IO_{3}^{-} + 5I^{-} + 6H^{+}$$
 (3)

$$I_{2,aq} + I^-$$
 I_3^- (4)

$$H_2O_2 + 2H^* + 2I^- - I_2 + 2H_2O$$
 (5)

Scheme 20 Main equilibria involved in the hydrolytic disproportionation of iodine and reaction with hydrogen peroxide.

at T = 60 °C with dodecyl sulfate sodium salt as surfactant and hexadecane as hydrophobe, yielding a stable and colorless latex with the expected molecular weight (e.g., $M_{n,SEC} = 7900 \text{ g mol}^{-1}$, $M_w/M_n = 1.46$, styrene conversion = 78%, $M_{n,\text{theoretical}} = 7900 \text{ g mol}^{-1}$).^{38,134} This was also applied to RITP of butyl acrylate and MMA in miniemulsion.^{135,136}

The hydrolytic stability of the chain ends can be an issue in controlled radical polymerization. However, the PBuA-I and PS-I chain ends were shown to be stable enough provided that the experimental conditions were carefully chosen: for instance, basic pH, high temperature, and low ionic strength of the continuous phase should be avoided (these are not strong constraints).¹³⁷

3.06.6.5 Emulsion Polymerization

Aqueous emulsion polymerization is of industrial importance. Therefore, special efforts have been concentrated to apply ITP and RITP to emulsion polymerization.

First trials of ITP of styrene with C_6F_{13} -I were unsuccessful due to mass transfer limitations of the hydrophobic transfer agent through the aqueous phase.²⁶ A less hydrophobic transfer agent, methyl-2-iodopropionate, was successfully used in ITP of styrene in emulsion, initiated by 2,2'-azobis[*N*-(2carboxyethyl)-2-methylpropionamidine] tetrahydrate (VA-057) at 68 °C in the presence of dodecyl sulfate sodium salt as surfactant, leading to stable and uncolored latexes with a good correlation between experimental and theoretical molecular weights.¹⁹ In the case of the iodine transfer copolymerization of VDF and α -trifluoromethacrylic acid in emulsion initiated by sodium persulfate at 80 °C, C_6F_{13} -I and IC₄F₈-I could be used as transfer agents and a pseudo-control of the polymerization was claimed.¹³⁸

Besides this, RITP of butyl acrylate was performed in emulsion at 85 °C with 4,4'-azobis(4-cyanopentanoic acid) as radical initiator and dodecyl sulfate sodium salt as surfactant. A careful analysis of the reaction medium revealed that disproportionation of iodine I₂ in water was an important side reaction causing an upward deviation of the molecular weight from the targeted values. Importantly, the latex was living as evidenced by a successful block copolymerization with styrene starting from a poly(butyl acrylate) latex.^{38,139–141} RITP of MMA in emulsion was also investigated.¹⁴² The main side reaction being identified, RITP of butyl acrylate in emulsion was then significantly improved by counterbalancing the disproportionation of iodine, thanks to the use of an oxidant to regenerate iodine I₂ from iodide (I⁻). Noticeably, persulfate can play the dual role of radical initiator and oxidant. Thus, RITP of butyl acrylate in emulsion was initiated by potassium persulfate at T = 85 °C with sodium 1-hexadecanesulfonate as surfactant, yielding a stable and colorless latex. The hydrolytically disproportionated iodine was regenerated by potassium persulfate as oxidant (also serving as radical initiator), leading to the expected targeted molecular weight (e.g., Bu conversion = 99%, acrylate $M_{\rm n, theoretical} = 10\,100\,{\rm g\,mol^{-1}},$ $M_{\rm n.SEC} = 9800 \,{\rm g \, mol^{-1}}, M_{\rm w}/M_{\rm n} = 1.8$, particle diameter $d_{\rm p} = 83$ nm with a monomodal particle size distribution).¹⁴³ An additional very important step was achieved when it was demonstrated that water-soluble, harmless, cheap, and nonhazardous sodium iodide (NaI) can be used in combination with potassium persulfate (K₂S₂O₈) instead of iodine I₂ itself to produce an uncolored living poly(Bu acrylate) latex of controlled molecular weight by RITP in emulsion (Scheme 21).^{135,144} Even surfactant-free acrylic latexes could be produced by RITP starting with NaI, thanks to the electrosteric stabilization of the latex provided by the in situ synthesized amphiphilic poly(acrylic acid-co-Bu acrylate) gradient copolymers.¹⁴⁵

3.06.6.6 Suspension Polymerization

Many of the SET-DTLRP works by Percec and co-workers^{61,88,95,146} were performed in aqueous heterogeneous media. Although the heterogeneous process was not described in detail, suspension polymerization is likely to occur in some of the reported systems.

3.06.7 Macromolecular Architectures Prepared by Degenerative Transfer with Iodo-Compounds

3.06.7.1 Telechelics

The use of transfer agents with two active iodine atoms allows one to prepare polymers bearing iodine at each end of the polymer chains such as I-P-I. These α , ω -functional chains are called telechelic polymers.^{20,147–152} Thanks to the large range of chemistry related to iodo-compounds (radical reaction,





Scheme 22 General scheme on telechelic polymers obtained by DT with alkyl iodides and their derivatization.

nucleophilic reaction, redox reaction, etc), the subsequent derivatization of the chain ends is also possible enabling new functionalities (e.g., amino, hydroxy, carboxy, azide) (Scheme 22).^{40,89,127,153–155} For instance, telechelic PVC (I-PVC-I) was prepared by SET-LRP initiated by iodoform (CHI₃). Then, reaction with 2-allyloxyethanol in DMSO at 70 °C catalyzed by sodium dithionite (Na₂S₂O₄) and sodium bicarbonate (NaHCO₃) provided a quantitative functionalization of the chain ends resulting in an $\alpha_i \omega$ -di(hydroxy)PVC.⁸⁹

Interestingly, telechelic polymers can also be prepared by coupling P-I polymers prepared by RITP (using functional initiators), thus offering a route to multiblock copolymers.¹¹

3.06.7.2 Alternated Copolymers

Iodine transfer copolymerization of MMA with styrene was performed in bulk at 60 °C in the presence of iodoacetonitrile or iodoform as transfer agents and Et_2AlCl as Lewis acid, which reduces the electron density of the double bond of MMA (Scheme 23a). However, this system was not investigated in detail and such studies would deserve more attention.¹⁵⁶

In another study, Koumura *et al.*¹⁵⁷ have shown that alternated copolymers of methyl acrylate and 1-hexene could be formed by $Mn_2(CO)_{10}$ -induced polymerization under weak visible light at 40 °C in a protic fluoroalcohol solvent such as $(CF_3)_2CHOH$ in the presence of ethyl-2-iodoisobutyrate as an initiator and molecular iodine I₂ as a cocatalyst (Scheme 23b).

3.06.7.3 Gradient Copolymers

Gradient-block copolymers of methyl acrylate and VAc were prepared by photo-induced copolymerization in PhC(CF₃)₂OH at 40 °C in the presence of $Mn_2(CO)_{10}$ and ethyl-2-iodoisobutyrate at 40 °C. For instance, a poly











Scheme 24 Cumulative ($F_{VAc,cum}$) and instantaneous ($F_{VAc,inst}$) VAc contents in methyl acrylate-vinyl acetate (MA-VAc) copolymers as a function of total conversion; $[VAc]_0 = [MA]_0 = 2.0 \text{ M}$ (in 1: m-C₆H₄ [(CF₃)₂COH]₂) or 5.1 M (in bulk); $[VAc]_0/[MA]_0/[ethyl-2-iodoisobutyrate]_0/[Mn_2(CO)_{10}]_0 = 100/100/1/1$. Reproduced with permission from Koumura, K.; Satoh, K.; Kamigaito, M. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 1343.¹⁵⁸ Copyright 2009 John Wiley and Sons.

(methyl acrylate-*grad*-VAc)-*b*-poly(VAc) copolymer of $M_n = 16500 \text{ g mol}^{-1}$ and PDI = 1.55 (methyl acrylate conversion > 99%, VAc conversion = 94%, methyl acrylate/VAc = 51/49) was prepared in one step (Scheme 24).¹⁵⁸ Similarly, a gradient-block copolymer of acetoacetoxyethyl-methacrylate (AAEM) and VAc was produced by RITP in toluene at 65 °C using a high ratio of [AIBN]/[I₂]of 6.7. A poly(AAEM-*grad*-VAc)-*b*-poly(VAc) of $M_n = 2500 \text{ g mol}^{-1}$ and PDI = 1.50 (AAEM conversion > 99%, VAc conversion = 28%, AAEM/VAc = 42/58) was thus produced in one step.⁴⁴

3.06.7.4 Block Copolymers

Block copolymers can be prepared by resuming the polymerization in the presence of another monomer or by transformation from one type to another type of controlled/living polymerization method.¹⁵⁹

Thus, several block copolymers have been prepared by ITP among which we can cite polystyrene-*b*-poly(butyl acrylate),^{16,132} perfluoropolyethers-*b*-poly(VDF-*co*-HFP),¹⁶⁰ poly-(VDF)-*b*-polystyrene,¹⁶¹ polystyrene-*b*-poly(acrylic acid)¹⁶² as well as polystyrene-*b*-poly(dimethylsiloxane)-*b*-polystyrene^{133,163} and poly(VAc)-*b*-poly(dimethyl siloxane)-*b*-poly (VAc).^{23,117,163}

Some block copolymers were also prepared by RITP, such as poly(vinylidene chloride-*co*-methyl acrylate)-*b*-polystyrene,^{45,80} poly(acrylic acid-*co*-butyl acrylate)-*b*-poly(butyl acrylate-*co*-styrene),¹⁴⁵ polystyrene-*b*-poly(acrylic acid),⁹³ poly-(vinyl benzyl chloride)-*b*-polystyrene quaternized with triethylamine,^{93,108} and poly(MMA)-*b*-poly(dimethyl(methacryloyloxy)methyl phosphonate)¹⁰⁰ as well as ABA and BAB copolymers where A is rich in styrene and B is rich in butyl acrylate.¹⁰⁷

Other copolymers involved two different methods of polymerization, such as for instance the sequential combination of ITP of VDF and ATRP of MMA to prepare poly(VDF)-*b*-PMMA and PMMA-*b*-poly(VDF)-*b*-PMMA block copolymers.¹⁶⁴

3.06.7.5 Graft Copolymers

Teodorescu²⁸ have reported the preparation of poly-(VAc)-g-polystyrene copolymers using two different strategies. Firstly, ITP of styrene with vinyl iodoacetate provided a PS macromonomer. The iodine chain end of PS was then replaced by -N3 azido group, and the PS macromonomer, whose reactivity was similar to that of VAc $(1/r_{VAc} = 1.07)$, was copolymerized with VAc to obtain the PVAc-g-PS copolymer. In another work, a statistical copolymer poly(VAc-co-vinyl chloroacetate) was first prepared by radical copolymerization. Then, chlorine atoms were replaced by iodine atoms through reaction with KI in acetone. Finally, the resulting poly-(VAc-co-vinyl iodoacetate) was used as macrotransfer agent in ITP of styrene to obtain the PVAc-g-PS copolymer. The grafting efficiency was not very high (72 wt.% of graft copolymer) and the copolymer was contaminated with PS homopolymer (11 wt.%) and unreacted poly(VAc-co-vinyl iodoacetate) (11 wt.%).¹⁶⁵

ITP from a multifunctional macrotransfer agent was also used to prepare poly(ε-caprolactone) (PCL)-based graft copolymers. Thus, ITP of styrene, *n*-butyl acrylate, and *N*,*N*-dimethylacrylamide was performed in the presence of poly(ε-caprolactone-*co*-α-iodo-ε-caprolactone) to obtain PCL-*g*-PS, PCL-*g*-P*n*BuA and PCL-*g*-PDMA, respectively.¹⁶⁶

3.06.7.6 Brushes

Surface initiation is a commonly used method to prepare hybrid materials. Poly(vinyl alcohol) brushes have been obtained from surface-initiated ITP of VAc from a silicon wafer followed by hydrolysis of PVAc. The surface properties of the SiO₂-g-PVA and SiO₂-g-PVAc were examined by atomic force microscopy.¹⁶⁷

3.06.7.7 Hyperbranched and Star (Co)Polymers

The use of a monomer bearing two reactive sites, such as p-iodomethylstyrene (one polymerizable double bond and one benzyl iodide transfer site), can lead to branched structures. This system was studied by Kowalczuk-Bleja et al.¹⁶⁸ for the polymerization of *p*-iodomethylstyrene initiated by AIBN in benzene at 67 °C. NMR and size exclusion chromatography (SEC) characterizations with absolute molecular weight determination by multiple-angle light scattering (MALLS) detection were performed to characterize the branched polymer chains. It was shown that ITP of *p*-iodomethylstyrene was possible and led to soluble well-defined branched products of M_n varying between 1500 and 3000 g mol⁻¹. This core was also utilized as macrotransfer agent in the bulk polymerization of styrene initiated with AIBN at 67 °C to obtain star-like polymers with poly(p-iodomethylstyrene) core and PS arms. Similarly, star-like polymers with poly(p-iodomethylstyrene) core and poly(tert-butyl acrylate) arms were obtained.169,170 Finally, polystyrene-b-poly(tert-butyl acrylate) arms could also be grown from the poly(p-iodomethylstyrene) core. The thermal

properties of these star-like polymers were investigated by dynamic scanning calorimetry.

Star copolymers are also attainable by using a well-defined $R(I)_n$ alkyl iodide as CTA. Thus, 1,1,1-trimethylolpropane tri (2-iodoisobutyrate) was synthesized and used as an $R(I)_3$ CTA for the polymerization of styrene in benzene initiated by AIBN at 65 °C, yielding $R(PS)_3$.¹⁷¹ Then, polymerization of butyl acrylate afforded $R(polystyrene-b-poly(tert-butyl acrylate))_3$. Finally, an amphiphilic star-block copolymer $R(polystyrene-b-poly(acrylic acid))_3$ was obtained by acidic hydrolysis in dichloromethane with trifluoroacetic acid (Scheme 25).

In another study, iodinated sucrose, glucose, and cyclodextrin cores were used as control agent in combination with a half-metallocene iron carbonyl complex (FeCp(CO)₂-I) and titanium(IV) isopropoxide (Ti(OiPr)₄) for the polymerization of styrene in toluene at 80 °C to afford star polymers with 5, 8, and 18 PS arms.¹⁷²

3.06.7.8 Stereospecific Reversible-Deactivation Radical Polymerization

The simultaneous control of the molecular weights and stereochemistry of a polymer chain is still challenging in radical polymerization.¹⁷³ ITP can provide molecular weight control while the tacticity can be directed by specific interactions with protic solvents like fluoroalcohols. Thus, the polymerization of VAc in $m-C_6H_4(C(CF_3)_2OH)_2$ initiated by 2,2'-azobis(4methoxy-2,4-dimethylvaleronitrile) (V70) at 20 °C in the presence of ICH₂C(O)OEt as CTA improved both the syndiotacticity (content of racemo dyad r = 59%) and the molecular weight control (PDI=1.20), but also decreased the content of head-to-head linkages (hh = 0.8%) and the proportion of poorly reactive primary iodide end group $(-CH_2-I=30\%)$ in comparison with bulk polymerization $(r = 52\%, PDI = 1.47, hh = 1.2\%, -CH_2 - I = 70\%)$.^{126,174} PVAc with $M_{\rm n}$ up to 70 000 g mol⁻¹ and PDI < 1.6 could be obtained with the same system.



Scheme 25 Preparation of amphiphilic star-block copolymers R(PS-b-PAA)₃

3.06.8 Applications of Polymers Prepared by Degenerative Transfer with Iodo-Compounds

Some fluoropolymers prepared by DT with iodo-compounds have already been commercialized such as Daiel, Viton, and Technoflon.^{8,175} Such fluoroelastomers may find applications in high technology such as in O-rings, gaskets, hoses, transportation, medical devices, and electronics. The control of the architecture and functionality of the polymer chains makes possible the preparation of peroxide curable fluoroelastomer with improved properties as well as the development of advanced fluorinated thermoplastic elastomers.^{78,176} Another application of functional fluoropolymers prepared by DT with iodo-compounds is the preparation of membranes for fuel cells.¹⁵¹

The preparation of polymers with well-defined architectures from a wide range of monomers, not only fluoromonomers, opens the door to many other applications, from toughened materials¹⁷⁷ to thermoplastic elastomers,¹⁰⁷ and macromolecular surfactants.^{93,108} The low cost of RITP is especially attractive in the latter case, where relatively low molecular weights and thus high concentrations of control agent are desirable. The potential of new methods like RITP is also important to combine effectiveness and sustainability,¹⁴⁴ in accordance with the principles of green chemistry.

3.06.9 Prospects

The combination of different controlled/living polymerization and derivatization techniques is a promising direction to reach novel materials with new properties. The emphasis should be not only on the mechanisms and kinetics but also on the characterization of the polymers, not obligatory targeting of clean and very well-defined polymers but copolymers with improved properties, prepared in a green way, and industrially viable. Completely new products could also be targeted, leading to new challenges, and the imagination and strong collaboration between the chemists and engineers of academia and industry will be necessary to reach the goal.

3.06.10 Conclusions

Degenerative chain transfer with iodo-compounds is compatible with most of the common monomers, as well as with halogenated monomers, and it has been performed successfully in aqueous emulsion polymerization, which is industrially relevant. Furthermore, it allows one to prepare various architectures such as block, graft, hyperbranched, star, and brush (co)polymers. Although being one of the very first techniques developed for reversible-deactivation radical polymerization, DT with alkyl iodide has retained only a little attention compared to nitroxide-mediated polymerization, ATRP, and RAFT. However, recent studies have revealed that degenerative chain transfer is very powerful and RITP, RTCP, and SET-DTLRP techniques have paved the way to imagine new, efficient, inexpensive, and greener solutions. Iodine chemistry is extremely rich and, with no doubt, it will allow the chemists to propose even more elegant and practical ways for the preparation of smart (multi)functional copolymers and hybrid materials of controlled architecture at the nanoscale.

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Biographical Sketches



Patrick Lacroix-Desmazes was born in Caen, France, in 1968. He graduated from the National School of Chemistry of Montpellier, France, in 1992. He obtained his PhD degree in 1996 at the University Claude Bernard Lyon I, where he studied, within a European Program and in collaboration with Elf Atochem, the use of macromonomers as steric stabilizers in dispersion polymerization in polar media. After postdoctoral research on suspension polymerization to develop a new range of expandable polystyrene, done with BP Chemicals in Wingles in 1997, he joined the Laboratory of Macromolecular Chemistry in Montpellier as a CNRS research scientist. In 1999, he developed RITP, a promising method for reversible-deactivation radical polymerization. He received his habilitation degree in 2004. He was awarded the 2004 Innovative Research ADER Award in collaboration with Solvin Company and he was laureate of the 2009 'Chercheur d'Avenir' Languedoc-Roussillon Award. His research interests cover reversible-deactivation radical polymerizations (photo-iniferters, NMP, ATRP, RAFT, ITP, RITP), including in dispersed media (emulsion, miniemulsion, dispersion, suspension polymerization), as well as the synthesis and use of polymers in liquid or supercritical carbon dioxide. Since 2009, he has been the Directeur de Recherche at CNRS within the Institut Charles Gerhardt where he leads topics on controlled polymerizations as well as on polymers in unconventional media and clean processes. He is a member of the Groupe Français d'Etudes et d'Applications des Polymères.



Jeff Tonnar was born in Luxembourg, Luxembourg, in 1979. He graduated from the National School of Chemistry of Montpellier in France in 2004. He obtained his PhD degree in 2007 at the University Montpellier II, working under the direction of Dr. P. Lacroix-Desmazes in the laboratory of Professor Bernard Boutevin. His research covered iodine-mediated polymerization ((reverse) ITP), especially in dispersed aqueous media (suspension, miniemulsion, and *ab initio* emulsion polymerization). In 2007, he obtained a postdoctoral research position in the laboratory of Pr. S. Armes (Sheffield University, UK). There he worked on the synthesis of polymer-silica nanocomposites in emulsion polymerization. Then, in 2008, he joined CIBA where he worked as a project manager on emulsion polymerization for paper coatings. He received in 2008 the Thesis Award from Groupe Français d'Etudes et d'Applications des Polymères. Since October 2009, he has been working as an R&D scientist for ADOCIA in the field of biotechnologies.

3.07 Radical Addition–Fragmentation Chemistry and RAFT Polymerization

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3.07.1	Introduction	181
3.07.1.1	Addition–Fragmentation Chain Transfer	182
3.07.1.2	Reversible Addition–Fragmentation Chain Transfer	184
3.07.2	Compounds Providing Irreversible Addition–Fragmentation Chain Transfer	187
3.07.2.1	Vinyl Ethers	187
3.07.2.1.1	Addition-fragmentation chain transfer agents	187
3.07.2.1.2	Ring-opening monomers	188
3.07.2.2	Allyl Sulfides, Sulfones, Halides, Phosphonates, and Silanes	189
3.07.2.2.1	Addition-fragmentation chain transfer agents	189
3.07.2.2.2	Ring-opening monomers	190
3.07.2.3	Allyl Peroxides	190
3.07.2.4	Thionoester and Related Transfer Agents	192
3.07.3	Compounds Providing Reversible Addition–Fragmentation Chain Transfer	193
3.07.3.1	Macromonomers	194
3.07.3.2	Thiocarbonylthio Compounds	196
3.07.3.2.1	RAFT agent synthesis	197
3.07.3.2.2	Dithioesters	201
3.07.3.2.3	Trithiocarbonates	203
3.07.3.2.4	Dithiocarbamates	204
3.07.3.2.5	Switchable RAFT agents	205
3.07.3.2.6	Xanthates	209
3.07.3.2.7	Other RAFT agents	212
3.07.3.3	Reaction Conditions	212
3.07.3.3.1	Temperature	212
3.07.3.3.2	Pressure	212
3.07.3.3.3	Initiator	212
3.07.3.3.4	Solvent	213
3.07.3.3.5	RAFT in heterogeneous media	213
3.07.3.4	Polymer Architectures	214
3.07.3.4.1	Functional polymers	214
3.07.3.4.2	Gradient copolymers	214
3.07.3.4.3	Block copolymers	215
3.07.3.4.4	Star polymers	216
References		219

3.07.1 Introduction

This chapter is a condensation and an update of our review on Radical Addition Fragmentation Chemistry in Polymer Synthesis that appeared in 2008.¹ It traces the development of addition–fragmentation chain transfer agents and related ring-opening monomers highlighting recent innovation in these areas. However, the major part of this chapter deals with reagents that give reversible addition–fragmentation chain transfer (RAFT) which is now recognized as one of the most versatile methods for conferring living characteristics on radical polymerizations.

The first reports of radical addition–fragmentation processes appeared in the synthetic organic chemistry literature in the early $1970s.^{2,3}$ Well-known examples of processes that involve a reaction step with an S_H2' mechanism include allyl transfer reactions with allyl sulfides⁴ and stannanes (the Keck

reaction)⁵ and the Barton–McCombie deoxygenation process with xanthates.⁶ A survey of these reactions is included in the review by Colombani and Chaumont.⁷ The first reports of the direct use of addition–fragmentation transfer agents to control radical polymerization appeared in the 1980s.^{8–10}

In an ideal living polymerization, all chains are initiated at the beginning, grow at the same rate, and survive polymerization (there is no termination). The propensity of free radicals to undergo radical-radical termination means that in radical polymerization all chains cannot be simultaneously active. To confer living character on radical polymerization, it is necessary to suppress or render insignificant all processes that terminate chains irreversibly. Thus, in radical polymerization, living characteristics are only seen in the presence of reagents that react with the propagating radicals (P_n^{\bullet}) by reversible coupling (Scheme 1) or reversible chain transfer (Scheme 2) such that the majority of living chains are maintained in a dormant form







(P_n–X). The average concentration of the active propagating species in a reversible deactivation radical polymerization (RDRP) may be similar to that for the conventional process. However, the cumulative lifetime of an individual chain as an active species will be lower. Rapid equilibration between the active and dormant forms ensures that all chains possess an equal chance for growth and that all chains will grow, albeit intermittently. These polymerizations, termed reversible deactivation radical polymerizations (RDRPs),¹¹ provide for the molecular weight to increase linearly with conversion (**Figure 1**) and can give narrow molecular weight distributions (e.g., $\overline{M}_w/\overline{M}_n \sim 1.1$, **Figure 2**).

The RDRP techniques that have recently received greatest attention are nitroxide-mediated polymerization (NMP),^{13,14} atom transfer radical polymerization (ATRP),^{15–18} and RAFT. RAFT polymerization, devised in our laboratories,¹⁹ is arguably the most convenient and versatile.



Figure 1 Evolution of molecular weight with monomer conversion for a conventional radical polymerization with constant rate of initiation (— — —) and a living polymerization (———). Reproduced from Moad, G.; Rizzardo, E.; Thang, S. H., Living Radical Polymerization by the RAFT Process. *Aust. J. Chem.* **2005**, *58*, 379–410.¹²



Figure 2 Typical molecular weight distributions for a conventional radical and a RAFT polymerization. Data shown are from gel permeation chromatography (GPC) analysis of polystyrene prepared by thermal polymerization of styrene at 110 °C for 16 h (\overline{M}_n 324 000, $\overline{M}_w/\overline{M}_n$ 1.74, 72% conversion) and a similar polymerization in the presence of curryl dithiobenzoate (0.0029 M) (\overline{M}_n 14 400, $\overline{M}_w/\overline{M}_n$ 1.04, 55% conversion). Reproduced from Moad, G.; Rizzardo, E.; Thang, S. H., Living Radical Polymerization by the RAFT Process. *Aust. J. Chem.* **2005**, *58*, 379–410.¹²

3.07.1.1 Addition–Fragmentation Chain Transfer

The generic structures of addition-fragmentation transfer agents are shown in Scheme 3. Unsaturated compounds of general structure 1 or 4 act as transfer agents by a two-step addition-fragmentation mechanism. In these compounds C=X is a double bond that is reactive toward radical addition. 'X' is most often CH₂ or S. 'Z' is a group chosen to give the transfer agent an appropriate reactivity toward propagating radicals and convey appropriate stability to the intermediate radicals 2 or 5. Examples of 'A' are CH₂, CH₂=CHCH₂, O, or S. 'R' is a homolytic leaving group and for efficient chain transfer R• must be capable of efficiently reinitiating polymerization. In all known examples of transfer agents 4, A is CH₂, B is O, and R is alkoxy. Since functionality can be introduced to the products 3 or 6 in either or both the transfer (typically from Z) and reinitiation (from R) steps, these reagents offer a route to a variety of end-functional polymers including telechelics.

Addition–fragmentation chain transfer agents and their application to control molecular weight and end-group functionality have been reviewed by Rizzardo and coworkers, ^{1,20–22} Colombani and Chaumont, ⁷ Colombani, ²³ Yagci and Reetz, ²⁴ Yamada and coworkers, ^{25,26} and Moad and Solomon.²⁷

Rates of addition to transfer agents 1 and 4 with $X = CH_2$ are determined by the same factors that determine rates of addition to monomer. Thus, substituents at A (i.e., R, B–R) have only a minor influence on reactivity; consequently the double bonds of the transfer agents 1 and 4 with $X = CH_2$ have a reactivity toward radical addition that is similar to that of the common monomers they resemble. Thus, with efficient fragmentation, transfer constant (C_{tr}) is often close to unity. A C_{tr} of unity has been called 'ideal' since the transfer agent and monomer are consumed at the same rate and, as a consequence, the



Scheme 3 Mechanisms for addition–fragmentation chain transfer.

molecular weight should remain essentially constant with monomer conversion.²⁸

In addition–fragmentation chain transfer, the rate constant for chain transfer (k_{tr}) is defined in terms of the rate constant for addition (k_{add}) and a partition coefficient (ϕ) which defines how the adduct is partitioned between products and starting materials (eqns [1] and [2])²⁹ – refer Scheme 3.

$$k_{\rm tr} = k_{\rm add} \frac{k_{\rm \beta}}{k_{\rm -add} + k_{\rm \beta}} = k_{\rm add} \phi \qquad [1]$$

$$\phi = \frac{k_{\beta}}{k_{-\text{add}} + k_{\beta}} \tag{2}$$

The transfer constant is defined in terms of k_{tr} and the propagation rate constant (k_p) in the usual way ($C_{tr} = k_{tr}/k_p$).

Efficient transfer requires that the radical intermediates formed by addition undergo facile β -scission (for 1) or rearrangement (for 4) to form a new radical that can reinitiate polymerization. The radical intermediates 2 and 5 typically have low reactivity toward further propagation and other intermolecular reactions because of steric crowding about the radical center.

The driving force for fragmentation of the intermediate radical is provided by cleavage of a weak A-R or B–R bond and/or formation of a strong C=A bond (for 1). If both addition and fragmentation are rapid and irreversible with respect to propagation the polymerization kinetics differ little from those seen in polymerization with conventional chain transfer. If the overall rate of β -scission is slow relative to propagation then retardation is a likely result. If fragmentation is slow, the adducts (2 or 5) also have a greater potential to undergo side reactions by addition to monomer (copolymerization of the transfer agent) or radical–radical termination. Retardation is often an issue with high k_p monomers such as vinyl acetate (VAc) and methyl acrylate (MA). In designing transfer agents and choosing an R group, a balance must also be achieved

between the leaving group ability of R and reinitiation efficiency of R• since, as with conventional chain transfer, the rate constant for reinitiation by R• should be $\geq k_p$. Factors discussed later with respect to RAFT agents are also important here. If fragmentation leads preferentially back to starting materials the transfer coefficients are low and concentration dependent.

The methods used for evaluating transfer coefficients are the same as for conventional chain transfer and involve evaluating the molecular weight (as in Mayo method³⁰) or the chain length distribution (CLD) (as in the Log CLD method^{31,32}) in low-conversion polymerizations or relative rate of consumption of transfer agent and monomer.^{33,34} Transfer coefficients for addition–fragmentation chain transfer agents from the literature are summarized in the sections that follow.

When the product of the reaction is itself a potential transfer agent or a macromonomer, further reaction to form a block, graft, or hyperbranched copolymer formation may occur particularly at high conversions.^{10,35} The design of transfer agents that give RAFT has provided one of the more successful approaches to living radical polymerization and is described in the next section. The reverse pathway can also be blocked by choice of A. For example, when A is oxygen (e.g., vinyl ethers, Section 3.07.2.1, and thionoesters, Section 3.07.2.4) or bears a substituent (e.g., $A = CH-CH_3$), the product is rendered essentially unreactive to radical addition.

If R and Z, R and A, or, in principle, R and X in structure 1 are connected to form a ring structure the result is a potential ring-opening monomer as shown in **Scheme** 4. For many of the transfer agents described, there are analogous ring-opening monomers. Radical ring-opening polymerization has been reviewed by Moad and Solomon,³⁶ Sanda and Endo,³⁷ Klemm and Schulze,³⁸ Cho,³⁹ Moszner and Salz,⁴⁰ Endo and Yokozawa,⁴¹ Stansbury,⁴² Bailey,⁴³ and Moad *et al.*¹



Scheme 4 Potential propagation mechanisms in ring-opening polymerization. Reproduced from Moad, G.; Rizzardo, E.; Thang, S. H., Radical addition-fragmentation chemistry in polymer synthesis. *Polymer* **2008**, *49*, 1079–1131.¹

3.07.1.2 Reversible Addition–Fragmentation Chain Transfer

'Macromonomers' (7, $X = CH_2$; Scheme 5) have been known as potential reversible transfer agents in radical polymerization since the mid-1980s.¹⁰ However, RDRPs which involve a 'degenerate' reversible chain transfer step for chain equilibration and which display at least some characteristics of living polymerization were not reported until 1995.^{44,45}

Reversible chain transfer may, in principle, involve homolytic substitution (Scheme 6) or addition–fragmentation (RAFT) or some other transfer mechanism.⁴⁶ An essential feature is that the product of chain transfer is also a chain transfer agent with similar activity to the precursor transfer agent. The overall process has also been termed degenerate or degenerative chain transfer since the polymeric starting materials and products have equivalent properties and differ only in molecular weight (Schemes 5 and 6, where R• and R'• are both propagating chains).

Polymerization of styrene and certain fluoro-monomers in the presence of alkyl iodides provided the first example of the reversible homolytic substitution process. This process is also known as iodine transfer polymerization.^{45,47} Other examples of control by reversible homolytic substitution chain transfer are polymerizations conducted in the presence of derivatives of organotellurides telluride-mediated radical polymerization (TERP)⁴⁸ or organostibines⁴⁸ and tin, germanium, or phosphorus iodides reversible chain transfer catalyzed polymerization (RCTP).⁴⁹

In 1995 it was reported that polymerizations of methacrylic monomers in the presence of methacrylic macromonomers $(7, X = CH_2, Z = CO_2R)$ under monomer-starved conditions display many of the characteristics of living polymerization.^{44,50} These systems involve the RAFT mechanism (Scheme 7).

In 1982, Otsu *et al.*^{51,52} proposed that living characteristics observed for polymerization in the presence of dithiocarbamate photoiniferters might be attributable to both reversible chain transfer and reversible radical–radical coupling steps as part of the mechanism. However, it is now known that degenerate chain transfer is a minor pathway for the reagents and reaction conditions used in those pioneering experiments.⁵³ RAFT with thiocarbonylthio compounds (7, X = S) was first reported in 1998¹⁹ and is the most versatile and well-known process of this class.^{54,55} It is compatible with most monomer



Scheme 5 Reversible addition–fragmentation chain transfer. Reproduced from Moad, G.; Rizzardo, E.; Thang, S. H., Radical addition-fragmentation chemistry in polymer synthesis. *Polymer* **2008**, *49*, 1079–1131.¹



Scheme 6 Reversible homolytic substitution chain transfer. Reproduced from Moad, G.; Rizzardo, E.; Thang, S. H., Radical addition-fragmentation chemistry in polymer synthesis. *Polymer* **2008**, *49*, 1079–1131.¹



Scheme 7 Mechanism of RAFT polymerization. Reproduced from Moad, G.; Rizzardo, E.; Thang, S. H., Radical addition-fragmentation chemistry in polymer synthesis. *Polymer* **2008**, *49*, 1079–1131.¹

types and with a very wide range of reaction conditions. Recent reviews which relate specifically to RAFT polymerization with thiocarbonylthio compounds include general reviews by Moad et al.,⁵⁴⁻⁵⁸ Mayadunne and Rizzardo,⁵⁹ Chiefari and Rizzardo,²² Perrier and Takolpuckdee,⁶⁰ Favier and Charrevre,⁶¹ and Barner-Kowollik and coworkers.^{62,63} A book entitled Handbook of RAFT Polymerization,64 which comprises reviews on all aspects of RAFT polymerization, has also been published. Other reviews deal with specific applications of RAFT polymerization such as computational studies related to RAFT agents and RAFT polymerization, 65,66 the kinetics and mechanism of RAFT polymerization,^{67–72} the control of molecular weight distributions produced by RAFT polymerization,⁷³ the use of RAFT to probe the kinetics of radical polymerization,74,75 the use of RAFT in organic synthesis,76-79 amphiphilic block copolymer synthesis,^{80,81} the use of trithiocarbonate RAFT agents,⁸² the use of xanthate RAFT agents (macromolecular design by interchange of xanthate (MADIX)),⁸³ RAFT polymerization in aqueous media,⁸⁴⁻⁸⁸ the use of RAFT polymerization in heterogeneous media,⁸⁸⁻⁹⁵ RAFT polymerization initiated with ionizing radiation,⁹⁶ the synthesis of end-functional polymers,⁹⁷⁻¹⁰¹ the synthesis of star polymers and other complex architectures, 63,102,103 the synthesis and properties of stimuli-responsive block and other polymers,^{87,101,104,105} the preparation of honeycomb structures,¹⁰⁶ surface and particle modification,^{107,108} green chemistry,¹⁰⁹ RAFT-synthesized polymers in drug delivery,^{80,110} bioapplications of RAFT polymerization,^{111,112} and the synthesis of polymers for optoelectronic applications.¹¹³

RAFT polymerization is also reviewed within works which deal more generically with radical polymerization. The literature through 2005 is comprehensively reviewed within the chapter *Living Radical Polymerization* in *The Chemistry of Radical Polymerization*¹¹⁴ and is given substantial coverage in many recent works that relate more generically to polymer synthesis, living polymerization, or novel architectures.^{115–126} Other relevant reviews include those focussing on the synthesis and organic chemistry of dithioesters and other thiocarbonylthio compounds in a nonpolymerization context.^{127,128}

The literature is expanding very rapidly; an update review⁵⁵ covering the period mid-2005–mid-2006 revealed more than 200 papers dealing directly with the use and application of RAFT polymerization. A second update covering the period mid-2006–mid-2009 covered a further 550 papers. Our first communication on RAFT with thiocarbonylthio compounds¹⁹ now has more than 1650 citations and is one of the most highly cited papers in *Macromolecules* while the first RAFT patent¹²⁹ was seventh on the list of most cited patents in the field of chemistry and related science in 2005 and continues to be highly cited (**Figure 3**).¹³⁰ It should be noted that not all papers on RAFT polymerization cite these sources nor are all of the papers citing these documents specifically on RAFT polymerization.

The key feature of the mechanism of RAFT polymerization with thiocarbonylthio compounds as proposed in our first communication on the subject¹⁹ is the sequence of addition–fragmentation equilibria shown in Scheme 7.¹³¹ Initiation and radical–radical termination occur as in conventional radical polymerization. In the early stages of the polymerization, addition of a propagating radical (P_n^{\bullet}) to the thiocarbonylthio compound [RSC(Z)=S (7)] followed by fragmentation of the intermediate radical provides a polymeric thiocarbonylthio compound [$P_nSC(Z)=S$ (9)] and a new radical (R^{\bullet}). Reaction of this radical (R^{\bullet}) with monomer forms a new propagating radical ((P_m^{\bullet})). Rapid equilibrium



Figure 3 (a) Cumulative citations for our first communication on RAFT (Δ),¹⁹ our first patent (\Box),¹²⁹ and our 2005 (\circ) review on RAFT polymerization⁵⁴ and that published in Polymer in 2008 (\diamond).¹ Based on SciFinder[®] search carried out in February 2011. (b) Total publications, papers, and patents on RAFT polymerization based on SciFinder[®] search of terms 'RAFT polymerization', 'reversible addition–fragmentation transfer' and 'radical', and 'MADIX' and 'radical'. The term 'papers' includes journal, articles, communications, letters, and reviews but does not include conference abstracts.

between the active propagating radicals $(P_n^{\bullet} \text{ and } P_m^{\bullet})$ and the dormant polymeric thiocarbonylthio compounds (9) provides equal probability for all chains to grow and allows for the production of low dispersity polymers. When the polymerization is complete (or stopped), the vast majority of chains retain the thiocarbonylthio end group and can be isolated as stable materials.

The reactions associated with RAFT equilibria shown in **Scheme 7** are in addition to those (i.e., initiation, propagation, and termination) that occur during conventional radical polymerization. In an ideal RAFT process, the RAFT agent should behave as an ideal transfer agent. Thus, as with radical polymerization with conventional chain transfer, the kinetics of polymerization should not be directly affected beyond those effects attributable to the differing molecular weights of the reacting species. Radical-radical termination is not suppressed by the RAFT process. Living characteristics are imparted only when the molecular weight of the polymer formed for a given reaction time (t) is substantially lower than that which might be formed in the absence of a RAFT agent and the number of polymer molecules with RAFT agent-derived ends far exceeds the number formed as a consequence of termination.

For less active RAFT agents ($C_{tr} \le 1$), transfer coefficients may be determined using the usual methods with little loss of accuracy. For more active transfer agents, where the transfer agent-derived radical (\mathbb{R}^{\bullet}) may partition between adding to monomer and reacting with the polymeric RAFT agent (\mathbb{P}_{n}^{T}) even at low conversions, transfer coefficients measured by the Mayo or related methods will appear to be dependent on the transfer agent concentration (and on the monomer conversion).^{132–134} These values should be called apparent transfer constants C_{tr}^{app} and be regarded as a minimum value of the transfer constant. The actual transfer constant may be higher by several orders of magnitude.¹³³ The reverse transfer coefficient (C_{-tr}) is defined as follows (eqn [3]):

$$C_{-\rm tr} = \frac{k_{-\rm tr}}{k_{\rm iT}}$$
[3]

where k_{iT} is the rate of reinitiation by the RAFT agent-derived radical R•, and the rate of transfer agent consumption is then given by eqn [4]:

$$\begin{aligned} \frac{d[T]}{d[M]} &\approx C_{tr} \frac{[T]}{[M] + C_{tr}[T] + C_{-tr}[P_n^T]} \\ &= C_{tr} \frac{[T]}{[M] + C_{tr}[T] + C_{tr}([T]-[T]_0)} \end{aligned} \qquad [4]$$

where [T] is the RAFT agent concentration, [M] is the monomer concentration and $[T]_0$ is the initial RAFT agent concentration. This equation can be solved numerically to give estimates of $C_{\rm tr}$ and $C_{\rm -tr}$.^{132,134}

The rate constant for the reverse transfer is defined analogously to that for the forward reaction (eqn [1]) as shown in eqn [5]:

$$k_{-\rm tr} = k_{-\beta} \frac{k_{-\rm add}}{k_{-\rm add} + k_{\beta}}$$
[5]

If the reverse reaction can be neglected eqn [4] simplifies as follows

$$\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}[\mathrm{T}]} \approx C_{\mathrm{tr}} \frac{[\mathrm{M}]}{[\mathrm{T}]} + 1$$
[6]

which suggests that a plot of log (M) versus log (T) should be a straight line with the slope proving the transfer coefficient. This equation has been used to evaluate C_{tr}^{app} for a range of RAFT agents. For the more active RAFT agents, the values so obtained are a minimum value for $C_{tr}^{.132,133}$ Some values of C_{tr}^{app} and, where available, estimates of C_{tr} and C_{-tr} are included in Section 3.07.3.

Systems that give reversible chain transfer can display the characteristics of living polymerization. Narrowed dispersities will generally only be observed when $C_{tr} > 2$ and $C_{tr} > 10$ are required to achieve the characteristics often associated with living polymerization (i.e., significantly narrowed molecular weight distributions, molecular weights predictable from reagent concentrations that increase linearly with conversion). The more effective RAFT agents have $C_{tr} \gg 100$. The dependence for



Figure 4 Predicted dependence of (a) degree of polymerization and (b) dispersity (\mathcal{B}) on conversion in polymerizations involving reversible chain transfer as a function of the chain transfer coefficient (C_{tr}). Predictions are based on equations proposed by Müller *et al.*^{135,136} with $\alpha = 10^{-7}$ (the concentration of active species), β (the transfer constant) as indicated, and $\gamma = 605$ (the ratio monomer to transfer agent). Experimental data points are for methyl methacrylate (MMA, 7.02 M) polymerization in the presence of dithiobenzoate esters (0.0116 M) where R = C(Me)₂CO₂Et (o) and C(Me)₂Ph (\Box). Reproduced from Chong, Y. K.; Krstina, J.; Le, T. P. T.; *et al. Macromolecules* **2003**, *36*, 2256–2272.¹³³ Copyright 2003 American Chemical Society.

molecular weight and dispersity on monomer conversion for various values of $C_{\rm tr}$ for a hypothetical polymerization without termination is shown in Figure 4.¹³³ Various factors will cause deviations from this ideal behavior (see, in particular, Section 3.07.3.3.3 below). The observation, that dispersities decrease only slowly with conversion when RAFT agents with lower $C_{\rm tr}$ are used, has been termed 'hybrid behavior'.⁶⁷

The properties of RAFT agents are often discussed in terms of the value of the equilibrium constants associated with radical addition to the thiocarbonylthio compound. Rates of addition are typically high (k_{add} , $k_{-\beta}$, $k_{addP} \sim 10^6 - 10^8 \text{ M}^{-1} \text{s}^{-1}$). Thus a high equilibrium constant generally implies a low fragmentation rate constant (k_{-add} , k_{β} , k_{-addP}) and consequently an increased likelihood for retardation and/or side reaction involving the adduct species. However, values of the equilibrium constants do not, by themselves, provide sufficient information to predict the ability of a RAFT agent to control polymerization.

In a given RAFT polymerization, there are at least four equilibrium constants that need to be considered. $K_{\rm P}$ (= $k_{\rm addP}/k_{\rm -addP}$) associated with the chain equilibration process (Scheme 7). This step is sometimes called the main equilibrium. K (= $k_{\rm add}/k_{\rm -add}$) and K_{β} (= $k_{-\beta}/k_{\beta}$) associated with the initial reversible chain transfer step sometimes known as the pre-equilibrium. $K_{\rm R}$ (= $k_{\rm addR}/k_{\rm -addR}$) associated with the reaction of the expelled radical with the initial RAFT agent (Scheme 8). This process only becomes significant if the intermediate formed has a significant lifetime.

There may be other equilibrium constants to consider if penultimate group effects are significant (there is theoretical data^{137,138} and some experimental evidence^{133,139} to indicate that this is the case). There are also a further series of reactions that need to be considered that involve initiator radical-derived

Reversible chain transfer



Scheme 8 Mechanism for reversible chain transfer between expelled radical (R•) and a RAFT agent. Reproduced from Moad, G.; Rizzardo, E.; Thang, S. H., Radical addition-fragmentation chemistry in polymer synthesis. *Polymer* **2008**, *49*, 1079–1131.¹

RAFT agents. In principle, RAFT agents of differing reactivity might be derived from each radical species present.

It should be possible to estimate values of *K* by determining the concentrations of the radical intermediates in RAFT polymerization by EPR (electron paramagnetic resonance) spectrometry and some effort has been directed to this end.^{140–143} Coote and coworkers^{65,137,138,144–147} have devised methods for calculating absolute values of *K* by applying *ab initio* methods. Values of *K* have also been estimated on the basis of simulation of the polymerization kinetics.^{148–150} Values of *K* estimated on the basis of the measured concentrations of the radical intermediates are substantially lower than those predicted by theoretical calculations.

3.07.2 Compounds Providing Irreversible Addition–Fragmentation Chain Transfer

3.07.2.1 Vinyl Ethers

3.07.2.1.1 Addition-fragmentation chain transfer agents

Vinyl ethers $(1, X = CH_2, A = O)$ can be very effective additionfragmentation chain transfer agents.^{8,21,151,152} The mechanism for chain transfer is shown in Scheme 9 for the case of α -benzyloxystyrene (15). The driving force for fragmentation is provided by formation of a strong carbonyl double bond. It is also important that R is a good radical leaving group. The vinyl carbonate 13152 gives only copolymerization, the ketene acetal 11¹⁵³ and the methyl vinyl ether 14¹⁵² give both copolymerization and chain transfer in styrene polymerization, whereas with the benzyl vinyl ethers, 12^{153}_{15} , $15^{8}_{15}_{15}$ and 16–18,¹⁵¹ chain transfer is the only reaction detected. Transfer constants for some vinyl ether transfer agents are provided in Table 1. The examples with R = benzyl are appropriate for use in S or (meth)acrylate ester polymerization but give retardation in polymerization of VAc and related monomers because benzyl radical is slow to initiate these polymerizations. Reagents 1 with X = CH₂, A = O, R = tertiary alkyl or cyclopropylcarbinyl have been shown to be effective as addition-fragmentation transfer agents in organic synthesis but have not been used in polymerization.154,155



The polymers formed have a ketone end group (e.g., 19, **Scheme** 9). Functionality can be introduced on 'Z' or 'R' to modify reactivity or to tailor the end groups as in the examples (20–22).²¹ The vinyl ether transfer agents, like other vinyl ethers generally show marked acid sensitivity and are not suited for use with acidic monomers (e.g., acrylic acid (AA), methacrylic acid (MAA)). Even traces of acidic impurities in the monomer or the polymerization medium can catalyze decomposition of the transfer agent.

3.07.2.1.2 Ring-opening monomers

The ring-opening polymerization of ketene acetals (23, X = O) provides a route to polyesters by radical polymerization and many examples have been reported (Scheme 10).^{157–161} A disadvantage of these systems is the marked acid sensitivity of the monomers which makes them relatively difficult to handle and complicates characterization. The early literature in this area is covered by a series of reviews by Bailey *et al.*^{43,162–166} and an updated summary has been provided by Moad and Solomon.³⁶

The nitrogen $(23, X = N-CH_3, n = 0)^{167}$ and sulfur $(23, X = S, n = 0)^{168}$ analogues of ketene acetals undergo ring-opening polymerization with selective cleavage of the C–O bond to give polyamides and polythioesters, respectively (Scheme 10). The specificity is most likely a reflection of the greater bond strength of C=O versus the C=S or C=N double bonds. The corresponding dithianes do not give ring-opening even though this would involve cleavage of a weaker C–S bond.^{169,170}

The competition between ring-opening and propagation is dependent on ring size and substitution pattern. For the five-membered ring ketene acetal (23, X = O, n = 0) ring opening is not complete except at very high temperatures. However, with the larger ring system (23, X = O, n = 2) ring opening is quantitative. This observation (for the n = 2 system) was originally attributed to greater ring strain. However, it may also reflect the greater ease with which the larger ring systems can accommodate the stereoelectronic requirements for β -scission.¹⁷¹ β -Substituents (e.g., CH₃, Ph) which lend stabilization to the new radical center, or which increase strain in the breaking bond, also favor ring opening.

 Table 1
 Transfer constants for vinyl ethers at 60 °C^{a,27}

Transfer agent	C_{tr} for m				
	St	MMA	MA	VAc	References
15 16 17	0.26 0.036 0.046	0.76 0.081 0.16	5.7 ^b 0.3 ^b 0.54 ^b	9.7 ^b 12 ^b 20 ^b	8, 151 151 151
18	0.2	0.5	1.1 ^b		151

^a Bulk, medium comprises only monomer and transfer agent.

^b Significant retardation observed.

St, styrene; MMA, methyl methacrylate; MA, methyl acrylate; VAc, vinyl acetate.



Scheme 9 Mechanism of addition-fragmentation chain transfer with a vinyl ether transfer agent. Reproduced from Moad, G.; Rizzardo, E.; Thang, S. H., Radical addition-fragmentation chemistry in polymer synthesis. *Polymer* **2008**, *49*, 1079–1131.¹



Much has recently been published on radical ring-opening (co)polymerization with 5,6-benzo-2-methylene-1,3-dioxepan and derivatives. The monomer provides quantitative ring opening, copolymerizes readily with styrenic and acrylic monomers,^{172–181} and is compatible with RAFT¹⁸² and ATRP.^{175,178,180,181}

3.07.2.2 Allyl Sulfides, Sulfones, Halides, Phosphonates, and Silanes

3.07.2.2.1 Addition-fragmentation chain transfer agents

Allyl transfer agents (1, $X = CH_2$, $A = CH_2$) include allyl sulfides (e.g., 24, 26–30) (Table 2),^{9,183,184} allyl sulfones (e.g., 31–35)¹⁸⁵ and sulfoxides (e.g., 35) (Table 3),^{185,186} and allyl halides (e.g., 36–38),^{185,187–192} phosphonates (e.g., 39),¹⁸⁵ silanes (e.g., 41),¹⁸⁵ and related compounds (Table 4). Rates of addition are determined by the activating group 'Z' as discussed above. The low transfer constant of 30 in styren

polymerization demonstrates the importance of choosing 'Z' to suit the particular monomer. The main driving force for fragmentation is the weak single A–R bond of 2. In many cases the chain transfer constants are close to the 'ideal' value of unity.

The mechanism of chain transfer is shown in Scheme 11 for allyl sulfide 24. The product, macromonomer (25), may undergo further reaction under the polymerization conditions particularly at high conversion (Section 3.07.3).

Allyl bromides **36a**, **37**, and **38a** give predominantly chain transfer whereas the chlorides (e.g., **36b** and **38b**) also copolymerize.^{185,193} The silane **41** also gives both copolymerization and chain transfer.¹⁸⁵ Allyl ethers (1, R = alkoxy, $X = A = CH_2$) are generally not addition–fragmentation chain transfer agents but are comonomers that may give degradative chain transfer by hydrogen abstraction.





 Table 2
 Transfer constants for allyl sulfides at 60 °C^{a,27}

	C _{tr} for monomer					
Transfer agent	St	MMA	MA	MAN	VAc	
26 , $Z = Ph$ 26 , $Z = CN$ 26 , $Z = CO_2Et$ 27 , $Z = Ph$ 27 , $Z = CO_2Et$ 27 , $Z = CO_2Et$ 27 , $Z = CO_2H$ 28 , $Z = Ph$ 29 , $Z = Ph$ 29 , $Z = CO_2H$ 29 , $Z = CO_2CH_2CH_2OH$ 30 , $R = CH_2CO_2CH_3^{-d}$	0.80 ⁹ 1.90 ⁹ 0.95 ⁹ 0.95 ¹⁸³ 1.72 ¹⁸³ 1.27 ¹⁸³ 0.68 ¹⁸³ 0.77 ¹⁸³ 1.81 ¹⁸³ 0.77 ¹⁸³ 0.77 ¹⁸³	$\begin{array}{c} 1.2^9 \\ 1.35^9 \\ 0.74^9 \\ 1.1^{183} \\ 0.65^{183} \\ 0.74^{183} \\ 1.04^{183} \\ 0.27^{183} \\ 0.40^{183} \end{array}$	3.9 ^{21b} 1.6 ^{21b} 2.2 ^{21b} 1.49 ^{183,c} 1.88 ^{183,c}	0.42 ^{425,426}	~20 ^b ~60 ^b ~27 ^{426,t}	

^a Bulk polymerization.

^b Significant retardation observed.

^c BA.

^d Transfer constants similar for various R.

St, styrene; MMA, methyl methacrylate; MA, methyl acrylate; MAN, methacrylonitrile; VAc, vinyl acetate



Table 3 Transfer constants for allyl sulfones and allyl sulfoxides at 60 $^\circ C^{a,27}$

	C_{tr} for				
Transfer agent	St	MMA	BA	VAc	Reference
31 32 33	4.2 ^c 5.8 0.02	0.72 ^{<i>c</i>} 1.1 0.065	1.1 ^c 2.3 ^c 0.20 ^e	d d 2.8	186 185 185
34 35		1.9		3.9	22 185

^a Bulk, medium comprises only monomer and transfer agent.

^b Transfer constants rounded to two significant figures.

^c 3.46 M monomer in benzene solution.¹⁸⁶

^d Significant retardation observed.

^e MA

St, styrene; MMA, methyl methacrylate; BA, butyl acrylate; MA methyl acrylate; VAc, vinvl acetate

Table 4Transfer constants for allyl halides, phosphonates,
silanes, and stannanes at $60 \, ^{\circ}C^{a,27}$

	C _{tr} for monomer ^b				
Transfer agent	St	MMA	MA	VAc	Reference
36a, Hal = Br 37 38a, Hal = Br 38b, Hal = Cl 39 40 41	2.9	1.5 2.3 2.2 0.0075 ^c 0.4 3.0 0.08 ^c	2.3 5.3 3.0 0.046 ^c		185 185 185 185 185 185 185

^a Bulk, medium comprises only monomer and transfer agent.

^b Transfer constants rounded to two significant figures.

^c Copolymerization observed.

St, styrene; MMA, methyl methacrylate; MA, methyl acrylate; VAc, vinyl acetate

3.07.2.2.2 Ring-opening monomers

Cyclic allyl sulfide derivatives (42–47; Table 5) are stable in storage and handling and do not show the acid sensitivity of the cyclic ketene acetal monomers mentioned above. The monomers with seven- or larger membered rings undergo facile polymerization even at relatively low temperatures^{194,195,198,199} with quantitative ring opening (Schemes 12 and 13). The monomers also undergo facile ring-opening copolymerization with methyl methacrylate (MMA) and St.^{196,203,204} The corresponding six-membered ring compound (42) appears unreactive in homopolymerization.

Ring opening provides a thiyl radical propagating species. Although the polymers have a double bond on the backbone it is possible to conduct polymerization such that there is little or no cross-linking. There is, however, evidence of reversible addition and addition–fragmentation involving such double bonds.^{201,205,206} Monomers containing multiple double bonds have been designed to provide ring-opening polymerization with cross-linking.¹⁹⁹

3.07.2.3 Allyl Peroxides

In the case of allyl peroxides (4, $X = CH_2$, $A = CH_2$, B = O, R = O-alkyl),^{4, 211–214} intramolecular homolytic substitution on the O–O bond gives an epoxy end group as shown in Scheme 14 (1,3-S_H*i* mechanism). The allyl peroxides usually are thermally stable under the conditions used to determine their chain transfer activity and conditions typically used in polymerizations. They may, however, be thermally unstable at higher temperatures. The transfer constants (Table 6) are more than two orders of magnitude higher than those for dialkyl peroxides such as di-*t*-butyl peroxide ($C_1 = 0.000 \ 23 - 0.001 \ 3$) or di-isopropyl peroxide ($C_1 = 0.000 \ 3$) which are believed to give chain transfer by direct attack on the O–O bond.²⁰⁸ This is circumstantial evidence in favor of the addition–fragmentation mechanism.



Scheme 11 Mechanism of addition-fragmentation chain transfer with an allyl sulfide transfer agent. Reproduced from Moad, G.; Rizzardo, E.; Thang, S. H., Radical addition-fragmentation chemistry in polymer synthesis. *Polymer* **2008**, *49*, 1079–1131.¹



Table 5Cyclic allyl sulfide monomers





44a

Scheme 12 Mechanism of ring-opening polymerization of cyclic allyl sulfide (**44a**). Reproduced from Moad, G.; Rizzardo, E.; Thang, S. H., Radical addition-fragmentation chemistry in polymer synthesis. *Polymer* **2008**, *49*, 1079–1131.¹



Scheme 13 Mechanism of ring-opening polymerization of cyclic allyl sulfide (**45b**). Reproduced from Moad, G.; Rizzardo, E.; Thang, S. H., Radical addition-fragmentation chemistry in polymer synthesis. *Polymer* **2008**, *49*, 1079–1131.¹



Scheme 14 Mechanism of addition-fragmentation chain transfer with an allyl peroxide transfer agent. Reproduced from Moad, G.; Rizzardo, E.; Thang, S. H., Radical addition-fragmentation chemistry in polymer synthesis. *Polymer* **2008**, *49*, 1079–1131.¹





Peroxyacetals 53²⁰⁹ and peresters such as 55²⁰⁷ can also be effective transfer agents. However, at typical polymerization temperatures (~60 °C) they are thermally unstable and also act as initiators. Compounds such as 57 which may give addition and 1,5-intramolecular substitution with fragmentation have also been examined for their potential as chain transfer agents (1,5-S_H*i* mechanism).²¹⁰

3.07.2.4 Thionoester and Related Transfer Agents

Thione derivatives (e.g., **58–60**, **Table 7**)^{4,226} also are very effective as addition–fragmentation chain transfer agents. The thiohydroxamic esters (e.g., **59**) are sometimes known as Barton esters because of the work of Barton and coworkers who explored their use in organic synthesis.^{215–217} When the initiating species formed are acyloxy radicals they may undergo decarboxylation
Table 6 Transfer constants for allyl peroxide and related transfer agents at 60 $^\circ C^{a,27}$

Transfer agent	C _{tr} for m	C _{tr} for monomer ^b					
	St	MMA	MA	VAc	References		
50 51 52 53 54 55 56	0.9 1.6 2.0 0.9 0.22 0.82 ^b 0.35 ^c	0.8 0.6 0.9 0.012 0.31 ^b 0.05 ^c	1.0 0.7 0.08 0.46 ^{c,d}	3.7 1.3°	21, 428 21, 428 21 209 429 207 430, 431		

^a Bulk, medium comprises only monomer and transfer agent.

^b Compound is also an initiator under the polymerization conditions. Transfer constant obtained using a modified Mayo equation.²⁰⁷

^c In benzene.

^d BA.

St, styrene; MMA, methyl methacrylate; BA, butyl acrylate; MA, methyl acrylate; VAc, vinyl acetate

before initiating a new chain. Thus for the example shown in Scheme 15, products with benzoyloxy and phenyl chain ends are expected (61 and 62, respectively).

 Table 7
 Transfer constants for thionoester and related transfer agents at 60 °C^{a,27}

C _{tr} for				
St	MMA	MA	VAc	References
1.0	~0	1.2 ^b	> 20 ^c	432
3.8	4.0	~20 ^b	~36 ^c	433
3.9	4.3		~80 ^c	433
	2.8			433
0.3	0.6	3.1	9.7 ^b	433
1.0	1.0		18 [°]	433
	C _{tr} for St 1.0 3.8 3.9 0.3 1.0	C _{tr} for monomer St MMA 1.0 ~0 3.8 4.0 3.9 4.3 2.8 0.3 0.6 1.0 1.0 1.0	$\begin{tabular}{ c c c c } \hline C_{tr} for monomer \\\hline St MMA MA \\\hline 1.0 $$ \sim0$ 1.2^b \\\hline 3.8 $$ 4.0 $$ $$ \sim20^b$ \\\hline 3.9 $$ $$ 4.3 \\\hline 2.8 \\\hline 0.3 $$ $$ 0.6 $$ 3.1 \\\hline 1.0 $$ 1.0 \\\hline \end{tabular}$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

^a Bulk, medium comprises only monomer and transfer agent.

^b Significant retardation observed.

^c Strong retardation observed.

St, styrene; MMA, methyl methacrylate; MA, methyl acrylate; VAc, vinyl acetate

Thiohydroxamic esters have also seen application in grafting of polyacrylonitrile onto polyethylene,²¹⁸ of polystyrene (PSt), polyacrylamide (PAM), and poly(*N*-isopropylacrylamide) onto cellulose,^{219,220} and of PS, PMMA, poly(vinyl pyridine), and polyacrylamide onto poly(arylene ether sulfone).²²¹ The process involves derivatization of a parent carboxy-functional polymer to form the thiohydroxamic ester **59** with R = polymer, which then behaves as a polymeric transfer agent.



Benzyl thionobenzoate (58) is believed to be ineffective as a transfer agent in MMA polymerization because of an unfavorable partition coefficient. Poly(methyl methacrylate) radical (PMMA•) is a much better radical leaving group than benzyl radical. Analogous benzyl thiocarbonylthio compounds (e.g., benzyl dithiobenzoate or dibenzyl trithiocarbonate) are also ineffective as RAFT agents in MMA polymerization.

58

3.07.3 Compounds Providing Reversible Addition–Fragmentation Chain Transfer

A wide variety of macromonomer $(7, X = CH_2)$ and thiocarbonylthio RAFT agents (7, X = S) have now been reported. The effectiveness of RAFT agent depends on the monomer being polymerized and depends strongly on the properties of the



Scheme 15 Mechanism of addition-fragmentation chain transfer with Barton ester (**58**). Reproduced from Moad, G.; Rizzardo, E.; Thang, S. H., Radical addition-fragmentation chemistry in polymer synthesis. *Polymer* **2008**, *49*, 1079–1131.¹

radical leaving group R and the group Z which can be chosen to activate or deactivate the thiocarbonyl double bond and to modify the stability of the intermediate radicals. For an efficient RAFT polymerization, ⁵⁴

- the RAFT agents (7) and (9) should have a reactive C=X double bond (high k_{add});
- the intermediate radicals (8) and (10) should fragment rapidly (high k_{β} , weak X–R bonds) and give no side reactions;
- the intermediate (8) should partition in favor of products (k_β≥k_{-add}); and
- the expelled radicals (R•) should efficiently reinitiate polymerization.

3.07.3.1 Macromonomers

Macromonomers (7, X = CH₂, R = polymer chain) can react by a RAFT mechanism as shown in **Scheme 16** for 'MAA trimer' (63).^{10,35} The product (65) is also a 'macromonomer', thus chain transfer is reversible and 'degenerate'.^{44,50} These chain transfer agents are frequently called 'macromonomers' even when used as transfer agents. This may appear to be a misnomer, since, when used in this context, they should not behave as macromonomers. Copolymerization when it occurs is a side reaction. The most reported transfer agents of this class are the methacrylate macromonomers (e.g., 66–68) and α -methylstyrene (AMS) dimer (77).

addition-fragmentation chain transfer agents (1) with $X = A = CH_2$ described in Section 3.07.2. The macromonomer chain end is also identical in structure to the unsaturated chain end formed by termination by disproportionation.²²³

Transfer coefficients for selected macromonomers are tabulated in Table 8. The rate constants (k_{add}) for addition of the MMA propagating radical²²⁴ (and other radicals³⁵) to macromonomers (e.g., 66-68) are believed to be essentially independent of the macromonomer chain length (n). However, the rate constants for addition and fragmentation are subject to significant penultimate unit effects and are dependent on the chain length of the propagating radical for n < 5. This is attributed to steric factors.^{34,224} One consequence is that the transfer coefficient of 'dimer' (66) is more than an order of magnitude lower than that for 'trimer' (67) and higher macromonomers 68 due to an unfavorable partition coefficient. Fragmentation of 72 preferentially gives back 66 and the MMA propagating radical (69) rather than 70 and the monomeric radical (71) (Scheme 17).

Transfer coefficients of the methacrylate macromonomers in MMA polymerization appear independent of the ester group. Those for MAA dimer and trimer are slightly higher than for the corresponding esters. End-functional trimers 74 and 75 can be synthesized from the MMA



Methacrylic macromonomers are conveniently synthesized by catalytic chain transfer.²²² They can also be synthesized by polymerizations in the presence of other trimer (67) by selective hydrolysis or hydrolysis and reesterification, respectively, and offer a route to telechelic polymers.³⁴



Scheme 16 Mechanism of reversible addition-fragmentation chain transfer with MMA trimer. Reproduced from Moad, G.; Rizzardo, E.; Thang, S. H., Radical addition-fragmentation chemistry in polymer synthesis. *Polymer* **2008**, *49*, 1079–1131.¹



Table 8 Transfer coefficients for macromonomers^{a,27}

	Tamparatura	C _{tr} for mono	mer ^b		
Transfer agent	(°C)	St	MMA	EA	References
66 (MMA dimer) 67 (MMA trimer) 68, <i>n</i> = 2 68, av. <i>n</i> = 14 73 (MAA dimer) 63 (MAA trimer) 74 75 76 77 (AMS dimer) 77 (AMS dimer) 78 80 82 83 84 85	60 60 60 60 60 60 60 60 60 110 120 120 120 120 60 60 60 60	0.55° 0.24 0.28 0.16 0.11 0.15 0.552°.° 0.004 0.15	0.013 0.19 0.31 0.21 0.18 0.26 0.18 0.27 0.015 0.09 ^d 0.13 0.14 ^d 0.123 ^{c.e} 0.004 0.015 0.004	0.12 ^c 0.84 ^c 0.02 ^f 0.20 0.45	224, 434 224, 434 224 34 34 34 34 35 400 26, 400, 436 400 400 400 231 437 437

^a Bulk, medium comprises only monomer and transfer agent.

^bAll transfer coefficients rounded to two significant figures.

^c Copolymerization observed as side reaction.

^d BMA.

^e Significant retardation observed.

^f MA, 80 °C.

EA, ethyl acrylate; St, styrene; MMA, methyl methacrylate.



Scheme 17 Mechanism of addition-fragmentation chain transfer with MMA dimer (**66**). Reproduced from Moad, G.; Rizzardo, E.; Thang, S. H., Radical addition-fragmentation chemistry in polymer synthesis. *Polymer* **2008**, *49*, 1079–1131.¹

In polymerization of monosubstituted monomers (e.g., St, butyl acrylate (BA)), copolymerization of the macromonomer to form a graft copolymer is invariably a significant pathway.¹⁰ Fragmentation and chain transfer is favored by elevated reaction temperatures.^{50,225,227} The process of backbiting and β -scission that occurs during radical polymerization of acrylate monomer can be considered as a RAFT process.²²⁸ The intermediate formed by polymerization of monosubstituted monomers in the presence of a 'trimer' such as **81** (*n*=1) is similar to that produced by backbiting β -scission during polymerization. High-temperature polymerization of acrylate monomers is a convenient source of macromonomers (e.g., **81**).^{225,227}

For polymerization of MMA in the presence of the macromonomers $81^{225,229,230}$ where the leaving group is a primary or secondary radical, the adduct radical partitions between fragmentation and propagation. In the case of 82, where the leaving group is a more stable radical, fragmentation becomes the favored pathway but copolymerization is still observed.²³¹ macromonomers were made *in situ* by catalytic chain transfer was developed.^{44,50} Molecular weights up to 28 000 that increase linearly with conversion as predicted, molecular weight distributions that narrow with conversion down to *D* (dispersity) < 1.3, and block purities > 90% can be achieved.^{44,50} Surfactant-free emulsion polymerizations are made possible by use of an MAA macromonomer as the initial RAFT agent to create 'self-stabilizing lattices'. Some examples of block copolymers synthesized by macromonomer RAFT polymerization are provided in Table 9.²³²

3.07.3.2 Thiocarbonylthio Compounds

Thiocarbonylthio RAFT agents include certain dithioesters, trithiocarbonates, xanthates, dithiocarbamates, and other compounds. Figure 5 provides general guidance on how to select the appropriate thiocarbonylthio RAFT agent for a particular monomer. It should be clear that with just two RAFT agents it should be possible to exert effective control over the vast



Because transfer coefficients of the macromonomers are typically low (<0.5) it is necessary to use starved–feed conditions to take full advantage of RAFT, achieve low dispersities, and make block copolymers. Best results have been achieved using emulsion polymerization^{44,50} where rates of termination are lowered by compartmentalization effects. A 'one-pot' process where

majority of polymerizations. For example, a tertiary cyanoalkyl trithiocarbonate (e.g., 119–121) provides excellent control and no or little retardation in RAFT polymerizations of (meth) acrylates, (meth)acrylamides, and styrene. A cyanoalkyl dithiocarbamate (e.g., 143) or xanthate (e.g., 167) enables similar control in RAFT polymerizations of VAc, vinyl pyrrolidone

 Table 9
 Block copolymers prepared by macromonomer RAFT polymerization under starved–feed conditions^{44,50}

Macro ^a	M _n	Ð	Monomer	Solvent	Temperature (°C)	M _n	Ð
MAA	950		MMA	Emulsion	80	3 000	1.4
MMA	3500	1.6	BMA	Emulsion	80	28 000	1.4
MMA	2050	1.7	EHMA	Emulsion	80	11 800	1.3
<i>t</i> BMA	2400	2.1	BMA	Emulsion	80	5 800	1.3
PhMA	1100	2.2	BMA	Emulsion	80	14 500	2.3
HEMA	1550		MMA	H ₂ 0/ <i>i</i> Pr0H	80	3 600	1.8
BMA	1050	2.0	St	BuAc	125	4 700	2.4 ^b
MMA-MAA	1030	1.5	BA	BuAc	125	2700	1.8 ^c
MAA	1600	1.4	BA	<i>i</i> PrOH	80	3 500	1.6 ^d

^a Macromonomer made from monomer shown by catalytic chain transfer.^{44,50}

^b After subtraction of residual macromonomer

^c Contains graft copolymer impurity.

^dBatch reaction. Block purity not determined.⁴³³

EHMA, 2-ethylhexyl methacrylate; PhMA, phenyl methacrylate; /PrOH, propan-2-ol; BuAc, butyl acetate.

BA, butyl acrylate; MAA, methacrylic acid, BMA, *n*-butyl methacrylate; *i*BMA, *t*-butyl methacrylate; HEMA, 2-hydroxyethyl methacrylate; MMA-MAA, methyl methacrylate-*co*-methacrylic acid



Figure 5 Guidelines for selection of RAFT agents for various polymerizations.^{54,55,82} For Z, addition rates decrease and fragmentation rates increase from left to right. For R, fragmentation rates decrease from left to right. Dashed line indicates partial control (i.e., control of molecular weight but poor dispersity or substantial retardation in the case of VAc).

(VPr), and similar monomers. Other RAFT agents may be required for solubility or compatibility with particular polymerization media or to provide specific end-group functionality. The use of bis- and multi-RAFT agents (see Section 3.07.3.4.4) permits the synthesis of polymers with complex architectures. Symmetrical trithiocarbonates can be considered as a member of the class of bis-RAFT agents.

A listing of the more popular RAFT agents and the polymerizations in which they have been applied can be found in the following sections (3.07.3.2.1-3.07.3.2.7). Monomer/RAFT agent combinations that have proved ineffective or which are less effective are indicated by the monomer being in parentheses. The criteria for effectiveness are that there is polymerization, that the molecular weight should be controlled, and that dispersity obtained should be < 1.4 under the conditions reported. There is some subjectiveness in these criteria since the level of control is dependent on polymerization conditions. It should be pointed out that a broad molecular weight distribution is not by itself an indication that there is a low fraction of living chains and thus it should not be taken as an indication that the RAFT agent is not useful for preparing block copolymers or for preparing end-functional polymers based on the indicated monomer. A more comprehensive listing of RAFT agents and polymerizations can be found in our recent reviews.^{1,54,55,58}

A more quantitative indication of effectiveness is provided by transfer coefficient data. Some representative data are provided in **Table 10**.¹ However, such data are, as yet, available for few systems. Moreover, most reported transfer coefficients (even when not indicated as such) are 'apparent transfer constants' (C_{tr}^{app} , see discussion above) and care should be taken when using these data to extrapolate to polymerization conditions different to those under which the data were obtained.

3.07.3.2.1 RAFT agent synthesis

This section is taken largely from our recent reviews.^{54,55,58,234} Currently, a few RAFT agents are available in research quantities from Strem²³⁵ and Aldrich.²³⁶ RAFT agents are available in moderate to excellent yields by a variety of methods, and

				T				10 ⁻⁶ k _{add}		
Agent	Ζ	R	Monomer	(°C)	C_{tr}^{app}	C _{tr}	C _{-tr}	$(M^{-1} S^{-1})$	ϕ	Reference
87	Ph	PMMA	MMA	60 ^a	140	140	140		0.5	405
88	CH₃	PMMA	MMA	40	40	40	40		0.5	139
90	CH ₃	PSt	MMA	40	0.83					139
91	Ph	C(CH ₃) ₂ Ph	MMA	60	5.9	56 ^b	2 500 ^b			133
92	Ph	C(CH ₃) ₂ CN	MMA	60	6.8	25 ^b	450 ^{b,c}			133
89	Ph	PSt	Styrene	60	~6 000	~6000	~6000	~2	0.5	405
90	CH_3	PSt	Styrene	60 ^a	180	180	180	0.05	0.5	405
90	CH ₃	PSt	Styrene	40	220	220	220		0.5	139
88	CH ₃	PMMA	Styrene	40	420					139
91	Ph	C(CH ₃) ₂ Ph	Styrene	60	> 500	2000 ^b	10 000 ^b	2	0.2	133
91	Ph	$C(CH_3)_2Ph$	Styrene	60	25 000 ^c			4.0	1.0 ^d	439
103	Ph	CH₂Ph	Styrene	60	50	400 ^{<i>b</i>}	11 600 ^b	2	0.034	133

 Table 10
 Transfer and rate coefficients for dithioester RAFT agents

^a Arrhenius parameters are provided in the reference indicated.

^b Estimated by kinetic simulation. Actual values may be higher.¹³³

^c C_{tr} corresponding to value of k_{add} shown ($C_{tr} = k_{add}/\phi/k_p$) with k_p (MA, 60 °C) 27 800 M⁻¹ s⁻¹ ²²⁸ and k_p (St,60 °C) 160 M⁻¹ s⁻¹.

^d Value of ϕ assumed in cited reference.



RAFT agent ^a	Synthesis ^a	Polymerizations ^b
S S S S S S S S S S S S S S S S S S S	B ^{12,246}	St ^{12,19,132,133,148,239,281,405,439–440} BA, ⁴⁴¹ MA ^{133,272,309,442,443} DMAM, ⁴⁴⁴ NIPAM ³⁶⁹ (AN) ⁴⁴⁵ BMA, ⁴⁴⁶ <i>BMA</i> , ^{19,129} MMA, ^{19,131,133,134,150,239,284,291,447,448 <i>MMA</i>¹²⁹}
$ \begin{array}{c} $	E ^{133,258} C ^{12,248}	St ^{12,129,132,133,286} BA, ¹³³ MA ^{133,271} AA ²³⁹ AN ⁴⁴⁹ <i>BMA</i> , ³⁵³ MMA, ^{129,133,134,239,273,450,451} <i>MMA</i> ³⁵³ VBz ^{19,129}
$S \rightarrow S$ S $\sim CN$	C ⁴⁵²	MA, ⁴⁵³ /BA ⁴⁵³ MMA, ^{453,454} MAA ⁴⁵⁵
S S CN S CN S CN S CN S S CN S CN S S CN S S CN S S CN S S CN S S S CN S S S CN S S CN S S S CN S S S S S S S S S S	C ²⁴⁸	St, ^{129,239} <i>St</i> ⁴⁵⁶ DMAM, ^{369,457} AM ⁴⁵⁸ MMA ⁴⁵⁶ HPMAM, ^{459,460} MAM ⁴⁶¹
S $CO_2C_2H_5$ 95	A ¹³³	St ¹³³ (MMA) ¹³³
S	B ¹³³	St ¹³³ (MMA) ¹³³
S 97	D ^{133,254} F ^{348,462}	BA, ⁴⁶³ EHA ⁴⁶⁴ AA ²⁶¹ (MMA) ¹³³
S S CN	A ⁴⁶⁵	St ⁴⁶⁵ BA ⁴⁶⁵ MMA ⁴⁶⁵
$S \xrightarrow{Ph} S \xrightarrow{Ph} N(C_2H_5)_2$	A ⁴⁶⁶	St ⁴⁶⁶ MA ⁴⁶⁶ MAM ⁴⁶⁶

Table 11	Dithioesters (Z = aryl) used as RAFT agents
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Table 11 (Continued)		
RAFT agent ^a	Synthesis ^a	Polymerizations ^b
	A ⁴²⁰	St ⁴²⁰ MA ⁴²⁰ DMAM ⁴²⁰ MMA ⁴²⁰
S S S S	B ^{133,246} D ²⁵⁴ F ²⁶¹	(<i>St</i>) ^{12,354,467} MA, ^{129,131,271,305} BA ^{12,129,131,133} AA ^{19,129,261} (MMA) ¹³³
101		
S $CO_2C_2H_5$	A ⁴⁶⁸ 469	St ⁴⁶⁸ BA ⁴⁶⁸ (MMA) ⁴⁶⁸
102		
	A ¹³³ D ²⁵⁴ F ²⁶⁰	St, ^{133,470} (<i>St</i>) ^{12,467} (MA), ⁴⁷¹ MA, ¹³³ BA ¹³³ DMAM ⁴⁴⁴ (MMA) ¹³³
	C ^{273,472}	St ^{287,473} MMA ^{273,294,472,474}
104		
S CN S CN	A ⁴⁶⁵	St ⁴⁶⁵ BA ⁴⁶⁵ MMA ⁴⁶⁵
105		

^a References cited in this column provide a synthesis of RAFT agent. The letter indicates the method used (see Section 3.07.3.2.1). ^b References cited provide details of polymerization of the monomers indicated. Heterogeneous polymerizations (emulsion, miniemulsion) are indicated by the monomer being in italics. Monomer/RAFT agent combinations that are relatively ineffective are indicated by the monomer being in parentheses. DMAM, *N*,*N*-dimethylacrylamide; EHA, 2-ethylhexyl acrylate; HPMAM, *N*-(2-hydroxypropyl) methacrylamide; MAM, methacrylamide; NIPAM, *N*-isopropyl acrylamide; *BA*, *tert*-butyl acrylate; VBz, vinyl benzoate.

syntheses are generally straightforward. References to syntheses of some specific RAFT agents are provided in Tables 11–19.

The methods most commonly exploited include the following:

 Reaction of a carbodithioate salt with an alkylating agent (Scheme 18).^{132,133,237,238} Often this will involve sequential treatment of an anionic species with carbon disulfide and an alkylating agent in a one-pot reaction. For example, this process was used to prepare 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate (95),¹³² 2-cyanoprop-2-yl dithiobenzoate (91),²³⁹ and benzyl dithiobenzoate (103).¹³²

Similar chemistry is used in the synthesis of unsymmetrical trithiocarbonates (Scheme 19).^{240,241} Yields are generally high (> 70%) for substitution of primary and secondary alkyl halides but can be low for tertiary halides (5–40%).

PhBr
$$\xrightarrow{Mg}$$
 PhMgBr $\xrightarrow{CS_2}$ PhCH₂Br \xrightarrow{S} PhCH₂Br \xrightarrow{S} Ph
50 °C Ph \xrightarrow{S} Ph

Scheme 18 Synthesis of benzyl dithiobenzoate (**103**). Reproduced from Moad, G.; Rizzardo, E.; Thang, S. H., Living Radical Polymerization by the RAFT Process. *Aust. J. Chem.* **2005**, *58*, 379–410.⁵⁴



Scheme 19 Synthesis of butyl phenylethyl trithiocarbonate (**126**). Reproduced from Moad, G.; Rizzardo, E.; Thang, S. H., Living Radical Polymerization by the RAFT Process. *Aust. J. Chem.* **2005**, *58*, 379–410.⁵⁴

Thiocarbonylbisimidazole may be used as an alternative to carbon disulfide in the synthesis of some RAFT agents (e.g., Scheme 20).^{242–244}

 Addition of a dithioacid across an olefinic double bond.^{133,245-247} This procedure has been used to prepare cumyl dithiobenzoate (91) (Scheme 21).²³⁹ Electron-rich olefins (St, AMS, isooctene, and VAc) give the desired Markownikov addition (sulfur at substituted position). However, similar reactions with electron-deficient olefins (MMA, MA, acrylonitrile (AN)) give Michael-like addition (sulfur at the unsubstituted position) and therefore do not give useful RAFT agents.

3. *Radical-induced decomposition of a bis(thioacyl) disulfide*.^{100,132,248,249} This is probably the most used method for the synthesis of RAFT agents requiring tertiary R groups. An example is the synthesis of the tertiary trithiocarbonate (Scheme 22).¹⁰⁰ The source of radicals may also be an ATRP







Scheme 21 Synthesis of cumyl dithiobenzoate (91) by addition of a dithioacid across a double bond. Reproduced from Moad, G.; Rizzardo, E.; Thang, S. H., Living Radical Polymerization by the RAFT Process. *Aust. J. Chem.* 2005, *58*, 379–410.⁵⁴



Scheme 22 Synthesis of (S)-4-cyano-4-(((dodecylthio)carbonothioyl)thio)pentanoic acid from a bis(thioacyl) disulfide. Reproduced from Moad, G.; Rizzardo, E.; Thang, S. H., Living Radical Polymerization by the RAFT Process. *Aust. J. Chem.* **2005**, *58*, 379–410.⁵⁴



Scheme 23 Synthesis of *t*-butyl dithiobenzoate by sulfuration of a thioloester. Reproduced from Moad, G.; Rizzardo, E.; Thang, S. H., Living Radical Polymerization by the RAFT Process. *Aust. J. Chem.* **2005**, *58*, 379–410.⁵⁴

initiator.^{250,251} It is also possible to use this chemistry to generate RAFT agents *in situ* during polymerization.²⁵² A new synthesis of bis(thioacyl) disulfides has appeared.²⁵³

- 4. Sulfuration of a thioloester (Scheme 23)¹³³ or a mixture of a carboxylic acid with an alcohol, halide, or $olefin^{254-256}$ with P_4S_{10} , Davy, or Lawesson reagent.²⁵⁷
- 5. Radical-induced ester exchange.^{12,132,133,258} For this method to be effective the R group of the precursor RAFT agent should be a good free radical leaving group with respect to that of the product RAFT agent. For example, the cyanoisopropyl radical generated from azobis(isobutyronitrile) (AIBN) can replace the cumyl group of cumyl dithiobenzoate (91) (Scheme 24).²³⁹ The use of macro-RAFT agents in this process provides a method of end-group removal and a method for regenerating a (low molecular weight) RAFT agent.²⁵⁹
- 6. Transesterification^{260,261} (thiol exchange by reaction of a dithioester with a thiol). Thioglycolic acid-based dithioesters are poor RAFT agents. However, they can serve as precursors to other RAFT agents as they undergo facile reaction with other thiols to provide new dithioesters. For example, reaction of dithioester 86 with benzylmercaptan provides benzyl dithiobenzoate (103) in high yield (Scheme 25).²⁶⁰



Scheme 24 Synthesis of 2-cyano-2-propyl dithiobenzoate by radical induced ester exchange. Reproduced from Moad, G.; Rizzardo, E.; Thang, S. H., Living Radical Polymerization by the RAFT Process. *Aust. J. Chem.* 2005, *58*, 379–410.⁵⁴



Scheme 25 Synthesis of benzyl dithiobenzoate using a thiol exchange reaction.

- *Ketoform reaction.* The symmetrical carboxy-functional trithiocarbonate 131 can be synthesized using a ketoform reaction as shown in Scheme 26.²⁶² Carboxy-functional trithiocarbonates,²⁶² xanthates,²⁶³ or dithiocarbamates²⁶³ can be prepared by a similar procedure with addition of a thiol, alcohol, or secondary amine, respectively (Scheme 27).
- 8. *Reaction of thiochloroformate with thiol*. The esterification of the appropriate thiol with a thiochloroformate (Scheme 28) has been used in the synthesis of phenyl xanthates^{132,261} and phenyl trithiocarbonates.²⁴⁴ This method was also used to synthesize the 'F-RAFT' agent 173.²⁶⁴ The thiochloroformate may be replaced with the corresponding imidazole to avoid use of thiophosgene.²⁴⁴
- 9. Single monomer unit insertion.²⁶⁵ The success of this process relies on the addition of R• to the monomer being substantially faster than the subsequent monomer additions and requires a very active RAFT agent such that the number of monomer additions per activation cycle is < 1. The methodology was applied in the synthesis of the bis-RAFT agent shown in Scheme 29.²⁶⁶ The process has also been adapted for end-functionalizing macro-RAFT agents by addition of a single monomer unit to form a new macro-RAFT agent. Recent examples of this involve attachment of a maleic anhydride (MAH) to a polystyrene macro-RAFT agent²⁶⁷ and a single maleimide unit to a poly(2-(dimethylamino)ethyl methacrylate) (PDMEAMA) macro-RAFT agent²⁶⁸ (Tables 20 and 21).

3.07.3.2.2 Dithioesters

A wide range of dithioester RAFT agents has been reported. Common examples of mono-RAFT agents and their application are provided in **Tables 11** (Z = aryl) and 13 (Z = alkyl or aralkyl). RAFT agents can contain various unprotected functionality on the 'R' fragment of dithiobenzoate including hydroxy, carboxylic acid/carboxylate, sulfonic acid/sulfonate, olefin, and siloxane. Examples of bis- and multi-dithioester RAFT agents (Z = aryl) that may be used for triblock or star synthesis are shown in **Tables 12** and **22**, respectively. Bis-dithioesters can be used to synthesize triblock copolymers in a two-step process.



Scheme 26 Synthesis of a symmetrical trithiocarbonate (131) using a ketoform reaction.

$$C_{12}H_{25}SH + CS_2 + CHCI_3 + H + CS_2 + CHCI_3 + H + CS_2 + CHCI_3 + C_{12}H_{25}S + C_{$$

Scheme 27 Synthesis of a non-symmetrical trithiocarbonate using a ketoform reaction.



Scheme 28 Synthesis of S-t-butyl O-phenyl xanthate (161) by reaction of a thiochloroformate with a thiol.



Scheme 29 Synthesis of a RAFT agent by single unit monomer insertion. Reproduced from Moad, G.; Rizzardo, E.; Thang, S. H., Living Radical Polymerization by the RAFT Process - A Second Update. *Aust. J. Chem.* **2009**, *62*, 1402–1472.⁵⁸

RAFT agent ^a	Synthesis ^a	Polymerizations ^b
'R'-connected core		
$S \rightarrow S \rightarrow$	B ^{129,475}	St ⁴⁷⁶ BA ¹²⁹ AA ⁴⁷⁶ NAM ⁴⁶² BMA, ¹³¹ DMAEMA, ⁴⁷⁶ MMA, ^{129,475} LMA ⁴⁷⁵
$ \begin{array}{c} $	A ⁴⁷⁷	MMA ⁴⁷⁷
108	A ^{129,475}	St ⁴⁷⁵ BA ¹²⁹
	D ²⁵⁵	St ²⁵⁵ <i>t</i> BA ²⁵⁵
^S 109		

 Table 12
 Bis-dithioesters (Z = aryl) used as RAFT agents

^a References cited in this column provide a synthesis of RAFT agent. The letter indicates the method used (see Section 3.07.3.2.1). ^b References cited provide details of polymerization of the monomers indicated.

LMA, lauryl methacrylate lauryl (dodecyl methacrylate); NAM, N-acryloylmorpholine; t BA, tert-butyl acrylate.

Dithiobenzoates and similar dithioesters with Z = aryl are amongst the most active RAFT agents and, with appropriate choice of 'R', have general applicability in the polymerization of (meth)acrylic and styrenic monomers.^{54,55} However, their use can give retardation, particularly when used in high condithiobenzoate RAFT agents in MMA polymerization, electron-withdrawing groups render the thiocarbonyl sulfur more electrophilic, enhance the rate of addition to the C=S double bond, and provide narrower dispersities from the early stages of polymerization (Figure 6).^{54,273}



centrations (to provide lower molecular weight polymers) and with high k_p monomers (acrylates and acrylamides). They are also more sensitive to hydrolysis and decomposition by Lewis acids⁸² than, for example, dithioesters with Z = alkyl or trithio-carbonate RAFT agents.

An IUPAC task group Towards a Holistic Mechanistic Model for RAFT Polymerizations: Dithiobenzoates as Mediating Agents was formed in 2005 under the auspices of the IUPAC Subcommittee on Modeling of Polymerization Kinetics and Processes. This dilemma paper summarized the current situation with respect to the polymerization kinetics, possible side reactions, and mechanisms for retardation.⁷²

In polymerization of methacrylates and styrene with cumyl dithiobenzoate (91), retardation may be observed that is directly correlated with consumption of the initial RAFT agent and which is strongly dependent on the RAFT agent concentration. Other dithiobenzoates (e.g., cyanoisopropyl dithiobenzoate (92)) and aliphatic dithioesters (e.g., cumyl 2-phenylethanedithioate (110)) have fewer issues with respect to retardation. The aliphatic dithioesters are also less active and offer poorer control, with methacrylates.

For the case of acrylates, retardation with dithiobenzoate RAFT agent is independent of 'R' and is not directly related to consumption of the initial RAFT agent, which is rapid with the dithiobenzoate being completely consumed at very low monomer conversion. Thus in polymerization of MA with benzyl (103) or cyanoisopropyl dithiobenzoate (92) as RAFT agent at 60 °C, substantial retardation of similar magnitude was found from the onset of polymerization.^{12,133,134,269} Use of an aliphatic dithioester, benzyl dithioacetate (113), provided substantially less retardation under the same polymerization conditions. Quinn et al.²⁷⁰ observed that 1-phenylethyl 2-phenylethanedithioate (115) enabled RAFT polymerization of MA at ambient temperature whereas 1-phenylethyl dithiobenzoate (101) strongly retarded polymerization under the same conditions. The observation of less retardation in RAFT polymerization of acrylate esters with aliphatic (Z=alkyl or aralkyl) and trithiocarbonate RAFT agents (Section 3.07.3.2.3) than is seen with dithiobenzoate RAFT agents has also been reported under other circumstances.270-272 It should be stressed that these retardation issues do not prevent formation of low-dispersity or block polymers.

Electron-withdrawing groups can enhance the activity of dithiobenzoate RAFT agents. For ring-substituted cyanoisopropyl For polymeric RAFT agents used in homopolymerization where R and the propagating radical differ only in chain length and chain length is significant (> 5), C_{tt}^{app} and C_{tt} (= C_{-tr}) are expected to be similar. In all other cases, because of the assumptions with respect to values of C_{-tr} and ϕ , C_{tr}^{app} should be regarded as a minimum value for C_{tr} . The difference between the measured C_{tr}^{app} may exceed several orders of magnitude (Table 13).

3.07.3.2.3 Trithiocarbonates

The utility of trithiocarbonate RAFT agents was disclosed in the first RAFT patent¹²⁹ and many papers now describe their application.⁸² Trithiocarbonates are less active than dithiobenzoate and similar RAFT agents (Section 3.07.3.2.1) yet can still provide good control over the polymerization of (meth)acrylic and styrenic monomers. More importantly, they give substantially less retardation, are less prone to hydrolytic degradation, and, typically, are more readily synthesized. Ideally, to avoid odor issues with the RAFT agent and polymer the 'Z', and preferably the 'R(S)' groups, should be based on thiols with low volatility (e.g., dodecanethiol).^{82,100}



Figure 6 Evolution of dispersity (*D*) with conversion for MMA polymerizations carried out with ring-substituted cyanoisopropyl dithiobenzoate RAFT agents: (a) 2,6-dimethyldithiobenzoate (Δ); (b) 4-methoxydithiobenzoate (\circ); (c) dithiobenzoate (Δ); (d) 3,5-di(trifluoromethyl)dithiobenzoate (\Box). Reproduced from Moad, G.; Rizzardo, E.; Thang, S. H. *Aust. J. Chem.* **2005**, *58*, 379–410. Based on data from Benaglia, M.; Rizzardo, E.; Alberti, A.; Guerra, M. *Macromolecules* **2005**, *38*, 3129–3140.²⁷³

RAFT agent ^a	Synthesis ^a	Polymerizations ^b	RAFT agent ^a	<i>Synthesis</i> ^a	Polymerizations ^b
H ₃ C – S S – S	B ²⁴⁶	MMA ^{139,239}	$H_{3}C \xrightarrow{S} CN$	C ¹³²	St ¹³²
110 H ₃ C – (S S – (S	B ²⁴⁶	St ^{139,405}	H ₃ C – (S	A ¹³²	St, ^{132,467} <i>St</i> ^{12,129} BA ^{12,19}
	B ⁴⁷⁸	St, ^{478,479} <i>St</i> ^{317,328} BA, ⁴⁴¹ MA ^{272,441} AA ⁴⁸⁰ AM, ⁴⁵⁸ NIPAM ⁴⁸¹ MMA ⁴⁷⁸		B ²⁷⁰	St, ^{247,354,482} (St ⁴⁸³), <i>St</i> ³⁵⁴ MA ^{247,270,272} NIPAM ⁴⁸¹ (NVP) ⁴⁸⁴
	A ⁴⁸⁵	MA, ^{441,485,486} BA, ⁴⁸⁷ DA ⁴⁸⁸	S S О ОН	A ^{489,490}	NIPAM, ⁴⁹¹ DMAM ⁴⁹⁰
S 118	A ³⁶⁹	MA, ⁴⁷¹ BA ³⁶⁹			

	Table 13	Dithioesters	(Z = alkyl	or alkylary	I) used as RAFT	agents
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^a References cited in this column provide a synthesis of RAFT agent. The letter indicates the method used (see Section 3.07.3.2.1).

^b References cited provide details of polymerization of the monomers indicated. Heterogeneous polymerizations (emulsion, miniemulsion) are indicated by the monomer being in italics. Monomer/RAFT agent combinations that are relatively ineffective are indicated by the monomer being in parentheses.

DA, dodecyl acrylate; DMAM, *N*,*N*-dimethylacrylamide; NIPAM, *N*-isopropyl acrylamide.

A wide range of trithiocarbonate RAFT agents has now been reported; two classes are distinguished. Nonsymmetrical trithiocarbonates (Table 14) have only one good homolytic leaving group. The other S-substituent is usually primary alkyl or aryl.²⁴⁴ Symmetrical trithiocarbonates have two good homolytic leaving groups (Table 15) and the trithiocarbonate group remains in the center of the structure. The bis-trithiocarbonates shown in Table 16 also have two good homolytic leaving groups

3.07.3.2.4 Dithiocarbamates

Examples of dithiocarbamate RAFT agents are shown in **Table 17**. *N*,*N*-Dialkyl dithiocarbamates and *N*-alkyl-*N*-aryl dithiocarbamates are suited for polymerization of 'less-

activated' monomers (LAMs) such as VAc, *N*-vinylpyrrolidone (NVP), and related vinyl monomers. However, they have low activity in polymerization of styrenic and (meth)acrylic monomers. The low transfer coefficients can be qualitatively understood in terms of the importance of the zwitterionic canonical forms (**Figure 7**). The interaction between the nitrogen lone pairs and the C=S double bond reduces the double bond character of the thiocarbonyl group.^{12,132}

When the nitrogen lone pair is less available for delocalization into the thiocarbonyl group by virtue of being part of an aromatic ring (e.g., a pyrrole or imidazole ring 138–141) or by possessing an adjacent electron-withdrawing substituent dithiocarbamates can be effective in controlling

RAFT agent ^a	<i>Synthesis</i> ^a	Polymerizations ^b	RAFT agent ^a	Synthesis ^a	Polymerizations ^b
$H_3CS \xrightarrow{S}_{CN}$	C ^{132,248}	St ^{132,239} MA ²⁶⁹ MMA ^{239,284}	$C_{12}H_{25}S \xrightarrow{S}_{CN}$	C ³⁰⁴	MMA ³⁰⁴
$C_{12}H_{25}S \xrightarrow{S} CO_{2}H$ S CN 121	C ¹⁰⁰	MMA ^{54,100}	С ₁₂ H ₂₅ S - К S - СО ₂ H 122	G ^{492,493}	BA ^{451,492} EA ²⁶² MA ²⁹¹ AA ^{262,494} NIPAM ⁴⁹⁵ DMAM ⁴⁹⁵ AN ⁴⁹⁴ (NVP ⁴⁹⁶)
$C_{12}H_{25}S \xrightarrow{S} Ph S \xrightarrow{CN} CN$	A ⁸²	MMA ⁸²	$H_3CS \xrightarrow{S} Ph S \xrightarrow{CO_2H} 124$	A ⁴⁹⁷	St, ^{239,498} BA ⁴⁹⁹
$H_3CS \xrightarrow{S} Ph S \xrightarrow{CO_2CH_3}$ 125	A ^{420,500}	St ⁴²⁰ MA ⁴²⁰ DMAM ⁴²⁰ (MMA ⁴²⁰)	$R = C_4H_9 \text{ or } C_{12}H_{25}$	A ²⁴⁰	St ²⁴⁰ ODA ^{81,403}
$C_2H_5S \xrightarrow{S} OC_2H_5$	A ²⁴³	St ⁵⁰¹ MA, ²⁴³ <i>t</i> BA ⁵⁰¹	$\begin{array}{c} C_{12}H_{25}H_{2}C \xrightarrow{S} \\ S \xrightarrow{CO_{2}H} \\ 128 \end{array}$	A ³³²	MA ^{291,451,492} AA ³³²
	A ²⁴⁰	St ^{100,240,280} MA ^{81,280} NIPAM ²⁸⁰	$C_{12}H_{25}S - \sqrt{S} C_{N}$ S C_{N} 130 R = C ₁₂ H ₂₅	A ³⁰⁴	St ³⁰⁴ MA ³⁰⁴

Table 14	Nonsymmetrical	trithiocarbonates	(Z = thioalkyl)	used as RAFT	agents
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^a References cited provide a synthesis of RAFT agent. The letter indicates the method used (see Section 3.07.3.2.1).

^b References cited provide details of polymerization of the monomers indicated. Monomer/RAFT agent combinations that are relatively ineffective are indicated by the monomer being in parentheses.

DMAM, N,N-dimethylacrylamide; EA, ethyl acrylate; NIPAM, N-isopropyl acrylamide; tBA, tert-butyl acrylate.

polymerization of 'more-activated' monomers (MAMs). These RAFT agents tend to inhibit polymerizations of LAMs. Inhibition is thought to be a consequence of greater stability of the intermediate radicals which is then more prone to undergo side reactions such as intermediate radical termination (Table 18).

3.07.3.2.5 Switchable RAFT agents

RAFT agents such as dithioesters or trithiocarbonates suitable for controlling polymerization of MAMs, for example, MMA, S, MA, acrylamide (AM), and AN, inhibit or retard the polymerizations of LAMs, for example, VAc, NVP, and N-vinylcarbazole (NVC). Similarly RAFT agents suitable for controlling





^a References cited in this column provide a synthesis of RAFT agent. The letter indicates the method used (see Section 3.07.3.2.1).

^b References cited provide details of polymerization of the monomers indicated. Monomer/RAFT agent combinations that are relatively ineffective are indicated by the monomer being in parentheses.

DA, dodecyl acrylate; EA, ethyl acrylate; NIPAM, N-isopropyl acrylamide.

Table 16 Bis-trithiocarbonates used as RAFT agents

RAFT agent ^a	Synthesis ^a	<i>Polymerizations</i> ^b
'R'-connected core		
S S S S S S S	A ^{509,510}	St ^{509,510} BA, ⁴⁰⁷ <i>t</i> BA ⁵⁰⁹ NIPAM ⁵¹⁰
R-S		
135 R = CH ₃ , C ₃ H ₇ , C ₁₂ H ₂₅		
H ₃ CO ₂ C S SC ₄ H ₉	A ⁵¹⁰	St ⁵¹⁰ NIPAM ⁵¹⁰
H ₃ CO ₂ C S S S		
C ₄ H ₉ S [´] 136		
'Z'-connected core		

(Continued)

^a References cited in this column provide a synthesis of RAFT agent. The letter indicates the method used (see Section 3.07.3.2.1).
 ^b References cited provide details of polymerization of the monomers indicated.
 NIPAM, *N*-isopropyl acrylamide; *t*BA, *tert*-butyl acrylate.

Table 17 Dithiocarbamates (Z = N<) used as RAFT agents</th>



Table 17(Continued)



^aReferences cited in this column provide a synthesis of RAFT agent. The letter indicates the method used (see Section 3.07.3.2.1).

^b References cited provide details of polymerization of the monomers indicated. Monomer/RAFT agent combinations that are relatively ineffective are indicated by the monomer being in parentheses.

EA, ethyl acrylate; NIPAM, N-isopropyl acrylamide.



Figure 7 Canonical forms of dithiocarbamates

polymerizations of LAMs such as *N*,*N*-dialkyl- or *N*-alkyl-*N*-aryl dithiocarbamates and xanthates tend to be ineffective with MAMs.

A new class of stimuli-responsive RAFT agents that can be switched to offer good control over polymerization of both MAMs and LAMs and a route to polyMAM-*block*-polyLAM has



^a References cited in this column provide a synthesis of RAFT agent. The letter indicates the method used (see Section 3.07.3.2.1).

^b A/B copolymerization of monomer A with monomer B. Heterogeneous polymerizations (emulsion, miniemulsion) are indicated by the monomer being in italics. A-b-B block copolymers are triblocks.

EA, ethyl acrylate; EHA, 2-ethylhexyl acrylate; iOA, isooctyl acrylate; NIPAM, N-isopropyl acrylamide; iBA, tert-butyl acrylate.

RAFT agent	Synthesis ^a	<i>Polymerizations</i> ^b	Switched RAFT agent	Polymerizations ^b
N S CN N 153	A ²⁷⁴	(BA), ²⁷⁴ VAc ²⁷⁴	^N − ^S ⊂N + ^N − ^S ⊂N ⁺ 153-H ⁺	BA ²⁷⁴
N S CO_2CH_3 154	A ²⁷⁴	NVP, ²⁷⁴ NVC ²⁷⁴	N − S − CO ₂ CH ₃ + N − 154-H ⁺	MA, ²⁷⁴ St ^{274,275} (NVC), ²⁷⁴ MA-b-NVC, ^{274,c} St-b-VAc ²⁷⁵
N N S CN 155	C ²⁷⁴		× N − S − CN + N − S − CN H 155-H⁺	MMA, ²⁷⁴ MMA-b-VAc ^{274,c}

Table 19	RAFT agents and RAF	l polymerizations	 switchable (dithiocarbamat	e RAF	T agents
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^a References cited in this column provide a synthesis of RAFT agent. The letter indicates the method used (see Section 3.07.3.2.1).

^b A-b-B block of monomer A then monomer B.

^c RAFT agent was switched (neutralized) to make second block. Monomer/RAFT agent combinations that are relatively ineffective are indicated by the monomer being in parentheses.



Scheme 30 Block copolymer synthesis using a switchable RAFT agent.

been reported.²⁷⁴ *N*-(4-Pyridinyl)-*N*-methyldithiocarbamates (**Table 19**) are effective with LAMs and, in the presence of a strong acid, the protonated form of the *N*-(4-pyridinyl)-*N*-methyldithiocarbamates provides excellent control over the polymerization of MAMs.^{274,275} The process is illustrated in **Scheme 30** for the preparation of PMMA-*block*-PVAc. Thus in the first step the protonated RAFT agent (formed by adding 4-toluenesulfonic acid) is used to control the polymerization of MMA to form poly(MMA). This macro-RAFT agent is then neutralized *in situ* by adding a

stoichiometric amount of *N*,*N*-dimethylaminopyridine (DMAP). RAFT polymerization of VAc then provided the desired block copolymer.

3.07.3.2.6 Xanthates

RAFT polymerization with xanthates is sometimes called MADIX.^{54,276} Xanthate RAFT agents are listed in **Table 20**.

O-Alkyl xanthates have been widely exploited for RAFT polymerization of VAc, NVP, and related vinyl monomers (such as NVC and *N*-vinylindole (NVI)) where the propagating

RAFT agent ^a	<i>Synthesis</i> ^a	Polymerizations ^b	RAFT agent ^a	<i>Synthesis</i> ^a	Polymerizations ^b
$\begin{array}{c} & S & O \\ & & & \\ & & \\ & & \\ & & \\ C_2H_5O & OC_2H_5 \\ & &$	A ⁵²⁰	St, ⁵²⁰ (St) ⁵²⁰ EA	$F_{3}C \xrightarrow{S} O \\ F_{3}C \xrightarrow{P_{=}O} C_{2}H_{5}O \\ C_{2}H_{5}O \\ 157 \\ C_{2}H_{5}O \\ C_{$	A ⁵²⁰	St ⁵²⁰ EA ⁵²⁰
$F \rightarrow F \qquad $	H ¹³²	(St) ^{132,242} MA, ²⁴² <i>t</i> BA, ²⁴² ODA ⁸¹	$F_3C \xrightarrow{O}_{S} \xrightarrow{S}_{O} OC_2H_5$		(St), ⁵²⁰ <i>St</i> ³³⁴ EA ⁵²⁰
	H ¹³²	(St) ^{132,242} MA ²⁴²		H ²⁶¹	AA ²⁶¹
	A ²⁶¹	(EA) ⁵²⁰ (AA) ²⁶¹		C ^{242,248}	(St) ⁵²⁰ (fBA), ²⁴² (MMA), ²⁴² VAc, ²⁴² VBz ²⁴²
$- S - CO_2 C_2 H_5$ 164	C ²⁴²	VAc ²⁴²		A ^{242,318,484}	St, ²⁴² (St), ^{318,483} (BA) ²⁴² (AA) ²⁶¹ NVP ⁴⁸⁴
	A ^{243,318}	(St), ⁵²⁰ (<i>St</i>) ³¹⁸ (EA), ⁵²⁰ MA ²⁴³ AA ⁵²¹ VAc, ^{286,520,522} <i>VAc</i> ³⁵⁶	S S CN	A ²⁴²	VAc ²⁴²
$100 H = CH_3 \text{ or } C_2H_5$	A ²⁸⁰	VAc ²⁸⁰ NVP ^{280,523}	0	A ^{132,261,484}	(St) ¹³² (AA) ²⁶¹ NVP ⁴⁸⁴

Table 20	Xanthates	(dithiocarbonates)) (Z = alkoxy,	aryloxy)	used as RA	FT agents ^a
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(Continued)

Table 20(Continued)					
RAFT agent ^a	<i>Synthesis</i> ^a	<i>Polymerizations</i> ^b	RAFT agent ^a	Synthesis ^a	Polymerizations ^b
S 0 170	A ²⁷⁸	VAc ^{278,522}			

^a References cited in this column provide a synthesis of RAFT agent. The letter indicates the method used (see Section 3.07.3.2.1).

^b References cited provide details of polymerization of the monomers indicated. Heterogeneous polymerizations (emulsion, miniemulsion) are indicated by the monomer being in italics. Monomer/RAFT agent combinations that are relatively ineffective are indicated by the monomer being in parentheses.

EA, ethyl acrylate; tBA, tert-butyl acrylate; VBz, vinyl benzoate.



Figure 8 Canonical forms of xanthates.

radical is a relatively poor homolytic leaving group. They are generally less effective (have low transfer coefficients) in polymerization of styrenic and acrylic monomers and offer no control with methacrylic polymers. This can be qualitatively understood in terms of the importance of the zwitterionic canonical forms (Figure 8).^{12,132} As is the case with *N*, *N*-dialkyl dithiocarbamates, electron-withdrawing substituents on *Z* can enhance the activity of RAFT agents¹³² so that they are more effective in polymerization of styrenic and (meth)acrylic monomers. Thus transfer coefficients of the *O*-aryl xanthates are higher than those of simple *O*-alkyl xanthates. Those of fluorinated xanthates (**158** and **159**) are higher than those of nonfluorinated analogs (**160** and **166**, respectively).^{242,277}

O-Alkyl xanthates with appropriate selection of R have transfer coefficients with acrylates in the range 2–7. This is sufficient to provide end-group control at high conversion (it may be possible to make block copolymers) and some trend for increase in molecular weight with conversion. It is not sufficient to provide very narrow molecular weight distributions, thus most entries appear in parentheses in **Table 20**.

In the case of O-alkyl xanthates, the choice of the alkyl is crucial.^{278,279} It is important that the alkyl on oxygen is a very poor homolytic leaving group with respect to the alkyl group on sulfur for cleavage of the 'S–R' bond to be favored over cleavage of the 'O–alkyl' bond.²⁷⁹ For example, control (predicted \overline{M}_{n} , low $\overline{M}_w/\overline{M}_n$) can be obtained in RAFT polymerization with O-methyl, O-ethyl (**170**), O-isopropyl, and O-aryl xanthates but not with the O-tert-butyl xanthate.²⁷⁸

It is also important to choose 'R' such that the radical R• is able to efficiently reinitiate polymerization. For example, benzyl radical is slow to add to VAc and is therefore also a poor choice for 'R'. RAFT polymerization of VAc and NVP with the *S*-phthalimidomethyl xanthate **168** gave good control over both molecular weight and dispersity (Table 21).²⁸⁰

RAFT agent ^a		Polymerizations ^b	RAFT agent ^a		Polymerizations ^b
$\begin{array}{cccc} C_2H_5O & O & S \\ P & & \\ C_2H_5O & S & \\ & $	C ²⁵⁸	St ²⁵⁸ MMA ²⁵⁸	C_2H_5O O S P \sim C_2H_5O S \sim	A ^{129,258,524}	St ^{129,525–527}
F	H ²⁶⁴	(St) ^{144,264}	172		
173					

 Table 21
 Other RAFT agents

^a References cited in this column provide a synthesis of RAFT agent. The letter indicates the method used (see Section 3.07.3.2.1).

^b References cited provide details of polymerization of the monomers indicated. Monomer/RAFT agent combinations that are relatively ineffective are indicated by the monomer being in parentheses.

3.07.3.2.7 Other RAFT agents

RAFT agents with Z = phosphonate (e.g., 171, 172) are active RAFT agents with transfer coefficients similar to those of the analogous dithioesters.²⁵⁸

On the basis of computational studies on RAFT agents, Z–C (=S)SR, a RAFT agent with Z = fluorine was proposed^{144,147,264} as a 'universal' RAFT agent able to efficiently control the polymerization of both activated monomers (e.g., acrylates and styrene) and LAMs (e.g., VAc). The full utility of this class of RAFT agent has yet to be demonstrated experimentally. The only example reported is the benzyl RAFT agent **173** and this has only been tested in styrene polymerization where limited control was observed (poor correspondence between found and calculated molecular weights, slightly narrowed dispersity).²⁶⁴

3.07.3.3 Reaction Conditions

Some aspects of reaction conditions to specific classes of RAFT agent have already been discussed above. This section is intended to cover generic issues related to the reaction conditions used for RAFT polymerization.

3.07.3.3.1 Temperature

Temperatures reported for RAFT polymerization range from ambient to 180 °C.²⁸¹ There is evidence with dithiobenzoates that retardation, when observed, is less at higher temperatures. Higher temperature does allow higher rates of polymerization, allowing a given conversion to be achieved in a shorter reaction time. There are also some data that show narrower molecular weight distributions can be achieved at higher temperatures.²² This is consistent with rate constants for fragmentation of the RAFT intermediates and transfer coefficients of RAFT agents, both increasing with reaction temperature.

There have been several studies on the thermal stability of RAFT agents and RAFT-synthesized polymers and the possible influence of this on the outcome of RAFT polymerization. Cumyl dithiobenzoate 91 appears substantially less stable than benzyl or phenylethyl dithiobenzoate and degrades rapidly at temperatures > 100 °C.²⁸² The instability was attributed to reversible formation to AMS and dithiobenzoic acid. The success of high-temperature polymerization (of, e.g., styrene) was attributed to the fact that the RAFT agent 91 was rapidly consumed and converted to more stable polymeric RAFT agents. It was also reported that the poor control in synthesis of PMMA with dithiobenzoate RAFT agents at higher temperatures (120 °C) could be attributed to the lability of the dithiobenzoate end group.²⁸³ More recent work,²⁸⁴ while confirming that thermolysis is a suitable method for end-group removal, indicates that dithiobenzoate end groups of RAFT-synthesized PMMA are stable to much higher temperatures.

RAFT polymerization of 'polar' monomers (MMA, MA,²⁸⁵ and VAc²⁸⁶) was reported to be substantially accelerated by microwave heating. Less but still substantial acceleration was observed for styrene polymerization.^{285–287} It is expected that monomers with a higher dielectric constant will be more effectively heated by microwave irradiation. However, the effect particularly with MMA and MA was substantially greater than expected for an effect of temperature alone.²⁸⁵ An explanation for the microwave effect was not provided.²⁸⁵

3.07.3.3.2 Pressure

RAFT polymerization of styrene with cumyl dithiobenzoate (91) under very high pressure (5 kbar) has been reported.^{281,288–290} At very high pressure, radical-radical termination is slowed and this allows the formation of higher molecular weight polymers and higher rates of polymerization than are achievable at ambient pressure.

3.07.3.3.3 Initiator

For optimal control of the RAFT process, it is important to pay attention to such factors as initiator concentration and selection.54 RAFT polymerization is usually carried out with conventional radical initiators. In principle, any source of radicals can be used¹²⁹ but most often thermal initiators (e.g., AIBN, azobis(2-cyanopentanoic acid (ACP), and K₂S₂O₈) are used. Styrene polymerization may be initiated thermally between 100 and 120 °C. Polymerizations initiated with ultraviolet (UV) irradiation,²⁹¹⁻²⁹³ a gamma source,²⁹⁴⁻³⁰² or a plasma field³⁰³ have also been reported. In the latter polymerizations, radicals may be generated directly from the RAFT agent and these may be responsible for initiation. It was initially suggested by Pan and coworkers that the mechanism for molecular weight control in UV²⁹² and gamma-initiated^{298,299} processes might involve only reversible coupling and be similar to that proposed by Otsu et al.53 to describe the chemistry of dithiocarbamate photoiniferters. However, Quinn et al. 293,300,302 demonstrated the living behavior observed in these polymerizations can be attributed to the standard RAFT mechanism.

The initiator concentration and rate of radical generation in RAFT polymerization should be chosen to provide a balance between an acceptable rate of polymerization and an acceptable level of dead chains (radical-radical termination). One useful guideline is to choose conditions such that the target molecular weight is ~10% of that which would have been obtained in the absence of RAFT agent. A common misconception is that it is necessary to use very low rates of polymerization in order to achieve narrow molecular weight distributions. Sometimes, using a high rate of polymerization and a correspondingly short reaction time can provide excellent results (for a narrow molecular weight distribution see, for example, Reference 132). However, it is very important not to use prolonged reaction times when retention of the RAFT functionality is important. Once the monomer is fully converted, continued radical generation may still lead to formation of dead chains by termination (combination or disproportionation) and consequent loss of the thiocarbonylthio end group. Addition of initiator to a RAFT-synthesized polymer is one recognized method for thiocarbonylthio end-group removal.^{259,304}

Side reactions of the initiator or initiator-derived radicals with the RAFT agent are possible. However, these are not always readily discernable or of significance because of the high RAFT agent:initiator ratios used in well-designed experiments. It follows from the mechanism of the RAFT process that there should be a fraction of dead chains formed which relates directly to the number of initiator-derived radicals. Ideally, this fraction should be taken into account when calculating the molecular weights of polymers formed by the RAFT process.¹³² The molecular weight of the polymer formed for a given reaction time (t) can usually be estimated ($[M]_0-[M]_t$) knowing the concentration of the monomer

consumed and the initial RAFT agent conentration $([T]_0)$ using the relationship [7]. Positive deviations from eqn [7] indicate incomplete usage of RAFT agent. Negative deviations indicate that other sources of polymer chains are significant. These include the initiator-derived chains.

$$\overline{M}_{n}(calc) \sim \frac{[M]_{0} - [M]_{t}}{[T]_{0}} m_{M}$$
[7]

If initiator-derived chains are significant, eqn [8] should be used to calculate molecular weights.⁵⁴

$$\overline{M}_{n}(\text{calc}) = \frac{[M]_{0} - [M]_{t}}{[T]_{0} + df([I]_{0} - [I]_{t})}m_{M} + m_{\text{RAFT}}$$
[8]

where $m_{\rm M}$ and $m_{\rm RAFT}$ are the molecular weights of the monomer and the RAFT agent respectively, *d* is the number of chains produced from radical–radical termination ($d \sim 1.67$ in MMA and $d \sim 1.0$ in styrene polymerization), $[I]_o-[I]_t$ is the concentration of initiator consumed, *f* is the initiator efficiency, and *t* is the reaction time.

If the initiator decomposition rate constant is known, the initiator consumption can be estimated using eqn [9]:

$$[I]_0 - [I]_t = [I]_0 (1 - e^{-k_d t})$$

The fraction of living chains (L) in RAFT polymerization (assuming no other side reactions) is given by eqn [10].

$$L = \frac{[T]_0}{[T]_0 + df([I]_0 - [I]_t)}$$
[10]

Some initiators (e.g., dibenzoyl peroxide and potassium peroxydisulfate) and the derived radicals may oxidize RAFT agents to sulfine or other products.³⁰⁵ Other initiator radicals may react with the RAFT agent to form a stable thiocarbonylthio compound. It is important that the initiator-derived radical is a good leaving group with respect to the propagating radical. For example, use of an aliphatic diacyl peroxide (e.g., dilauroyl peroxide) will provide a relatively stable 'RAFT agent' with R = primary alkyl. Similarly, azobis(methyl isobutyrate) (AIBMe) is not a suitable choice for RAFT polymerization of MMA.¹³⁴

The mechanism of decomposition of AIBN and other azonitriles is complicated by the formation of ketenimines as unstable intermediates.³⁰⁶ In the presence of high concentrations of RAFT agents, the ketenimine is intercepted and converted to by-products, which reduce the initiator efficiency and may cause some retardation.

3.07.3.3.4 Solvent

Generally, the polymerization conditions for solution or bulk RAFT polymerization are the same as those for conventional radical polymerization. The RAFT process is compatible with a wide range of reaction media including all common organic solvents, protic solvents such as alcohols and water,^{19,84,307} and less conventional solvents such as ionic liquids³⁰⁸ and supercritical carbon dioxide.^{309,310} It is important that the RAFT agent should be selected for solubility in the reaction medium. In polar media and in the presence of Lewis acids, RAFT agents can show hydrolytic sensitivity.^{311–313} We have found that this order roughly correlates with RAFT agent activity (dithiobenzoates > trithiocarbonates ~aliphatic dithioesters).

3.07.3.3.5 RAFT in heterogeneous media

Much has now been written on the use of RAFT in emulsion and miniemulsion polymerization, and many reviews relating to the use of RAFT in heterogeneous media have appeared.^{88–92,314–316} Our first communication on RAFT polymerization briefly mentions the successful emulsion polymerization of butyl methacrylate with cumyl dithiobenzoate as a table entry.¹⁹ Additional examples and brief discussion of some of the important factors for successful use of RAFT polymerization in emulsion and miniemulsion were provided in two patents^{129,242} and in a subsequent paper.¹²

It is established that success in RAFT emulsion polymerization depends strongly on the choice of RAFT agent and polymerization conditions.^{12,317–327} Most work has focused on styrene polymerization,^{12,317,320,321,326,328–331} although RAFT emulsion polymerizations of BA^{322,332,333} and methacrylates^{12,19} have also been reported.

The emulsion recipes we reported in our first publications^{12,19} were feed processes in which conversions of monomer to polymer were maintained at a high level (often >90%). In a first *ab initio* step, a low molecular weight polymeric RAFT agent was prepared which served as the seed latex and in which ideally all chains were living, that is, capped by a thiocarbonylthio end group. Control during this stage may be relatively poor. However, the poor control obtained in this stage does not substantially affect the control exerted during the later stages of polymerization as long as the ultimate molecular weight required is significantly higher than that of the initial polymeric RAFT agent. The use of cumyl dithiobenzoate (91) as RAFT agent in *ab initio* emulsion polymerization of styrene was not recommended,¹² a finding which has been borne out by many subsequent studies. However this reagent has been successfully used for emulsion polymerization of butyl methacrylate (BMA).¹⁹ Better control in styrene emulsion polymerization is attained through the use of less active RAFT agents, such as dithioacetates or trithiocarbonates, than is achieved with dithiobenzoates.^{12,317,328} The use of xanthate RAFT agents has also been recommended in this context.^{318,334}

An approach to RAFT emulsion polymerization allows emulsion polymerization to be performed without added surfactant. Macro-RAFT agents are used as stabilizers in 'surfactantless' emulsion polymerization, 333, 335-345 miniemulsion polymerization, ^{335,346} suspension polymerization, ³⁴⁷ and nonaqueous dispersion polymerization in both organic media³⁴⁸ and in supercritical CO₂.³⁴⁹⁻³⁵² The process is analogous to the 'self-stabilizing lattices' approach we have previously used in macromonomer RAFT polymerization which involves sequential polymerization of MAA and nonpolar methacrylates (Section 3.07.3.1).44 In a first step, a water-soluble monomer (AA) was polymerized in the water phase using a water-soluble RAFT agent to form a low molecular weight macro-RAFT agent. A hydrophobic monomer (BA^{332,333} and styrene^{329,330}) was then added under controlled feed conditions to give block oligomers which form rigid micelles. These constitute a RAFT agent-containing seed. Continued controlled feed of hydrophobic monomer may be used to continue the emulsion polymerization. A related approach to surfactant-free emulsion polymerization was reported by Freal-Saison et al.331 In this case, the RAFT agent-containing seed was formed by bulk copolymerization of AA and styrene with a water-insoluble RAFT agent (134)

which was neutralized before being dispersed in water. Gilbert³³⁰ has proposed a simple theoretical model for particle formation by self-assembly during RAFT emulsion polymerization and has applied this to analyze data for styrene polymerization. Particle nucleation and growth during RAFT emulsion polymerization of styrene and BA mediated by macro-RAFT agents of various compositions has been studied by calorimetry.³³⁷ More hydrophilic amphipathic macro-RAFT agents (e.g., AA 10 units–S 10 units) were thought to be promising for producing latex products with best control over particle number and particle size distribution. In most cases, this work has involved use of a hydrophilic or an amphiphilic macro-RAFT agent. Examples based on dextran³⁴³ or poly(ethylene oxide) (PEO)^{335,339,346} have also been exploited.

The use of RAFT to control miniemulsion polymerization has also been reported.^{239,353–367} We showed that RAFT in miniemulsion can be used to produce narrow dispersity polystyrene in a batch process.²³⁹ Some retardation is observed with dithiobenzoate RAFT agents.^{12,354} However, this is markedly reduced when aliphatic dithioesters³⁵⁴ or trithiocarbonate RAFT agents are used.³⁶⁵ One of the issues with traditional miniemulsion polymerization is the high level of surfactant and co-stabilizer that is typically employed. Pham *et al.*³⁶⁵ have described surfactant-free miniemulsion polymerization. As with the emulsion procedure referred to above, amphipathic macro-RAFT agents synthesized *in situ* by polymerization of AA were used as the sole stabilizers. This process eliminated secondary nucleation of new particles and leads to a latex with no mobile surfactant and good particle size control.

3.07.3.4 Polymer Architectures

3.07.3.4.1 Functional polymers

RAFT polymerization is compatible with a wide range of unprotected functionality in the monomer and RAFT agent. Tolerated monomer functionality includes fluorine,^{346,368} tertiary amino (in N,N-(dimethylamino)ethyl methacrylate (DMAEMA)), quaternary amino (e.g., in 2-(trimethylammonium) ethyl methacrylate (TMAEMA)), carboxylic acid (e.g., in MAA, AA), betaine,³⁶⁹ hydroxyl (e.g., in 2-hydroxyethyl acrylate (HEA), 2-hydroxyethyl methacrylate (HEMA)), epoxy (e.g., in glycidyl methacrylate (GMA)), and thiirane.³⁷⁰ RAFT agents are generally not compatible with primary and secondary amino or with thiol functionality, though He et al.³⁷¹ have recently shown that RAFT is possible with primary amino functionality as long as it is fully protonated (in 2-aminoethyl methacrylate hydrochloride (AEMA)). RAFT polymerization of functional monomers has been used as a route to structures as diverse as glycopolymers,^{54,313,372-378} possible hole or electron transport materials,^{379,380} photochromic materials,^{381,382} and light harvesting polymers (e.g., from acenapthalene (AcN)³⁸³⁻³⁸⁵). RAFT polymerization of activated monomers such as N-acryloylsuccinimide (NAS) and N-methacryloylsuccinimide (NMS)³⁸⁶⁻³⁸⁸ also provides a means of synthesizing functional (co)polymers.

One major advantage of RAFT polymerization over many other RDRP techniques, such as ATRP,^{15,18,123} single electron transfer living radical polymerization (SET-LRP),³⁸⁹ and NMP,¹⁴ is its tolerance of functionality which is such that a wide range of groups can be introduced as substituents on 'R' or 'Z' groups. This functionality includes for use in 'click' reactions. Characteristics of 'click' reactions are (1) high yields with by-products (if any) that are simply removed by nonchromatographic processes; (2) high regiospecificity and stereospecificity; (3) insensitivity to oxygen and water; (4) mild, solventless reaction conditions; (5) orthogonality with other reactions; and (6) amenability to a wide variety of readily available starting materials. A number of recent reviews have focused on the combination of 'click' chemistry and polymer chemistry.^{390–395}

A key feature of RAFT polymerization is that the thiocarbonylthio groups, present in the initial RAFT agent, are retained in the polymeric product. This feature is responsible for the living character of RAFT polymerization and renders the process suitable for synthesizing block copolymers and end-functional polymers. However, the presence of the thiocarbonylthio groups is detrimental to some applications. Removal or transformation of the thiocarbonylthio group is therefore an integral part of many polymer syntheses.

The reactions of the thiocarbonylthio group are well known from small molecule chemistry^{77,78,127,396} and much of this knowledge has been shown to be applicable to transforming the thiocarbonylthio groups present in RAFT-synthesized polymers.¹⁹ Many of the methods used for thiocarbonylthio group removal are summarized in **Scheme 31**. Thiocarbonylthio groups undergo reaction with nucleophiles and ionic reducing agents typically to produce a polymer with a thiol end group. They also react with various oxidizing agents and are sensitive to UV irradiation. These reactions, which leave reactive end-group functionality, are not appropriate in all circumstances. Thermolysis and radical-induced reactions are other solutions and can provide complete desulfurization.

The thiocarbonylthio group may also be transformed or, in some cases, used directly in other forms of radical polymerization, such as ATRP^{397,398} or NMP,³⁹⁹ and, as we have recently demonstrated, certain thiocarbonylthio groups can be 'switched' to enable control over polymerization of a wider range of monomers in the RAFT process.^{274,275}

Reviews focussing on end-functional polymers include those by Willcock and O'Reilly,⁹⁸ Moad *et al.*,^{99,100} and Barner and Perrier.⁹⁷ Other reviews that include significant sections on end-functional polymers and end-group transformation include our reviews of the RAFT process,^{1,54,55,58} that by Boyer *et al.*¹¹¹ on biomedical applications, and that by Moad *et al.*¹¹³ on optoelectronic applications.

3.07.3.4.2 Gradient copolymers

In most copolymerization, the monomers are consumed at different rates dictated by the steric and electronic properties of the reactants. Consequently, both the monomer feed and copolymer composition will drift with conversion. Thus conventional copolymers are generally not homogeneous in composition at the molecular level. In RAFT polymerization processes, where all chains grow throughout the polymerization, the compositional drift is captured within the chain structure (Scheme 32). All chains will have similar composition and the copolymers formed have a gradient or tapered structure – poly(monomer A-grad-monomer B).

Reactivity ratios are generally unaffected by the RAFT process. However, for very low conversions when molecular weights are low, copolymer composition may be different from that seen in conventional copolymerization because of



Scheme 31 Processes for RAFT end-group transformation (R' = radical, [H] = H atom donor, M = monomer, $Co^{II} = square planar cobalt complex$). Adapted from Moad, G.; Rizzardo, E.; Thang, S. H. *Polym. Int.* **2011**, *60*, 9–25.⁹⁹



Scheme 32 Gradient copolymer synthesis.

specificity shown in the initiation step by the radical (R). The same phenomenon is observed in radical polymerization with conventional chain transfer when molecular weights are low.^{400–402} Note that these conditions also equate to those most frequently used for measuring reactivity ratios. It is likely that the few reports of apparent dependence of reactivity ratios on the presence of RAFT agent can be attributed to this.

A wide variety of copolymers have been synthesized by RAFT polymerization and many examples are provided in the tables (Section 3.07.3.2). RAFT copolymerization can be successful (provide molecular weight control and narrow molecular weight distributions) even when one of the monomers is not amenable to direct homopolymerization using a particular RAFT agent. For example, severe retardation is observed for NVP polymerization in the presence of trithiocarbonate RAFT agents (e.g., with 129²⁸⁰), yet copolymerization of NVP with an acrylate provides good control and little retardation (e.g., NVP/octadecyl acrylate (ODA) with 12.6,⁴⁰³ Scheme 33).

3.07.3.4.3 Block copolymers

RAFT polymerization is recognized as one of the most versatile methods for block copolymer synthesis and numerous examples of block synthesis have now appeared in the literature. RAFT polymerization proceeds with retention of the thiocarbo-nylthio group. This allows an easy entry to the synthesis of AB diblock copolymers by the simple addition of a second mono-mer.^{131,404} Higher order (ABA, ABC, etc.) blocks are also possible by sequential addition of further monomer(s).

Of considerable interest has been the ability to make hydrophilic–hydrophobic or double hydrophilic block copolymers where the hydrophilic block is composed of unprotected polar monomers such as AA or DMAEMA.

As with other RDRPs, the order of constructing the blocks can be very important.^{131,133} In RAFT polymerization the propagating radical for the first formed block should be chosen such that it is a good homolytic leaving group with respect to that of the second block. For example, in the synthesis of a methacrylate–acrylate or methacrylate–styrene blocks, the methacrylate block should be prepared first.^{131,133,139,405} The propagating radicals sited on a styrene or acrylate unit are very poor leaving groups with respect to methacrylate propagating radicals and thus the corresponding macro-RAFT agents have extremely low transfer coefficients in polymerizations of methacrylate monomers.





The use of feed addition protocols, where the monomer concentration is kept low with respect to the RAFT agent concentration, can be used to circumvent this requirement.^{12,406} Such strategies can also allow RAFT agents with lower transfer coefficients ($C_{tr} \sim 0.1-5$) to be used in syntheses of polymers with narrow molecular weight distributions. Thus, while a polystyrene macro-RAFT agent appears essentially inert in batch solution polymerization of MMA, PSt-*b*-PMMA has been successfully prepared by feed emulsion polymerization starting with a polystyrene macro-RAFT agent.¹² This strategy is also applied when synthesizing block copolymers from macromonomer RAFT agents (Section 3.07.3.1). Another work-around is to maintain a small amount of an appropriate comonomer in the feed.⁵⁴

For block copolymers where the leaving group ability of the propagating species is similar, the order on construction is less critical. Thus, in the synthesis of block copolymers of styrene with AA or with acrylate esters either block can be made first.

Block copolymers based on polymers formed by other mechanisms can be made by first preparing an end-functional prepolymer which is converted to a polymer with thiocarbonylthio groups by end-group transformation. This is then used as a macro-RAFT agent in preparation of the desired block copolymer (Scheme 34). We first exploited this methodology to prepare PEO-*block*-PSt from commercially available hydroxy end-functional PEO.^{129,131,407}

Use of a bis-RAFT agent allows the direct synthesis of triblock copolymers in a 'one-pot' reaction. Bis-RAFT agents are described in **Table 12** (bis-dithioesters), **Table 16** (bis-trithiocarbonates), and **Table 18** (bis-dithiocarbamates). The RAFT agent functionalities may be connected through the 'Z' or 'R' groups to give ABA (**Scheme 35**) or BAB blocks (**Scheme 36**), respectively. The limitations of the two forms of RAFT agents are discussed under Star Polymers (Section 3.07.3.4.4). Symmetrical mono-trithiocarbonates (Table 15) can be considered as 'Z-connected' bis-RAFT agents (n = 0 in Scheme 35).

3.07.3.4.4 Star polymers

There is now a large body of literature on the synthesis of star polymers using the RAFT process.^{12,63,102,239,407–411} A frequently used approach begins with a compound containing multiple thiocarbonylthio groups of appropriate design – a multi-RAFT agent. The multi-RAFT agent may be a small organic compound (for examples see **Tables 22–25**), an organometallic complex,^{412,413} a dendrimer,^{414–418} a hyperbranched species,⁴¹⁹ a macromolecular species,^{420,421} a particle,^{422,423} or indeed any moiety possessing multiple thiocarbonylthio groups (though here the distinction between star and graft copolymers may become blurred). The first RAFT patent¹²⁹ recognized two limiting forms of star (or graft/brush copolymer) growth depending on the orientation of the thiocarbonylthio group with respect to the core. The advantages and disadvantages of the two approaches have been discussed in detail in a number of papers.^{408,409}

• In the first strategy the propagating radicals are linear chains that are dissociated from the core. 'Z-connected' RAFT agents (174, Scheme 37) are employed. The advantage of this strategy is that by-products from star-star coupling are unlikely. The thiocarbonylthio functionality is retained at the core of the star. A potential disadvantage of the 'propagation away from core' strategy is that reactions that cleave the thiocarbonylthio groups (e.g., hydrolysis and thermolysis) cause destruction of the star structure. A further potential issue is



Scheme 34 AB diblock synthesis from end-functional polymers via RAFT process











Table 22 Multi-dithioesters	(Z = aryl)	used as	RAFT	agents
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^aReferences cited in this column provide a synthesis of RAFT agent.

^b References cited provide details of polymerization of the monomers indicated. Monomer/RAFT agent combinations that are relatively ineffective are indicated by the monomer being in parentheses. A-b-B block of monomer A then monomer B. The second mentioned block is core, for 'Z'-connected examples, or the two arms, for 'R'-connected examples.

NIPAM, N-isopropyl acrylamide; tBA, tert-butyl acrylate.

RAFT agent ^a	Synthesis ^a	Polymerizations ^t
'R'-connected		
Ar 1,3,5-substitution	B ⁵³⁰	St ⁵³⁰
	A ⁴⁰⁹	AcS, ⁵³¹ St ⁴⁰⁹ MA ⁵³²
Ar 1,2,4,5-substitution		

Table 23 Multi-dithioesters (Z = aralkyl) used as RAFT agents

^aReferences cited in this column provide a synthesis of RAFT agent.

^b References cited provide details of polymerization of the monomers indicated.

AcS, 4-acetoxystyrene; St, styrene; MA, methyl acrylate

Polymerizations^b RAFT agent Synthesis^a 'Z'-connected core A^{241,533} St^{417,418,533} C S BA,417,418 St-b-BA417 H₃C BA-b-St417 3 3-arm 'generation 1' dendrimer St^{417,418} A⁴¹⁷ BA,417,418 St-b-BA417 BA-b-St⁴¹⁷ H₃C Ô Ö S 3 6 arm 'generation 2' dendrimer A⁴¹⁷ St417,418 BA,^{417,418} St-b-BA⁴¹⁷ BA-b-St417 H₂ ö ŝ Ô C 2^{_]} 2-3 12-arm 'generation 3' dendrimer St⁵³³ A⁵³³ H_3 S 3 A^{241,408,533,534} St,^{12,408,533,534} MA,⁴⁰⁸ tBA,⁵³⁵ NIPAM⁵³⁶ tBA-b-St535 S St-b-MA408 A⁵³³ St⁵³³ S Ph S A^{241,534,537} St^{533,534,537} S S S 0 Ph C R A^{533,537} St^{533,537} S S Ph 2 A⁴¹⁰ BA,410 DA,410 MA410 0 `O S `S CO₂CH₃ 2 'R'-connected core A⁴⁰⁸ St^{12,408} MA⁴⁰⁸ S St-b-MA⁴⁰⁸ 5 ¹4

Table 24 Multi-trithiocarbonates used as RAFT agents

^a References cited in this column provide a synthesis of RAFT agent.

^b References cited provide details of polymerization of the monomers indicated. A-b-B block of monomer A then monomer B.

DA, dodecyl acrylate; NIPAM, N-isopropyl acrylamide; tBA, tert-butyl acrylate.



Table 25 Multi-xanthates used as RAFT agents

^a References cited in this column provide a synthesis of RAFT agent.

^b References cited provide details of polymerization of the monomers indicated.



Scheme 37 Star polymers synthesis by the 'propagation away from core' strategy using a 'Z-connected' RAFT agent.



Scheme 38 Star polymers synthesis by the 'propagation attached to core' strategy using a 'R-connected' RAFT agent.

that the thiocarbonylthio functionality may become sterically inaccessible as polymerization proceeds.

• In the second strategy most propagating radicals remain attached to the core, and 'R-connected' RAFT agents (175, Scheme 38) are used. Most thiocarbonylthio functionality remains on the periphery of the star. However, linear macro-RAFT agent is released to the polymerization medium by the RAFT process. Since propagating radicals are attached to the core, termination by star-star coupling is a complication. Because the thiocarbonylthio groups are end groups, they can be cleaved without destroying the star structure.

Acknowledgments

Sections of this chapter where indicated are adapted with permission from the previous reviews of Moad, Rizzardo, and Thang first published in the *Australian Journal of Chemistry*^{54,55,58} or in *Polymer*,¹ or from Moad and Solomon *The Chemistry of Radical Polymerization*⁴²⁴ © 2006 Elsevier.

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257-288

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Biographical Sketches



Graeme Moad was born in Orange, NSW, Australia. He obtained his BSc (Hons, First Class) and PhD from the Adelaide University in the field of organic free radical chemistry. After undertaking postdoctoral research at Pennsylvania State University in the field of biological organic chemistry he joined CSIRO in 1979 where he is currently a chief research scientist and a research group leader. He is also a project leader within the Cooperative Research Centre for Polymers. Dr. Moad is author or co-author of over 150 publications, co-inventor of 33 patent families (9 relate to the RAFT process), and co-author of the book *The Chemistry of Radical Polymerization*. More than 11 500 papers cite his work and his h-index is 51. His research interests lie in the fields of polymer design and synthesis (radical polymerization, reactive extrusion, polymer nanocomposites) and polymerization kinetics and mechanism. Dr. Moad is a Fellow of the Royal Australian Chemical Institute and has recently been elected as a titular member of the International Union of Pure and Applied Chemistry.



Ezio Rizzardo was born in Onigo, Italy, in 1943. He graduated with first-class honors in applied organic chemistry from the University of NSW and was awarded a PhD in Organic Chemistry by the University of Sydney in 1969. He joined David Solomon's group at CSIRO in 1976 after postdoctoral work on the synthesis of biologically active compounds with Richard Turner at Rice University (Houston), Sir Derek Barton at RIMAC (Boston), and Arthur Birch at the ANU (Canberra). His research at CSIRO has focused on the development of methods for understanding and controlling polymerization processes. Research highlights from the teams he has led include radical trapping with nitroxides, NMP, chain transfer and ring-opening polymerization by addition–fragmentation, and the RAFT process. He is co-author of some 200 journal papers, which to date have received over 12 000 citations, and co-inventor on 44 worldwide patents. He is a Fellow of the Royal Society of London, the Australian Academy of Science, the Australian Academy of Technological Sciences and Engineering, and the recipient of the Australian Polymer Medal, the CSIRO Chairman's Gold Medal, and the Australian Government's Centenary Medal for contributions to society and polymer science.



San Thang came to Australia as a refugee from Vietnam in 1979. He completed his BSc (Hons) in 1983 with Prof. Gus Guthrie at Griffith University; and PhD in 1987 with Prof. Ian Jenkins and Associate Prof. Ken Busfield (Griffith University) and Dr. Ezio Rizzardo and Dr. David Solomon (CSIRO) as supervisors. He joined CSIRO in 1986 as a Research Fellow and in late 1987, he moved to ICI Australia to undertake the challenge of industrial research in synthetic UV sunscreens and agrochemicals. San rejoined CSIRO in late 1990 and currently is a Senior Principal Research Scientist at CSIRO Materials Science and Engineering where his research focuses on the interface between biology and polymer chemistry. San has published over 100 papers in refereed journals which to date have received over 9250 citations. He is responsible for several key inventions in the area of controlled/living radical polymerization; significantly, he is a co-inventor of the RAFT process. San is a Fellow of the Australian Academy of Technological Science and Engineering and Fellow of the Royal Australian Chemical Institute. Currently, he also serves as Adjunct Professor of Monash University and Treasurer of the Federation of Asian Chemical Societies.

3.08 Other Degenerative Transfer Systems

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3.08.1	Introduction	227
3.08.2	Background	228
3.08.3	Organoheteroatom-Mediated LRP	229
3.08.3.1	Initiators and CTAs	229
3.08.3.2	Polymerization Conditions	230
3.08.3.3	Homopolymerization	231
3.08.3.4	Random and Alternating Copolymerization	233
3.08.3.5	Emulsion Polymerization	234
3.08.4	Mechanism	234
3.08.4.1	Activation/Deactivation Mechanism of Dormant Species	234
3.08.4.2	Role of Diheteroatom Compounds	236
3.08.5	Macromolecular Engineering	237
3.08.5.1	End Group Transformations	237
3.08.5.2	Block Copolymer Syntheses	240
3.08.5.3	Synthesis of Functional Polymers	242
3.08.5.3.1	Thermosensitive micelles	242
3.08.5.3.2	Polymer monoliths	244
3.08.5.3.3	Adhesives, dispersants, and compatibilizers	245
3.08.6	Conclusions	245
References		245

3.08.1 Introduction

The development of living radical polymerization reactions, by analogy with the progress of living $anion_{1,2}^{1,2}$ cation₁³⁻⁵ and coordination polymerizations,⁶⁻⁸ has been a long-standing goal for synthetic polymer chemists. Since radicals are neutral, 'soft', and highly reactive species, the conventional radical polymerization takes full advantage of these characteristics;⁹⁻¹² it can successfully take place in the presence of various polar functional groups and polar solvents including water under mild thermal conditions. The conditions are in sharp contrast to anionic, cationic, and coordination polymerizations, which usually require stringent reaction conditions to avoid the occurrence of undesirable side reactions. Therefore, the living version of radical polymerization has become an indispensable method for the synthesis of structurally well-controlled polymers with rich functionalities, which would lay essential foundations for new polymeric materials with improved and/or new properties.13,14

The difference between controlled or living radical polymerization (LRP) and conventional radical polymerization is that the activity of polymer-end species is preserved throughout the polymerization period by reversible generation of the radical from a so-called dormant species, which possesses appropriate functional groups at the polymer end for radical generation (Scheme 1(a)).^{15,16} This 'pseudo' deactivation of the polymer-end radical to the dormant species decreases the concentration of radical species in solution and minimizes undesirable side reactions leading to dead polymers. Furthermore, the rapid deactivation makes it possible to elongate all of the polymer chains with similar chain lengths. The faster deactivation leads to higher control of molecular weight distribution (MWD) under an ideal condition without any termination reactions.

There are two activation/deactivation mechanisms of the dormant/radical species so far known. One is the reversible termination (RT) reaction in which homolytic cleavage of P-X bond (P denotes polymer here) in a dormant species generates polymer-end radical P and persistent radical X or its equivalent (Scheme 1(b)), and the selective deactivation of P and X radicals is controlled by the persistent radical effect.¹⁷ The other mechanism is the degenerative chain transfer (DT) reaction in which polymer-end radical P' undergoes homolytic substitution reaction with dormant species P-X to generate new radical P and new dormant species P'-X (Scheme 1(c)). The characteristic feature of the DT process is that activation and deactivation reactions are coupled with each other and controlled simultaneously. On the contrary, these reactions are controlled independently in the RT process, and enhancement of the activation reaction sometimes results in the loss of control due to insufficient deactivation reaction. A disadvantage of the DT is, however, the necessity of the influx of initiating radical species usually from radical initiators, because the number of radical species does not change in the DT. The addition of initiator results in the formation of a polymer possessing a-structure derived from the initiator, and the complete control of the polymer is, in principle, unachievable.

Several LRP methods have been developed to achieve efficient activation/deactivation reactions to control macromolecular structure of the resulting polymers. LRPs that have been widely used include nitroxide-mediated radical polymerization (NMP),¹⁸ atom transfer radical polymerization (ATRP),^{19–21} and reversible addition–fragmentation chain transfer radical polymerization (RAFT).^{22–25} Organotellurium-,



(b) Reversible termination (RT)

$$P-XL_n \rightarrow P \cdot + \cdot XL_n$$

(c) Degenerative transfer (DT)

 $P-XL_n$ $-XL_n$



organostibine-, and organobismuthine-mediated LRP (TERP, SBRP, and BIRP, respectively) $^{26-29}$ are relatively new methods developed by the author's group. New variants of LRP, such as single-electron transfer LRP,³⁰ titanium-catalyzed polymerization,³¹ have also emerged, and cobalt-mediated radical polymerization (CMRP)³² and organoiodine-mediated LRP (IRP)^{33,34} have revived. Each method utilizes unique chemical structures and activation/deactivation mechanisms of the dormant species, and these differences make each LRP method unique both mechanistically and synthetically.

NMP and ATRP exclusively proceed by RT mechanism and RAFT by DT mechanism. TERP, SBRP, BIRP, and IRP predominantly proceed via the DT mechanism, but the RT also contributes to a small extent. While CMRP by both RT and DT depending proceeds on the conditions, RT plays more important role than DT for the MWD control. As NMP (see Chapter 3.10), ATRP (see Chapters 3.12 and 3.13), RAFT (see Chapter 3.07), IRP (see Chapter 3.06), and organometallic-mediated radical polymerization (see Chapter 3.11) including CMRP are discussed in the previous and following chapters, this chapter deals with synthetic and mechanistic aspects of TERP, SBRP, and BIRP.

3.08.2 Background

Radical-mediated atom transfer addition reactions of haloalkanes to alkenes in the presence of a radical initiator were first reported by Kharasch in 1945 (Scheme 2(a)).^{35,36} This type of reaction has caught the attention of organic chemists since the rediscovery of the iodine group transfer radical addition reaction by Curran in 1986.37-39 Phenylselenyl group transfer and phenyltellanyl group transfer radical addition reactions of organoselenides and organotellurides, respectively, were subsequently reported by several groups.⁴⁰⁻⁴⁹ The reaction proceeds by a radical chain reaction, and carbon-centered radical R generated from an organoheteroatom compound, R-X, reacts with an alkene or alkyne to generate a new carbon-centered radical (1), which reacts with R-X to give the addition product with the regeneration of R radical (Scheme 2(b)).

Repetition of atom or group transfer addition reactions to alkenes leads to the formation of living polymers possessing heteroatom functionality X at the ω-polymer end (Scheme 2(a)). The effect of heteroatom compounds





X = halogen atom or charcogen group



Scheme 2 (a) Atom and group transfer radical addition reaction and (b) its mechanism.

on the control of MWD was recognized for the first time by Tatemoto, who observed the living character of radical polymerization of fluorinated monomers by the addition of organoiodine compounds.⁵⁰ Matyjaszewski and coworkers^{51,52} showed that organoiodine compounds are also effective for the MWD control in the radical polymerization of conventional monomers.

Kwon and coworkers^{53–55} have utilized diaryldiselenides as a photoiniferter or radical trapping agent,⁵⁶ which generate organoselenium dormant species in situ by the reaction of the monomers. They also employed phenylselenyl-substituted chain transfer agents (CTAs) for the polymerization of styrene under photo-irradiation.⁵⁷ The polymerization showed living character as judged from a linear increase of M_n upon monomer conversion and successful synthesis of block copolymers. However, the control of MWD was insufficient, and polymers with considerably high MWDs were obtained $(M_w/M_n > 1.5)$. This is primarily due to the low reactivity of organoselenides toward the DT reaction. High reactivity of arylselenyl radical to monomers initiating a new polymer chain also contributes to loss of the control. The same group also reported the effect of diphenylditelluride on the conventional AIBN-initiated radical polymerization of styrene.⁵⁸ They found that MWD becomes narrow $(M_w/M_p = 1.26 - 1.18)$ with the addition of more than 0.5-2.0 equiv of diphenylditelluride to AIBN, whereas the addition of more ditelluride led to the formation of polystyrene with lower M_n . They also propose the existence of a phenyltellanyl-substituted w-polymer end group, but there was no direct evidence to support the end group structure.

On the basis of the findings of reversible radical generation from organotellurium compounds via carbon-tellurium bond thermolysis and photolysis^{59,60} and its applications to organic synthesis, 61-68 Yamago and coworkers 27-29 developed TERP, SBRP, and BIRP. These methods are versatile and produce a variety of well-defined polymers with several different functional groups. The details of these methods are discussed below.
3.08.3 Organoheteroatom-Mediated LRP

3.08.3.1 Initiators and CTAs

Besides the requirement of the efficient activation/deactivation reaction in LRP for the control of MWD, the general requirement for the control of MWD in living polymerization is the efficient initiation reaction. This step must be faster than or at least similar to the propagation step. To ensure the fast activation reaction, CTAs mimicking the polymer-end structure have been used for TERP, SBRP, and BIRP. The same structural features are also reported for other LRP methods.

Structures of organoheteroatom CTAs are summarized in **Scheme 3**. These CTAs mimic the polymer-end structure of polymethacrylate, polymethacrylonitrile, polyacrylate, or polystyrene. The radicals generated from these compounds are considerably stabilized by conjugation with ester and nitrile groups about 40 kJ mol⁻¹ and phenyl groups about 70 kJ mol⁻¹ compared to radicals without such stabilizing groups.⁶⁹ An alkyl group also stabilizes its α -radical to a small extent by hyperconjugation about 15~20 kJ mol⁻¹. Therefore, CTAs having polymethacrylate and polymethacrylonitrile structures show higher control than polyacrylate structures, and phenylethyl-substituted CTAs mimicking PSt polymer end are better CTAs than benzyl derivatives.

The availability of CTAs is a key issue with respect to practical applications of LRPs. Many of the organoheteroatom CTAs shown in **Scheme 3** are easily prepared on large scales and easily purified by simple vacuum distillation. Though heteroatom CTAs are moderately air (oxygen) sensitive, they can be stored for long periods under a nitrogen atmosphere and are handled using standard syringe techniques. Organotellurium derivatives are the most resistant to oxidation by air among these CTAs. Organotellurium CTAs are usually prepared under basic conditions as shown in **Scheme 4(a)**. The reaction of alkyl or aryl lithium reagents with tellurium metal affords the corresponding organotellanyl lithium species,⁷⁰ which reacts with organochlorides, bromides, and iodides to give the desired CTA.⁷¹ CTAs **Te-1–Te-14** are prepared by using this route. Since many organolithium reagents and organohalogen compounds are readily available, this is a practical and scalable synthetic route to organotellurium CTAs.

The reaction of an organostibanyl anion, which was reductively generated from the diorganostibanyl bromide and sodium metal, with 1-phenylethyl bromide afforded the organostibanyl transfer agent **Sb-1**.⁷² However, due to the difficulty in generating the stibanyl anions and their low reactivities, the synthetic scope of this route is limited.

Organostibanyl transfer agent Sb-2 was prepared by the reaction of lithium enolate generated from ethyl 2-methyl-2-propanoate and lithium diisopropylamide with dimethylstibanyl bromide as an electrophile (Scheme 4(c)).⁷² The same method was used for the cyano-derivative Sb-3 and Sb-4 from 2-methyl-2-propionitrile and dimethylstibanyl and diphenyl-stibanyl bromides, respectively. Organobismuthine transfer agents Bi-1 and Bi-2 were also prepared via this route using dimethylbismuthanyl and diphenylbismuthanyl bromides, respectively, as an electrophile.⁷³

Despite the high synthetic efficiencies of the routes shown in **Scheme** 4(a)-4(c), it is difficult to introduce polar functional groups into the CTAs. As the heteroatom functional groups in the CTAs are moderately sensitive to oxygen and also reactive under various conditions, postmodifications to introduce functional groups starting from the existing CTAs are limited. In addition, as synthesis of the CTAs requires basic conditions, many polar functional groups are not compatible. The fourth method shown in **Scheme** 4(d), which relies



Scheme 3 Structures of CTAs for TERP, SBRP, and BIRP.

(a)
$$R^{1}Li \xrightarrow{Te} [R^{1}TeLi] \xrightarrow{R^{2}-X} R^{2}-TeR^{1}$$

(b) $R^{1}_{2}SbX \xrightarrow{Na} [R^{1}_{2}SbNa] \xrightarrow{R^{2}-X} R^{2}-SbR^{1}_{2}$
(c) $R' \xrightarrow{CO_{2}R} LDA \begin{bmatrix} LiO & OR \\ R' & R' \end{bmatrix} \xrightarrow{R^{1}_{n}YBr} R' \xrightarrow{CO_{2}R} R' \xrightarrow{T} YR^{1}_{n}$
(d) $1/2 \begin{pmatrix} CN \\ R' & N \end{pmatrix} \xrightarrow{heat} [R' & CN \\ R' & (-N_{2}) \end{pmatrix} \begin{bmatrix} CN \\ R' & N \end{pmatrix} \xrightarrow{R' & CN} R' \xrightarrow{CN} R' \xrightarrow{T} YR^{1}_{n}$

Scheme 4 Synthetic route to organoheteroatom CTAs. Reprinted with permission from Yamago, S. *Chem. Rev.* 2009, *109*, 5051.²⁹ Copyright 2009 American Chemical Society.

on the reaction of a radical generated from an azo initiator with ditellurides⁷⁴ and distibines,⁷⁵ proceeds under neutral conditions and is applicable to the synthesis of functional CTAs.

Organotellurium CTAs Te-7 and Te-8 were prepared by reacting AIBN with dimethyl- and diphenylditelluride, respectively, but in low yields (8–18%).⁷⁴ This route has the practical advantage that both AIBN and ditellurides are stable in air and can be handled without special precautions. Furthermore, the air-sensitive CTAs formed can be directly used for polymerization without purification because the only side product is a dimer of AIBN-derived radicals, which does not affect the polymerization reaction. Despite the simplicity of this procedure, the use of purified initiators is the method of choice for obtaining living polymers with the highest level of control of MWD.

The reaction of azo initiators with tetramethyldistibine, on the other hand, took place with high coupling efficiencies.⁷⁵ Yields of the CTAs were about 60% when a 1:1 mixture of an azo initiator and the distibine was employed. Since about 40% of the radicals generated from the azo initiators dimerize within a solvent cage,⁷⁶ the result indicates that almost all the radicals that diffused from the cage were captured by the distibine. Organostibine CTAs **Sb-2**, **Sb-3**, **Sb-5~Sb-8** were prepared via this route starting from the corresponding azo initiators. Ester, ether, terminal alkene, and alcohol groups were incorporated into the CTAs. α -Functional polymers were synthesized starting from these functional CTAs (see below).

Diheteroatom compounds, such as dimethyl ditelluride, diphenyl ditelluride, tetramethyl distibine, tetraphenyl distibine, and 2,6-dimesitylphenylthiodiphenylbismuthine 2 (Scheme 5), were used as cocatalysts to increase the MWD control. As these cocatalysts do not generate initiating radical species for the polymerization, a binary system consisting of an



Scheme 5 Structures of diheteroatom cocatalyst for TERP, SBRP, and BIRP.

organoheteroatom CTA and a diheteroatom compound was employed for the LRP. Synthetic scope and the role of the diheteroatom compounds are discussed in the following section.

3.08.3.2 Polymerization Conditions

Three conditions have been developed for conducting TERP, SBRP, and BIRP. The first condition (A in **Table 1**) is a purely thermal condition, in which a CTA and a monomer are typically heated between 80 °C and 110 °C.^{71,79} The second condition (B) is a ternary system consisting of a radical initiator, typically azo initiators, a CTA, and a monomer.⁷⁷ The polymerization conditions depend on the decomposition temperature of the azo initiator used, and it usually proceeds at lower temperature than that of condition A. The third condition (C) proceeds under photo-irradiation of a mixture of an organotellurium CTA and a monomer,⁷⁸ and the polymerization proceeds under much milder conditions, such as temperatures in the range of 0 °C to room temperature. These differences depend on the mechanism of the polymerization reaction, as discussed in the following section.

Effects of the conditions on the polymerization of *n*-butyl acrylate (BA), styrene (St), and methyl methacrylate (MMA) in the presence of organotellurium CTAs **Te-1**, **Te-3**, and **Te-7** are summarized in **Table 1**. Polymerization of BA (100 equiv) under condition A was sluggish and monomer conversion reached 70% after being heated at 100 °C for 24 h. Despite the long reaction time required in order to achieve high monomer conversion, PBA with high MWD control ($M_w/M_n = 1.12$) was obtained. Polymerization under condition B, on the other hand, completed within 0.5 h at 60 °C and gave well-controlled polymers ($M_w/M_n = 1.17$). Uncontrolled free radical polymerization did not compete with LRP even in the presence of azo initiators. Polymerization proceeded even at 0 °C under condition C, and PBA with a narrow MWD ($M_w/M_n = 1.16$) was also obtained with high monomer conversion.

Polymerization of St and MMA under conditions A and B has been reported. Polymerization of St and MMA under condition A proceeded in the temperature range of 80–100 °C, and that under condition B with AIBN as an initiator proceeded at 60 °C with a high monomer conversion. Polymerization of St using condition B took place at 40 °C with 2,2'-azobis(4-

Monomer	<i>Condition</i> ^a	Temperature (°C)	Time (h)	Yield (%)	<i>M</i> _n	M _w / M _n
BA	А	100	24	69	8 300	1.12
	В	60	0.5	92	10700	1.17
	С	0	4	86	10 500	1.16
St	А	100	98	98	9400	1.15
	В	60	11	94	11 300	1.17
	B ^b	40	23	82	7 400	1.21
MMA ^c	А	80	13	81	8 300	1.12
	В	60	2	98	9600	1.15

 Table 1
 Polymerization of styrene (St), n-butyl acrylate (BA), and methyl methacrylate (MMA) under different conditions

^a Condition A: A mixture of chain transfer agent (**Te-1**) and monomer (1:100) was heated.⁷¹ Condition B: A mixture of AIBN, chain transfer agent (**Te-1** or **Te-7**), and monomer in a ratio of 1:1:100 was heated.⁷⁷ Condition C: A mixture of chain transfer agent (**Te-3**) and monomer was irradiated with a 500 W high-pressure Hg lamp through a cutoff filter.⁷⁸

^b2,2'-Azobis(4-methoxyvaleronitrile) was used instead of AIBN.

^c One equivalent of dimethyl ditelluride was added.

methoxyvaleronitrile) as an initiator, which decomposes at a lower temperature than AIBN does. A high level of control of MWD ($M_w/M_n = 1.12-1.21$) was observed regardless of the method used.

Since polymerization takes place at lower temperatures and with shorter reaction times under conditions B and C than those under condition A, these methods should be suitable for monomers that undergo unwanted side reactions at high temperatures. The high energy efficiencies of conditions B and C are also useful for industrial applications.

Since thermolysis of the dormant species is the rate determining step in condition A (see Mechanistic section), the rate of polymerization is strongly affected by the strength of the carbon-heteroatom bond of the dormant species. Since PBA-dormant species have a stronger carbon-heteroatom bond than the PSt- and PMMA-dormant species, the polymerization of BA required a higher temperature and a longer reaction time than those of St and MMA. On the contrary, the rate control step is the propagation reaction in condition B because the initiating radicals are provided from azo initiators. Therefore, the rate of polymerization is similar to the propagation rate; BA is the fastest followed by MMA and then St.

TERP, SBRP, and BIRP are routinely carried out without solvent (bulk polymerization), but several solvents have also been used. Polar solvents, such as *N*,*N*-dimethylformamide (DMF) and tetrahydrofuran (THF), were used for the polymerization of *N*-isopropylacrylamide (NIPAM), acrylonitrile (AN), *N*-vinyl carbazole (NVC), and acrylic acid (AA).^{73,78–80} TERP of NIPAM was also carried out in a DMF/water mixture at 20 °C under condition C.⁷⁸ TERP has been also applied to emulsion polymerization in an aqueous dispersed media (see below). The results clearly indicate the high compatibility of these methods for polar functional groups and solvents.

3.08.3.3 Homopolymerization

A synthetic advantage of TERP, SBRP, and BIRP is their high versatility in polymerizing a variety of monomer families using the same CTAs. Selected monomers homopolymerized by using these methods are summarized in **Scheme 6**. The monomer conversions are usually high (> 90%), and polymers with narrow MWDs were obtained in all cases.

St was polymerized under conditions A and B, and structurally well-defined PSt with M_n close to the theoretical values and low MWDs formed.^{71,73,74,77,81} M_n increased linearly with an increase in the St/CTA ratio, and PSts with M_n in the range of 3000–87 000 and narrow MWDs ($M_w/M_n < 1.3$) were prepared. *p*-Chlorostyrene (*p*ClSt) and *p*-methoxystyrene (*p*MeOSt) were also successfully polymerized.⁷¹ Although the MWD control in *p*ClSt polymerization was less efficient than those in St and *p*MeOSt polymerizations, presumably due to the higher propagation rate of the former than the latter, the level of control was still acceptable.

A binary system consisting of a ditelluride and organotellurium CTA⁸² and a distibine and organostibine CTA^{75,83} was effective in increasing the MWD control of St polymerization, but the effect was less pronounced than that in methacrylate polymerization as discussed below. Both low and high molecular weight PSts with M_n s in the range of 1.0×10^4 to 2.0×10^5 and narrow MWDs ($M_w/M_n = 1.07 - 1.15$) were synthesized with high monomer conversion (> 90%) by adding a catalytic amount of thiobismuthine cocatalyst 2 to organobismuthine CTA **Bi-1**.⁸⁴

Although methacrylates could be polymerized, the control of MWD was not always sufficient via TERP. Polymerization of MMA using organotellurium CTAs resulted in the formation of PMMAs with considerably broad MWDs ($M_w/M_n > 1.37$). However, the control increased with the addition of ditellurides as a cocatalyst, such as dimethyl, dibutyl, and diphenylditelluride, and PMMAs with narrow MWDs ($M_w/M_n = 1.12-1.16$) and M_n in the range of 8600–79400 were obtained depending on the monomer/CTA ratio.^{74,79} A catalytic amount of ditelluride was effective when the targeted molecular weight was small, but substoichiometric to excess amounts of ditelluride were used when the targeted molecular weight was large.

SBRP and BIRP exhibited higher MWD control than TERP, and PMMAs with narrow MWDs ($M_w/M_n = 1.10-1.25$) and M_n in the range of 1000–10 000 were obtained without the addition of additives. Distibines are also effective in controlling the



Scheme 6 Selected monomers polymerized by TERP, SBRP, and BIRP.

MWD in SBRP. For example, SBRP of MMA using Sb-2 proceeded with reasonable MDW control ($M_w/M_n = 1.24$), and that in the presence of 0.1 equiv of tetramethyldistibine afforded PMMA with highly controlled structures ($M_w/M_n = 1.05$).⁷⁵ The addition of further distibine, on the other hand, had virtually no effect on the MWD control, and significant rate retardation of the polymerization was observed. PMMAs of higher molecular weights ($M_n = 34700-122900$) and very narrow MWDs ($M_w/M_n = 1.05-1.15$) were prepared by increasing the ratio of MMA to Sb-4 in the presence of 0.1 equiv of tetramethyldistibine. It is worth mentioning that the use of a tiny amount of distibine is effective (0.1 equiv to the CTA and $10^{-3}-10^{-5}$ equiv to the monomer) for achieving a high M_n and MWD control.

Acrylates, acrylamides, and acrylonitrile were polymerized in a controlled manner under conditions A, B, and C. High temperature and long reaction times were required to reach high monomer conversion under condition A due to inefficient generation of the initiating radicals from the dormant species.⁷⁹ The high temperatures were also unsuitable because a considerable amount of branching occurred due to a backbiting reaction.^{85–87} Therefore, conditions B⁸⁸ and C⁷⁸ at low to ambient temperature are more suitable for the polymerization of these monomers. Poly(butyl acrylate)s (PBAs) with narrow MWDs ($M_w/M_n = 1.10-1.20$) and M_n in the range of 11000–122000 were successfully synthesized at 60 °C by using BIRP under condition B with AIBN as the initiator. Polymerization of BA proceeded in the temperature range of 0–50 °C by using TERP under UV-vis irradiation (condition C), and PBAs with narrow MWDs ($M_w/M_n = 1.08-1.19$) and M_n in the range of 13 000–223 000 were synthesized.

Addition of thiobismuthine cocatalyst 2 was especially suitable for the synthesis of ultrahigh molecular weight polyacrylates. PBAs with M_n s in the range of 1.2×10^4 to 2.8×10^6 and narrow MWDs ($M_w/M_n = 1.06-1.43$) were prepared under mild thermal conditions under a ternary system consisting of **Bi-1**,2, and AIBN. The GPC traces of all of the PBAs were unimodal, and the peak maxima shifted to higher molecular weights as the targeted molecular weight increased (**Figure 1**). A PBA with an M_n of 1.4×10^6 and a narrow MWD ($M_w/M_n = 1.22$) was obtained at 47% monomer conversion when 20 000 equiv of BA was employed. Moreover, a PBA with an M_n of 2.8×10^6 was obtained at 41% monomer conversion when 50 000 equiv of BA was employed. Although the MWD was slightly large ($M_w/M_n = 1.43$), it is still acceptable.

A significant drawback of LRP is the synthesis of high molecular weight polymers because the polymer-end radicals are always subject to irreversible termination reactions.⁸⁹ Only a few examples have been reported for the synthesis of ultrahigh molecular weight polyacrylates and polymethacrylates with M_n s exceeding 1×10^6 and with narrow MWDs: RAFT⁹⁰ and ATRP^{91,92} under high pressure conditions, single-electron transfer LRP using a copper catalyst,⁹³ and ATRP under mini-emulsion conditions.⁹⁴ Therefore, BIRP in the presence of **2** provides a new route to structurally well-defined ultrahigh molecular weight polymers.



Figure 1 GPC traces of PBAs prepared by a ternary system consisting of **Bi-1, 2**, and AIBN. GPC columns with exclusion limits of (a) 2×10^6 and (b) 2×10^7 were used. Reprinted with permission from Kayahara, E.; Yamago, S. *J. Am. Chem. Soc.* **2009**, *131*, 2508.⁸⁴ Copyright 2009 American Chemical Society.

Since TERP, SBRP, and BIRP are performed under thermal or photochemical conditions without catalysts that are incompatible with the functionalities of the monomers, controlled polymerization of various monomers possessing functional groups can be achieved. For example, methacrylates and acrylates with a free hydroxyl group, such as 2-hydroxyethyl methacrylate (HEMA) and 2-hydroxyethyl acrylate (HEA), a carboxylic acid group, such as AA, and an amine group, such as N,N-dimethylaminoethyl acrylate (DMAEA), were polymerized by using TERP in a controlled manner.78,79 Acryl amides, such as N,N-dimethylacrylamide (DMA) and NIPAM, and AN also gave the corresponding controlled polymers. Protection of the acidic proton in the hydroxyl, carboxylic acid, and amide groups was not necessary because polymerization proceeded under neutral conditions and carbon-heteroatom bonds in the dormant species are resistant to polar functional groups.

The most notable feature of these LRP methods is that they can control the polymerization of both conjugated and unconjugated monomers using the same CTAs.^{73,78,80,95} Since polymer-end radicals generated from unconjugated monomers are less stable than those from conjugated monomers, the

dormant species of unconjugated monomers possess stronger carbon–heteroatom bond than those of conjugated monomers. Therefore, conditions B and C are effective for the polymerization of unconjugated monomers. TERP, SBRP, and BIRP of *N*-vinylpyrrolidone (NVP) afforded poly(NVP)s (PNVPs) with M_n in the range of 3100–83500 and narrow MWDs (M_w/M_n = 1.06–1.29). *N*-Vinylimidazole (NVI) and NVC were also polymerized in a controlled manner by using TERP under photo-irradiation. Polymerization of vinyl acetate (VAc) by using TERP⁹⁶ and SBRP⁸⁰ gave the controlled poly(vinyl acetate)s (PVAcs), but the control was limited to low molecular weight polymers (M_n < 5000) due to the formation of dormant species by head-to-head addition reaction.⁹⁶

3.08.3.4 Random and Alternating Copolymerization

While there are no reports on random copolymerization of conjugated monomers by TERP, SBRP, and BIRP, it is reasonable to assume that the copolymerization will proceed in a controlled manner. Mishima and Yamago⁹⁷ reported that copolymerization of (meth)acrylate monomers and vinyl ethers took place with high MWD control and high control of monomer sequence by employing an excess amount of vinyl ethers (5~10 times) over (meth)acrylates (Scheme 7). For example, when a 1:1 mixture of 2,2,2-trifluoroethyl acrylate (TFEA) and isobutyl vinyl ether (IBVE) was polymerized in the presence of organotellurium CTA Te-1, the resulting copolymer possessed low MWD ($M_w/M_p = 1.12$) with mole fraction of IBVE $(MF_{IBVE}) = 0.43$. The polymerization did not proceed further after all of the TFEA was consumed, and IBVE remained even under the polymerization conditions. This is because vinyl ethers do not homopolymerize under radical conditions. A polymer-end radical formed from TFEA reacts with TFEA and IBVE, but that formed from IBVE only reacts with TFEA. Therefore, more TFEA than IBVE was incorporated.

When the amount of IBVE was increased (IBVE/TFEA = 5), nearly complete alternating copolymer with MF_{IBVE} = 0.49 and controlled MWD ($M_w/M_p = 1.18$) was formed. The alternating structure was confirmed by two-dimentional NMR and mass spectroscopy analyses. This alternating copolymerization took place for the combination of various (meth)acrylates and vinyl ethers: TFEA and t-butyl vinyl ether (tBVE), TFEA and trimethyl(vinyloxy)silane (TMVS), BA and IBVE, BA and TMVS, tBA and tBVE, MMA and IBVE, and trifluoroethyl methacrylate (TFEMA) and IBVE (Scheme 8). Highly controlled alternating copolymers with respect to MWD and monomer sequence were formed in all cases under TERP, SBRP, and BIRP conditions.



Scheme 7 Controlled alternating copolymerization of (meth)acrylates and vinyl ethers.



Scheme 8 Combination of (meth)acrylate/vinyl ether monomers in random and alternating copolymerization by TERP, SBRP, and BIRP.

3.08.3.5 Emulsion Polymerization

Due to the high compatibility of water, TERP was applied to a mini-emulsion condition by Okubo.⁹⁸ Polymerization of MMA, St, and BA under mini-emulsion condition was carried out under condition B with CTA Te-2 and AIBN as an initiator in an aqueous solution containing sodium dodecyl sulfate at 60 °C. In the case of MMA polymerization, dibutylditelluride was added to increase the MWD control. The polymerization proceeded in a controlled manner with a high monomer conversion and afforded stable latexes with controlled sizes, though the MWDs of the resulting polymers were broader ($M_w/M_n = 1.23-1.76$) than those obtained under homogeneous conditions. Diblock copolymers composed of St, MMA, and BA were prepared by using a two-step procedure, both of which were carried out in an aqueous dispersed system.

Okubo also reported that TERP of BA and St could be carried out under emulsifier-free emulsion polymerization conditions by employing a water-soluble macro CTA, PMAA₃₀-TeMe, and a water-soluble azo initiator (Scheme 9).^{99–101} Polymerization at moderate temperature ($50 \sim 60 \circ$ C) with efficient stirring resulted in the formation of PBA and PSt with narrow MWD and controlled nanometer-sized particle. The control was achieved by the *in situ* nucleation via self-assembly of the propagating amphiphilic polymer chains derived from the macro CTA in the early stage of the polymerization (Scheme 9). The vigorous stirring ensures homogeneous distribution of the macro CTA leading to the uniform nucleation. The amount of initiating radicals from an azo initiator increases with an increase in temperature, and this leads to the formation of submicrometer-sized particles by homogeneous nucleation and the loss of MWD control. These results demonstrate the applicability of TERP in aqueous heterogeneous systems.

3.08.4 Mechanism

3.08.4.1 Activation/Deactivation Mechanism of Dormant Species

Both RT and DT mechanisms (Scheme 1(b) and 1(c)) involve TERP, SBRP, and BIRP for the activation/deactivation of the dormant species/polymer-end radicals, and the contribution of RT and DT depends on the reaction conditions.^{77,88,96} Involvement of the two mechanisms makes these LRP methods unique, and it is the origin of the different polymerization conditions described in the previous section.

The first-order rate constant for the activation of the dormant species via RT (k_d), the second-order rate constant for the activation via DT (k_{ex}), and the DT constant C_{ex} in TERP,^{77,81,96} SBRP,^{80,88} and BIRP⁷³ are summarized in **Table 2**. Although the rate constants are affected by the heteroatom species and the substituents on the heteroatom, the contribution of the DT mechanism is predominant over the RT mechanism. Therefore, once the initiating radical species have formed, they predominantly undergo the DT-mediated polymerization reaction in all cases.

Under condition A, the initiating radicals are provided via the thermolysis of the heteroatom CTA. The high temperatures and long reaction times required for the polymerization are due to the high activation energy required for the thermolysis. The initiating radicals are generated from azo initiators under mild thermal conditions under condition B, and the



Scheme 9 Structure of macro CTA, PMMA₃₀-TeMe, and mechanism for particle formation in emulsifier-free emulsion polymerization. Reprinted with permission from Kitayama, Y.; Chaiyasat, A.; Minami, H.; Okubo, M. *Macromolecules* **2010**, *43*, 7465.¹⁰⁰ Copyright 2010 American Chemical Society.

 Table 2
 Kinetic parameters for the activation of organotellurium,^{77,81,96}
 organostibine,^{80,88,102}
 organobismuthine⁷³
 dormant spices at 60 °C in homopolymerization^a

P-X ^b	k _d (s ⁻¹)	$k_{\rm ex} \ (M^{-1} s^{-1})$	$k_{\rm p} \ (M^{-1} s^{-1})$	C _{ex}
PSt-TeMe	1×10^{-5} $(2 \times 10^{-4})^c$	5.7×10^3	3.4×10^2	17
PSt-TeBu- <i>n</i>	1 × 10 ⁻⁵	$3.4 imes10^3$		10
PSt-TePh	1×10^{-5}	$9.6 imes10^3$		28
PSt-TeC ₆ H ₄ OMe-p	$4 imes 10^{-5}$	$1.2 imes 10^4$		35
PSt-TeC ₆ H ₄ CH ₃ -p	$5 imes 10^{-5}$	$1.4 imes 10^4$		41
PSt-SbMe ₂	~0	1.1×10^{4}		32
PSt-SbPh ₂	~0	$4.0 imes 10^4$		118
PSt-BiMe ₂	$(3 \times 10^{-4})^{c}$	$1.8 imes 10^4$		53
PMMA-TeMe	5 × 10 ⁻⁶	$3.0 imes10^3$	$8.3 imes 10^2$	3.6
PMA-TeMe	$\leq 1 imes 10^{-3}$	4.6×10^5	2.4×10^4	19

^a The k_d , k_{ex} , and k_p are the rate constant for reversible termination (RT) (**Scheme 7(a**)), degenerative transfer (DT) (**Scheme 7(b**)), and propagation, respectively. C_{ex} is the degenerative chain transfer constant ($=k_{ex}/k_p$).

^b PMA, poly(methyl acrylate); PMMA, poly(methyl methacrylate); PSt, polystyrene.
^c Data obtained at 100 °C.

polymerization proceeds exclusively via the DT mechanism. Under condition C, direct carbon-tellurium bond photolysis occurs to afford the initiating radicals from the dormant species. Since photochemical reactions do not require heat, polymerization also proceeds at low temperatures exclusively via DT. It is worth noting that, as the rate of polymerization becomes slower at lower temperatures, heating is sometimes necessary to complete the polymerization within a reasonable timescale when monomers with low propagation rates are employed under conditions B and C.

When LRP proceeds by DT mechanism, MWD of polymers can be estimated by using eqn [1] under steady-state conditions without any side reactions leading to dead polymers, where $DP_{nv} c$, C_{ex} (= k_{ex}/k_p), k_{ex} , and k_p are the number-average degree of polymerization, monomer conversion, a DT constant, a rate constant for DT, and a rate constant for the propagation reaction,⁹ respectively.

$$M_{\rm w}/M_{\rm n} = 1 + 1/{\rm DP_n} + (2/c - 1)/C_{\rm ex}$$
 [1]

Since k_p is the same when the same monomer is considered, a faster k_{ex} and thus a higher C_{ex} lead to higher MWD control of the resulting polymer at the same monomer conversion.

The $C_{\rm ex}$ (=17) of methyltellanyl group transfer reaction at PSt polymer-end radical and PSt-TeMe dormant species in St polymerization is sufficiently fast to achieve high MWD control. Although $C_{\rm ex}$ (=10) of the butyltellanyl group transfer reaction is slightly smaller than that of the methyltellanyl group transfer reaction, it is still faster than that of the iodine atom transfer reaction ($C_{\rm ex}$ =3.5).¹⁰³ The DT in the phenyltellanyl, *p*-methoxyphenyltellanyl, and *p*-trifluoromethylphenyltellanyl group transfer reactions takes place much faster than that in methyltellanyl group transfer reactions ($C_{\rm ex}$ =28~41). The kinetics data are consistent with the observed higher MWD control using CTAs Te-3–Te-5 possessing aryl substituents than that using methyltellanyl derivative Te-1.

High values of k_{ex} and C_{ex} were also observed in dimethylstibanyl and dimethylbismuthanyl group transfer reaction in SBRP (C_{ex} = 32~118) and BIRP (C_{ex} = 53) in St

polymerization. Among the same methyl-substituted heteroatom groups, bismuth is the fastest followed by antimony and then tellurium for the DT reaction. The kinetics data are also consistent with the general trend that organostibine, such as **Sb-2** and **Sb-3**, and organobismuthine CTAs, such as **Bi-1**, show higher MWD control than organotellurium CTAs **Te-1** and **Te-7** do.

The DT of diphenylstibanyl group at PSt polymer end in styrene polymerization occurs faster than that of dimethylstibanyl group (C_{ex} = 118). However, the MWD control of polymerization using diphenylstibanyl CTA **Sb-3** was lower than dimethylstibanyl CTA, such as **Sb-2**. The insufficient control of diphenylstibanyl group is attributed to the occurrence of frequent termination.¹⁰² The results indicate that the rate of DT is not the exclusive factor for the MWD control.

The kinetics parameters of the polymerization of MMA and methacrylate (MA) involving an organotellurium dormant species with a methyltellanyl group are also summarized in Table 2.⁹⁶ The C_{ex} (=3.6) of the MMA polymerization becomes ~5 times smaller than that of the St polymerization. This C_{ex} value is too small to yield PMMAs with narrow MWDs $(M_w/M_p < 1.28)$. The result is consistent with the fact that the MWD control of the TERP of MMA was not sufficient $(M_w/M_n > 1.35)$, and the addition of ditellurides was required to yield PMMA with a narrow MWD $(M_w/M_n \approx 1.1)$.⁷⁹ SBRP and BIRP of MMA gave PMMA with a low MWD ($M_w/M_p < 1.25$) without the addition of additives. The results suggest that the Cex values under these conditions are larger than that under TERP, as in the polymerization of St, and that organostibines and bismuthines generally have a higher reactivity in the DT reaction than organotellurium compounds have.

The C_{ex} (=19) in MA polymerization was similar to that in St polymerization, despite the rate of propagation of MA is ~70 times faster than that of St. This is because the rate of DT of the MA polymer-end species is ~80 times faster than that of PSt. The result is also consistent with the fact that the polymerization of acrylates usually gives resulting polymers with a low MWD ($M_w/M_n < 1.2$).



Figure 2 Hypothetical reaction coordinate of DT in (a) RAFT and (b) TERP. The lines in gray show the energy diagram when less stabilized radical P and P' are involved. Reprinted with permission from Yamago, S. *Chem. Rev.* **2009**, *109*, 5051.²⁹ Copyright 2009 American Chemical Society.

Although RAFT also proceeds by DT polymerization,^{24,25} the microscopic energy profiles of the DT in RAFT are completely different from those of TERP, SBRP, and BIRP, as schematically shown in Figure 2. The DT in RAFT proceeds stepwise with the addition of radical P to thiocarbonyl compound 3 (a RAFT reagent) to form intermediate radical 4 (Figure 2(a)). Subsequent fragmentation of the S-P' bond in 4 generates RAFT reagent 3' and radical P'. All the elementary processes are reversible, and the addition of radical P' to 3' also generates radical P and 3 through intermediate 4.¹⁰⁴ Though the lifetime of 4 must be short in order to minimize unwanted radical-radical termination processes, capture of intermediate 4 in acrylate polymerization occurs as ascertained by Monteiro¹⁰⁵ and Fukuda.^{106,107} This chain breaking reaction causes the rate retardation in acrylate polymerization when phenyl-substituted RAFT CTA (Z=Ph) was used. Stability of 4 is strongly affected by the Z substituent because it directly attaches to the radical center, while effects of P and P' radicals on 4 are marginal. When the same Z group is considered, relative stability and, thus, concentration of 4 increase as the polymer-end radical P and P' become less stable as shown in the gray line. This enhances the probability of 4 undergoing the chain breaking reaction. Therefore, appropriate choice of the Z group is necessary depending on the monomer families being polymerized so as to undergo efficient DT reaction.

In sharp contrast, the DT in TERP proceeds through hypervalent tellurium intermediate or transition state 6, which forms by the reaction of radical P with organotellurium dormant species 5 to generate radical P' and new dormant species 5' (Figure 2(b)). Although the existence of a trivalent tellurium radical intermediate is still a controversial issue, 65,108-110 the intermediate, if any, should be very close in energy to the transition state. Therefore, the DT in TERP virtually proceeds in a concerted manner, and involvement of a long-lived intermediate, which may cause unwanted side reactions, is unlikely. In addition, since the DT process becomes faster when less stable polymer-end radicals are involved as shown in the gray line, CTAs with the same Z group can be used for controlling LRP. Energy profiles of SBRP and BIRP should be very similar to TERP, though more experimental and theoretical investigations are needed. 111,112

The contribution of RT is small compared to DT, but it plays a crucial role under condition A especially in TERP and BIRP (**Table 2**).⁹⁶ The results indicate that CTAs in TERP and

BIRP also serve as radical initiators. As the rate of thermal dissociation of organobismuth compounds is about 2 times faster than that of organotellurium compounds, the former is the best radical initiator among the heteroatom compounds.

3.08.4.2 Role of Diheteroatom Compounds

Addition of ditellurides and distibines in TERP and SBRP, respectively, is effective for increasing MWD control in styrene and especially in methacrylate polymerization, as mentioned in the previous section.^{75,79} Thiobisumthine **2** is also effective for the controlled synthesis of ultrahigh molecular weight polymers.

A polymer-end radical reacts with a ditelluride through a homolytic substitution reaction to form a dormant species (Scheme 10(a)). Kinetics studies have revealed that the rate for the deactivation of PSt polymer-end radical by dimethylditelluride is ~100 times faster than that of PSt polymer-end radical with PSt dormant species by the DT mechanism.⁹⁶ The rate for the deactivation of PMMA polymer-end radical by dimethylditelluride is also 40–80 times faster than that of PMMA polymer-end radical by PMMA dormant species. Therefore, the deactivation mechanism completely changes from the DT to the ditelluride trapping by the addition of a substoicheometric amount of ditelluride, and the increase of the deactivation frequency of polymer-end radicals by ditelluride is the origin of the increase of MWD control.

The liberated tellanyl radical reacts with an organotellurium dormant species to regenerate a polymer-end radical and ditelluride. However, it is virtually inert to monomer and does not initiate new polymer chains.¹¹³ If it did, the observed high controllability would not be realized. These seemingly conflicting reactivities of tellurium-centered radicals also play crucial roles in the control of MWD in TERP in the presence of ditellurides.

Though there are no kinetics studies on the effects of distibines in SBRP, the increased MWD control in the presence of distibine can also be ascribed to the higher efficiency of the deactivation of the polymer-end radical by distibine via a homolytic substitution reaction (Scheme 10(b)). The effect on the control using distibine is more noticeable than ditelluride, and this may be attributed to the higher reactivity of distibine than ditelluride, as in the DT reaction of polymer-end dormant species (Table 2).⁷⁵ The observed rate retardation in



Scheme 10 Deactivation mechanism of polymer-end radical P by diheteroatom compounds.

the presence of distibine is likely to shift the equilibrium from the polymer-end radical to the dormant species. This shift is probably due to the low reactivity of the dimethylstibanyl radical to an organostibine dormant species. In such a case, the stibanyl radical may dimerize to a distibine.

The role of thiobismuthine **2** is to react reversibly with the polymer-end radical to generate an organobismuthine dormant species and 2,6-dimesitylphenylthiyl radical 7 (Scheme 10(c)).¹¹⁴ The bulky 2,6-dimesitylphenyl group attached to the sulfur atom prevents the addition of thiyl radicals to the vinyl monomers generating a new polymer chain, as thiyl radicals are reactive toward alkenes.¹¹⁵ Since thiyl radicals are highly reactive toward organobismuthines,¹¹⁶ the liberated thiyl radical 7 reacts with the orgnobismuthine dormant species to regenerate the polymer-end radical P and 2.

3.08.5 Macromolecular Engineering

3.08.5.1 End Group Transformations

A characteristic advantage of the TERP, SBRP, and BIRP is the versatility of the transformations that can be carried out on the polymer-end groups. Since polymer-end radicals are easily generated from the organoheteroatom dormant species, several polymer-end group transformations mediated by radical species have been developed.

Radical-mediated reduction of organoheteroatom ω -end groups is the simplest route to ω -protonated and deuterated polymers.^{71,73,74,80} For example, treatment of PMMA 8 bearing dimethylstibanyl group with tributyltin hydride gave end-protonated PMMA 10 in quantitative conversion through radical 9 (Scheme 11(a)).¹¹⁷ Not only tin hydrides, which pose environmental concerns, but also arylthiols can be used as reducing agents.¹¹⁶ When 8 was treated with ethyl-[(tributylstannyl)methyl]acrylate $(11)^{118}$ in the presence of AIBN, ω-vinylidene-functionalized PMMA 12 formed (Scheme 11(b)).^{71,117} Structurally related ω-vinylidenefunctionalized PMMA 13 also formed when PMMAs prepared by using BIRP, SBRP, and TERP were treated with 2,2,6,6tetramethylpiperidine 1-oxyl (TEMPO) under thermal or photochemical conditions (Scheme 11(c)).¹¹⁷ The formation of 13 is due to the abstraction of a β -hydrogen adjacent to the radical center by TEMPO. The same protocol could be used for the synthesis of ω-vinylidene-functionalized polymethacrylonitrile. The high end-group fidelity must be due to the high efficiency of radical generation by direct carbon-heteroatom homolysis.

Thermogravimetric analysis revealed that ω -protonated PMMA **10** ($M_n = 4100$, $M_w/M_n = 1.22$) started to degrade at approximately 370 °C and all polymer completely degraded around 450 °C (**Figure 3(a)**). Degradation of ω -vinylidene PMMA **13** ($M_n = 3300$, $M_w/M_n = 1.19$), on the other hand, began at approximately 270 °C and ended about at 340 °C (**Figure 3(b)**). The clean single-step decomposition of each PMMA sample is consistent with the defined polymer-end structure.¹¹⁷ While the relative stability of these PMMAs is similar to



Scheme 11 Radical-mediated transformations of heteroatom-substituted PMMA polymer-end.



Figure 3 TGA thermograms of (a) ω -hydrogenated PMMA **10** ($M_n = 4100, M_w/M_n = 1.22$), and (b) ω -vinylidene PMMA **13** ($M_n = 3300, M_w/M_n = 1.19$). Reprinted with permission from Yamago, S.; Kayahara, E.; Yamada, H. *React. Function Polym.* **2009**, *69*, 416.¹¹⁷ Copyright 2009 Elsevier.

the previous reports,^{119–121} selective and controlled synthesis of each endo-modified PMMA was difficult. The current method, thus, provides structurally homogeneous PMMA samples with respect to molecular weight, MWD, and end groups.

The selective ω -end group transformation combined with the use of functional CTAs, such as **Sb-7** and **Sb-8**, have led to the synthesis of structurally well-controlled telechelic polymers.⁷⁵ For example, PSt 14, which possesses an alkene functionality at the α -polymer end prepared from **Sb-7** and St, was heated with allylstannane 11 in the presence of AIBN at 80 °C to give telechelic polymer 15 as the sole product (**Scheme 12(a)**). Aerobic oxidation of an organostibanyl group to a hydroxyl group has been reported,¹²² and application of this procedure to 14 resulted in the selective formation of ω -hydroxylated PSt 16 (**Scheme 12(b**)). The different functional groups at the α -polymer and ω -polymer ends of these PSts should be useful for further selective synthetic transformations.

The reaction of living polymers prepared by using RAFT with an excess amount of AIBN has recently been reported to form the bis-functionalized polymers by Perrier,¹²³ and this method has been applied to organstibine substituted living polymers (Scheme 13).⁷⁵ For example, the reaction of azo initiator 17 with tetramethyldistibine gave CTA **Sb-8** (Scheme 4(d)). PSt 18, which was prepared by using SBRP of St with **Sb-8**, was treated with 40 equiv of 17 to give

 α, ω -bisfunctionalized PSt **19**. These results indicate that not only homotelechelic polymers but also heterotelechelic polymers, which possess different functional groups at their α -polymer and ω -polymer ends, can be synthesized by arbitrary choice of the azo initiator for preparation of the CTA and the subsequent ω -polymer end transformation.

Organotellurium compounds are excellent precursors not only for carbon-centered radicals, but also for carbanions and carbocations.^{26,70,124} Once such ionic species can be selectively generated from the polymer-end organotellurium compounds, they are highly effective intermediates for the end functionalization (Scheme 14). Tellurium–lithium transmetallation^{125,126} was achieved by the treatment of PSt 20 possessing methyltellanyl group at the polymer end with butyllithium to give benzyllithium 21, which was trapped with an electrophile, such as carbon dioxide, giving carboxylic acid functionalized PSt 22.⁷¹ The carboxylic acid was further transformed to different functional groups by using standard techniques, such as esterification. Treatment of 20 with phenyltellanyl triflate in the presence of 1,3,5-trimethoxybenzene afforded Friedel–Crafts product 24 through benzilic cation 23.¹²⁷

Since carbanions occupy a central position in organic synthesis, 128, 129 the end-group modification via a polymer-end anionic species, for example, 21, is an attractive method. However, carbanions are usually uncompatible with many of polar functional groups which often present in polymers prepared by LRP. Kayahara and Yamago recently reported that organostibines and organobismuthines are highly reactive to stibine-metal and bismuthine-metal exchange reaction, respectively, and that the exchange reaction proceeds much faster than the reaction of organometallic species reacting to polar functional groups. The method was applied to the end group modification of living polymers prepared by SBRP and BIRP.83 For example, the exchange reaction between PMMA 25 bearing dimethylstibanyl group prepared by SBRP and n-BuLi selectively occurred to give anion 26, which was treated with H₃O⁺ or D₃O⁺ to give end-protonated or deuterated PMMA (Scheme 15). The exchange reaction starting from PMMA bearing dimethylbismuthanyl group also selectively gave 26. The exchange reaction with tetraalkylzincates, Me₄ZnLi₂¹³⁰⁻¹³² and $tBu_4ZnLi_{2i}^{133-135}$ and $iPrMgCl \cdot LiCl^{136,137}$ also took place chemoselectively despite the excess number of ester groups in PMMA 25. Once polymer-end lithium species 21 was generated, subsequent reaction with carbon electrophiles afforded various end-functionalized PMMAs. For example, the reaction of 26 with carbon dioxide, benzoyl chloride, benzaldehyde, and allyl iodide proceeded giving PMMAs possessing



Scheme 12 Synthesis of telechelic polymer starting from functional CTA **Sb-7** and ω -end functionalization.



Scheme 13 Synthesis of diol-functionalized telechelic polymer through radical coupling reaction. Reprinted with permission from Yamago, S. Chem. Rev. 2009, 109, 5051.²⁹ Copyright 2009 American Chemical Society.



Scheme 14 Carbanion- and carbocation-mediated transformation of PSt-TeMe.



Scheme 15 Synthesis of ω-functionalized PMMA through chemoselective heteroatom–lithium exchange reaction.

carboxylic acid, benzoate, δ -lactone, and alkene functionalities, respectively. ¹H NMR and MALDI-TOF mass spectra (MS) analyses revealed the high-end group fidelity (90~>99%) for the end group transformation. As the reactivity of organotellurium compounds toward the exchange reaction is very similar to organostibine and organobismuthiene compounds, the same type of anion-mediated transformations of organotellurium-polymer end group would also be possible.

The exchange reaction can also be applicable for polyacrylates and polyacrylamides possessing acidic hydrogen in the main chain as well as the side chain (Scheme 16). While the stibine–lithium exchange reaction of PBA **27** with *n*-BuLi occurred selectively, the resulting anionic species underwent side reactions. However, the exchange reactions with t-Bu₄ZnLi₂ in THF proceeded selectively and afforded stable anionic species, which reacted with electrophile, for example, benzoyl chloride, to give the desired product **28** quantitatively (Scheme 16(a)). The exchange reaction successfully took place even with PHEMA **29** possessing free hydroxyl group at the pendant group by the treatment of t-Bu₄ZnLi₂ in DMSO without protection of the free hydroxyl group. Subsequent trapping of the anionic species with benzoyl chloride desired



Scheme 16 Chemoselective stibine–zincate exchange reaction in the presence of acidic hydrogens.

PHEMA **30** in quantitative transformation (Scheme 16(b)). Polymer-end dimehylstibanyl group in PNIPAM **31** was also successfully transformed to the corresponding anionic species by tBu_4ZnLi_2 in DMF without protection of the amide protons. Subsequent addition of benzoyl chloride (5.0 equiv) gave the desired product **32** with quantitative incorporation of the benzoyl group (Scheme 16(c)).

Due to the high chemoselectivity, the current method was applied to the synthesis of an ω -biotinylated polymer (Scheme 13(d)). Treatment of PNIPAM 31 with tBu_4ZnLi_2 in DMF followed by the addition of biotin chloride exclusively afforded ω -biotinylated PNIPAM 33. The structure of 33 was unambiguously confirmed by using ¹H NMR and MALDI-TOF MS analyses. PNIPAM is a thermoresponsive polymer and possesses lower critical solution temperature in water. On the other hand, biotin is a good ligand for proteins, such as avidin and streptavidin. Therefore, this polymer and its analogs would make it possible to thermally modulate the properties of biomaterials for biological applications.¹³⁸

3.08.5.2 Block Copolymer Syntheses

Another notable feature of TERP, SBRP, and BIRP is their versatility in the synthesis of block copolymers. Although the success of block copolymer synthesis is, in general, highly dependent on the order of monomer addition, especially when different monomer families are used, these methods are more tolerant toward the order of addition than other LRP methods.^{139–142} For example, blockcopolymer syntheses starting from the PSt macro CTA were successfully carried out with MMA and tBA, and the desired AB-diblock copolymers with narrow MWDs were obtained in both cases (Scheme 17).⁷⁹ The essentially complete disappearance of the starting macro CTAs and the formation of the desired diblock copolymers were observed. The addition of ditelluride is necessary when MMA is used as a monomer, as is also the case for the homopolymerization of MMA. The controlled syntheses of

AB-diblock copolymers starting from a PMMA macro CTA with St and tBA, or from a poly(*t*-butyl acrylate) (PtBA) macro CTA with St and MMA, were also carried out by the successive addition of a second monomer. The desired diblock copolymers with narrow MWDs were obtained in all cases. Due to the stronger carbon–tellurium bonds found in PBA dormant species compared with those found in PSt and PMMA species, the MWD control of diblock copolymers initiated by the PtBA CTA was slightly less efficient than that starting from PSt and PMMA, but still at an acceptable level ($M_w/M_n < 1.35$).

As the order of monomer addition is less important in TERP compared to that in other LRP methods, it was possible to prepare ABA- and ABC-triblock copolymers starting from diblock macro CTAs (Scheme 17). Treatment of PMMA-*block*-PSt and PMMA-*block*-PtBA macro CTAs with MMA gave the desired ABA-triblock copolymers with narrow MWDs. ABC-triblock copolymers with different monomer sequences of St, MMA, and tBA, namely, PSt-*block*-PtBA.*block*-PtBA, PMMA-*block*-PtBA, and PMMA-*block*-PtBA, were also synthesized in a controlled manner by the successive addition of each monomer. These triblock copolymers were all obtained in a highly controlled manner with narrow MWDs.

The insensitivity toward the order of monomer addition in TERP was partly verified via kinetic studies on the block copolymerization of St and MMA by measuring the activation rate of PMMA-TeMe macro CTA in the St polymerization and the reverse reaction.⁹⁶ The C_{ex} values for PMMA polymer-end radical to PMMA-TeMe CTA (homopolymerization) and PSt-TeMe CTA (block copolymerization) are similar (17 vs. 31), and those for PSt radical to PSt-TeMe CTA (homopolymerization) are also similar (3.6 vs. 2.8). The results indicate that the transfer of PSt block to MMA, as well as that of PMMA block to St, occurs efficiently to give the second PMMA or PSt block.

The results are in sharp contrast to the sensitivity of the C_{ex} values in RAFT polymerization. Fukuda reported that, although the C_{ex} values for PSt polymer-end radical to PSt-SCSMe CTA



Scheme 17 Synthesis of AB-diblock, ABA-triblock, and ABC-triblock copolymers using St, MMA, and BA starting from **Te-11**. Reprinted with permission from Yamago, S. *Chem. Rev.* **2009**, *109*, 5051.²⁹ Copyright 2009 American Chemical Society.

and PMMA-SCSMe CTA are similar (220 vs. 420), those for PMMA polymer-end radical to PMMA-SCSMe CTA (homopolymerization) and PSt-SCSMe CTA (block copolymerization) are very different (40 vs. 0.83).¹⁴³ The results are consistent with the fact that the order of monomer addition is important in RAFT.¹⁴² The origin of the monomer dependence of the kinetic parameters between TERP and RAFT is not clear at this moment. However, the difference in the DT mechanism between TERP and RAFT, as shown in Figure 2, may well contribute to the observed differences.

Block copolymers comprised of conjugated and unconjugated monomers were also synthesized in a controlled manner by using TERP, SBRP, and BIRP.^{72,73,80,95} Synthesis of these block copolymers is more difficult than that from both conjugated monomers because stabilities and reactivities of the dormant species and polymer-end radicals derived from conjugated and unconjugated monomers are quite different. Polymerization of organostibine and organobismuthine PSt macro CTAs with NVP in the presence of AIBN in DMF at 60 °C resulted in the complete consumption of the CTAs and the formation of desired PSt-block-PNVP in high monomer conversion (Scheme 18). The diblock copolymers composed of different compositions of PSt and PNVP segments were successfully synthesized in a controlled manner $(M_w/M_n = 1.05 - 1.28)$ by altering the molecular weight of PSt macro CTAs and the amount of NVP. PMMA-block-PNVP was also synthesized in a controlled manner ($M_n = 20500$, $M_{\rm w}/M_{\rm n}$ = 1.31) by treating an organostibine-PMMA macro CTA with NVP in the presence of AIBN. Although the blocking



Scheme 18 Structures of diblock copolymers containing a PNVP segment. Reprinted with permission from Yamago, S. *Chem. Rev.* **2009**, *109*, 5051.²⁹ Copyright 2009 American Chemical Society.

reaction of PNVP macro CTA to St was inefficient, that to MMA proceeded smoothly in the presence of AIBN to give highly controlled PNVP-*block*-PMMA with a narrow MWD ($M_w/M_n = 1.18$). These are the first examples of the successful block copolymerization of both conjugated and unconjugated monomers. Since these block copolymers are comprised of hydrophobic PSt or PMMA and hydrophilic PNVP blocks, their physical properties will be of great interest.

New block copolymers were synthesized using alternating copolymerization of acrylates and vinyl ethers as described in the previous section. For example, poly(BA) macro CTA with a



Scheme 19 Synthesis of block copolymers containing a poly(BA-alt-IBVE) segment.

methyltellanyl group at the polymer end prepared by reacting Te-1 with BA was treated with a mixture of BA and IBVE. Conversion of BA reached 92% and block copolymer poly[BA-*block*-(BA-*alt*-IBVE)] with controlled MWD $(M_n = 27700, M_w/M_n = 1.22)$ was obtained (Scheme 19(a)). The MF of IBVE in the second block was 0.44, suggesting that highly alternating copolymerization occurred.

An alternating copolymer was also used as a macro CTA. Poly(BA-*alt*-IBVE) ($M_n = 3900$, $M_w/M_n = 1.20$, $MF_{IBVE} = 0.49$) was prepared by copolymerizing BA (20 equiv) and IBVE (100 equiv) in the presence of **Te-1**. Since ~80 equiv of unreacted IBVE remained in the reaction mixture, addition of tBA (50 equiv) triggered to reinitiate the polymerization, affording poly[(BA-*alt*-IBVE)-*block*-(*t*BA-*co*-IBVE)] with a controlled MWD ($M_n = 11700$, $M_w/M_n = 1.20$) (Scheme 19(b)).

As vinyl ethers do not homopolymerize, the group transfer radical addition reaction of poly(meth)acrylate prepared by LRP to vinyl ethers can be used for selective end-group transformation reaction. The resulting adduct, for example, 34, was used for the macro CTA for living cationic polymerization of vinyl ethers in the presence of Lewis acid giving poly[(meth) acrylate-block-(vinyl ether)] (Scheme 20).144 This one-pot, three-step reaction was applied for the combination of BA and IBVE, BA and n-butyl vinyl ether, BA and n-octyl vinyl ether, and MMA and IBVE. Desired block copolymers with Mn ranging from 8000 to 20000 with controlled MWD $(M_w/M_p = 1.21 \sim 1.46)$ were successfully synthesized. Starting from a bifunctional CTA Te-14, ABA-triblock copolymer, poly(IBVE-block-BA-block-IBVE), was successfully synthesized by TERP of BA, the radical addition reaction to IBVE, and living cationic polymerization of IBVE by employing BF₃·OEt₂ (Scheme 21).

(Meth)acrylates and vinyl ethers are orthogonal monomer families under radical and cationic polymerization conditions, and they cannot be polymerized under cationic and radical conditions, respectively. However, a selective chain-end transformation via a radical-mediated tellurium group transfer addition reaction of poly(meth)acrylate macro initiator to vinyl ethers alternates the reactivity of ω -polymer end group, which is suitable for living cationic polymerization.

Moreover, macro CTAs prepared by alternating copolymerization of (meth)acrylates and vinyl ethers were used as initiators for living cationic polymerization.⁹⁷ Since an excess amount of vinyl ethers is employed over (meth)acrylates to achieve highly alternating monomer sequence, polymer-end unit is derived from vinyl ethers. Therefore, the copolymer formed by LRP is directly used as a macro CTA for the cationic polymerization. For example, copolymer 35 ($M_{\rm p}$ = 3900, $M_{\rm w}/M_{\rm n}$ = 1.19, MF_{IBVE} = 0.50) was prepared by TERP of TFEA (20 equiv) and IBVE (200 equiv) in the presence of Te-1. After the reaction mixture was diluted with CH₂Cl₂, the remaining IBVE was polymerized under living cationic polymerization conditions with $BF_3 \cdot OEt_2$ as an activator. Desired block copolymer poly[(TFEA-alt-IBVE)-block-IBVE] formed with a controlled macromolecular structure ($M_n = 23300$, $M_{\rm w}/M_{\rm n}$ = 1.32) (Scheme 22).

3.08.5.3 Synthesis of Functional Polymers

3.08.5.3.1 Thermosensitive micelles

Yusa and coworkers⁹⁵ have reported the synthesis of diblock copolymers composed of PNIPAM and PNVP and their solution properties in water. PNIPAM is a representative thermosensitive polymer and has a lower critical solution temperature (LCST) in water,¹⁴⁵ and PNVP is a water-soluble polymer.^{146,147} Therefore, the block copolymers reversibly form micelles in water depending on the solution temperature (Figure 4).







Scheme 21 Synthesis of a ABA-triblock copolymer by successive living radical and living cationic polymerization reaction starting from a bifunctional CTA **Te-14**. V-601 refers to dimethyl 2,2'-azobis(2-methylpropionate).







Figure 4 (a) Structure of thermoresponsive diblock copolymer poly(NIPAM-*block*-NVP) and (b) schematic illustration of the micellization of the block copolymer as a function of temperature and the formation of a polymer-coated gold nanoparticle. Reprinted with permission from Yusa, S.; Yamago, S.; Sugahara, M.; *et al. Macromolecules* **2007**, *40*, 5907.⁹⁵ Copyright 2007 American Chemical Society.

The synthesis was achieved by treating PNIPAM organotellurium macro CTA ($M_n = 10\,900$, $M_w/M_n = 1.09$), which was prepared from Te-2 and NIPAM in DMF with 100% monomer conversion, with NVP (300 equiv) in the presence of AIBN. The blocking reaction proceeded cleanly, and the desired diblock copolymer formed with 76% monomer conversion and a narrow MWD ($M_n = 36\,700$, $M_w/M_n = 1.15$). By changing the amount of each monomer, diblock copolymers with different block lengths were also prepared in a controlled manner ($M_n = 17\,000-26\,300, M_w/M_n = 1.09-1.11$) (Figure 4(a)).

Heat-induced association of the diblock copolymers was confirmed by using ¹H NMR, turbidity, and light-scattering studies as a function of temperature. The diblock copolymer dissolves in water as an unimer below the aggregation temperature (T_a), but it starts to aggregate near the LCST of PNIPAM. T_a is a function of the chain length of each polymer block, and it

becomes lower as the block length of PNVP becomes shorter. On the other hand, the T_a becomes higher as the block length of PNIPAM becomes shorter. Each block copolymer reversibly forms spherical core–corona micelles above T_a with unique aggregation numbers (300–27 000) depending on the block lengths of each segment.

Although there have been a number of reports concerning the synthesis of thermoresponsive block copolymers containing PNIPAM segment,^{148–150} this is the first example of the synthesis of diblock copolymer comprised of PNIPAM and PNVP. Since PNVP is a water-soluble and biocompatible polymer, this block copolymer is a good candidate for several biological applications, such as in thermosensitive drug delivery vehicles.¹⁵¹

The same diblock copolymer encapsulates gold nanoparticles in water via coordination of the PNVP block to the gold particle, as schematically shown in **Figure 5(b)**.¹⁵² The polymer-coated gold nanoparticles show a temperature dependent color change of the solution from pink to bluish purple above the LCST of PNIPAM determined on the basis of the surface plasmon band. The polymer-coated gold nanoparticles may be separately dissolved in water when the temperature is below the LCST for the PNIPAM block. However, they may associate with each other due to hydrophobic interactions between the dehydrated PNIPAM blocks at temperatures above LCST, inducing a color change. This phenomenon may be applied to colloidal sensors.

3.08.5.3.2 Polymer monoliths

Kanamori and coworkers¹⁵³ have reported that TERP of 1,4-divinylbenzene in the presence of poly(dimethylsiloxane) and 1,3,5-trimethylbenzene gave macroporous cross-linked polymeric gels (Figure 5(a)). Well-defined macroporous monolithic dried gels with bicontinuous structures on the micrometer scale were obtained after removing poly(dimethylsiloxane) and 1,3,5-trimethylbenzene by simple washing and drying (Figure 5(b)). Inside the skeletons that comprise the macroporous structure, 'skeletal pores' with various sizes on the nanometer scale were found. The controlled pore formations are based on polymerization-induced phase separation by spinodal decomposition in the course of the homogeneous network formation during LRP. An unreactive polymeric agent present in solution induces the phase separation during gelation to give a well-defined bicontinuous porous structure. Pore size and volume can be independently controlled by changing the starting composition.¹⁵⁴

Conventional free radical polymerization in the presence of a 'porogen', which is usually a poor solvent for the network-forming components and induces phase separation, is widely used for the preparation of porous polymeric materials (polymer monoliths).^{155–157} Polymer monoliths thus prepared have been applied especially as liquid-phase separation or reaction media.^{158,159} However, fine-tuning of the pore properties, such as pore size, volume, and morphology, is relatively difficult because the pores are formed in between segregated microgel particles that aggregate at random. Since



Figure 5 (a) Synthesis and (b) morphology of polydivinylbenzene (PDVB) gel prepared by TERP. Reprinted with permission from Hasegawa, J.; Kanamori, K.; Nakanishi, K.; *et al. Macromolecules* **2009**, *42*, 1270.¹⁵³ Copyright 2009 American Chemical Society.

the more homogeneous macroporous morphology with a bicontinuous structure obtained from spinodal decomposition will improve liquid transport throughout the media, liquid-phase applications, such as chromatography and catalyst supports, are expected.

The same group has recently reported the synthesis of rigid crosslinked polyacrylamide monoliths with well-defined macropores derived from N,N-methylenebis(acrylamide) by using TERP accompanied by spinodal decomposition with polyethylene oxide as a porogen.¹⁶⁰ They are promising materials with highly hydrophilic polyacrylamide surfaces and have enough strength to withstand the surface tension arising from repetitive swelling and drying, which is inevitable in many applications. Kanamori¹⁶¹ has also reported the synthesis of polymer monoliths with controlled pore properties by using NMP of 1,4-divinylbenzene and ATRP of 1,3-glycerol dimethacrylate.¹⁶² Therefore, the synthesis of polymer monoliths with controlled pore sizes is not limited to TERP. However, the synthetic advantages of TERP, such as high functional compatibility and high versatility of polymerizable monomer families, should be beneficial for the future design of new monoliths with various functionalities.

3.08.5.3.3 Adhesives, dispersants, and compatibilizers

Otsuka Chemical Co. (Kawauchi, Tokushima, Japan) recently announced that they had started selling several adhesives prepared by using TERP (http://chemical.otsukac.co.jp/advanced/ about01.html). Although detailed polymer compositions and chain lengths are not shown, control of MWD and the distribution of the crosslinking functionality of the polymer are the key for improving the properties. For example, a model random copolymer formed by TERP has an M_w of 581 600 with a narrow MWD $(M_w/M_p = 1.24)$, whereas a control polymer prepared by conventional radical copolymerization has a broad MWD $(M_w = 703\ 800,\ M_w/M_n = 3.44)$. A model adhesive prepared from the model polymer by crosslinking reaction has about 10 times longer holding time than a control adhesive prepared from the control polymer, although they have similar peel strengths. The properties of adhesives, such as the peel strength and the tack, are easily tuned by changing the composition of functional groups and/or chain lengths. Otsuka Chemical Co. has also succeeded in the development of polymer compatibilizers and pigment dispersants consisting of block copolymers prepared by TERP.

3.08.6 Conclusions

DT polymerization using organotellurium, organostibine, and organobismuthine compounds, namely, TERP, SBRP, and BIRP, are versatile and robust methods for the preparation of structurally well-controlled macromolecules. Characteristic features of these methods include wide applicability to the polymerization of a variety of monomer families, high functional group compatibility, and a strong ability for the syntheses of block copolymers and end-modified polymers. These features clearly demonstrate that TERP, SBRP, and BIRP could rival current LRP methods for the preparation of functionalized macromolecules with well-defined structures, although more work is needed to clarify the full scope of these methods.

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7186

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Biographical Sketches



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3.09 Cobalt-Catalyzed Chain Transfer Polymerization: A Review

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3 09 1	Introduction and Overview	250
3.09.1.1	Broad Overview of Patent Literature	251
3.09.1.2	General Polymerization Considerations	251
3.09.2	Polymerization Mechanism	252
3.09.2.1	Evidence of Catalytic Process	252
3.09.2.2	Points to Consider with the Proposed Mechanism	252
3.09.2.3	Analytical Methods Employed to Investigate Mechanism	253
3.09.2.4	Model Compound Studies	255
3.09.3	Catalysts	255
3.09.3.1	Catalyst Screening	255
3.09.3.2	Measuring Catalytic Activity	256
3.09.3.3	Factors Affecting $C_{\rm e}$ Values	257
3.09.3.3.1	First generation of Co(II) complexes	257
3.09.3.3.2	Second generation of Co(II) complexes	257
3.09.3.3.3	Third generation of Co(II) complexes	258
3.09.3.3.4	Use of axial coordinating ligands in conjunction with Co(II) complexes	258
3.09.3.3.5	Solvent effects	258
3.09.3.3.6	Viscosity effects	258
3.09.3.3.7	Effect of impurities	259
3.09.4	Monomers for CCT	259
3.09.4.1	CCT Active Monomers	259
3.09.4.1.1	Reactive methacrylates	262
3.09.4.1.2	Stimuli-responsive methacrylates	262
3.09.4.1.3	Hyperbranched polymers from methacrylates	262
3.09.4.2	CCT of Less Active Monomers	262
3.09.4.2.1	Styrene	263
3.09.4.3	Further Polymerization Processes	263
3.09.4.3.1	Emulsion polymerization	263
3 09 4 3 2	Postpolymerization 'click' chemistry	263
3.09.4.3.3	Postpolymerization conclumerization	264
3.09.4.3.4	Copolymers with both active and nonactive CCT monomers	264
3.09.4.3.5	Addition-fragmentation chain transfer	264
3.09.4.3.6	Cobalt-mediated radical polymerization	264
3.09.4.3.7	Atom transfer radical polymerization and CCT	264
3.09.4.3.8	CCT polymers generated from new Co macrocycles	265
3.09.5	Applications	265
3.09.5.1	CCTP Emulsion Polymerization	265
3.09.5.2	Direct Industrial Applications of CCTP	265
3.09.5.3	Semiconductor Nanocrystal Polymer Hybrids	266
3.09.5.4	CCTP Polymers as Additives for Road Pavement Manufacture	266
3.09.5.5	Glyconolymers	267
3.09.5.6	Polymers for Use in the Hair Care Industry	267
3.09.5.7	Branched Polymers	267
3.09.5.8	Macromonomers for Industrial Applications	268
3.09.5.9	Macromonomers for Photonic Crystals	269
3 09 5 10	Macromonomers for Graft/Comb Conolymers	269
3 09 5 10 1	Automotive industrial applications of graft/comb polymers	270
3 09 5 10 2	Automotive hase coats/color coats	270
3 09 5 10 3	Automotive ton coats/clear coats	271
3 09 5 11	Macromonomers for Star Polymers	271
3 09 5 12	Macromonomers for Hydrogels	271
3.09.6	Summarv	272
References		272

3.09.1 Introduction and Overview

The use of Co(II) macrocycles as catalytic chain transfer agents (CCTAs) in free radical polymerization is a convenient method for the synthesis of low-molecular-weight polymers with vinyl end-functionality.^{1,2} Catalytic chain transfer polymerization (CCTP) is an extremely efficient form of industrially useful controlled polymerization. The history of CCTP is very well documented by one of its founders, Alexei Gridnev, on the occasion of its 25th anniversary.³ CCTP originated in Moscow in 1975 in the laboratory of Smirnov and Marchenko with the later involvement of Enikolopyan. This groundbreaking and important work was the subject of a series of papers in the Russian literature, which went largely unnoticed in the late 1970s.⁴⁻⁸ Initially, it was discovered during an investigation into the effect transition metal-containing compounds had on free radical polymerization and prompted by a porphyrin chemist, Ponomarev, who was promoting the application of this class of compounds. Smirnov noticed that the addition of Co(II) porphyrins seemed to inhibit the polymerization of methyl methacrylate (MMA). However, in what can only be described as an outstanding scientific observation, the importance of this somewhat negative result was realized. The fact that an azo free radical initiator had been put under polymerization conditions with MMA and the product remained a liquid as opposed to a high-molecular-weight plastic meant something very interesting had occurred.

Gridnev describes how this was patented in the Russian patent literature in 1980, which added to its dormancy in the literature. This was the time when group transfer polymerization (GTP) was being developed and discovered at DuPont Central Laboratories with much of the focus on new polymerization methods for methacrylates. CCTP's jump from Russia seemed to occur on a visit by Enikolopyan to DuPont in 1979 when Owen Webster and Steve Ittel realized the interesting effect these catalysts had on polymerizations. Early patents were filed by the Glidden paint company on cobaloximes and specifically the parent Co(II) cobaloxime (1).9,10 A very important problem for this catalyst is acid stability and any acid present will hydrolyze the ligand back to the free ligand and the Co(II) salt. The role of Co(II) in vitamin B₁₂ was also the subject of intense activity at the same time. It is noted here that vitamin B_{12} (2) contains a Co(II) in a square planar arrangement with four nitrogen donor ligands of a porphyrin with two axial ligands giving an overall octahedral geometry. One of these ligands is a nitrogen donor and the final ligand is either an alkyl group giving a Co(III) compound or a solvent ligand, such as water. Vitamin B₁₂ is involved in the metabolism of most cells in the body, DNA synthesis and regulation, fatty acid synthesis, and energy production. In addition, it can exchange an alkyl group with a hydrogen atom on adjacent carbon atoms in a biomolecule. With this wide-ranging role, it is perhaps very surprising to note that the total amount of vitamin B₁₂ in the body is approximately 2-5 mg with around 50% of this being stored, and relatively dormant, in the liver. It is also probably surprising that the recommended daily allowance (RDA) is $2-3 \mu g day^{-1}$. From the fact that much less than 5 mg is distributed throughout the whole body and that vitamin B₁₂ is so important for many chemical reactions, we see immediately that it must be an extremely efficient catalyst, and if we only need to replenish it by approximately

3 orders of magnitude less than the total concentration, it must be extremely robust to a range of chemical environments.



A range of different Co(II) compounds were investigated for CCT activity by Gridnev and co-workers and some rules of thumb developed on what made a Co(II) compound effective, as many were not.3 It was concluded that active catalysts should have a planar arrangement of four donors with a conjugated π -system in the plane, whereby at least two of the donors should be nitrogen ligands. Cobaloximes such as cobalamin proved to be not only an excellent model compound for looking at the mode of action of vitamin B_{12} but also very efficacious CCTAs. One aspect was the hydrolytic stability of the cobalamin that was solved in the bioinorganic literature by ring closure with a -BF2 group and the resulting cobaloxime (CoBF (3)) was reported to be stable indefinitely at elevated temperatures even at pH=1. This is mostly true but the catalyst will tend to hydrolyze under certain emulsion polymerization conditions, 70-80 °C and pH < 3.0, which is solved by a slow feed of catalyst into the reaction mixture to compensate for this.



3.09.1.1 Broad Overview of Patent Literature

Outside of Russian patents, the first US patent on CCTP was filed by Glidden paint company as a process for preparing oligomers presumably for high solids coatings.^{9,11} Interestingly, the patent was very brief and had very limited claims to the parent cobaloxime (1) that was explicitly claimed in claim 1. This meant that other effective Co(II), Co(III), and indeed other transition metals could be claimed as long as an advantage could be demonstrated. It also meant that no later patents could blanket claim all Co(II) and/or Co(III) catalysts. Thus, when Janowicz discovered that the closely related but much more hydrolytically stable CoBF (3) was very effective, specific compounds had to be claimed.^{12,13} In order to satisfy the US patent office that as structure 1 was effective, it was not obvious to anyone not skilled in the art that structure 3 would also be effective - an important and essential point in any patent filing - Janowicz filed an affidavit stating that as cobalt salen and salophen complexes were ineffective for CCTP and these compounds had very similar chemistry to both structures 1 and 3 then it was not possible to predict if new compounds would be effective toward CCTP without trying them. It turned out that in the CoBF patent DuPont had claimed many different substituents for R in structure 4. However, they had defined R as potentially being phenyl but not aryl. As the same patent agent had filed a patent concerning GTP on the same day using the word aryl coupled with the affidavit filed on behalf of DuPont, it was difficult to argue against further patents filed by ICI/Zeneca covering substituted aryl such as structures 5 and 6, which showed a distinct solubility advantage without affecting the catalytic activity.^{14,15} This led to a family of patents that allowed for use of catalysts in a range of media with good control over the solubility by changing the substituents on the aromatic rings.



3.09.1.2 General Polymerization Considerations

The products from CCTP of methacrylates are a-substituted acrylate macromonomers with structure 10 (Section 3.09.2.3). Thus, CCTP is an attractive method for the synthesis of lowmolecular-weight polymers and macromonomers since it couples the versatility of a radical system with the unique properties of these CCTAs. These α-substituted acrylate macromonomers can also be made to undergo a facile β-scission, making themselves useful as chain transfer agents (CTAs) (by an addition-fragmentation mechanism) and as intermediates in the synthesis of telechelics, block copolymers, and other macromonomers.¹⁶ Oligomeric and functionalized materials are important to the polymer industry since there is a continual drive, due to environmental legislation, toward low volatile organic compound (VOC) products, such as high solids coatings, radiation cure systems, and powder coatings. Likewise, macromonomers are of considerable interest since they are important building blocks for materials such as graft copolymers. The utility of CCTP products in these applications has been recognized by the polymer industry and is reflected in the patent literature.^{9,11,14,15,17-20}

The majority of publications deal with the application of catalytic chain transfer (CCT) in bulk or solution, but examples in the patent literature do apply CCT to emulsion and suspension. These patents report only limited data and full details of the experimental procedures are not revealed. Molecular weight data for the final products are given, but information on coagulation, conversion, and particle size are often not provided. The use of CoBF in MMA emulsion polymerization has been reported outside the patent literature but efficient CCT was not achieved, suggesting the process may be sensitive to at least some of the reaction components.

Often, it is desirable to have the CCTP products in the form of an emulsion or dispersion. At least one case exists where a monomer solution of macromonomer from CCT was homogenized in an aqueous phase to make an emulsion. The resultant macromonomer dispersion was then used in miniemulsion polymerization to ultimately yield a block copolymer.

Studies of CCTP have focused primarily on methacrylates, although cobalt macrocycles active in CCTP of methacrylates have been investigated with other monomers.^{21–23} CCT occurs with styrene with a much lower transfer constant^{2,6} but the chain transfer is complicated by secondary processes, which manifest themselves as a decrease in polymerization rate, and by 'poisoning' of the catalyst.^{6,21}

Janowicz disclosed that molecular weight reductions result from addition of the cobaloxime derivative (3) to most acrylates, but little or no effect is seen in vinyl acetate polymerizations.

Many of the examples in the patent literature have applied CCTP to multicomponent copolymerizations where not all of the monomers are methacrylates. CCTP of methacrylates with other monomers has received rather limited attention in the scientific literature.²³ CCT occurs in copolymerizations of styrene with methacrylates and when acrylates are a minor component in the polymerization system. CCT is reduced or ceases in systems containing larger quantities of acrylates or vinyl acetate and inhibition is reported. Thus, CCT can be applied to copolymerizations of vinyl monomers where methacrylates are at least a major component of the monomer feed.

3.09.2 Polymerization Mechanism

3.09.2.1 Evidence of Catalytic Process

Following the discovery of CCT, evidence was provided that it is a catalytic process in 1980, when isolation of the regenerated cobalt porphyrin complex was achieved following polymerization.^{4–7,24} Three mechanisms for H transfer have been proposed (Figure 1).

 R_n and R_1 are the polymeric and monomeric radical, respectively, M monomer, Co(II)-L cobalt chelate, and $P_n^{(=)}$ an unsaturated polymer chain end. The first mechanism is improbable due to the expectation that a methacrylate would abstract a hydrogen atom; evidence is already available that shows monomer does not directly participate in the hydrogen abstraction step in CCT.²⁵ The second mechanism suggests that the CCT rate is dependent on monomer concentration; however, this has also been disproved.²⁶ In the case of the third mechanism, H-Co(III)-L is highly reactive, making it difficult to observe. However, the kinetic studies carried out by Smirnov *et al.* proved the formation of cobalt hydride and soon after, evidence provided by O'Driscoll and co-workers has led to general agreement with the third proposed mechanism.^{1-3,25,27–38}

3.09.2.2 Points to Consider with the Proposed Mechanism

The mechanism of CCTP has usually been described from a radical polymerization approach. The Co(II) macrocycle has been considered to behave as a reusable CTA in that it terminates a growing polymer chain by hydrogen atom abstraction. CCT differs from normal transfer in that the nonpolymeric product of this reaction, that is, the Co(III)-H can reinitiate polymerization. The overall effect is to reduce molecular weight without affecting the kinetic chain length or the overall rate of polymerization, as is true for conventional chain transfer. A proposed mechanism has already found its way into catalysis textbooks.³⁹ The commonly accepted mechanism at present can be shown as a catalytic cycle (Figure 2), but it should be noted that a number of observed anomalies have not been fully explained. It is unlikely that hydrogen abstraction occurs via a β-elimination. Although no conclusive evidence exists, a 'normal' hydrogen abstraction via a radical pathway is more likely and Gridnev supported this with kinetic isotope effect experiments³³

Due to termination by conventional radical-radical coupling and disproportionation, a continual supply of radicals is required in order for effective CCT. Typically, reactions are carried out in the presence of a thermal initiator, usually azo



Figure 1 Proposed mechanisms for catalytic chain transfer polymerization.



Figure 2 Generally accepted catalytic chain transfer polymerization mechanism.

initiators, at temperatures and timescales where a roughly constant radical flux is maintained over the timescale of the polymerization as in conventional free radical polymerization. If the temperature of the reaction is lowered or the thermal initiator is depleted, then oligomer formation is curtailed as in normal free radical polymerization.¹ An interesting reaction is CCT with a primary radical fragment that results in the disproportionation of the organic radical, for example, azobisisobutyronitrile (AIBN) catalyzed by Co(II) producing methacrylonitrile (MAN), eqn [1].



3.09.2.3 Analytical Methods Employed to Investigate Mechanism

The mechanism is difficult to investigate, as there are very low levels of catalyst employed, the catalyst is paramagnetic, precluding NMR even if there were signals to be followed. Conventional free radical polymerization gives three different polymer end groups: 7 and 8 from disproportionation, 7 from chain transfer, and 9 from polymer–polymer coupling.





The CCTA introduces a massive increase in the rate of loss of a hydrogen atom to 8 giving a product with an unsaturated end group, a macromonomer. β-Hydride abstraction to Co(II) leads to structure 8. The most established method to determine between structures 7, 8, and 9 is by thermal gravimetric analysis (TGA), as the three different structures thermally decompose at different temperatures,⁴⁰⁻⁴² and it was used by DuPont as the analytical method of choice in patents claiming polymer compositions comprising at least 15 mol.% methacrylate macromonomer with the end group $C(X_1)(X_2) = C(X_3)$ (CH₂)-, structure 8. All examples quoted in this patent are prepared by CCTP.43 While TGA is a suitable tool for poly-(methyl methacrylate) (PMMA) homopolymer, the determination of the different structures for other acrylic homopolymers and copolymer compositions is more complicated by TGA and thus a different method is necessary. Indeed, small amounts of acrylate comonomer are often added to commercial PMMA to improve thermal stability.

Subsequently, DuPont described a more general method utilizing ¹H and ¹³C NMR to measure the amount of vinylidene

groups per polymer chain.⁴⁴ This study concluded that >82% of polymer chains are vinyl terminated from hydrogen abstraction; the authors do not discuss the structure of the non-vinyl-terminated polymer except to say there is no evidence from ¹H or ¹³C NMR for structure 7.

Subsequent advances in matrix-assisted laser desorption time-of-flight mass spectrometry (MALDI-ToF-MS) have made mass spectra of poly(methacrylate)s easily available at high resolution to well over 15 000 atomic mass units (amu) allowing masses of less than 5 amu, arising from different end groups, to be easily distinguished.^{1,45,46} In the case of CCTP, it is facile to distinguish between hydrogen-initiated polymer and polymer resulting from radicals originating from the thermal initiator, for example, in the case of AIBN initiation the polymers will differ in mass by approximately 63 amu, structures **10** and **11**.





MALDI-ToF-MS can be seen in Figures 3(a) and 3(b) from CCTP of MMA with the azo initiator 2,2'-azobis-(2-methylbutyronitrile) (AMBN) in the presence of CoBF in butanone (also known as methyl ethyl ketone (MEK)) solution at 60 °C. Note that in all cases a monocation adduct of the molecular peak, usually Na⁺, with no fragmentation is observed. Under normal CCTP conditions with 0.62 mass% AMBN with respect to monomer and [MMA]/[2] = 130 000, the vast majority of the polymer molecules are initiated by a hydrogen atom as opposed to an AMBN fragment (Figure 3(a)). By addition of very large amounts of thermal initiator and smaller amounts of CCTA, 6.2 mass% AMBN and [MMA]/[2] = 800 000, some AMBN-initiated polymer is observed (Figure 3(b)). Thus, once an organic radical is formed by thermal degradation of the azo initiator, at least two competing reactions are possible, that is, reaction with monomer to subsequently produce polymer with structure 10 and reaction with Co(II) to produce Co(III)-H, which in turn initiates polymerization by transfer of H to monomer. It is important to note that both reactions occur but even with extremely small amounts of Co(II) and unusually high levels of initiator, production of Co(III) is the predominant pathway.

At the time this work was carried out in order to distinguish between saturated and unsaturated terminal groups, the MALDI source had to be connected to a much higher resolution detector. Note that in **Figures 3(a)** and **3(b)** the width at half height of each peak is approximately 3-5 amu.



Figure 3 MALDI-ToF-MS of CCTP for methyl methacrylate.

Organocobalt porphyrin complexes have also yielded

useful mechanistic information. The reactions of (tetrakis(p-

methoxyphenyl)porphyrinato)cobalt(II) ((TAP)Co(II)) with

Two distinct initiation pathways were observed in the presence of relatively large amounts of thermal initiator, as described above. The smaller peaks at 16 amu higher than all of the main peaks are due to K⁺ adducts as opposed to Na⁺ adducts. Molecular structures **12** and **13** have predicted molecular masses of 1523.776 ($C_{75}H_{120}O_{30}Na$) and 1590.818 ($C_{79}H_{125}O_{30}NNa$), respectively, as compared with 1523.774 and 1590.808 from MALDI-Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). **Table 1** lists the observed peaks along with their observed and predicted peak heights.



These spectra unequivocally demonstrate both initiating and terminating groups within the polymer from CCTP. Although the majority of molecules have structure 12, there is a higher than expected occurrence of both M+2and M+3 peaks for both 1523.774 and 1590.808, indicating a small amount of saturated polymer arising from termination other than β -H transfer for both methods of initiation.

3.09.2.4 Model Compound Studies

The mechanism has also been studied using organo-porphyrin model compounds, which although not nearly as effective CTAs as CoBF, have similar chemical environments and mode of action. The use of a second-row transition metal rhodium in (octaethylporphyrinato)rhodium(III), [(OEP)Rh(III)]₂, dimer results in reduction of the vinyl unit and a two-carbon alkyl-bridged dimeric rhodium complex with acrylates.⁴⁷ The use of the more bulky tetramesitylporphyrin, (TMP)Rh(II), gives coupling of the acrylate. With the more bulkier MMA, both (OEP)Rh(II) and (TMP)Rh(II) form (Por)Rh(II)–CH₂C(CO₂CH₃) = CH₂ (14), that is, not the desired intermediate for efficient polymerization. This study concluded that although (Por)Rh(II) radicals are not effective in the polymerization of acrylics, they can, however, catalyze photopromoted living polymerization.



radicals derived from dialkylazo thermal initiators with acrylic
monomers provide evidence for the intermediacy of Co(III)-H
species in CCTP. Reaction of (TAP)Co(II) with tertiary alkyl
radicals, for example, as derived from AIBN in the presence of
monomers that form stable Co-alkyl complexes, such as
methyl acrylate, results in quantitative formation of Co(III)-
alkyl. Whereas with monomers leading to tertiary C-Co bonds,
such as MMA, the Co(II) is very much a spectator as normal
polymerization ensues. ³² Thermodynamic and activation
parameters have been measured for the dissociation of
(TAP)Co(III)-C(CH ₃) ₂ CN to Co(II) and organic radical in
solution as a probe into CCTP mechanism by low-spin Co(II). ⁴⁸

3.09.3 Catalysts

3.09.3.1 Catalyst Screening

Effective CCTAs are invariably low-spin Co(II) complexes with octahedral geometry derived from a square planar ligand and two available axial sites.³² Co(II) is d^7 and can exist as high spin, with three unpaired electrons, or low spin, with one unpaired electron. Interestingly, this is an important consideration in designing a CCTA, as the nature of the ligands surrounding the central cobalt can easily result in spin crossover from low to high spin, as the relative energy levels are close together; to date, no reason has been found for this empirical observation. For example, cobalt macrocycles containing two O atoms and two N atoms, or four O atoms directly bonded to cobalt result in poor CTAs, such as structures **15** and **16**.



Most Co(II) complexes of nonmacrocyclic tetradentate ligands with either N or O donors are high spin, whereas a number of tetradentate macrocycles contain sufficiently high-field ligands to exist in a low-spin environment. Distinguishing between low- and high-spin complexes is relatively straightforward, and is achieved by measuring

<i>Observed mass for 12 (Da)</i>	Observed relative intensity	Calculated relative intensity	Observed mass for 13 (Da)	Observed relative intensity	Calculated relative intensity
1523.774	100	100	1590.808	18.792	18.79
1524.781	83.6	87.21	1591.812	16.983	17.22
1525.78	50.88	42.68	1592.827	13.073	8.94
1526.81	25.09	15.88	1593.814	9.674	3.26

Table 2	Magnetic	moments	for se	lected	Co(II)
macrocycles	;				

Catalyst	Magnetic moment (µ _B)	Spin state	CTA
15	4.48	High	No
16	4.28	High	No
2	1.82	Low	Yes
3	1.92	Low	Yes

the magnetic moment. Low-spin Co(II) has a spin-only value of approximately 1.73 $\mu_{\rm B}$, which is indicative of a single unpaired electron. High-spin Co(II) has a spin-only value of approximately 3.46 $\mu_{\rm B}$ (usually 4.9–5.2 $\mu_{\rm B}$).⁴⁹ Table 2 lists magnetic moments of four Co(II) macrocycles, two of which are effective and two ineffective and, thus, measurement of the magnetic susceptibility is an excellent primary test for catalyst screening.

Due to the paramagnetic nature of low-spin Co(II) macrocycles, assignable ¹H NMR spectra cannot be obtained. However, high-spin Co(II) macrocycles give acceptable ¹H NMR spectra. Conversely, low-spin Co(II) give excellent electron spin resonance (ESR) spectra contrary to high-spin Co(II). Therefore, a further simple first screening, but not conclusive, test for catalytic activity is to attempt to record the ¹H NMR spectra.

3.09.3.2 Measuring Catalytic Activity

The most commonly used measure of catalytic activity and indeed catalyst purity is measurement of the chain transfer constant, $C_{\rm s}$, defined as the ratio of the rate constant for the chain transfer reaction to the rate constant for propagation $(k_{\rm tr,S}/k_{\rm p})$. The $C_{\rm s}$ values for conventional CTAs, such as mercaptans, are approximately 1–10 for methacrylates. In contrast, $C_{\rm s}$ values for cobaloximes can be 4 orders of magnitude greater and the catalysts are not consumed during the reaction. This makes them highly effective catalysts, hence only parts per million (ppm) amounts are often required to achieve very large reductions in the molecular weight.⁵⁰

Traditionally C_s values are determined using variations of the Mayo equation (eqn [2]):

$$\frac{1}{DP_n} = \frac{1}{DP_{n0}} + C_s \frac{[S]}{[M]}$$
[2]

where DP_n is the number-average degree of polymerization of the polymer, DP_{n0} the number-average degree of polymerization of the polymer under the same conditions but in the absence of CTA, and [S] and [M] the concentrations of CTA and monomer, respectively.

From eqn [2], a linear Mayo plot of the inverse of DP_n versus [S]/[M] can be plotted, the gradient of which is a measure of the C_s value for that particular CTA under the conditions used in the polymerization, the intercept of which gives the inverse of DP_{n0} . Polymerizations carried out in order to obtain a Mayo plot must be under the same conditions, preferably using more than three CTA

concentrations, and should be terminated at low conversions in order to ensure that [S]/[M] remains constant throughout the polymerization; hence, polymerizations should be terminated before 5% conversion is achieved.

 DP_n can be calculated in one of two ways, either by division of the M_n (usually obtained by gel permeation chromatography (GPC)) by the monomer mass or by division of the M_w by 2 times the monomer mass. Use of M_w as a measure of DP_n is only justified when the polymerization is fully controlled by chain transfer; hence, a polydispersity index (PDI = M_w/M_n) value of approximately 2 is obtained, but in general practice this method has proved more accurate than measurements based on $M_{n\nu}$ as it is less susceptible to baseline deviations.^{34,50,51}

The C_s can also be measured by chain length distribution (CLD), also described as molecular weight distribution (MWD), which can be obtained directly by GPC.^{28,50–52} The CLD of a polymer contains a history of the kinetic events that have occurred throughout the polymerization. Information on chain transfer kinetics can be readily extracted from the CLD of a polymer. Equation [3] was derived by Clay and Gilbert.⁵²

$$\lim_{i \to \infty} P_i \propto \exp\left\{\frac{k_{\text{tr},M}[M] + k_{\text{tr},S}[S]}{k_p[M]}i\right\}$$
[3]

where P_i is the instantaneous CLD obtained by GPC, $k_{tr,M}$ the transfer rate to monomer, $k_{tr,S}$ the transfer rate to CTA, and k_p the rate of propagation. Differentiation gives the limiting slope of P_i versus *i* (eqn [4]).

$$\frac{\mathrm{d}(\ln P_{\mathrm{i}})}{\mathrm{d}i} = -\left\{\frac{k_{\mathrm{tr},\mathrm{M}}[M] + k_{\mathrm{tr},\mathrm{S}}[S]}{K_{\mathrm{p}}[M]}\right\} = -\left\{C_{\mathrm{M}} + C_{\mathrm{S}}\frac{[S]}{[M]}\right\} \quad [4]$$

where $C_{\rm M}$ is chain transfer to monomer. The slope of this can be represented by eqn [5] as $P_{\rm i} = (1-T) T^{i-1}$:

$$\frac{\mathrm{d}(\ln P_{\mathrm{i}})}{\mathrm{d}i} = \ln T \tag{5}$$

where

$$T = \frac{R_{\rm p}}{R_{\rm p} + R_{\rm tr} + R_{\rm t}}$$
[6]

where R_{pr} , R_{trr} and R_t are the rates of propagation, transfer, and termination, respectively. Hence, the slope of a plot of ln P_i versus *i* gives ln *T*. From this, the transfer constant can be obtained from the slope of the plot ln *T* versus [*S*]/[*M*], preferably for more than three concentrations of CTA, where the intercept will be the inverse of DP_{n0}.⁵³

An advantage to using this method for estimation of the C_s is that essential information can be obtained by analysis of a small portion of the CLD, providing high-molecular-weight end data are used. As the whole CLD is not analyzed, the CLD method is less sensitive to noise, poor baseline selection, and the presence of artifacts in the GPC spectra.

The catalytic activity of Co(II) complexes can vary dramatically depending on a number of factors, such as sterics and electronics of ligands, solvent, viscosity, monomer, and impurities. As it is difficult to measure purity of CCTAs, often measurement of C_s is the most reliable measure.

3.09.3.3 Factors Affecting C_s Values

3.09.3.3.1 First generation of Co(II) complexes

On first discovery of CCTP, the Co(II) complexes were based on porphyrin complexes, for example, Co(II) hematoporphyrin IX tetramethyl ether (17).



This first generation of CTAs produced $C_{\rm s}$ values of 2.4E3,⁵⁴ but due to the expensive isolation and purification of porphyrins, the cost was considered too high for application of CCTP in industry. Other disadvantages included their high color and insolubility in a range of solvents; hence, alternative catalysts were required.

A number of catalyst structures were tested during this search for more efficient CTAs, and so a better picture of the requirements for a successful CTA was obtained. CTAs must have a central cobalt atom surrounded by a tetradentate chelating planar ligand system of conjugated π -electrons, which must be able to maintain the ring current, containing at least two N atoms in the coordination plane. It was found that the macrocycle could be open or closed, but a closed macrocycle provides a more efficient CTA.

3.09.3.3.2 Second generation of Co(II) complexes

The second generation of Co(II) complexes were cobaloximes (18), which are an order of magnitude more active than porphyrins (C_s values of 2.0E4–2.28E3), with the added benefit that the synthesis is less costly, are low in color compared to porphyrins, have good solubility, and their properties can be

tuned through the axial ((18), L ligands) and equatorial ligands ((18), R ligands).³



The effect of substituents on catalytic activity of cobaloximes can be dramatic (**Table 3**). When L₁ is a primary alkyl, CN or NO₂ catalytic activity is inhibited (**18a–f**, **Table 3**). Use of a secondary alkyl, halogen, or pseudohalogen, however, provides an adequate level of catalytic activity (**18g–k**, **Table 3**). Variation of the R groups has a significant effect on the catalytic activity (**18l–o**, **Table 3**), increasing it several fold, but the biggest increase in catalytic activity is seen with the presence of basic L₂ ligands, with an apparent increase in C_s value with increasing ligand field (**18p–r**, **Table 3**).²⁹

A disadvantage to this generation of cobaloximes was that they are susceptible to hydrolysis and oxidation; hence, the third generation of cobaloximes incorporates a BF₂ bridge that stabilizes the cobaloxime toward these reactions (C_s value of 4E4).²⁸ These complexes were given the general name CoBF, which is commonly used to describe CTAs of general structure **19**.



Compound	R_1	R_2	L ₁	L ₂ (base)	C_s
18 a	Me	Me	Me	H ₂ O	< 50
18 b	-(Cł	l₂)₄−	Et	H₂O	< 50
18 c	Me	Me	CN	Py	< 50
18 d	Me	Me	NO_2	Py	< 50
18 e	Ph	Ph	CN	Py	< 50
18f	Ph	Ph	Et	H_2O	< 50
18 g	Me	Me	CI	Py	5 000
18 h	Me	Me	I	Py	1 000
18 i	Me	Me	CNS	Py	4 000
18 j	Me	Me	<i>Sec</i> -Bu	H_2O	13 000
18k	Ph	Ph	CNS	Py	25 000
18	Me	COOEt	CI	Py	12 000
18 m	Me	COMe	CI	Py	25 000
18 n	-(CH	$(1_2)_4 -$	CI	Py	4 0 0 0
18 0	α-Furyl	α-Furyl	CI	Py	100 000
18 p	Ph	Ph	CI	H_2O	25 000
18 q	Ph	Ph	CI	Py	30 000
18r	Ph	Ph	CI	P(Ph) ₃	100 000

Table 3 Effect of substituents on MMA CCT activity for cobaloxime 18

3.09.3.3.3 Third generation of Co(II) complexes

The enhanced stability of the cobaloxime complex by introduction of the $-BF_2$ bridge was an important aspect with respect to its useful application, as little handling/storage precautions of the solid catalyst are necessary. The CoBF complex in a solid state is air stable; the only precaution required is that liquids are degassed prior to preparation of CoBF solutions as often solvent molecules can coordinate as an axial ligand that can change oxidative stability, for example, solutions in nondeaerated acetone give a green precipitate after 10–15 min. The hydrolytic stability of CoBF complexes widens the applicability of these catalysts, especially toward making emulsion polymerization of acidic monomers or with acidic initiators such as methacrylic acid possible,²⁹ although at very low pH and elevated temperatures decomposition of these compounds will occur slowly.⁵⁵

Although it would appear that the second- and third-generation cobaloximes have a break in π -conjugation due to the OH or BF₂ bridge, their resonance structures complete delocalization around the macrocycle by hydrogen jumping from one O atom to another (Figures 4);³ hence, their pronounced catalytic activity.

The third generation of cobaloximes is less affected by ligand choice than previous CTAs, but due to the electron-withdrawing nature of the $-BF_2$ bridge, in the absence of an electron-donating R group (10), the catalytic activity is reduced. This is due to the strong electron withdrawing behavior of the BF_2 group, which reduces electron density, causing the unpaired electron on cobalt to act less like a free radical. By use of an electron-donating R group, this radical behavior, and hence catalytic activity, can be restored.²⁹ The hydrogen-abstracting ability of CoBF is carried out so effectively that it has not only been used in CCTP but also in energy-efficient solar hydrogen production to catalyze H₂ evolution from protic solvents.⁵⁶

3.09.3.3.4 Use of axial coordinating ligands in conjunction with Co(II) complexes

Square planar Co(II) complexes contain ligands in the axial positions coordinated to the metal. The nature of these ancillary ligands depends on the synthetic route. For example, if the product is purified by a recrystallization in methanol, then the axial ligands will be methanol, structures **18** and **19**.

However, if the synthesis is carried out in the presence of coordinating bases such as pyridine, these will usually occupy the axial positions. The mechanism of CCTP involves the interaction of Co(II) with a carbon-based radical, forming a Co(III)–C species at some intermediate or transition state. The axial ligand is known to affect the nature of this bond (**Table 3**). For constant steric influences, the Co(III)–C bond strength increases with the electron donor ability (pK_a) of the ligand, and for constant $pK_{a'}$ increasing the steric requirements

of the ligands decreases the bond strength.⁵⁷ Bases have thus been utilized in an attempt to weaken the cobalt–polymer bond and so increase catalytic activity, although this gives rise to an additional complication outlined by Gridnev *et al.*³² Once Co(III)–H has been formed, deprotonation can occur yielding $[Co(I)]^-$ and pyH⁺, when using pyridine. Active Co(II) may be regenerated by the reaction of $[Co(I)]^-$ with Co(III)–H, forming 2[Co(II)] and H₂.

3.09.3.3.5 Solvent effects

It has also been noted that polar aprotic solvents can promote activity. These reactions are thought to be fast relative to competing radical polymerization. Suddaby *et al.*⁵⁸ described the effect of CTAs in N',N-dimethyl formamide (DMF) as catalytic inhibition. DMF forms a complex with the Co(II) in the axial ligand positions, binding through its O group. Reaction of this complex with AIBN produces hydrogen and MAN, thus removing initiator radicals from the reaction.

The monomer in these reactions becomes inert and cannot take part in the reaction. Thus, bases and polar aprotic solvents should be avoided as they represent radical sinks. It is also observed that the catalytic activity is lowered when using coordinating solvents as competing reactions occur.⁵⁹ Solvents with a weak coordinating ability such as toluene or butyl acetate have no discernible effect on the polymerization,²⁵ although it has been shown that solvent impurities such as peroxides and trace acid can have a detrimental effect on the $C_{\rm s}$ value,^{54,60} therefore, purification of solvents by distillation is usually essential.

3.09.3.3.6 Viscosity effects

Chain transfer reaction is diffusion controlled^{54,61,62} and thus comparison of the chain transfer rate coefficient to bimolecular termination of two radicals, which is known to be diffusion controlled, yields similar rates of approximately $10^7 \,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$. Forster *et al.*⁶³ suggested a diffusion-controlled chain transfer mechanism, as they observed a reduction in rate for high-viscosity monomers.

Very little difference is observed in the rate of CCTP for low-viscosity monomers such as MMA under bulk or organic solution conditions. However, when using higher viscosity monomers, a difference in rate is seen between bulk and solution experiments, with a significant reduction in the rate for bulk reactions.⁶⁴ This observation is consistent with a chain transfer mechanism where the rate-determining step is diffusion controlled. Further agreement with Forster *et al.* was seen when the CCTP of MMA was carried out in the low-viscosity medium, supercritical CO₂. Under these conditions, chain transfer was significantly higher when compared with a toluene medium or bulk MMA.⁶³ A direct relationship was found between viscosity of medium and C_s value; hence, the higher



Figure 4 Delocalization of cobaloxime 18.

the viscosity the lower the $C_{\rm s}$ value (eqn [7]), where $\eta^{\rm a}$ is solvent viscosity.⁶³

$$C_{\rm s} \propto \frac{1}{\eta^{\rm a}}$$
 [7]

It has also been postulated that lower $C_{\rm s}$ values for bulky catalysts are due to diffusion control, as the cross-sectional areas are larger, slowing down the diffusion process.⁵⁴

3.09.3.3.7 Effect of impurities

Vollmerhaus *et al.* investigated the effect of the deliberate introduction of impurities on the catalytic cycle, observing any changes by the use of Mayo plots⁶⁵ on addition of controlled amounts of oxygen and by the use of decreasing concentrations of unpurified initiator.

The effect of using non-recrystallized AIBN was seen as being significant, with an induction period seen in the Mayo plots, which was more pronounced at high concentrations of initiator. It was found that for low concentrations of initiator this effect was not as significant. The induction period observed suggests that the impurity is consumed during the polymerization. Attempts to identify the impurity, however, only revealed that it was introduced at the manufacturing stage, as use of AIBN that had undergone prolonged heating or atmospheric storage did not recreate the effects seen when using unpurified AIBN.

The effect of oxygen introduction was less significant than expected. It was found that long-term exposure of cobalt solutions to oxygen prior to initiation was detrimental, but short-term exposure posed no real problem. Problems only arose when large volumes of oxygen were introduced (\sim 20 ppm), which decreased the C_s values significantly, indicating a reaction between oxygen and the cobalt catalyst, thus proving that CCTP is a robust technique with respect to oxygen toleration.

It has also been observed that low levels of peroxides, at concentrations similar to that of the CTA itself, have a detrimental effect on the polymerization, effectively poisoning the catalyst. Presence of peroxides can oxidize the catalyst from the active species Co(II) to a deactivated Co(III) form, that is why the use of peroxide initiators is probably less well developed.²⁷

$$R_n O_2^{\bullet} + Co(II) \to Co(III) - O_2 R_n$$
[8]

3.09.4 Monomers for CCT

3.09.4.1 CCT Active Monomers

Monomers that are able to undergo CCT must be able to easily facilitate the transfer of H since this is the key mechanistic step in CCT. Monomers that contain an α -methyl group are able to do this resulting in the formation of Co(III)–H and a terminal unsaturated double bond. Tertiary radicals formed with α -methyl group containing monomers lead to labile Co–C bonds. ⁶⁶ Scheme 1 shows the general trends observed with monomers for CCT and examples of such monomers are shown in Table 4 along with some measured chain transfer constants, $C_{\rm s}$.



Scheme 1 Generalization of monomer properties and the resulting outcome of CCT.

Monomer	<i>Catalyst^a</i>	\mathcal{C}_s	Solvent	Temperature (°C)	References
Methyl methacrylate	CoBF	24 000-40 000 (40 000)	Bulk	60	38,50,54,61,62,85
	CoPhBF	18 000-24 000	Bulk	60	25,34,54,61
	Co(dma) ₂	2200–20 000 (2200)	Bulk	60	86
	cvcCoBF	13 700	Bulk	60	54
	CoP	3600	Bulk	60	61,65
	CoTMHP	2400	Bulk	60	6
	CoBE	41 000-60 000	Toluene	60	87
	CoBE	26 500	Butanone	60	54
	CoBE	10 100	Methanol	60	54
	CoPE	16 000 25 000	Ethanol	60	63
		10,000-23,000	Ethanoi SoCO	00 50	88
		1200	Sc002	50	89
		1300		00	90
		32 000	BUIK	00	91-93
	60(L _S)	17.5	Butanone	70	94
Eduction of the	TAP60			60	61
Ethyl methacrylate	COBF	27 000	Buik	60	60
<i>n</i> -Butyl methacrylate	COBF	16 000-28 000	Bulk	60	05.06
	COIMHP	670	Bulk	60	93,90
	CoPhBF	11 900–46 700 ^a	ScCO ₂	50	07
	CoPhBF	13 200–43 000 ^a	ScCO ₂	60	97
t-Butyl methacrylate	CoBF	14 000–16 800	Bulk	60	54
Hexyl methacrylate	CoTMHP	430	Bulk	60	95,96
Heptyl methacrylate	CoTMHP	250	Bulk	60	
Octyl methacrylate	CoTMHP	250	Bulk	60	
Nonyl methacrylate	CoTMHP	150	Bulk	60	
Decyal methacrylate	CoTMHP	110	Bulk	60	
Hexadecyl methacrylate	CoTMHP	130	Bulk	60	
2-Hydroxyethyl methacrylate	CoBF	600	Bulk	60	
	Co(ipp)BF	900	H ₂ O	60	90
	CoBF	1100	H ₂ O/MeOH (2:1)	80	67
	TAPCo	_	CDCI ₃	60	94
2-Phenoxyethyl methacrylate	CoPhBF	2000	Bulk	60	64
3-[Tris(trimethylsilyloxy)silyl]propyl methacrylate	CoBF	800–1700	Toluene	60	98
	CoBF	~ 7500	2-Butanone	60	99
3-(Trimethoxysilyl) propyl methacrylate	CoBF	~27000	2-Butanone	60	99
2-[3-(2 <i>H</i> -Benzotriazol-2-yl)-4-hydroxyphenyl]ethyl methacrylate	CoBF	~ 4000	Toluene	60	99
Lauryl methacrylate	CoBF	~20000	2-Butanone	60	99
2-Dimethylaminoethyl methacrylate	CoBF	~ 4400	Bulk	70	100
2-Phthalimidoethyl methacrylate	CoBF	500	30% sol toluene	80	101
Glycidyl methacrylate	CoBF		MIRK	105	70
3-0-MethacrylovI-1 2.5 6-di-0-isopropylidene-p-alucofuranose	CoBE	_	Distilled water	80	67
Renzyl methacnylate	CoBE	5700-6900	Bulk	60	35
2-Fthylhexyl methacrylate	CoBF	11 900	Bulk	60	102
	0000		Duin	00	

Table 4 Selection of monomers employed in CCT homopolymerizations and associated reaction conditions

Ethyl α-hydroxymethacrylate	CoBF	700	Bulk	60	103
Trimethylsilane-protected propargyl methacrylate	CoBF	_	Toluene	60	104,105
Glycerol methacrylate	CoBF	1000	H ₂ O/MeoH (2:1)	80	67
Methacrylic acid	CoBF	1100	H ₂ 0	55	67
Dimethyl itaconate	CoBF	7300–9500	Bulk	60	36
Styrene	CoBF	350-8300 (~ 8000)	Bulk	60	50,54,62,102,106
•	TAPCo		CDCl ₃	60	94
	CoPhBF	100–1200 ^a	ScCO ₂	50	97
α-Methyl styrene	CoBF	89 300	Bulk	50	106
Phenylallyl alcohol	CoBF	138 000–157 000	10% in MMA	60	107
Methyl acrylate	CoBF	8–22	Bulk	60	35,38
	TAPCo	_	CDCl ₃	60	94
Butyl acrylate	CoBF	700	Bulk	60	102
Acrylamide	CoPc	100	Acetic acid	60	108
Di(ethylene glycol) methyl ether methacrylates	CoBF	7600	Acetonitrile	70	73
Poly(ethylene glycol) ₄₇₅ methyl ether methacrylate	CoBF	1800	Acetonitrile	70	73
	Co(ipp)BF	_	H ₂ 0	60	90
Poly(ethylene glycol) ₁₁₀₀ methyl ether methacrylate	CoBF	180	Acetonitrile	70	73
Poly(ethylene glycol)2000 methyl ether methacrylate	Co(ipp)BF	15–20	H ₂ 0	60	90
Ethylene glycol dimethacrylate	CoBF	—	1,2-	55	109,110
			Dichloroethane		
	CoTMHP	_	_	_	111
Methylolpropane trimethacrylate	CoBF	_	1,2-	70	110
			Dichloroethane		
Poly(ethylene glycol) ₄₀₀₀ dimethacrylate	Co(ipp)BF	_	H ₂ 0	60	90
Methacrylonitrile	TAPCo	_		60	94
2-Methacryloxyethyl phosphorylcholine	CoBF	—	Water/MeoH (2:1)	80	67
2-Aminoethyl methacrylate hydrochloride	CoBF	_	Water	80	67
1,1,2,2-Tetrahydroperfluoroalkyl methacrylate	CoBF	110	Acetone	65	112,113
Cyclohexene	TAPCo	_	CDCl ₃	60	94
Methyl crotonate	TAPCo	_	CDCl ₃	60	94
Vinyl acetate	TAPCo	_	CDCl ₃	60	94
Cis-2-pentenenitrile	TAPCo	_	CDCl ₃	60	94
Vinyl benzoate	TAPCo	—	CDCI ₃	60	94

^aValue dependent on pressure.

CoBF, bis[(difluoroboryl)dimethylglyoximato]cobalt(II); CoPhBF, bis[(difluoroboryl)diphenylglyoximato]cobalt(II); Co(dmg)₂, bis(dimethyl glyoximato)cobalt(II); cycCoBF, bis[(difluoroboryl)cyclobutylglyoximato]cobalt(II); CoPh, cobalt(II); cycCoBF, bis[(difluoroboryl)cyclobutylglyoximato]cobalt(II); CoCDFP, cobalt(II); CoPh, cobalt(II); CoTMHP, tetramethyl ether of cobalt hematoporphyrin IX; CoTFPP, cobalt tetrafluorophenyl porphyrin; CoPc, cobalt(II) 2,16-bis(4-butanamidoyl) phthalocyanine; MIBK, methyl isobutyl ketone; TAPCo, (tetrakis(*p*-methoxyphenyl)porphyrinato)cobalt(II); Co(ipp)BF, bis(borondifluorodimethylglyoximato)isopropyl-pyridine cobalt(II); —, *C*_s value has not been determined; Co(L_s), Co(II) thiophenolate complex.

3.09.4.1.1 Reactive methacrylates

MMA has been the most commonly used monomer in CCT; most of the mechanistic studies have used this monomer, making it a standard for comparison when investigating different monomers. In addition to alkyl methacrylates, more exotic methacrylates are also suitable including functional monomers with reactive groups that can undergo additional chemistry after CCTP. Hence, the macromonomers formed have dual functionality: a reactive terminal vinyl group and reactive groups on the pendent chains. Macromonomers with such properties are appealing to chemists because they are suitable to undergo a variety of postpolymerization transformations for use in a wide array of applications. Examples of such functionality include carboxylic acids,^{67–69} epoxy groups,⁷⁰ isocyanates, hydroxyl groups,⁶⁷ and aldehydes.^{71,72}

3.09.4.1.2 Stimuli-responsive methacrylates

Stimuli-responsive monomers have been used with CCT, with a range of poly(ethylene glycol) methyl ether methacrylate undergoing CCTP readily. Postpolymerization functionalization by click chemistry was carried out on these polymers demonstrating the versatility of CCTP. Thermoresponsive polymers such as those containing polyethylene glycol are of great importance in many biological applications, but the ability to further functionalize these polymers improves their usefulness.⁷³

3.09.4.1.3 Hyperbranched polymers from methacrylates

Methacrylate monomers that normally form cross-linked gels during free radical polymerization are di- and trimethacrylates since they contain more than one point where the propagating radical can attack. When they are used in conjunction with CCTP, the CCT keeps the overall molecular weight low resulting in a polymer that has branching points between the monomers with some unreacted vinyl groups. This leads to a hyperbranched polymer that is soluble since the gelation point is much higher compared to a free radical polymerization. When trimethacrylates are used, this is termed cascade branching and these hyperbranched polymers have been shown to have interesting solution properties; the intrinsic viscosity of hyperbranched poly(ethylene glycol) dimethacrylate was much lower compared to linear PMMA of the same molecular weight.⁷⁴ In fact, no dependence exists of intrinsic viscosity on the molecular weight for these polymers.

Another example of polymer architecture with high surface functionality is possible when CCT macromonomers are reacted with cross-linked cores, giving access to star polymers.⁷⁵ Copolymerization of ethylene glycol dimethacrylate (EGDMA) with other monomers such as styrene and MMA has also been demonstrated.^{76–81} A recent paper discusses polymerizations containing 1,4-butanediol diacrylate and triethylene glycol dimethacrylate along with copolymerizations with MMA, all providing reactive pendent groups capable of further transformations.⁸² A direct comparison between butane-1,4-diol dimethacrylate and its structural analog butane-1,4-diol diacrylate was also made in a separate paper.⁸³

Overall, a wide range of homopolymerizations of methacrylates have been utilized in CCT; there are many more that to the best of our knowledge have been discussed in patents but have not yet been published in scientific journals such as glycidyl methacrylate⁷⁰ and 2-isocyanatoethyl methacrylate, work is underway to investigate such monomers.⁸⁴ While there is still scope for many more to be applied to CCT.

3.09.4.2 CCT of Less Active Monomers

Monomers without α -methyl groups need to form internal double bonds in CCTP due to the formation of stable Co(III)–C bonds when propagating radicals attack the cobalt catalyst instead of hydrogen abstraction taking place. These monomers form secondary radicals with thermodynamically stronger Co–C bonds, leading to very low activity in terms of CCT. The dissociation of such complexes was found to be irreversible.^{4,114} Four points that have an impact on the strength of the Co–C bond formation are the following: (1) the number of radical pathways formed from the monomer, (2) the number of radical types, (3) the stability of these radicals, and (4) the relative propagation rate of the monomer.^{22,94} Examples of these less active CCT monomers include acrylates,¹¹⁵ vinyl acetate, acrylonitrile, tetrafluoroethylene, vinyl chloride, dimethyl itaconate,³⁶ and styrene(s).

Acrylates form these relatively stable Co–C bonds between the catalyst and the propagating radical and related oligomers, and have even been observed by MALDI-ToF.³⁵ Increasing the reaction temperature can overcome this problem to some extent. Backbiting is also a common issue in growing acrylate chains, which leads to a mixture of vinyl-terminated polymers. More side reactions are possible such as the anti-Markovnikov addition Co–H to the double bond.¹⁰⁸

A further low CCT activity monomer is dimethyl itaconate as it is a bulky monomer giving rise to a low polymerization rate. It forms a tertiary propagating radical but has a very low value for the termination rate coefficient, which shows chain length-independent behavior – this is the opposite of monomers such as MMA where the rate of termination is diffusion controlled and shows chain length dependence.³⁶ The reason for this is still not fully understood; two proposed explanations given are the following: it is caused by either the interaction between radical substituent and the Co center or the large substituents lead to a more rigid polymer chain and reduced segmental diffusion rate.

Investigations involving MAN for use in CCT have shown that MAN monomers produce additional radicals generated from the initiator while monomers such as cyclohexene produce only monomer-derived radicals.³¹ Further work in this field has led to the conclusion that the initiator-derived radicals react with the Co CTA by hydrogen transfer and rapidly form an equilibrium concentration of MAN.94 This causes a competition between the MAN generated from the initiator radicals and the added vinyl compound in binding to the Co CTA. In general, it can be noted that the formation of Co(II) CTA needed for hydrogen abstraction is much slower when using MAN as an almost static ratio of Co(II)/Co(III) exists. This paper discusses a wide range of monomers and ranks them in terms of relative Co-C bond strengths. Some of the more diverse monomers discussed include vinyl benzoate, cis-2-pentenenitrile, methyl crotonate, and vinyl acetate.

The analog of MAN, acrylonitrile, also has issues with polymerization due to the insolubility of its polymer. In both cases, the incorporation of amines makes it possible that they may labilize the Co–C bond with formation of a π -complex instead.²⁹

3.09.4.2.1 Styrene

In the case of styrene, CCT takes place but the C_s value is much lower than that for MMA. The reason given is that it is more difficult to abstract the β -hydrogen atom from a propagating polystyrene (PS) radical than to abstract α -methyl group found in PMMA. The secondary radicals are formed and due to styrenes' π -ring system these are able to complex with the cobalt catalyst as an additional axial ligand and complete the conju-gation of the macrocycle.^{22,63,116,117} In doing so, two different forms of the catalyst are found, unbound catalyst and monomer-bound catalyst. It should be noted that when copolymerized with MMA, high C_s values are found.¹¹⁸ The size of monomer was also shown to influence CCT, with lower Cs values found as monomer size increased.^{6,96} α-Methyl styrene (AMS) has a high chain transfer constant and when copolymerized with styrene, the C_s value for PS increases as more AMS is added. The rate of the reaction slows and in most cases the polymer chain end group was AMS.^{96,106} A more recent influx of reports on the CCT of styrene has shown that there is still an incomplete understanding of its mechanism.^{119,120}

Fluorinated polymers have also been shown to facilitate CCT.^{112,113} 2,2-Tetrahydroperfluoroalkyl methacrylate was successfully polymerized although the chain transfer constant was much lower than that for MMA but similar instead to longer alkyl methacrylates. As the reaction proceeds, it becomes more heterogeneous in nature as polymer is formed, as the catalyst has low solubility in the monomer and polymer. This fact most likely has an impact on the C_s value; however, control over the reaction was achieved. The monomer and polymer are not very soluble in the solvent, GPC analysis was carried out with α , α , α -trifluorotoluene as the mobile phase and another study by the same authors was conducted on this topic.^{119,120}

More monomers are mentioned in patent literature but details of the reaction conditions are discrete. One such example is the CCTP of a hydrophilic acrylic macromonomer. Sodium acrylate and ammonium acrylate homopolymers are mentioned and most likely to be examples of cobalt-mediated radical polymerization (CMRP) rather than of CCTP.¹²³

3.09.4.3 Further Polymerization Processes

3.09.4.3.1 Emulsion polymerization

Although many reports involve bulk or solution polymerization, the majority of papers concerning CCTP, which have been published in recent years, involve emulsion polymerization, a steady interest most likely caused by its use in industry. In general, the C_s values for monomers decrease when moving from solution to emulsion. The reaction kinetics become more complex; however, the advantage of using this method is that no or very little solvent is needed.¹²⁴ Graft polymers can be synthesized by a two-stage emulsion polymerization, an example of this is the copolymerization of butyl acrylate (BA) and MMA.¹²⁵ Incorporation of sulfonated groups into CCT polymers was carried out by emulsion polymerization. Butyl methacrylate (BMA), 2-acrylamido-2-methylpropane sulfonic acid (AMPS), and hydroxyethyl methacrylate (HEMA) were used to synthesize novel polymeric surfactants with uniform size distribution.¹²⁶ Investigation into the kinetics of emulsion polymerization of MMA is still being carried out.¹²⁷⁻¹³² However, it is noted that the available studies show that comb polymers are indeed produced, but no real structural

information exists about the exact composition of the grafts (as at present it is too difficult to measure). It is implicitly assumed that the graft consists of the methacrylic macromonomer 'tail', but it is more likely that one or more acrylate units will have been added between the terminal vinylic unit of the macromonomer and its 'tail'. This is indeed not well known and earlier reviews have not appreciated this.

3.09.4.3.2 Postpolymerization 'click' chemistry

Macromonomers synthesized by CCT have an instant handle for introducing functionality. The unsaturated vinyl end group allows hetero-Michael addition with thiols. By taking advantage of this, it is possible to introduce hydrophobic/hydrophilic groups, biological groups, to name only a few options. One example involves the generation of an amphiphilic graft copolymer from CCTP of BA and poly(*tert*-BMA). After which the poly(*tert*-BMA) section was quantitatively hydrolyzed under acidic conditions and neutralized to prepare the amphiphilic graft copolymer poly(BA)-g-poly(MAA⁻Na⁺) with hydrophobic backbone and hydrophilic side chains.¹³³

Glycopolymers have been synthesized by CCTP and 'click' chemistry.^{104,105} The CCTP of protected alkyne methacrylates enabled postpolymerization functionalization by facile Huisgen cycloaddition chemistry with sugar azides. The ability to further functionalize these CCT glycol macromonomers was demonstrated with the use of hetero-Michael addition (also known as 'thiol-ene click' chemistry) and benzyl mercaptan. This can be replaced with thiol-containing groups that have a specific purpose, for example, biologically active proteins.¹³⁴

In personal care applications, copolymers of oligo(ethylene) glycol methacrylates with allyl methacrylate have been synthesized by CCT. The activated vinyl end group has then been used to conjugate to a biological surface, α -keratin, found in human hair. The conjugation was carried out by hetero-Michael addition and reaction success monitored by measuring the denaturation temperature of the unfolded protein before and after conjugation. These copolymers have thermoresponsive behavior as well as pendent vinyl groups ready to undergo further reaction by traditional thiol–ene click chemistry.¹³⁵

A recent report describes the *in situ* polymerization of MMA on modified cadmium sulfide (CdS) nanocrystals (NCs) along with copolymers using poly(methacryloxypropyltrimethoxysilane) (PMPS). The terminal functional groups on the surface were then cross-linked by free radical polymerization to form CdS NC–polymer networks.¹³⁶ This work has been continued with incorporation of poly(styrene)-*co*-poly(methacrylic acid) microspheres by surfactant-free emulsion polymerization.¹³⁷

Hyperbranched polymers have also been utilized with thiol–ene chemistry to generate multiarm star block copolymers.¹¹⁰ In this report, CCTP of EGDMA was carried out followed by hetero-Michael addition with a range of thiol-containing groups on the terminal vinyl moiety. Polymers prepared by reversible addition-fragmentation chain transfer (RAFT) or transition metal-mediated living radical polymerization (TMM LRP) techniques can be easily attached in this way to generate star block copolymers. In addition, this report includes copolymerizations with MMA and methylpropane trimethacrylate to vary the level of branching in the products.

3.09.4.3.3 Postpolymerization copolymerization

After CCTP, it is difficult to reinitiate polymer growth with the addition of new monomer. Methacrylates are able to copolymerize with acrylates but less well with other methacrylates.¹¹⁵ The tertiary propagating radicals formed are so hindered that β-scission takes place rather than monomer addition. Styrene monomers are unable to reinitiate and copolymerize due to the resulting terminal 1,2-disubstituted double bond formed. An example using emulsion polymerization incorporates three monomers: n-BMA, n-BA, and 2-hydropropyl methacrylate. AB-block macromonomers act as surfactants during emulsion copolymerizations at concentrations much lower than those observed for random macromonomers. The CTAs are effective in emulsion copolymerization at low concentrations as they lower particle size, molecular weight, and polydispersity.¹³⁸ In a further example, dimethylacrylamide was added to a preformed MMA macromonomer in bulk conditions with γ -radiation to yield a hydrogel. Successful reaction on the terminal double bond was confirmed.139

CCT has also been applied to surface chemistry. Nanosilica surface-grafted PMMA macromonomers were prepared by CCTP. The first step involved CCTP of 3-(trimethoxysilyl) propylmethacrylate coupled to the nanosilica surface with terminal vinyl groups accessible on the surface. Subsequently, grafting of PMMA by CCTP was achieved.¹⁴⁰ Complex polymeric structures have been synthesized by grafting of copolymers. One example has St/BA/2-dimethylaminoethyl methacrylate (DMAEMA) as the 'trunk' chain composition with the lateral chain being composed of MMA/BMA for use in dispersants with quaternization able to occur.¹⁴¹

3.09.4.3.4 Copolymers with both active and nonactive CCT monomers

Introducing nonactive CCT monomers results in monotelechelic architecture. When the propagating radical from a nonactive CCT monomer reacts with an active CCT monomer, chain transfer is now able to take place, which results in the formation of the characteristic vinyl end group capping the polymer chain. There is a lot of literature on copolymers by CCT; Table 4 only discusses homopolymerizations but there are other monomers, such as 2-pentenenitrile and cyclopenten-1-one, that although do not undergo CCT by themselves, there have been reports on their copolymerization with more standard CCT monomers such as MMA.¹⁴² In this case, the end group formed is a germinal double bond and can undergo further polymerization to give arms on graft polymers. Investigations to provide fuller understanding into the CCTP of methacrylates are still being carried out after 20 years since the discovery of CCTs.143

A study on the copolymerization of MMA and BA was undertaken to gain further understanding into what affects the chain transfer constant. It was found to be dependent on the monomer feed composition and initiator concentration. A model using CCT and CMRP was used to explain this.¹⁴⁴ Copolymers of BA and either AMS or benzyl methacrylate (BzMA) generated interesting copolymers. AMS/BA consisted in most cases of BA polymer chains with AMS end groups while BA/BzMA generated BA polymer chains with BzMA end groups, also pure BA macromonomers were formed.¹⁴⁵ In both cases, only a few units (1–3) of the copolymer were incorporated into the backbone, which is what the authors set out to investigate. This feature is common in such copolymers.^{146,147}

Tubular reactor vessels using supercritical CO₂ have shown the ability to synthesize copolymers with almost complete monomer conversion.¹⁴⁸ Copolymers of styrene, MMA, and glycidyl methacrylate were produced. In a further report, supercritical CO₂ was shown to increase the chain transfer constant in MMA, when the monomer was first expanded in dense CO_2 . This technique could be carried out at lower pressures compared to supercritical CO2 reactions under homogenous conditions. The higher C_s value was also related to reduced viscosity of the medium, providing evidence of a diffusioncontrolled mechanism.⁸⁸ This work was expanded in a separate report in which the bulk viscosity effect was studied with CO₂-expanded monomers with different structures. In this case, styrene and BMA form secondary and tertiary radicals, respectively.⁹⁷ With BMA it was possible to increase the value of the chain transfer constant attributed to reduction in bulk viscosity of the medium. This report showed that using supercritical CO₂ also had a positive impact in the CCTP of less active CCT monomers such as styrene. Continuation of this investigation has moved into considering the volumetric expansion behavior of polymer-monomer mixtures in the presence of dense CO₂. In addition, the evolution of MWDs of polymer synthesized in this manner was also discussed. Modified Predici simulations were included to explain the experimental results.149

3.09.4.3.5 Addition-fragmentation chain transfer

PMMA oligomers made by CCT have proved to be excellent addition-fragmentation chain transfer (AFCT) agents. In this case, they act as traditional CTAs, as the polymeric radical prefers to undergo β-scission rather than monomer addition, while secondary propagating radicals result in copolymerization rather than AFCT. A recent report combines RAFT and CCT to form ω-unsaturated polymers with relatively low polydispersities. First the monomers (MMA and BMA) were synthesized by RAFT following which CoBF was introduced to the reaction mixture to generate terminal vinyl groups on the polymer chains. The loss of the RAFT end group was either due to radical addition of the initiator or due to transfer reaction caused by CoBF. Successful copolymerization was carried out with ethyl acrylate to yield graft copolymers.¹⁵⁰

3.09.4.3.6 Cobalt-mediated radical polymerization

CMRP makes use of the stable Co–C bond that forms in less active CCT monomers. The Co–C bond undergoes homolytic cleavage with release of a persistent cobalt radical and transient alkyl radical.^{151–154} Hence, the cobalt complex end-caps the polymer chain providing a level of control over the polymerization. This research area is quite large in its own right and is not discussed in this chapter; however, a more detailed description can be found in a review.¹⁵⁵

3.09.4.3.7 Atom transfer radical polymerization and CCT

A few reports have shown the use of atom transfer radical polymerization (ATRP) and CCT occurring almost in parallel. The polymerization is started using ATRP conditions to generate a living polymerization with polymer chains possessing lower PDIs than would be possible if using CCT. A CCTA is then added into the reaction to generate polymer chains with
unsaturated end groups. In this case, the CTA is not facilitating chain transfer but instead acting as a chain terminator. It is expected that no unfavorable side reactions take place and a well-defined polymer is produced with an unsaturated end group. This method is also suitable for use with preformed block polymers with examples using MMA with ethyl acrylate and BMA with almost no trace of the original macromonomer at the end of the reaction.¹⁵⁶

3.09.4.3.8 CCT polymers generated from new Co macrocycles

It is known that sulfur atoms incorporated into the macrocycle of Co significantly decrease CCT,²⁹ while a more recent report incorporating sulfur donors into the coordination sphere of the Co center has led to a mild CTA that can be used to produce controlled high-molecular-weight macromonomers using more practical concentrations of CCT catalyst.⁹³ The synthesis of a vinyl Co porphyrin that facilitates CCT as well as being a comonomer was reported.¹⁵⁷ Copolymerization with styrene was carried out and CCT behavior was observed. The resulting products are then suitable catalysts for anthracene photooxidation with oxygen to anthracene *endo*-peroxide. A further new catalyst type that has polymer-tethered ligands has been shown to undergo CCT to form copolymers of BMA and MMA with the catalyst being recoverable and has proved to be of interest for some applications.^{158–160}

3.09.5 Applications

3.09.5.1 CCTP Emulsion Polymerization

CCT is particularly effective under emulsion polymerization conditions provided the catalyst is able to partition freely between the oil and water phases. The number-average molecular weight of PMMA is decreased from over 120000 in the absence of cobalt CTA to less than 3000 on addition of 36 ppm of CoBF. Molecular weight remains constant throughout the reaction, while the PDI was maintained at approximately 2. End group fidelity was shown by MALDI-ToF-MS. The behavior of the catalyst in emulsion is more complicated than in solution, due to partitioning of the CCTA in the compartmentalized system, thus control of feed conditions are essential. CoBF partitions almost equally between the organic and aqueous phases with the best results being obtained when catalyst is fed continually as a solution in the monomer feed. A critical level of catalyst is required, which is shown to be related to the number of catalyst molecules per particle.55

When more hydrophobic monomers are used, the hydrophobicity of the CCT reagents can be altered and when tetraphenylcobaloxime boron fluoride (COPhBF) is used, it is found to reside predominantly in the organic phase. The best results are often achieved under monomer-flooded conditions that keep the glass transition temperature (T_g) of the monomer-filled particles below the reactor temperature.¹⁶¹ CCT does actually reduce the rate of polymerization such that the monomer can be fed at a rate that maintains the instantaneous conversion low enough for the particle to be swollen with monomer, allowing diffusion of the catalysts between the aqueous and monomer phases. If the amount of the catalyst is reduced and the rate increases, this can lead to viscous, glassy particles that prevent catalyst mobility, which is observed as a

breakdown in the polymerization mechanism and is observed primarily in the PDI. This can be circumvented by the addition of a shot of monomer, for example, 20% of the total, at the start of the reaction. The effective chain transfer coefficient decreases on increasing the length of the ester group of the methacrylate. In all cases, the CCT mechanism is shown to be maintained by excellent end group fidelity from MALDI-ToF-MS.¹⁶²

Thus, the effect that a Co(II)-based CCTA has on the course of the polymerization, and on the product properties of an emulsion polymerization, is governed by the intrinsic activity and the partitioning behavior of the catalyst. Radical desorption from the particle phase to the aqueous phase preceded by chain transfer is the main kinetic event controlling the course of the polymerization. The product properties in terms of the particle size distribution and the aqueous phase solubility of the CCTA are the key parameters controlling the course of the polymerization and the particle size distribution.¹³¹ Two limiting scenarios have been identified: in cases of fast CCTA entry and exit, monomodal MWDs can be obtained and with slow CCTA entry and exit, bimodal MWDs can be obtained; one peak can be attributed to the generation by bimolecular termination product produced in polymer particles devoid of CCTA, while a transfer-derived peak can be attributed to polymer particles containing one or more CCTA molecules.132

3.09.5.2 Direct Industrial Applications of CCTP

CCTP is used directly in a variety of applications, one of which is printing using toner processes. Water-miscible CTA is used, along with initiator, to facilitate the polymerization of monomers to form latex particles. Coalescence or fusion of these latex particles with colorants, pigments, and/or dyes gives sediment-free toner compositions used for electrographic imaging and printing processes.^{131,163}

Polymerization of MMA to form thermoforming sheets is a process that utilizes CCTP. Suitable compositions are placed between sheets of glass or two opposing metal bands, providing a sheet of thermoformable PMMA. The sheet is heated and then drawn into a mold under pressure or vacuum to manufacture items such as baths, sinks, and shower trays.¹⁶⁴

Emulsion polymerization is an important industrial process mainly used to create high-molecular-weight lattices. The need to create lower-molecular-weight lattices for certain applications became evident and CCTP was employed by the use of specific CTAs to control the molecular weight of resulting polymers.19,165 CCTP in emulsion polymerization facilitates the synthesis of macromonomers with a high degree of terminal vinyl groups and can also be used in the synthesis of copolymers. The stability of the boron fluoride-bridged cobaloxime catalysts toward hydrolysis enables the synthesis of methacrylic acid-containing polymers without catalyst degradation.¹⁶⁵ Due to the instability of cobalt CTAs toward peroxides, conventional inexpensive peroxide initiators are avoided, with more expensive azo initiators being used in their place. The evolution of nitrogen bubbles with initiator decomposition can cause problems of coagulation. This problem can be overcome, however, by conducting microemulsion polymerizations; the reduced particle size nucleation occurs predominantly in the monomer droplets, as opposed to creating a new particle phase, and so the CTA is separated from the primary initiator radicals.166

CCTP can be used for the removal of RAFT end groups to give vinyl-terminated polymers. The presence of RAFT end groups can sometimes be detrimental to the required application of the polymers as they can undergo aminolysis, hydrolysis, and thermolysis, and may possibly cause cytotoxicity in biological applications; hence, facile and complete removal of RAFT end groups is often desired. Once the RAFT polymerization is complete, a cobalt CTA is added and the reaction continued for several hours until the RAFT end groups are fully removed. Low concentrations of CTA are used so that no further polymerization should occur that may have a detrimental effect on the PDI of the synthesized polymer.¹⁵⁰

The terminal vinyl groups of CCTP polymers have been of interest due to their potential to be functionalized by click chemistry methodology. This would offer a route to a wide range of functional polymers. Several click chemistry methods are available for the functionalization of vinyl groups involving the attachment of a functional thiol, termed thio-Michael addition. Haddleton et al. investigated the validity of several of these methods for the functionalization of CCTP oligomers, including MMA dimer, HEMA, and ethylene glycol methyl ether methacrylate oligomers, using the nucleophilic amine catalysts triethylamine (TEA), pentylamine, and hexylamine, and phosphine catalysts dimethylphenylphosphine (DMPP) and tris(2-carboxyethyl)phosphine hydrochloride (TCEP). A range of commercial functional thiols were covalently attached by reaction with the terminal vinyl groups of the CCTP oligomers using all catalysts, thus providing a facile route for the formation of functionalized polymers.¹⁶⁷ Various thermoresponsive oligomers of ethylene glycol methyl ether methacrylate have also been synthesized by CCTP and functionalized by thio-Michael addition in this manner, forming functional thermoresponsive oligomers.⁷³

3.09.5.3 Semiconductor Nanocrystal Polymer Hybrids

Semiconductor NCs possessing a quantum confinement effect are crystalline structures of ≤ 100 nm in one direction, with confined excitons in all three spatial directions, also known as quantum dots.¹⁶⁸ Quantum confinement effect alters the properties of the semiconductor such that photons are absorbed at one wavelength and transmitted at another; hence, these materials are of considerable interest due to their applications as light-emitting devices, solar cells,¹⁶⁸ and biological labels.¹⁶⁹ The optical and electrical properties of semiconductor NCs are size dependent, so a synthesis route that can guarantee a monodisperse size is vital (Figure 5).

Work has found that specific combinations of NCs and polymers led to more easily processed materials, labeled NC–polymer hybrids.¹⁷⁰ Polymers have been used in two ways to create these hybrids: with the two components either existing as separate layers or where NCs are well dispersed in a polymer matrix.¹⁶⁹ CCTP has been exploited to create polymers for use in covalently linked CdS NC–polymer hybrids.¹³⁶

Both methods of creating NC–polymer hybrids were investigated using CCTP technique. The grafting-to approach (dispersed NCs in a polymer matrix) was carried out by first synthesizing hydroxyl-coated CdS NCs. These were formed by a reaction between cadmium chloride and mercaptoethanol, which yielded a hydroxyl-coated CdS suspension. PMPS and PMMA were copolymerized by CCTP to yield PMPS–PMMA



Figure 5 Example of nanocrystal photon absorption and reemission.

macromonomers that were then covalently attached to the hydroxyl-coated CdS NCs using an azo initiator. The terminal vinyl groups formed in this reaction were then cross-linked by further addition of initiator forming a polymer matrix with well-dispersed CdS NCs.

The grafting-from approach (separate covalently linked nanocrsytal/polymer layers) was carried out by surface modification of the hydroxylated CdS suspension with methacryloxypropyltrimethoxysilane (MPS) to which an *in situ* CCTP of MMA was conducted, forming covalently linked CdS– PMMA hybrids (Figure 6).

Both techniques were shown to have no detrimental effect on the size of the NCs and led to luminescent enhancement when compared to the lone NCs, giving two successful methods for the formation of NC-polymer hybrids by CCTP mechanisms. Intramolecular cross-linking was favored in this case, as it was shown to induce apparent fluorescent enhancement of the NC and should lower diffusion quenching effectively intensifying photoluminescence.¹³⁶

3.09.5.4 CCTP Polymers as Additives for Road Pavement Manufacture

An interesting potential application is in road building; bitumen is a key component of roads and pavements but is nonsustainable as it is derived from fossil fuels, hence other alternatives have been researched to provide sustainable materials so that the exclusive use of bitumen is no longer a necessity. Acrylic polymers such as poly(ethyl acrylate) and poly(methyl acrylate) were found to possess rheological properties similar to those of soft and hard bitumen, although the synthesis route was not commercially viable; hence, as CCTP is an industrially established technique, it was investigated for the synthesis of homo- and copolymers of methyl acrylate and BA. A range of polymers were synthesized using CCTP with varying monomer ratios, CTA concentrations, and initiator concentrations. Of 19 polymers synthesized, 4 showed rheological properties similar to those of hard, intermediate, and soft



Figure 6 Grafting-from and grafting-to approaches to nanocrystal polymer hybrids using CCTP.

bitumen. These were subject to rheological testing and found to be suitable as bitumen binders for use in road and pavement manufacture. The scope for functional changes also means that synthesis of a binder with improved mechanical performance may also be possible.¹⁷¹

3.09.5.5 Glycopolymers

Glycopolymers are synthetic polymer structures with pendent carbohydrate moieties. They play an essential role in biological recognition and are used in such events as cell–cell interaction, which is responsible for fertilization, cancer metastasis, cell migration, organ formation, and immune defense to name a few. These recognition processes are thought to proceed by specific carbohydrate–protein interaction, whereby proteins generically called lectins, which are commonly found on cell surfaces, bind specifically and noncovalently to carbohydrates.¹⁷² Due to this specific recognition and binding, glycopolymers have been of great interest for the synthesis of biocompatible materials for targeted drug delivery^{173,174} and tissue engineering.¹⁷⁵

Haddleton *et al.* exploited the terminal vinyl groups produced by CCTP to give macromonomers of trimethylsilane-protected propargyl methacrylate, whereby the resulting polymer possessed a high level of pendent alkyne bonds and one vinyl group per polymer. These macromonomers were termed dual clickable as once deprotected the alkyne groups could be selectively functionalized using Cu(I)-catalyzed azide–alkyne cycloaddition (CuAAC), a widely used click chemistry technique, while vinyl groups could be selectively functionalized using functional thiols by thio-Michael addition. Sugar azides of mannose, galactose, and cellobiose were synthesized for functionalization of the alkyne bonds forming a glycopolymer. Lectin recognition of mannose and galactose glycopolymers synthesized was investigated by turbidimetry and by high-performance liquid chromatography (HPLC). Results demonstrated that both mannose and galactose glycopolymers synthesized were able to function as multivalent ligands for the recognition of specific lectins, thus providing a facile method for the synthesis of dual clickable macromonomers as a tool in the synthesis of glycopolymers.¹⁷²

3.09.5.6 Polymers for Use in the Hair Care Industry

The reactive vinyl end group that is present in CCT polymers has been shown to react with α -keratin protein, present in human hair, by taking advantage of the hetero-Michael addition with thiol groups present in the protein.¹³⁵ The purpose of this conjugation is to create hair care products that protect damaged hair against further environmental damage. Differential scanning calorimetry was used to evaluate the success of the conjugation since the denaturation temperature of damaged hair is lower than that of healthy hair. After conjugation, the denaturation temperature of the protein increased compared to the damaged protein, indicating that the polymer can successfully protect the protein.

3.09.5.7 Branched Polymers

CCTP is a useful and facile tool for the synthesis of branched polymers from multivinyl monomers as originally demonstrated by Guan.⁷⁴ Guan polymerized EGDMA in the presence of a Co(II) catalyst, forming a branched polymer with a high degree of terminal vinyl functionality. The level of Co(II) catalyst was chosen to facilitate statistical trimerization forming a trimer radical, which then undergoes termination by β -hydride abstraction by the Co(II) chain transfer catalyst. The trimer may then be reinitiated by the Co(III)–H species and a



Figure 7 Synthesis of branched polymers by CCTP of EGDMA.

further trimerization reaction may proceed, causing a cascade trimerization effect, forming a branched polymer that retains a high level of terminal vinyl functionality. These materials can be taken to relatively high conversions and molecular weights before the products cross-link forming an insoluble network or gel (Figure 7).

This research was further investigated by Haddleton *et al.* by incorporation of copolymers of varying vinyl functionality, including a trivinyl methacrylate to increase the level of branching and monovinyl methacrylate to decrease the level of branching, providing a means to tailor the degree of branching of the resulting materials. The functionalization of the terminal vinyl groups was also investigated using phosphine-mediated thio-Michael addition, a facile, one-step reaction capable of covalently linking a range of functional thiol groups to vinyl groups of

the polymer by use of a phosphine catalyst such as DMPP, thus creating an array of products with varying degrees of branching and a wide scope for terminal functionality (Figure 8).

Tunable properties are of importance with respect to certain industrial applications as the material properties can be tailored for the needs of the application. Another avenue for consideration with regard to these products is that for low molecular weights, which may be used as branched macromonomers.

3.09.5.8 Macromonomers for Industrial Applications

Not only is the CCTP technique itself is an important technique in industry, but the macromonomers produced have also found a variety of unique uses. It was realized that copolymerization of CCTP macromonomers with acrylic monomers



Figure 8 Synthesis of hyperbranched polymers by CCTP and subsequent functionalization by phosphine-mediated thio-Michael addition.



Acrylic monomer (M) + Macromonomer \rightarrow Comb polymer

Figure 9 Synthesis of comb polymers by copolymerization of an acrylic monomer with a CCTP macromonomer.

yields comb-like architectures,¹⁷⁶ whereas copolymerization of macromonomers with methacrylic polymers yields poor copolymerization as rather than copolymerizing with methacrylic monomers, the macromonomers act as CTAs (Figure 9).^{131,177}

As macromonomers act as CTAs when copolymerized with methacrylic monomers, it results in a reduction in the molecular weight of the product. The macromonomer acts as a CTA by an AFCT mechanism (Figure 10), with a measurable chain transfer constant.^{29,66}

A good example where a CCTP macromonomer is used to limit the molecular weight of a polymerization is AMS dimer, which has been used in a range of industrial applications, such as PS manufacture,¹⁷⁸ to control hardening and polymerization temperature in dental adhesives cured by UV radiation,¹⁷⁹ and as part of a copolymer used as a fiber retention agent in the production of paper from pulp.¹⁸⁰ α-Methylstyrene has also been used in the food packaging industry. Ethylene vinyl acetate copolymers possess good gas-barrier properties and melt processibilities. These copolymers can be processed into melt films, sheets, pipes, tubes, and bottles for use in the food packaging industry; however, conventional ethyl vinyl acetate copolymers streak on extrusion, leaving deformities on the surface. If the CCTP-synthesized a-methylstyrene macromonomer is added after polymerization but before saponification, then polymers with no surface deformities are obtained, although it is unknown why this effect occurs.¹⁸¹

Macromonomers have also been used in the synthesis of telechelic polymers using benzyl mercaptan dimer in the synthesis of α, ω -dicarboxyl telechelic PMMA. This reaction proceeds through an addition-fragmentation reaction whereby the macromonomer dimer splits in half. One-half forms the ω -terminal end of each macromolecule, while the other is released as a functional initiating radical.¹⁸²

3.09.5.9 Macromonomers for Photonic Crystals

Photonic crystals are periodic dielectric structures that possess a band gap that forbids the propagation of certain frequency ranges of light, producing effects not possible with conventional optical devices,¹⁸³ with the potential to be used in optical communications, frequency conversion, and sensing.^{137,184}

Colloidal photonic crystals are often synthesized from monodisperse microspheres of PMMA, PS, and silica. The use of functionalized microspheres can increase the performance of certain photonic devices and CCTP has been successful in the synthesis of NC-loaded photonic crystals with a polymerizable macromonomer. Monodisperse microspheres composed of a PS core with a poly(methacrylic acid) (PMAA) shell were synthesized through an emulsion copolymerization of PMAA macromonomers synthesized by CCTP with PS. It was found that the CdZnS NCs capped with PMAA macromonomers could be anchored to the microsphere surface as the PMAA acts as a ligand. These colloidal crystals are then formed into a film, yielding well-ordered, hexagonal close packed structures that show pH-responsive behavior. All films with different hydrodynamic diameters simultaneously exhibit brilliant colors from red to blue, providing a promising avenue for the next generation of photonic devices.¹³⁷

3.09.5.10 Macromonomers for Graft/Comb Copolymers

Comb polymers synthesized by CCTP consist of macromonomer side chains grafted to a polymer backbone. Macromonomers



Figure 10 Addition-fragmentation chain transfer mechanism for CCTP-based oligomers

synthesized by CCTP are used to make a range of comb polymers and copolymers. In many cases, the macromonomer synthesized is a block copolymer, hence when it is copolymerized with an acrylic monomer to form a comb it will have side chains containing several different monomer functionalities. The block copolymer macromonomers formed can be random blocks or AB blocks. It was found that by increasing the temperature of the polymerization of these AB blocks highly pure segregation of the monomers blocks could be achieved and styrenic and acrylic monomers could be copolymerized.¹⁸⁵⁻¹⁸⁶ Tailoring of the segments of the block macromonomer can have a profound effect on the properties of the resulting comb polymers; more monomers can be incorporated into the block if required, and if copolymerized with several acrylic monomers, a copolymer backbone can also be achieved. The versatility of the technique is large and a vast number of different properties can be attained by monomer choice, ratio, and ratio of side chain to backbone.¹⁸⁷ Comb polymers synthesized by CCTP macromonomers have been used extensively utilizing both macromonomers and block macromonomers.

When polymerized in the absence of plasticizers or processing aids thermoplastic polymers of poly(vinyl chloride) (PVC) result in inferior heterogeneous melts of low strength and low elongation. Although plasticizers eliminate many of these problems and enable the formation of homogenous thermoplastics, they also result in the loss of physical properties, in particular loss of rigidity. Comb copolymers, synthesized by emulsion polymerization of a CCTP macromonomer and a vinyl monomer, can be incorporated into the thermoplastic blend and will act as plasticizers. Heating and mixing of these produces melt blends possessing improved melt behavior, applications of which includes extrusion, blow molding, injection molding, expansion into foam, and making of bioriented materials.¹⁸⁸

Aqueous dispersions also utilize macromonomers formed by CCTP for a variety of applications. Block copolymer macromonomers are synthesized by emulsion polymerization of vinyl monomers in the presence of cobalt CTA, further emulsion polymerization of macromonomer products with additional vinyl monomer yields comb copolymers in aqueous dispersions. By tailoring the ratio of macromonomer segment to polymer segment, which alters the overall T_{σ} of the resulting polymer, the hard to soft balance can be adjusted to form films that are neither too soft, leading to a tacky film, nor too hard, leading to a brittle film. The application of such films is broad, encompassing a range of architectural and industrial coatings such as paints, wood coatings, inks, paper coatings, textile and nonwoven binders and finishes, adhesives, mastics, asphalt additives, floor polishes, leather coatings, plastics, plastic additives, petroleum additives, and thermoplastic elastomers.¹⁸⁹ Comb polymers have also been synthesized in a similar manner using emulsion-polymerized macromonomers for applications in architectural and industrial coatings.¹⁹⁰

3.09.5.10.1 Automotive industrial applications of graft/comb polymers

One of the applications of CCTP polymers and macromonomers has been in the automotive industry. Typically, automobile steel panels require several paint layers to achieve hardwearing coatings. The first layer is commonly an inorganic rust proofing zinc or iron phosphate layer. Primer comprises the next layer, leading to a better appearance of the finished coating and better adhesion of the next layer known as the base coat layer. The base coat or color coat layer contains the pigment, and the final layer is a clear top coat, which protects the base coat from weathering.

Stringent legislations concerning the amount of VOCs in all paint types have caused many companies to seek alternatives to solvent-borne paint systems, making the move to waterborne systems, the main focus of which is to improve film properties to the level of conventional solvent systems. Hence, a combination of CCTP and emulsion polymerization was explored as a method of creating additives for waterborne paints.^{138,191}

3.09.5.10.2 Automotive base coats/color coats

Acrylic polymers containing hydroxyl groups are utilized in base coats as binders, which bind the pigments together, usually by a catalyzed cross-linking mechanism with a polyisocyanate hardener, providing a chip-resistant coating. These coatings are usually two-component systems, meaning the binder and cross-linker are stored separately and mixed to form a pot mix prior to application.

The acrylic polymers that comprise the binder can be synthesized by emulsion polymerization. It was found that emulsion polymerizations, which incorporated random and AB block copolymers synthesized using CCTP macromonomers, required no conventional surfactants to stabilize particles, as the block copolymers could be used as polymerizable surfactants.¹⁹¹

Block copolymers can be synthesized by alternative techniques to CCTP, but these have disadvantages. Cationic polymerization is limited by the amount of monomers applicable; anionic polymerization requires low temperature, which is not feasible for application to plant reactors; and GTP requires protection of any acidic monomers. Certain living free radical techniques have also been investigated but drawbacks still remain with respect to conversion, color, and catalyst removal.¹³⁸ CCTP provides a new way to prepare hydroxyl-functional graft copolymers that show excellent drying.

Work by Huybrechts et al. on waterborne pigment dispersants for automotive paints utilized CCTP for synthesis of macromonomer copolymers of BA and methacrylic acid by standard solution polymerization in the formulation of automotive base coats. These amphiphilic block copolymer macromonomers form stable anionic dispersions in water and could be further used in the surfactant-free emulsion polymerization of MMA and BA. MMA and BA copolymerize with the macromonomer to form comb structures that are water dispersible and stabilize the final emulsion. The molecular weight of these comb copolymers can be reduced by incorporation of MMA macromonomers, also synthesized by CCTP as the MMA macromonomers act as CTAs. Tuning the molecular weight of comb structures has a profound effect on drying with both physical and chemical drying processes taking place. Physical drying is the increase in film $T_{\rm g}$ caused by solvent evaporation, which is influenced by the $T_{\rm g}$ of the comb copolymers. Chemical drying is the increase in T_g due to cross-linking. On drying, hydroxyl groups will react with isocyanate cross-linkers leading to a network structure, with an overall drying performance comparable to solvent-borne systems when formulated correctly.¹⁹¹

Macromonomers are utilized for a range of other applications for both solvent-borne¹⁹² and aqueous systems used in the automotive industry,^{193–195} and are usually utilized in the synthesis of comb polymers. In solvent-borne systems, the macromonomer facilitates less selective anchoring of the pigment to dispersants, hence creating a better color quality in resulting coatings.¹⁹² In aqueous pigment dispersion, conventional coatings have an insufficient intensity of color with regard to jet black coatings; incorporation of macromonomers into the comb copolymer has been shown to increase the color intensity of jet black pigments.¹⁹³

Macromonomers have also been used in the production of fast drying coatings for the refinishing of base coats and clear coats. CCTP AB block macromonomers are first prepared; copolymerizing these in a sequential polymerization yields a comb polymer with random segmented side chains. Introduction of functional monomers is also possible creating more segments on the arm. These comb polymers can be added as binder resins to solvent- or water-based coatings for a range of paint compositions, such as primers, base coats, and clear coats, and many architectural compositions, such as house paints.¹⁹² It was found that this formulation was particularly useful in fast drying coatings such as air-dry acrylic lacquer color coat compositions to be coated in a clear coat finish, these fast drying coatings are of particular use to the paint repair industry, as much repair work is carried out in auto repair shops, where ovens are not used to cure the paint, hence the paint must dry quickly under ambient conditions.

3.09.5.10.3 Automotive top coats/clear coats

Top coats are of a similar composition to base coats but are not pigmented. Again these are usually two-component systems that comprise an acrylic comb polymer and a poly(isocyanate) hardener, which cross-links after application if a catalyst is used or cross-links under heating curing forming a clear, hard, chip-resistant coating.^{92,95,96} Macromonomers synthesized by CCTP are again used in the formation of acrylic comb polymers.

A hydroxyl functional comb polymer is made by the synthesis of block macromonomers by CCTP, which contain hydroxyl functionality and copolymerizing these with acrylic monomers to form a comb polymer. The amount of hydroxyl functionality of the macromonomer depends on the application, but by tuning this level it was found to increase the pot life of the paint and also the initial hardness. Acrylic comonomers can also be used to achieve properties such as hardness, appearance, and scratch resistance. This comb polymer is combined with a polyisocyanate or blocked isocyanate cross-linking agent in the presence of a catalyst. The polyisocyanate will react with the hydroxyl functionalities on the comb polymer creating a cross-linked network, forming a hard, chip-resistant coating.^{191,195,196}

3.09.5.11 Macromonomers for Star Polymers

Star polymers are commonly used as rheology modifiers in applications such as coatings and oil additives, but can also be used in a variety of other ways.

Synthesis of star polymers can be achieved by CCTP using an arm first method. Macromonomers are synthesized by CCTP forming the arms and are copolymerized with an acrylic divinyl monomer that forms a cross-linked core with macromonomer arms. Work by Antonelli *et al.* has used CCTP to create a range of star polymers for use as rheology modifiers. Random block macromonomers are first synthesized by CCTP, copolymerizing three monomers, iso-BMA, 2-ethylhexyl methacrylate, and HEMA, the ratio of which can alter the properties of the polymer, the molecular weight of which is in the range 4000–20 000. A copolymerization of the resulting macromonomers with a divinyl monomer such as butanediol diacrylate yields a cross-linked butanediol diacrylate core, where at least three macromonomer arms have been incorporated into the polymerization creating star polymers (Figure 11).

Preferably the star contains between 10–50% weight of core and 50–90% weight of macromonomer arm. The resulting star polymer can be used in conventional coatings to modify the rheology or properties of the composition. They may also be used as tougheners in plastic sheeting, as adhesives, and as an additive in motor oils to improve viscosity.⁷⁵

3.09.5.12 Macromonomers for Hydrogels

Hydrogels are commonly used in the biomedical industry as contact lenses, wound dressings, and biocompatible adhesives. These are polymeric structures that are capable of absorbing large quantities of water. The original material used for contact lenses was PMMA that formed rigid lenses, whose impermeability toward oxygen caused unwanted side effects, and thus hydrogels were investigated as gas-permeable soft lenses. One problem often encountered with hydrogels is their poor mechanical strength; this is because a significant portion of the material is made up of water. One method to overcome this effect is to synthesize



Figure 11 Star polymers synthesized by a grafting-to approach using divinyl acrylic monomers and CCTP macromonomers.

comb polymers from a hydrophobic macromonomer and a hydrophilic monomer, termed a self-reinforcing gel, creating a balance between hydrophilicity and mechanical strength.¹⁹⁷ CCTP has been utilized to synthesize hydrophobic macromonomers for copolymerization with hydrophilic monomers in the formation of comb polymers capable of exhibiting hydrogel function while retaining mechanical strength.¹⁹⁸ MMA macromonomers were copolymerized with N,N-dimethylacrylamide and other hydrophilic monomers by γ -radiation to form comb polymers with both hydrophobic and hydrophilic domains. It is postulated that theoretical cross-linking occurs in these materials that can be explained in two ways, y-radiation is known to cross-link acrylates, hence the acrylate polymer may have cross-linked in the γ -source, but what is known is that the MMA macromonomers clearly aggregated forming physical cross-links by hydrophobic interaction. On swelling in deionized water, these materials demonstrate a significantly higher rigidity than hydrogels synthesized without the inclusion of CCTP macromonomers, suggesting MMA aggregation is not as significant in statistical copolymerizations of the same composition.198

3.09.6 Summary

CCTP exploits CTAs with chain transfer constants orders of magnitude higher than conventionally used agents. In addition, if used correctly they give products with extremely high fidelity vinyl functionality. The mechanism is an unequivocal perturbation of a free radical polymerization. Due to its ease of use, it has found industrial application in many areas and in all types of free radial polymerization processes from solution to emulsion. Catalysts that were once protected by patents are now coming into the public domain and thus available for more generic use and application. It is interesting that academic study has been quite limited when compared to other innovations in radical polymerization and controlled polymerization methods that have emerged since the 1980s. The usefulness is limited mainly to methacrylates and copolymers of methacrylates. However, catalysts are robust and extremely effective.

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Biographical Sketches



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3.10 Nitroxide-Mediated Polymerization

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3.10.1	Introduction	277
3.10.1.1	Historical Background	277
3.10.1.2	General Considerations	278
3.10.2	Synthesis of Nitroxides and Alkoxyamines	279
3.10.2.1	Synthetic Strategies	279
3.10.2.1.1	Nitroxides	279
3.10.2.1.2	Alkoxyamines	284
3.10.2.2	Nitroxides and Alkoxyamines for NMP	287
3.10.2.2.1	Development of nitroxides	287
3.10.2.2.2	Development of alkoxyamines	293
3.10.3	Features of Nitroxide-Mediated Polymerization	294
3.10.3.1	Kinetics of Homogeneous NMP	294
3.10.3.1.1	Theoretical consideration	294
3.10.3.1.2	The dissociation rate constant $k_{\rm d}$	295
3.10.3.1.3	The recombination rate constant $k_{\rm c}$	297
3.10.3.1.4	Kinetics enhancement	298
3.10.3.2	Range of Monomers for NMP	298
3.10.3.2.1	Homopolymerization	299
3.10.3.2.2	Random copolymerization	300
3.10.3.3	Polymerizations in Aqueous Dispersed Media	302
3.10.3.3.1	Aqueous miniemulsion polymerization	302
3.10.3.3.2	Aqueous emulsion polymerization	304
3.10.4	Advanced Architectures and Materials by NMP	305
3.10.4.1	Chain-End Functionalized Polymers from NMP	305
3.10.4.1.1	Alpha-functional polymers	305
3.10.4.1.2	Omega-functional polymers	306
3.10.4.2	Diblock and Triblock Copolymers by NMP	307
3.10.4.2.1	General trends	307
3.10.4.2.2	Monomer sequence	333
3.10.4.2.3	Microphase separation/nanostructuration	334
3.10.4.2.4	Self-assembly in aqueous solution	334
3.10.4.3	Complex Macromolecular Architectures	334
3.10.4.3.1	Combination of NMP and other polymerization methods	334
3.10.4.3.2	Cyclic polymers	335
3.10.4.3.3	Star polymers	335
3.10.4.3.4	Grafted and comb polymers	336
3.10.4.3.5	Hyperbranched polymers	337
3.10.4.4	Biomaterials	337
3.10.4.4.1	Glycopolymers	338
3.10.4.4.2	Bioconjugates	338
3.10.5	Conclusions and Perspectives	341
Keferences		342

3.10.1 Introduction

3.10.1.1 Historical Background

Until 15 years ago, living anionic and cationic polymerizations were the only available methods to reach a high degree of structural and compositional homogeneity of polymers before recent developments in macromolecular synthesis provided a new synthetic tool to easily achieve complex macromolecular architectures: controlled/living radical polymerization (CLRP). This general term gathered several novel free-radical polymerization techniques that enable a high degree of control to be reached. Indeed, free-radical polymerization differs from ionic polymerization by (1) its relative ease of use (only dissolved oxygen has to be eliminated), (2) the broad range of vinylic monomers that can be polymerized by a radical mechanism, and (3) the numerous processes that can be implemented (bulk, solvent, emulsion, dispersion, etc.). However, the main limitation of free-radical polymerization is the total lack of



Figure 1 General concept of controlled radical polymerization (CLRP).

control over the molar mass, the molar mass distribution, the chain-end functionalities, and the macromolecular architecture. Therefore, bringing together the ease of use of free-radical polymerization with the high standard of control provided by living ionic polymerization, within a single polymerization process, simply brought about a revolution in the field of macromolecular synthesis.

In this view, various CLRP methods have been developed since the early 80s, each of them based on a different mechanistic approach and having encountered more or less success over the years. Basically, whatever the involved mechanism, their joint, key feature is the establishment of a dynamic equilibrium between propagating radicals, $[P^{\bullet}]$, and various dormant species (i.e., end-capped, thus unable to propagate) throughout the polymerization process in order to decrease the occurrence of irreversible termination reactions to an extremely low level. The so-obtained equilibrium (**Figure 1**) is triggered and governed by thermal, photochemical, and/or chemical stimuli. For the success of such an approach, a polymer chain should spend most of the polymerization time under its dormant state.

Among the most well-established methods deriving from this concept is nitroxide-mediated polymerization (NMP),¹⁻⁴ atom-transfer radical polymerization (ATRP),⁵⁻⁸ and reversible addition-fragmentation chain transfer (RAFT).⁹⁻¹¹ NMP was historically the first and represents perhaps the easiest CLRP technology to apply. The aim of this chapter is to offer the readers a global overview of NMP from its emergence to the latest advances. It covers achievements in the synthesis of nitroxides and alkoxyamines and their development for NMP, detailed kinetic aspects of NMP including the range of monomers that can be controlled as well as its application in homogeneous and heterogeneous media. Functionalization methods, along with the synthesis of block copolymers and complex architectures together with bioconjugates/biomaterials, are also presented. However, due to a too large number of publications, hybrid materials involving NMP and (in) organic supports (silica, quantum dots, magnetite, carbon nanotubes, titanium oxide, Merrifield resin, etc.) are not covered. The reader looking for a more exhaustive point of view about this field is referred to the following review articles: Ghannam et al.¹² and Brinks and Studer.¹³

3.10.1.2 General Considerations

In an ideal living polymerization process such as living anionic polymerization, all polymer chains are created at the beginning of the polymerization and then grow homogeneously until the monomer is depleted. However, this phenomenon cannot be observed in a radical process due to the propensity of radicals to undergo self-termination. The control/livingness can only be achieved in the presence of reagents able to reversibly deactivate propagating radicals and to establish a rapid equilibrium between active and dormant species. An ideal living polymerization system should exhibit (1) a linear evolution of the first-order kinetics ($\ln[1/(1 - \text{conversion})]$) with time, accounting for a constant propagating radical concentration, (2) a linear increase in the number average molar mass, $M_{n\nu}$, with monomer conversion, (3) low polydispersity indexes (PDIs), $M_w/M_{n\nu}$ (4) a quantitative α - and ω -functionalization, and (5) the possibility for polymer chains to grow again when additional monomer is introduced, allowing block copolymers to be synthesized.

The rate of termination (k_t) is proportional to the square of the total radical concentration, while the rate of propagation $(k_{\rm p})$ is directly proportional to the total radical concentration. Thus, a first strategy to suppress termination is to lower the macroradical concentration. This was achieved by Otsu and Yoshida¹⁴ and Otsu¹⁵ with dithiocarbamate compounds. Nevertheless, the first real system that led to a successful living and controlled polymerization was developed by Solomon et al.¹ In their patent, they describe the use of nitroxides and alkoxyamines as a route to control the radical polymerization of several monomers, including acrylates and styrenics. This work was derived from their previous studies on initiation, where they used nitroxides as radical-trapping agents.³ Since this pioneering work, Georges et al.,² followed by many others, provided experimental proofs that this system is effective for controlling the polymerization of several vinyl monomers. The NMP was born.

NMP is based on a reversible termination mechanism between the growing propagating (macro-)radical and the nitroxide, acting as a controlling agent, to yield a (macro) alkoxyamine as the predominant species. This dormant functionality generates back the propagating radical and the nitroxide by a simple homolytic cleavage upon temperature increase. When the latter is judiciously chosen, an equilibrium between dormant and active species, namely the activation-deactivation equilibrium, is established (**Figure 2**). This equilibrium presents the advantage of being a purely thermal process where neither a catalyst nor a bimolecular exchange is required. The polymerization kinetics are governed by both this activation-deactivation equilibrium (with $K = k_d/k_c$, the activation-deactivation equilibrium constant) and the persistent radical effect (PRE)¹⁶ (see Section 3.10.3.1.1 for details).

NMP was originally initiated by a bicomponent pathway, comprising a classical thermal initiator, such as 2,2'azobisisobutyronitrile (AIBN) or benzoyl peroxide (BPO), in combination with 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO, **Table 1**, 1) as the stable free nitroxide.² This system has the advantage of using classical radical polymerization processes with the only addition of free nitroxide. This initiating system can be also highly desirable from both the economic and practical points of view.



Figure 2 Activation-deactivation equilibrium in nitroxide-mediated polymerization. (a) Bicomponent initiating system and (b) monocomponent initiating system.

Fine-tuning the [nitroxide]₀/[initiator]₀ ratio is of high importance since it controls the kinetics of the polymerization. The polymerization rate is indeed governed by the amount of nitroxide in excess present after the initiation step.¹⁷ As a consequence, the activation-deactivation equilibrium is shifted toward dormant species that slow down the polymerization rate. All thermal initiators suffer from the difficulty to determine precisely the efficiency of the primary radicals produced by thermal decomposition to induce the polymerization (for instance, due to cage effect and induced decomposition) and also the nature of the initiating group since the majority of these primary radicals undergo rearrangement or fragmentation reactions.¹⁸ These phenomena lead to poorly reproducible polymerization kinetics and to ill-defined polymer end-groups. The [nitroxide]₀/[initiator]₀ ratio originally used was 1.3.² Recently, Dollin et al.¹⁹ revisited the influence of this ratio over the kinetics and showed that if this value is finely optimized (the ratio depends on the targeted molar mass and can be decreased down to 0.95 in certain conditions), the kinetics of the system could be strongly accelerated.

However, to circumvent this issue, the groups of Rizzardo¹ and Hawker^{20,21} developed the concept of unimolecular initiator that decomposes into both the initiating radical and the nitroxide. This compound, originally termed unimer, is called alkoxyamine initiator. Due to its particular structure, it leads, after dissociation, to a 1:1 release of initiating radical:nitroxide. Interestingly, the structure of the initiating end-group can be tuned to perform advanced macromolecular synthesis or postmodification chemistry (see Section 3.10.4.1 for details). Experimentally, it was observed that unimolecular initiators led to a better control over molar masses and molar mass distributions than bimolecular initiating systems.²⁰

3.10.2 Synthesis of Nitroxides and Alkoxyamines

3.10.2.1 Synthetic Strategies

3.10.2.1.1 Nitroxides

Numerous nitroxides have been designed and used for NMPs. The nitroxides discussed in the following paragraphs (1–65) are shown in Tables 1–3.

3.10.2.1.1(i) Nitroxide structures

Nitroxide radicals are compounds containing an aminoxyl group characterized by an unpaired electron delocalized in a π_{N-O} three-electron bond. This three-electron π system bond results from an overlap of the 2p_z orbitals of the nitrogen and the oxygen atoms. As a result, the N–O bond of an aminoxyl group has a bond order of 1.5 as indicated by the bond energy of about 100 kcal mol⁻¹, and the bond length d_{NO} (1.25 Å < d_{NO} < 1.30 Å), midway between the energy and the bond length of an N–OH single bond (53 kcal mol⁻¹; ~1.43 Å) and an N=O double bond (145 kcal mol⁻¹; ~1.20 Å).^{22,23} Therefore, the aminoxyl fragment can be seen as a combination of the two main mesomeric structures, which is the basis of nitroxide stabilization (Figure 3).

A considerable amount of research, both theoretical and experimental, has been devoted to the molecular and the electronic structure of nitroxides. From these works, it is well accepted that the spin density between the N and O atoms depends on various parameters such as the pyramidalization of the nitrogen atom, the resonance effects, or the polarity of the medium. The gain in energy from the delocalization of the unpaired electron has been calculated to be approximately $30 \text{ kcal mol}^{-1.24}$ It was recently suggested that this value was overestimated and a lower value of 23 kcal mol⁻¹, determined by Hel/HeII photoelectron spectroscopy, was proposed.²⁵

3.10.2.1.1(ii) Nitroxide stability

Nitroxide stability is a crucial parameter regarding almost all of their applications (NMP, spin trapping, organic synthesis, etc.). As previously mentioned, the stability of the nitroxyl radicals originates from the high delocalization energy of the strong π_{N-O} three-electron bond (23–30 kcal mol⁻¹). This phenomenon is responsible for the remarkable thermodynamic stability of nitroxides and explains why most of the reported nitroxides do not dimerize. Indeed, the gain in energy obtained from a weak O–O bond (~35 kcal mol⁻¹) deriving from the dimerization is lower than the loss of the resonance energy of the two aminoxyl groups.

Interestingly, nitroxide stability is strongly affected by the nature of the adjacent group attached to the nitrogen atom. For instance, depending on its nature, it can lead to an increase of its thermodynamic stability but also to side reactions that can

Entry	Structure	References	Entry	Structure	References
TEMPO 1		2, 21	14	N O	127
2a (R=H) 2b (R=Me)		128, 129	15		95
3	NH ₂	130	16	OH	95
4		115	17		95
5		116	18	OH N	119
6		126	19	OH N	119
7a (R=Me) 7b (R=Et)	HO R'N N R OH	124	20		120
8a (R=Me) 8b (R=Et)	HO R'' N R OH	124	21	OH N O	120
9a (R=Me) 9b (R=TBDMS)	RO N OR	124	22	OH N O.	118

Table 1 Structure of six-membered ring cyclic nitroxides

(Continued)



Table 2 Structure of acyclic nitroxides

Entry	Structure	References	Entry	Structure	References
DBNO 27		68	40a (R=OH) 40b (R=OTMS)		33
28		133	41		95
TIPNO 29		33	42		95
30		33	43	Me ₂ N O	95

(Continued)

Table 2 (Continued)

Entry	Structure	References	Entry	Structure	References
31	N O.	96	44		151
32	N O. C	140	45	HO	152
33		140	46		148
34		140	47	HO HO OH O	150
35		141	48	HO N OH O	148
BIPNO 36		143	49	HO HO N O	148
37a(R=Me) 37b (R=H)	N O. COOR	145	50		153
38		144	51		136
39		146			



Table 3 Structure of acyclic nitroxides bearing heteroatom



Figure 3 Mesomeric structures of nitroxides.

have the opposite effect. As an illustration, the delocalization of the single electron on the aromatic ring of compound **66** (Figure 4) not only leads to an extra-stabilization of the nitroxide but also to a high electron density on the carbon atom in para position, which is responsible for unwanted cross-combination reactions.²⁶

Most of the stable nitroxides are characterized by the presence of two sp³-carbon atoms as nitrogen substituents with no hydrogen atom directly attached to the vicinal carbon. However, if the steric strain induced by these groups is high enough, unimolecular decomposition of the nitroxide can occur via homolytic cleavage of the C–N(O) bond, leading to a nitroso compound and an alkyl radical.^{27,28}

Usually, nitroxides bearing a H atom in the α -position to the N atom are not stable and readily undergo disproportionation to form the corresponding hydroxylamine and a nitrone^{29–31} (Figure 5). The mechanism of this degradation has been thoroughly investigated by Bowman *et al.*³¹ who suggested the formation of a five-membered cyclic species during the transition state.



Figure 4 Instability of unprotected aryl nitroxides.

$$\begin{array}{c} 2 \\ R^{1} \\ R^{2} \\ R^{2} \\ R^{3} \\ H \end{array} \xrightarrow{R^{2} \\ R^{3} \\ H} \begin{array}{c} R^{1} \\ R^{2} \\ R^{3} \\ R^{3} \\ H \end{array} \xrightarrow{R^{1} \\ R^{2} \\ R^{3} \\ H \\ H \\ R^{3} \end{array} \xrightarrow{R^{1} \\ R^{2} \\ R^{2} \\ R^{2} \\ R^{2} \\ R^{3} \\ H \\ R^{2} \\ R^{2} \\ R^{3} \\ H \\ R^{3} \end{array} \xrightarrow{R^{1} \\ R^{1} \\ R^{-} \\ R^{-} \\ R^{3} \\ H \\ R^{3} \\ R^{3} \\ R^{3} \\ R^{3} \\ H \\ R^{3} \\ R^$$

Figure 5 Disproportionation of nitroxides.

However, some nitroxides containing a H atom in the α -position to the N atom are relatively stable and even isolable. For instance, bicyclic nitroxides are stable since the Bredt's rule excludes the formation of a double bond at the bridgehead of a bridged-ring system.³² Another interesting example is illustrated by nitroxides containing a H atom in the α -position to the N atom exhibiting a particularly high steric hindrance around the aminoxyl function. Many examples in the literature show that crowded nitroxides are stable, or at least persistent, even when bearing a H atom in the α -position to the N atom.^{33–37} Indeed, in such a situation, the five-membered cyclic species involved in the disproportionation mechanism is unfavored.³⁸ Consequently, access to the hydrogen atom, which is supposed to be abstracted, is strongly limited and leads to stable nitroxides.

3.10.2.1.1(iii) Nitroxide preparation

The synthesis of nitroxides can be carried out using various synthetic routes depending on the nature of the R^1 and R^2 groups.^{23,39-48} The most common pathways are briefly depicted in **Figure 6**. Typically, in almost all prepared and



Figure 6 Synthetic pathways to prepare nitroxides.

isolated nitroxides, the aminoxyl group is introduced by an oxidation step involving either an amine (route *a*) or a hydroxylamine (route *b*). Routes *c* and *e* rely on the spin trapping of alkyl radicals by nitrone⁴⁹ and nitroso compounds, respectively. These techniques demonstrated their efficiency for the *in situ* NMP⁵⁰ or more recently in the enhanced spin capturing polymerization process.^{51,52} Route *d*, which is less used, consists of the reduction of nitro compounds in the presence of sodium.⁵³ Route *f* is mainly devoted to electron spin resonance (ESR) experiments and consists of the oxidation of an aminyl radical in the presence of oxygen.⁵⁴

In the following paragraph, only oxidation of amines and hydroxylamines will be described. Usually, secondary amines are conveniently transformed into nitroxides in the presence of peracids, 41,42,55 alkyl hydroperoxide, 56 dimethyldioxirane, oxone, 57 or hydrogen peroxide. ⁵⁸ For instance, TEMPO (1) is prepared from oxidation of the corresponding piperidine⁴³ and *N-tert*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide (SG1, **Table 3, 52**) is produced at the industrial scale via oxidation of the corresponding aminosphophonate in the presence of peracetic acid. ⁵⁵ Direct oxidation of tertiary amines to nitroxides is also possible and is generally carried out using *m*-chloroperbenzoic acid (*m*CPBA) or H₂O₂/Na₂WO4.

The hydroxylamine or *N*-hydroxy compounds can be easily oxidized to nitroxides by a large number of oxidizing agents.⁶² The most suitable for this purpose are lead, mercury, or silver oxides. Air, in combination with a catalyst or used alone, may also turn hydroxylamines into nitroxides. For example, the 2,2,5-trimethyl-4-phenyl-3-azahexane-3-oxyl (TIPNO) nitroxide (**Table 2**, **29**) is obtained upon treatment of the corresponding hydroxylamine by a copper(II)-catalyzed oxidation at ambient temperature.³³ When multiple-step synthesis must be carried out prior to oxidation, the hydroxylamine can be protected either by O-acetylation⁶³ or O-silylation with *tert*-butylchlorodimethylsilane.^{64,65}

3.10.2.1.2 Alkoxyamines

The *N*-alkoxyamines R¹R²NOR, ³ also called O-alkyl hydroxylamines, consist of a large family of compounds, even if the most



Figure 7 Methods to prepare alkoxyamines.

studied molecules are the trialkyl-substituted ones, which could undergo a fragmentation into an alkyl R^{3*} and a stable nitroxide radical $R^1R^2NO^*$. Their syntheses have been recently reviewed.^{66,67} These compounds are mainly prepared according to four routes (Figure 7). Route *a* is based on the nucleophilic substitution of the hydroxylaminate anion on the corresponding alkyl halide. Route *b* involves the Meisenheimer rearrangement of allyl or benzyl amine oxides, whereas route *c* is related to the reaction between an oxoammonium salt with an olefin. Finally, route *d*, which is probably the most used, consists of the *in situ* generation of an alkyl radical followed by its trapping by a nitroxide. Routes *b* and *c* are quite specific and will not be detailed in the following section.

3.10.2.1.2(i) Reaction from a hydroxylaminate anion

This method requires the preparation of the corresponding hydroxylamine and its anion derivative. Nevertheless, the stability of both compounds is generally not very high, which explains the limited use of this pathway. For example, the hydroxylaminate anion of the SG1 is known to be unstable. Only the preparations of TEMPO²⁰ and di-*tert*-butyl nitroxide (DBNO, **Table 2**, 27)⁶⁸ alkoxyamine derivatives have been reported so far. In these examples, the hydroxylaminate anion

is generated by reaction of sodium hydride with the corresponding hydroxylamine, previously obtained by reduction of the aminoxyl radical with sodium ascorbate.

Moon and Kang⁶⁹ used the same nucleophilic substitution but prepared the hydroxylaminate anion of the TIPNO nitroxide by a one-electron reduction using potassium metal. Gigmes *et al.*⁷⁰ prepared alkoxyamines based on the 2,2-diphenyl-3phenylimino-2,3-dihydroindol-1-yloxyl (DPAIO) nitroxide by a one-pot process combining the reduction of the nitroxide by addition of phenyl hydrazine, the preparation of hydroxylaminate anion by addition of *t*BuOK, and then the nucleophilic substitution by the alkyl halide.

3.10.2.1.2(ii) Scavenging of an alkyl radical by an aminoxyl radical

Among the several methods already developed to prepare alkoxyamines, the easiest approach involves the *in situ* generation of carbon-centered radicals followed by its recombination with the nitroxide. Many different methods already exist to prepare carbon-centered radicals. The ones used to prepare alkoxyamines are described in Figure 8 and the most used are detailed in the following paragraphs.

3.10.2.1.2(ii)(a) Radical addition onto an olefin Addition of a radical species Y^* onto an olefin (Figure 8, route *a*) affords



Figure 8 Synthetic routes to generate alkyl radicals.

a new alkyl radical (with $R^3 = CH_2-Y$), which can be trapped *in situ* by the aminoxyl radical to yield the alkoxyamine. The nature of Y^{\bullet} can be varied with the structure of the radical precursor. Photochemical or thermal decomposition of common radical initiators (dialkyl, dialcyloxy, or diaryloxy peroxide,⁷¹ peroxalate, perester; etc.) generates oxygen-centered radicals (alkoxy and/or acyloxy radical), whereas azo derivatives⁷² generate alkyl radicals. The addition of acyloxy radicals is very interesting since the ester group can be easily converted into alcohol to afford telechelic polymers.⁷¹

Photochemical routes present a major advantage in these systems because the synthesis can be performed at room temperature to prevent decomposition of the alkoxyamine. However, the yields obtained are often moderate due to side reactions such as multiaddition or hydrogen abstraction.

3.10.2.1.2(ii)(b) Hydrogen abstraction Oxygen-centered radicals can be used to abstract activated hydrogens from carbon substrate to generate the carbon-centered radical (Figure 8, route b).⁷³ If the targeted alkoxyamine is stable enough, the alkoxy radical can be generated by thermal decomposition of dialkyl peroxide. For instance, the styryl-TEMPO alkoxyamine has been prepared by reacting ethylbenzene and di-tertbutylperoxide (DTBP) in the presence of TEMPO at 125 °C.^{20,74} In order to lower the reaction temperature, the hydrogen abstraction route has been employed under both photochemical and mild thermal oxygen-centered radical-generating conditions. The photolytic generation of alkoxy radicals can be achieved from dialkyl peroxide.75,76 Alternatively, generation of alkoxy radicals at relatively low temperature has been obtained from dialkylperoxyoxalate⁷⁷ and dialkyl hyponitrite.⁷⁶ Kirner et al.⁷⁸ and Sugimoto et al.⁷⁹ used the hydroperoxide decomposition catalyzed by cobalt complex,⁷⁹ copper halide, as well as by onium iodides.⁷⁸

3.10.2.1.2(ii)(c) Grignard reagent It was reported that alkylsamarium and other organometallic reagents (Grignard

reagent, alkyl lithium, alkyl titanium, etc.) can react with 2 equiv. of TEMPO to afford the corresponding alkoxyamine (**Figure 8**, route *c*).⁸⁰ Hawker *et al.*²⁰ used the same procedure to prepare benzylic TEMPO-based alkoxyamines. The proposed mechanism of this reaction is the oxidation of the organometallic compound by TEMPO to produce the alkyl radical, which is then trapped by the nitroxide. It was shown that this reaction cannot be used with aryl, alkenyl, or alkynyl Grignard reactants since their corresponding radicals are destabilized, thus preventing any oxidation.^{81,82} Only homocoupling of the reactant in good yield was observed but the mechanism was not elucidated.

The only alternative to prepare nonactivated alkyl-based alkoxyamine was recently proposed by Dichtl *et al.*⁸³ This new procedure is based on the β -fragmentation of an α -hydroxy alkoxyl radical that releases one alkyl radical (Figure 9). The α -hydroxy alkoxyl radical was produced by the reaction of H₂O₂ on a ketone giving an α -hydroxy hydroperoxide followed by a one-electron oxidation using CuCl.

The same group⁸⁴ extended this method to aldehydes RCHO and found that the reaction was more selective (only one alkyl group could be released) and generated less side products.

3.10.2.1.2(ii)(d) Reaction of metal complexes with alkenes Takeuchi and Kano⁸⁵ and Dao *et al.*⁸⁶ employed the commercially available manganese-based Jacobsen's catalyst, originally used for the enantioselective epoxidation of alkene,⁸⁷ to prepare a wide variety of functionalized alkoxyamines (Figure 8, route *e*). In this approach, the manganese complex is oxidized first (using DTBP) to the manganese-oxo species, which reacts with an activated olefin to afford the radical intermediate 67. The radical species is then trapped by the added nitroxide to give the compound 68, which leads to the desired alkoxyamine after reduction (Figure 10). This method can be performed under mild conditions with good yields (60–70%) and few side products.



 R^1 or $R^2 = Me$, Et, *i*Pr, cyclohexyl, ...

Figure 9 Synthesis of alkoxyamines from ketone/aldehyde compounds.



Figure 10 Synthesis of alkoxyamines using the Jacobsen's catalyst.

A similar approach was developed by Bothe and Schmidt-Naake⁸⁸ who used a Mn(salen)Cl complex, as a low-cost alternative to the Jacobsen's catalyst. In addition, it avoids the use of peroxide as long as the stirring of the reaction mixture can proceed in the presence of air. Krause *et al.*⁸⁹ modified the route developed by Hawker *et al.* for the preparation of alkoxyamines and employed the readily available manganese(III) acetate to obtain TEMPO and TIPNO derivatives in higher yields. Nevertheless, a stoichiometric amount of the manganese complex was necessary compared to the catalytic amount used in previous studies.^{86,88} Thiessen and Wolff⁹⁰ optimized this reaction by (1) applying ultrasound to obtain a better homogenization, and (2) developing an *in situ* generation of the active complex by continuous addition of Mn(OAc)₂ in the presence of KMnO₄ in toluene/acetic acid.

3.10.2.1.2(ii)(e) Decomposition of azo compounds Solomon *et al.*¹ together with Wang and Wu⁹¹ described the synthesis of the alkoxyamine from the direct reaction of AIBN with TEMPO at 60 °C for 4 h (Figure 8, route f). However, this method may appear limited because it concerns only commercially available azo compounds and the alkoxyamine have to be stable at the decomposition temperature of the azo initiator.

Guillaneuf *et al.*⁹² extended this approach by using ultraviolet (UV) irradiation to decompose azo compounds. Thermo-sensitive tertiary SG1-based alkoxyamines were synthesized using this very straightforward and metal-free procedure. This method requires a high [azo compound]/ [nitroxide] ratio since the cage effect is known to drastically decrease the azo compound efficiency at low temperature. A special one-pot procedure was also developed to prepare the 2-methyl-2-[*N-tert*-butyl-*N*-(1-diethoxyphosphoryl-2,2dimethylpropyl)aminoxy]propionic acid SG1-based alkoxyamine (BlocBuilder, **Table 4**, **71**).

3.10.2.1.2(ii)(f) Reaction of carbon-centered radicals with nitroso compounds or nitrones Akzo Nobel⁹³ and Ciba⁹⁴ companies have developed a one-pot synthesis of alkoxyamines from the reaction of AIBN with nitrosobenzene, nitric oxide, and nitrones (Figure 8, route *g*).

Closely related routes to alkoxyamines have also been described by Studer and Grubbs research groups. They both used nitroso compounds as radical traps. Studer *et al.*⁹⁵ used the reaction between hydrazine and lead oxide to promote the alkyl radical formation, whereas Grubbs *et al.*⁹⁶ generated the alkyl radical by reaction of an alkyl bromide with copper(I) complex. The advantage of this technique relies on the *in situ* production of the nitroxide. However, yields for alkoxyamines are often moderate and the method is limited to alkoxyamines bearing two identical alkyl groups in the structure.

Many authors and in particular Jerome and Detrembleur⁵⁰ developed the *in situ* NMP process by adding to a conventional radical polymerization mixture various nitroxide precursors such as sodium nitrite/nitric oxide,^{97,98} nitroso compounds,^{99,100} nitrones,^{94,101} amines,^{102,103} and hydroxylamines.^{104,105} In all cases, quite successful controlled/living polymerizations were obtained even if the nature of the control agent is difficult to identify.

3.10.2.1.2(ii)(g) Alkyl radical generation from halogenoalkane in the presence of metal complexes Tris-

(trimethyl)silyl radicals and organostannyl radicals are known to readily abstract halogen atoms from alkyl halides and then to produce alkyl radicals (**Figure 8**, route *i*). Braslau *et al.*¹⁰⁶ generated tris(trimethyl)silyl radical by hydrogen abstraction on tris(trimethyl)silane with *tert*-butoxyl radical (originated from the thermal decomposition of *tert*-butyl hyponitrite). Boger and McKie¹⁰⁷ showed that the mixture of an organo-iodide compound, TEMPO, and Bu₃SnH led to the formation of the corresponding alkoxyamine. The tributyltin radical, responsible for the halogen abstraction, can be obtained from hydrogen abstraction on tributyltin hydride by 1 equiv. of TEMPO. The same procedure was also used by other research groups to produce various alkoxyamines.^{108,109}

Matyjaszewski¹¹⁰ reported a simple and versatile method for the preparation of several TEMPO-derivative alkoxyamines based on atom-transfer radical addition (ATRA). This reaction involves halogen transfer from organic halides to Cu(I)complexes to produce the alkyl radical, which is then trapped by the nitroxide to afford the targeted alkoxyamine. Matyjaszewski *et al.*¹¹¹ and Matyjaszewski and Greszta¹¹² have shown that 1.05 equiv. of Cu(0) with respect to the alkyl halide is necessary for a quantitative reaction and a slight excess of nitroxide (1.2 equiv.) is needed to minimize alkyl radical termination reactions (**Figure 11(a**)).

The group of Tordo^{113,114} optimized the ATRA procedure to prepare various highly thermolabile SG1-based alkoxyamines in high yields in only 2 h at room temperature (Figure 11(b)).

A similar procedure was recently proposed by Thiessen and Wolff⁹⁰ who used various transition metals such as a combination of zinc and vitamin B12 or magnesium and SmI₂.

3.10.2.2 Nitroxides and Alkoxyamines for NMP

3.10.2.2.1 Development of nitroxides

The first study that demonstrated the viability of NMP was performed with styrene (S) and TEMPO as the nitroxide.² However, it rapidly appeared that TEMPO was only limited to styrene and styrene derivatives. In addition, high temperatures (125–145 °C) and long polymerization times (24–72 h) were usually required. To overcome these strong limitations, changes in the nitroxide structure were required. In this view, different families of nitroxides were synthesized and are detailed in the following paragraphs. We will focus here only on six-membered cyclic nitroxides and acyclic nitroxides since these compounds are the most used and the most efficient (see Tables 1–3).

3.10.2.2.1(i) Six-membered cyclic nitroxides

To expand the range of nitroxides as controlling agents for NMP, nitroxides with a structure similar to that of TEMPO (1) were first designed. Functionalized TEMPOs in para-position such as structures 2–4 were used to keep the same reactivity as TEMPO but with the introduction of a reactive group, able to prepare more complex macromolecular architectures (2) or to induce water solubility (3).

The first structure that allowed the range of monomers to be expanded was the 4-oxo-TEMPO (4). The group of Georges¹¹⁵ showed that acrylates could be polymerized at 145–155 °C in a pseudo-controlled fashion as long as polydispersities were still between 1.40 and 1.67 and the livingness of the polymerization was not totally proven. Matyjaszewski *et al.*¹¹⁶ developed

Table 4Functionalized alkoxyamines



(Continued)



Figure 11 Synthesis of alkoxyamines using the ATRA method.

nitroxide 5, substituted in the 4 position with a phosphonic acid group. An intramolecular H-bonding between the aminoxyl function and the phosphonic group induced an extra-stability and then significantly increased the polymerization rate.

It was however quickly realized that the main problem with TEMPO was the low value of the dissociation rate constant, k_{dy} of the corresponding alkoxyamine. Moad and Rizzardo¹¹⁷ showed that alkoxyamine homolysis rate is governed by a combination of polar, steric, and electronic factors; the steric one being predominant (see Section 3.10.3.1 for details). Many variations in the nature of the alkyl groups linked to the carbon in the α -position to the aminoxyl function were then investigated. For example, Mannan et al.¹¹⁸ and Miura et al.¹¹⁹⁻¹²¹ developed many six-membered cyclic nitroxides with spiro structures (18-24), which could be either mono (19) or disubstituted (21). The increase of the steric hindrance due to the spiro structure increased the dissociation rate constant of the (macro)alkoxyamines and led to successful NMP of S at 70 °C and n-butyl acrylate (nBA) at 120 °C using nitroxide 21.^{120,121} The nitroxide 24 was developed as a water-soluble analog to 21 and applied to the controlled polymerization of sodium 4-styrenesulfonate (SS) in water.¹²²

The group of Studer investigated the substitution of the methyl groups by ethyl moieties (15–17).¹²³ This change led to an important increase in the polymerization rate and a significant improvement of the control. Nevertheless, the best results were obtained with the tetraethyl-substituted nitroxide 17. However, its hydroxy analog 16 was found to be less stable and therefore less efficient.

The same group also developed TEMPO derivatives, in which the methyl groups at the 2 and 6 positions were replaced by hydroxymethyl and silyloxymethyl groups.^{124,125} To further increase the steric hindrance around the alkoxyamine oxygen atom, the remaining two methyl groups were also substituted with bulkier ethyl groups (7-8 and 10-11). It was shown that styrene polymerizations using hydroxy-substituted TEMPO derivatives were fast but not well controlled due to a high instability of these compounds. The substitution of the OH group by highly hindered silvloxy-group increased the nitroxide stability and made the corresponding alkoxyamines excellent mediator/initiators for styrene polymerization even at low temperatures (90-105 °C). Furthermore, well-controlled poly-(n-butyl acrylate)s (PnBA) with low PDIs have been prepared at the same temperature. It was also demonstrated that the separation of cis- and trans-compounds was not necessary since nitroxides 10 and 11 gave similar results. Siegenthaler and Studer¹²⁵ further increased the steric strain with structures 12-13 compared to nitroxide 11, leading to a marked change in the control of the polymerization. Controlled styrene polymerizations could be performed at a temperature as low as 70 °C using alkoxyamine 12. However, with too bulky substituents (13), fast and uncontrolled polymerizations were obtained.

Positioning of substituents on the ring was also investigated by Fischer *et al.*¹²⁶ They prepared the nitroxide 6 and observed a fivefold increase of the k_d value compared to 2. They explained this result by a decrease of the number of conformations that have to be 'frozen' in the transition state, which is costly in terms of activation entropy.

3.10.2.2.1(ii) Acyclic nitroxides

A drastic change of nitroxide structure was witnessed with the use of the commercially available DBNO (27). In particular, Moad and Rizzardo¹¹⁷ showed that the dissociation rate constant of a DBNO-based alkoxyamine was higher than any similar alkoxyamines based on cyclic nitroxides bearing tetra-methyl alkyl groups on the vicinity of the aminoxyl function. The first experimental studies were performed by the group of Catala^{68,131,132} where it was shown that the polymerization of styrene and substituted styrene monomers could be carried out at 90 °C with all the criteria of control/livingness. However, the polymerization rate was independent of the alkoxyamine concentration and remained governed by the production of thermal radicals in the medium.¹³² The *tert*-butyl-*tert*-amyl nitroxide 28 was tested by Moad *et al.*¹³³ to control the polymerization of MMA and appeared to be inefficient.

At that time, very few studies were devoted to open-chain or acyclic nitroxides. Only Reznikov et al.36 and Reznikov and Volodarsky³⁷ demonstrated that acyclic nitroxides bearing a hydrogen in the β -position could be stable without undergoing disproportionation if steric strain was high enough (see Section 3.10.2.1.1 for details). This led the groups of Tordo¹³⁴ and Hawker³³ to develop the TIPNO nitroxide (29). In his work, Benoit et al.³³ demonstrated for the first time that this nitroxide could be used for the controlled polymerization of a broad range of monomers (styrene and acrylate derivatives, dienes, etc.). They studied the effect of the variation of the alkyl substituents on the carbon bearing the hydrogen over the control and the living character of the polymerization. It was shown that a tert-butyl group (30) led to a loss of control and that substituted phenyl groups gave similar results to those found with the nonsubstituted counterparts. Grubbs et al.⁹⁶ developed the nitroxide 31 as an alternative to the TIPNO nitroxide with the advantage to be synthesized in situ before the polymerization from the commercially available tert-butyl nitroso compound. This nitroxide appeared to be less stable than TIPNO and then nonisolable. However, by an elegant process, the control of the polymerization of acrylate derivatives was possible using a preheating step at 125 °C before the monomer addition.¹³⁵ Using the same synthetic route, Guillaneuf et al.¹³⁶ developed a TIPNO analog bearing a chromophore (51) for application in nitroxide-mediated photopolymerization (NMP²) (Box 1).

Lagrille *et al.*¹⁴⁰ performed a study similar to the one reported by Hawker's group,³³ in which they prepared more hydrophobic and hindered nitroxides **32–34** by placing the phenyl group on the TIPNO backbone. Nitroxides with biphenyl **32**, *tert*-butylphenyl **33**, and phenanthryl **34** groups in place of phenyl moiety showed only little difference in the bulk polymerization of styrene.

The nitroxide **35** was prepared by substituting the isopropyl group by a phenyl group.¹⁴¹ The polymerization rate of styrene at 120 °C was higher than with TEMPO but similar to those reported with TIPNO and SG1. This nitroxide was also evaluated by Bertin¹⁴² who observed a very poor stability at 120 °C and low/moderate livingness of the resulting polymers. Flakus *et al.*¹⁴³ proceeded similarly by developing the 2,2,5-trimethyl-4-(isopropyl)-3-azahexane-3-oxyl (BIPNO, **36**), with two isopropyl groups in the β -position to the nitrogen. This compound presented similar results compared to TIPNO in term of control and livingness for the polymerization of S

Box 1

Nitroxide-Mediated Photopolymerization (NMP²)

By Y. Guillaneuf, University of Provence

Photopolymerization represents a rapidly emerging field in material science, mainly due to the numerous advantages associated with UV irradiation (very fast polymerization < 1 s, no volatile organic compounds released, etc.). For coatings, inks, photoresists, or dual-cure systems, the photopolymerization reaction is now recognized as particularly interesting and efficient. However, the main drawback of the photochemical processes is the lack of control of the polymer properties and the difficulty to prepare block copolymers. The photoiniferter technology, introduced by Otsu,¹³⁷ represents the only example to combine the photopolymerization process and the controlled radical polymerization. Despite very encouraging results, this method suffers from severe limitations and no other efficient controlled radical photopolymerization system has been described despite the industrial and academic growing needs in this field.

However, a significant breakthrough has been recently witnessed with the discovery that photolysis of alkoxyamines with a chromophore attached to the nitroxide moiety could lead to a reversible equilibrium between alkyl radicals and the nitroxide.¹³⁸ The chromophore must be located close to the aminoxyl function (i.e., one or two carbons) to enhance the intramolecular transfer responsible for the cleavage of the C–O bond.¹³⁶



Using an alkoxyamine based on nitroxide **51** (Table 2) as a photoiniferter for the polymerization of *n*BA, a linear growth of the polymer chain (80% conversion in 500 s) combined with a partial living character has been shown.¹³⁶ It also appeared that the k_d value can be modulated by simply varying the light intensity.¹³⁹ As a consequence, the NMP² behavior is governed by the value of the light intensity. This is a striking feature of NMP² compared to NMP, where the available temperature range is restricted by the nature of the monomers.

An original application of this novel technique was devoted to covalently bonded multilayered organic materials. Indeed, surface patterning with polymer layers is of high importance in many areas such as the production of integrated circuits, data storage devices, miniaturized sensors, microfluidic devices, biochips, and so on. By using the same alkoxyamine, a homogeneous acrylate-based film could be cured in less than 200 s followed by reinitiation to prepare a multilayered film with a thickness close to 50 mm and a good spatial resolution.¹³⁶



Beyond these achievements, this strategy will allow a novel chemistry based on photosensitive alkoxyamines to be developed, which could extend the range of monomers available for NMP and be implemented for controlled multilayered micropatterning applications.

and *n*BA, but exhibited lower polymerization times. Besides, this nitroxide is very stable (the half-life time of this nitroxide at 120 °C is above 24 h),¹⁴² which makes it one of the most stable and efficient nitroxides used in NMP.

Water-soluble TIPNO derivatives 37b-38 were also developped.^{144,145} The polymerization of SS was successfully achieved at temperatures below 100 °C using 37b under its deprotonated form and led to well-defined polymers. Nitroxide 38 is water-soluble under its protonated form and presents another interesting feature, which is its strong polarity. However, despite a more pronounced instability compared to TIPNO, nitroxide 38 is more efficient than TIPNO since no addition of free nitroxide is required for the controlled radical polymerization of *n*BA. This confirmed the result observed in the case of the polar SG1 nitroxide (see Section 3.10.3.1.2 for details), namely the strong influence of the polarity of the nitroxide on the efficiency of NMP.

Bisnitroxide **39** based on TIPNO was prepared by Ruehl *et al.*¹⁴⁶ and allowed a pseudo-controlled polymerization at temperatures as low as 70 °C to be performed. Decomposition of the corresponding styryl bisalkoxyamine presented an unusual behavior since the homolytic cleavage occurred twice as fast as the monofunctional counterpart. According to the ESR analyses, the authors claimed that conformational constraint induced strong spin–spin interaction and the near-proximity of the two nitroxide moieties led to an enhanced rate of homolysis. Nevertheless, Marque and Siri¹⁴⁷ showed that the analysis of Braslau could be erroneous due to both E_a/A compensation error effect (with E_a the activation energy and *A* the frequency factor) and the need for diastereoisomers purification prior to analysis of the decomposition kinetics.

Contrary to the previous studies, the groups of Braslau¹⁴⁸ and Studer⁹⁵ investigated the influence of the tertiary alkyl group (40–46) attached to the nitrogen due to its presumed influence on the outcome of the polymerization. Compared to TIPNO, structure **41** was more efficient as a regulator for the controlled polymerization of styrene and *n*BA.⁹⁵ However, the increased steric demand of the substituent also decreased its stability, hence providing a better control at lower temperature. The bulky adamantlyl group (**46**) led to only slightly better results than with TIPNO.¹⁴⁸

Various functional groups were also introduced on TIPNO via the tert-butyl group attached to the nitrogen. Hydroxy- (40a and 45), ketone- (44), and amido- (43) functionalized nitroxides were then designed with the same reactivity as TIPNO. A thorough analysis of styrene polymerization kinetics mediated by nitroxide 40a showed a slightly faster rate of polymerization when compared to results obtained with TIPNO.33 This was confirmed by the measurement of the k_d value that highlighted the occurrence of an intramolecular H-bonding,¹⁴⁹ stabilizing the free nitroxide and then increasing the alkoxyamine decomposition. This phenomenon led Harth et al.¹⁵⁰ to prepare the nitroxide 47 in order to maximize intramolecular H-bonding. The polymerization of various monomers presented all the characteristics of a controlled/living system with rates of polymerization of about 1 order of magnitude higher than with TIPNO. Following this concept, Braslau et al.¹⁴⁸ prepared the nitroxides 48-49, where the diol 48 exhibited a similar behavior compared to 40a, that is, a slight increase of the rate of styrene polymerization compared to TIPNO. However,

structure **49** showed a poorer control compared to TIPNO, which was explained by MOPAC calculations. The diols are expected to be proximal to the nitroxide oxygen in **48**, but distal to the nitroxide oxygen in **49**, thus preventing H-bonding to occur.

3.10.2.2.1(iii) Acyclic nitroxides bearing a heteroatom

A major breakthrough in NMP was witnessed when the group of Tordo proposed the β -phosphorylated nitroxide **52**, called SG1 or DEPN.¹⁵⁴ This nitroxide was found to be one of the most potent and versatile nitroxides used in NMP so far. This is due to the large value of the C–P bond length that allows a high steric demand in combination with a good thermal inherent stability.¹⁵⁵ In addition, the presence of the polar phosphoryl group allowed the dissociation rate constant of SG1-based alkoxyamine with the polarity of the alkyl moiety to be tuned¹⁵⁶ (see Section 3.10.3.1.2 for details).

Marchand *et al.*¹⁵⁷ investigated the substitution of the *tert*butyl group on the carbon in the α -position to the aminoxyl function by various fragments. For instance, with 2-ethylhexyl, they found that structure **53** was less efficient than SG1 for the polymerization of *n*BA. This study highlighted the delicate compromise already faced with SG1 and the difficulty to find other stable and efficient β -phosphorylated nitroxides for NMP. Kim *et al.*¹⁵⁸ prepared the nitroxide **54** as a SG1-type nitroxide, further involved in the synthesis of multifunctionalized alkoxyamines. Well-defined star polymers were then obtained at 115 °C, but the change of the *tert*-butyl group by a methyl group was not evaluated.

Contrary to hydroxyl-TIPNO **40a**, the hydroxyfunctionalized SG1 **55** developed by the group of Tordo¹⁵⁹ did not exhibit H-bonding between the alcohol and the aminoxyl function but between the alcohol and the phosphoryl group. Nevertheless, this interaction increased the k_d value since the stabilization occurred only for the nitroxide and not for the alkoxyamine since very high steric hindrance around the aminoxyl moiety should disrupt the intramolecular H-bonding.

The synthesis of new nitroxides, bearing either a *tert*-butyl **57** or a *tert*-octyl group **56** and various bulky phosphonate groups in the β -position to the nitrogen, was also reported.²⁷ The polymerization of styrene mediated by nitroxides **56** was controlled whatever the nature of the phosphonate group. Nevertheless, M_n s obtained where not in good agreement with theoretical values. A deeper investigation showed that the highly sterically hindered nitroxides **56** decomposed by homolytic cleavage of the C–N bond into a *tert*-octylnitroso compound and a cyclohexyl radical bearing the phosphonate group. A polystyrene (PS) macroradical was then trapped by the nitroso compound to form a TIPNO-type macronitroxide, able to control the polymerization.

Le Mercier *et al.*¹¹⁴ studied the influence of the substituents linked to the phosphorous atom (60–62). By replacing the ethoxy group by bulkier alkyl fragments, the dissociation rate coefficients increased drastically. For example, k_d of the styryl-alkoxyamine based on nitroxide 62 was 25 times higher than k_d of styryl-SG1 (52). This increase is still compensated by a lower thermal stability. Styrene polymerization was then performed at 75 °C with good control when low or moderate M_n s were targeted.¹¹⁴ The use of such a crowded nitroxide not only led to a lower reaction temperature but also to a lower rate of recombination due to the steric hindrance, causing a loss of control and livingness for high-molecular-weight polymers.¹⁶⁰ The nitroxide **58** was also prepared in order to investigate whether the β -hydrogen atom could be carried by a carbon other than the phosphonate-substituted carbon.³⁴ The polymerization of styrene carried out using **58** appeared much faster than in the presence of SG1 but with a poor control, which was certainly due to the difficulty of the nitroxide to efficiently trap alkyl radicals for steric reasons.

Drockenmuller and Catala¹⁶¹ introduced a sulfoxide moiety as a strong polar group in the γ -position to the oxygen atom (63), which allowed well-defined PSs to be synthesized at low temperature. The same authors also examined the effect of the stereochemistry on the polymerization kinetics of ethyl acrylate.¹⁶² Experiments were carried out in the presence of two enantiomerically pure mixtures of N-tert-butyl-N-(1-tert-butyl-2-ethylsulfinyl)propyl nitroxide; that is, a 1:1 $S_S R_B R_{\alpha}/R_S S_B S_{\alpha}$ and a 1:1 $S_S S_B S_{\alpha}/R_S R_B R_{\alpha}$ racemic mixtures. The different stereochemistry induced various conformations leading to different physical and chemical properties for nitroxides 63 and 64 (nuclear magnetic resonance (NMR) shifts, ESR couplings, etc.). This is due to the orientation of the sulfoxide dipole toward the nitroxide moiety. The dissociation rate constant is then strongly dependent on the stereochemistry, contrary to the recombination rate constant. The use of nitroxide 63 allowed the polymerization of ethyl and *n*BA to be controlled at 90 °C. Even though this nitroxide was among the more efficient compound developed for NMP, its synthesis required many steps and a tedious purification. Nesvadba et al.¹⁶³ prepared the easily accessible nitroxide 65 bearing an amido fragment. However, the polymerization of S and nBA exhibited a partial controlled only, which was explained by the low thermal stability of the nitroxide.

3.10.2.2.2 Development of alkoxyamines

Once the groups of Rizzardo and Hawker developed the concept of unimolecular initiator (see Section 3.10.1.2 for details), the influence of both the structure of the nitroxide and the released alkyl radical were studied.

The use of alkoxyamines exhibiting structures close to dormant species is an unwritten law and this explains why the 1-phenylethyl (also termed styryl) fragment represents the vast majority of the synthesized alkoxyamines, whatever the nature of the nitroxide. Functionalized styryl fragments were also designed to provide a selective attachment point for further conjugation (see Section 3.10.4.1 for details).

The 1-carboxyethyl radical, as a model of polyacrylates, was also occasionally found in the literature,^{118,164} although first studies showed that the styryl radical is also efficient to initiate the polymerization of acrylate derivatives.

However, the initiation step in NMP is rather complex. Chauvin *et al.*¹⁶⁵ investigated experimentally and theoretically the influence of the dissociation rate constant of the alkoxyamine initiator in the case of S and *n*BA polymerizations. It was shown that the control depends. on the alkyl fragment, whereas the livingness is influenced by the nitroxide structure (**Figure 12**).

The use of a very labile SG1-based alkoxyamine drastically improved the controlled character of a bulk styrene polymerization. In that case, a crowded tertiary alkyl radical moiety instead of a secondary alkyl one increased the k_{d1} value from 5.0×10^{-5} to $1.7 \times 10^{-2} \text{ s}^{-1}$ at 90 °C. Additionally, Bertin¹⁶⁵ and Charleux¹⁶⁶ research groups showed that a very labile SG1-based alkoxyamine (BlocBuilder, **Table 4**, **71**) allowed the polymerization of *n*BA to be successfully performed without any initial addition of free nitroxide. In this case, high k_{d1} leads to the *in situ* production of free nitroxide in the early stage of the polymerization and this forces the recombination of alkyl radicals with nitroxides even at low monomer conversion. Chauvin *et al.*¹⁶⁵ rationalized this phenomenon by eqn [1], linking the k_d value of the initiating alkoxyamine to the propagation rate constant of the monomer:

$$\frac{k_{\rm p}}{k_{\rm d1}} \le 6.0 \times 10^5 \,\,{\rm L}\,{\rm mol}^{-1}$$
[1]

Recently, it was shown that the chemical structure of the initial alkoxyamine had a strong effect on the outcome of the polymerization.¹⁶⁷ Using imidazolidin-*N*-oxyl nitroxide-based alkoxyamines, it was observed that the 1-phenylethyl alkyl moiety led to a successful living and controlled polymerization of styrene, whereas the *p*-nitrophenyloxycarbonyl-2-prop-2-yl



Figure 12 Evolution of the M_n vs. conversion for the bulk polymerization of styrene at 90 °C mediated by various alkoxyamines: experimental M_n (symbols), modeling M_n (dotted and dashed lines), and theoretical M_n (solid line).

alkyl moiety failed to initiate the polymerization. It was stated that a slow, first monomer addition in combination with intermolecular H-transfer reaction consumed the initiating radicals and inhibited the polymerization. From a theoretical point of view, Gigmes *et al.*¹⁶⁸ studied the influence of both the rate of the first monomer addition and of the rate of recombination for the initiating alkyl radical and obtained results in good agreement with the experimental work of Bagryanskaya *et al.*¹⁶⁷ although total inhibition was not observed. The influence of H-transfer reaction between the initiating radical and the nitroxide was also evidenced.¹⁶⁹ Various TEMPO-based alkoxyamines with different tertiary methacrylate fragments were prepared and variation of the polymerization kinetics of styrene due to the H-transfer side reaction was observed.

All these results highlighted the crucial role of the alkoxyamine structure for NMP. The best alkoxyamine should then present a high dissociation rate constant value and a rate constant of first monomer addition at least equal to the propagation rate constant. This makes the determination of the dissociation and recombination rate coefficients of model alkoxyamines of high importance for further improvement of this process.

3.10.3 Features of Nitroxide-Mediated Polymerization

3.10.3.1 Kinetics of Homogeneous NMP

3.10.3.1.1 Theoretical consideration

The final elucidation of the NMP mechanism was obtained by the groups of Fischer¹⁶ and Fukuda,¹⁷⁰ who theoretically explained the minimization of the irreversible terminations by the PRE. Previously, Johnson *et al.*¹⁷¹ emphasized this phenomenon using theoretical modeling but without performing a full rationalization.

The PRE could be qualitatively explained as follows (Figure 13). We consider a compound (RY) that decomposes into a transient (R[•]) and a persistent radical (Y[•]), with the initial concentration of radicals equals zero. At the beginning of the reaction, the concentrations of both radical species increase linearly, as governed by the decomposition rate coefficient $k_{\rm d}$. This period (the pre-equilibrium regime) lasts until the total radical concentration becomes large enough so that radical species could react by bimolecular reaction (either self-termination of R[•] or recombination between R[•] and Y[•]). The irreversible self-termination led to a decrease of the concentration of R[•] and consequently to a slow accumulation of the persistent species Y[•] (which cannot self-terminate). Therefore, the recombination of transient and persistent radicals becomes more and more favored compared to the self-reaction, which inhibits itself as it proceeds, although it never completely ceases. This is the intermediate regime. Then, after a long reaction time, the concentration of transient radicals drops to zero and the persistent radical reaches its highest concentration, which corresponds to the initial RY concentration.

Two different theoretical analyses performed by Fischer and Fukuda led to two unusual rate laws (eqns [2] and [3]) for R^{\bullet} and Y^{\bullet} during the intermediate regime (Figure 13(a)).

$$[R^{\bullet}] = \left(\frac{k_{\rm d}[\rm RY]_0}{3k_{\rm t}k_{\rm c}}\right)^{1/3} t^{-1/3}$$
[2]

$$Y^{\bullet}] = \left(\frac{3k_{\rm t}k_{\rm d}^2[{\rm RY}]_0^2}{k_{\rm c}^2}\right)^{1/3} t^{1/3}$$
[3]



Figure 13 Concentrations of RY, Y[•], and R[•] vs. time in a double logarithmic plot with $[RY]_0 = 5.0 \times 10^{-2} \text{ M}$, $k_d = 10^{-2} \text{ s}^{-1}$, $k_t = 10^8 \text{ M}^{-1} \text{ s}^{-1}$. (a) $k_c = 10^7 \text{ M}^{-1} \text{ s}^{-1}$, (b) $k_c = 10^4 \text{ M}^{-1} \text{ s}^{-1}$.

The combination of eqns [2] and [3] conducted to eqn [4], showing that an equilibrium is set up even if the radical concentrations are unequal, with $[Y^{\bullet}]$ being much larger than $[R^{\bullet}]$.

$$k_{\rm c}[R^{\bullet}][Y^{\bullet}] = k_{\rm d}[\mathrm{RY}]_0$$
^[4]

Nevertheless, it must be noted that the equilibrium exists providing that the activation–deactivation equilibrium constant, *K*, obeys eqn [5]:

$$\frac{k_{\rm d}}{k_{\rm c}} = K < \frac{k_{\rm c} [\rm RY]_0}{4k_{\rm t}}$$
^[5]

In case this, requirement is not fulfilled, the cross-reaction between the transient and persistent radicals is not favored, and Y^{\bullet} behaves as a spectator, which means that $[R^{\bullet}]$ reaches a steady state (as it happens with a classical thermal initiator) and $[Y^{\bullet}]$ still linearly increases with time to reach the initial RY concentration (Figure 13(b)).

If eqn [5] is satisfied, the lifetime of RY is then drastically prolonged compared with a classical first-order kinetic decomposition occurring if a radical scavenger such as oxygen is present in the medium. When conditions for eqn [5] are not met (for instance, $k_c = 1.0 \times 10^4$ instead of $1.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$), the degradation of RY is very fast, that is, 10 s compared to 10^5 s if eqn [5] is fulfilled (Figure 13(b)).

The Fischer¹⁷² research group proved experimentally the unusual kinetic law for the nitroxide concentration following a $t^{1/3}$ dependence by monitoring the decomposition of the cumyl-TEMPO alkoxyamine in the absence and in the presence of an alkyl radical scavenger. Under appropriate conditions and after a short time period (typically a few milliseconds), an equilibrium between the alkoxyamine and the transient radical is established and the polymerization occurs, leading to a living macroalkoxyamine. In this case, by neglecting propagation events before the equilibrium period, the monomer concentration is then given by eqn [6].^{173,174}

$$\ln \frac{[M]_0}{[M]} = \frac{3k_p}{2} \left(\frac{k_d [\text{RY}]_0}{3k_l k_c} \right)^{1/3} t^{2/3}$$
 [6]

With the same and with some further minor approximations, it is also possible to show analytically that the PDI of the dormant chains is given by:^{173,174}

$$PDI = 1 + \frac{1}{DP_n} + \frac{[M]_0^2}{DP_n^2[RY]_0^2} \left(\frac{\pi k_p^3[RY]_0}{k_d k_t k_c}\right)^{1/2} erf(z)$$
 [7]

where erf(z) is the error function

$$\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_{0}^{z} e^{-t^{2}} dt$$
 [8]

and

$$z = (3k_{\rm p})^{1/2} \left(\frac{K[\rm RY]_0}{3k_{\rm t}}\right)^{1/6} t^{1/3}$$
 [9]

Equation [7] could be, respectively, approximated for initial and long time by:

$$PDI_0 = 1 + \frac{1}{DP_n} + \frac{8}{3} (k_d t)^{-1}$$
 [10]

and

$$PDI_{\infty} = 1 + \frac{[RY]_0}{[M]_0} + \left(\frac{\pi k_p^3 [RY]_0}{k_d k_c k_t}\right)^{1/2}$$
[11]

All equations described above supposed an ideal mechanism, that is, no side reactions or additives. Fischer also developed various equations in the case of (1) the presence of excess nitroxide,¹⁷⁵ (2) the addition of a thermal initiator,¹⁷⁵ (3) disproportionation between macroradicals and nitroxide,¹⁷⁶ and (4) decomposition of the nitroxide.¹⁷⁵

These equations, and in particular eqn [6], could then be used to determine the rate coefficients such as the activation-deactivation equilibrium constant. Nevertheless, this was experimentally difficult to obtain when high conversions are reached.¹⁷⁷ This is based on the inaccurate assumption that the initiator concentration (RY or dormant species in polymerization) does not change as the reaction proceeds. Tang *et al.*¹⁷⁸ then derived new equations to take into account the consumption of the initiator.

Using the equations described in the previous part (eqns [6]–[11]), it is possible to determine analytically the final PDI value, and the final conversion and the final macroalkoxyamine concentration, providing all kinetic rate constants are known. Interestingly, Fischer developed a predictive phase diagram,^{179,180} linking k_d and k_c values for a defined system (monomer, targeted DP_n, polymerization temperature) and the above-mentioned criteria. This diagram was built using the following equations assuming only k_d and k_c are unknown.

$$\frac{k_{\rm d}}{k_{\rm c}} \le \frac{k_{\rm p}[\rm RY]_0}{2\log(10)k_{\rm t}}\Phi_{\rm lim}^2$$
[12]

$$k_{\rm d}k_{\rm c} \ge \frac{\pi k_{\rm p}^3 [\rm RY]_0}{k_{\rm t}} \frac{1}{\delta_{\rm lim}^2}$$
[13]

$$\frac{k_{\rm d}}{k_{\rm c}} \ge \frac{(2\log(10))^3 k_{\rm t}}{9[\rm RY]_0 k_{\rm p}^3 t_{\rm 20}^2}$$
[14]

with Φ_{lim} the maximum fraction of dead chains, δ_{lim} the maximum residual polydispersity ($\delta = \text{PDI} - 1 - [\text{RY}]_0/[\text{M}]_0$), and t_{20} the time to reach 90% conversion.

The double logarithmic k_d versus k_c plot is depicted in **Figure 14**. The area is then divided into several areas. Below the solid line, the amount of dead chains is lower than the chosen criterion. Similarly, above the dotted line and the dashed line, the residual polydispersity and the duration of the polymerization are lower than the chosen criteria.

In many cases, this phase diagram can help to select a suitable nitroxide for a successful NMP experiment. Besides, this approach could also help to choose the polymerization temperature prior any experiment due to the temperature dependence of the k_d - k_c values. For instance, in the case of the DPAIO nitroxide, it helped to find suitable experimental conditions for a successful NMP of MMA.¹⁸¹

3.10.3.1.2 The dissociation rate constant k_d

The main equilibrium between dormant and active species is the key step in the NMP process. If K is too high, the nitroxide acts only as a spectator and the macroradical concentration is close to the classical steady-state value. In contrast, if K is too low, the



Figure 14 Phase diagram for a system with $k_p = 2000 \text{ M}^{-1} \text{ s}^{-1}$, $k_t = 1.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, $[\text{RY}]_0 = 0.05 \text{ M}$, limit criteria $\Phi_{\text{lim}} = 0.2$, $\delta_{\text{lim}} = 0.5$, and $t_{90} = 20 \text{ h}$.

polymerization is inhibited.^{16,168} Contrary to the recombination rate constant k_c , that can only vary in the $10^5-10^8 \,\mathrm{L\,mol^{-1}\,s^{-1}}$ range, the k_d can take a much broader range of values $(10-10^{-10} \,\mathrm{s^{-1}})$ between 20 and 120 °C), thus representing an efficient leverage to tune the polymerization outcome.¹⁸²

To avoid tedious synthetic and polymerization studies, the estimation of the dissociation rate constant, predicted on the basis of alkoxyamine and nitroxide structures, is highly desirable.

3.10.3.1.2(i) Determination of the k_d value

Due to the PRE, the monitoring of nitroxide and alkoxyamine concentrations cannot be employed. To obtain accurate measurements, the reversible recombination reaction must be suppressed by adding either alkyl radical scavengers or nitroxide radical reductants. As nitroxides are paramagnetic species, ESR is the most suitable technique.¹⁸³ Various alkyl radical scavengers were used, such as iodine,¹⁸⁴ oxygen,^{183,185} styrene,¹⁸⁶ labeled¹⁸³ and unlabeled¹⁸⁷ nitroxides, galvinoxyl radical,^{172,183} or hydroquinone.¹⁸⁸ Values of k_d have also been obtained by high-performance liquid chromatography^{117,189,190} and NMR spectroscopy (¹H¹⁹¹⁻¹⁹⁶ and ³¹P¹⁹⁷). Goto and Fukuda,¹⁹⁸ Goto *et al.*,¹⁹⁹ and Fukuda and Goto²⁰⁰ have used size-exclusion chromatography (SEC) to estimate the $k_{\rm d}$ of polymeric species in the presence of monomers. Once the recombination reaction is suppressed (large excess of alkyl radical scavenger and/or aminoxyl reducing agent and/or stability of the nitroxide during the timescale of the experiment), the values of k_d are similar, whatever the technique or the nature of the scavenger/reducing agent.

Many Arrhenius parameters were obtained and Gigmes *et al.*¹⁸² established that the frequency factor *A* is constant whatever the alkoxyamine structure (both alkyl or nitroxide moities) and is equal to $2.4 \times 10^{14} \text{ s}^{-1}$. Different values were proposed in the literature, which could be due to the A/E_a compensation error effect, as highlighted for nitroxide 39.¹⁴⁷ This allowed the absolute comparison of the stability of different alkoxyamines by examining the value of the activation energy.

3.10.3.1.2(ii) Influence of the alkyl fragment

The first attempt to rationalize the $k_{\rm d}$ values was to plot $E_{\rm a}$ or $\log k_{\rm d}$ versus the bond-dissociation energy, BDE(C–H), of the corresponding alkane leading to the radical, since the reactivity of radical precursors are generally related to the stabilization of the radicals derived from the cleaved/formed bonds. The first E_a (C-ON) versus BDE(C-H) plot for alkoxyamines was proposed by Ciriano et al.²⁰¹ for a short series of molecules based on TEMPO. Marque *et al.*^{149,183} extended the analysis to a large series of alkoxyamines, varying both the nitroxide and the alkyl moieties. They established a relationship, strongly dependent on the accuracy of the value of BDE(C-H), giving a rough estimation of the k_d value. Indeed, other effects such as steric and polar effects seem to occur when the decomposition of SG1-based alkoxyamines was studied. In that case, the alkyl fragments have to be divided into various families to obtain a linear relationship.113

To establish more accurate k_d estimations, Bertin *et al.*¹⁵⁶ developed a multiparameter approach, in which $\log k_d$ is described using the Hammett constants corresponding to polar inductive/field ($\sigma_{\rm U}$), steric (v), and stabilization ($\sigma_{\rm RS}$) effects of the leaving alkyl radical (eqns [15] and [16] for TEMPO- and SG1-based alkoxyamines, respectively):

$$\log k_{\rm d}({\rm s}^{-1}) = -14.06(\pm 0.69) + 14.25(\pm 1.15) \times \sigma_{\rm RS} \\ + 13.17(\pm 2.91) \times \sigma_{\rm U} + 5.76(\pm 0.66) \times \nu$$
 [15]

$$log k_{d}(s^{-1}) = -14.19(\pm 0.48) + 15.13(\pm 1.08) \times \sigma_{RS} + 20.14(\pm 1.64) \times \sigma_{U} + 6.79(\pm 0.39) \times \nu$$
[16]

Hence, they were able to selectively compare the influence of these three intertwined effects and they concluded that each effect depends on the nitroxide structure. It was shown that the polar effect mainly depends on the nitroxide moiety. For instance, the influence of the polarity of the leaving alkyl group on the homolysis is weak for TEMPO ($\sigma_{\rm U}$ <0.10), in contrast to a more polar nitroxide such as SG1.

Among the various alkyl fragments that have been studied,¹⁸² little of the data did not follow eqns [15] and [16]. This is generally due to stereoelectronic effects,²⁰² strengthening or weakening the C–O bond. Due to the presence of several heteroatoms close to the cleaved bond, several anomeric^{149,203} and anchimeric²⁰² effects take place, which can exhibit antagonist influences. Other effects such as long-range polar^{149,204} and steric^{113,149} effects were also observed and could have a nonnegligible impact.

The k_d value of macromolecular species has also been determined. The influence of the macromolecular feature depends on the nature of the monomer. Bertin *et al.*¹⁸⁷ showed no influence of the chain length on k_d for a PS-SG1 macroalkoxyamine, whereas a weak influence (threefold increase between DP 1 and 200) for PnBA-SG1 was noticed.²⁰⁵ For MMA, Guillaneuf *et al.*²⁰⁶ estimated a k_d value 30 times higher than the model monomeric alkoxyamine. This led to a study concerning the influence of the penultimate unit effect over the dissociation rate constant.²⁰⁷ It was found that if the penultimate unit is a tertiary alkyl fragment, the k_d value of the alkoxyamine drastically increased.^{207,208}

3.10.3.1.2(iii) Influence of the nitroxide fragment

In a similar way, the effects (stabilization of the radical center, polar and steric effects) observed for the alkyl fragment should

also occur for the nitroxide moiety. This led Marque²⁰⁹ to develop a multiparameter analysis (eqns [15] and [16]) for the alkyl fragment. For the sake of simplicity, the k_d values were estimated for the 1-phenylethyl fragment. In case the k_d value of the styryl-based alkoxyamine was not determined, it was estimated using eqns [15] and [16].

Usually, the two carbons in the α -position to the aminoxyl function are bound to hydrogen atoms or alkyl groups, which inhibits the resonance effect (delocalized polar effect). Therefore, the stabilization and polar effects were described by the electrical Hammett constant (σ_1), whereas the steric effect was taken into account by the Fujita steric constant (E_s).

The description of cyclic nitroxides required the development of two new ring constants for five-, six-, and eight-membered ring aminoxyl fragments as well as three new ring constants for seven-membered ring aminoxyl fragments. The ring constant values depend on the hybridization (sp^3/sp^2) and/or on the presence of substituents.^{126,209} This hybridization effect is related to the relief of the cyclic strain (taken into account by different individual steric constants r_{ir} included in the total Fujita steric constant), whereas the position of the substituent on the ring is related to the activation entropy ΔS^{x} effect. The smaller the number of conformations that has to be 'frozen', the smaller the activation Gibbs energy ΔG^{x} and consequently the higher the k_d .¹⁸²

Due to a too high steric hindrance for acyclic nitroxides, the molecule adopt a new conformation, which, therefore, prevents the steric effect to be considered as the sum of the Taft-type steric constants E_s of the two alkyl groups attached to the aminoxyl function. A levelled steric effect should then be used.²¹⁰ After taking into account these features, the equation used to estimate the k_d value is summarized by eqn [17].¹⁸²

$$log k_{d}(s^{-1}) = -5.68(\pm 0.12) - 2.65(\pm 0.16)$$
$$\times \sigma_{I} - 0.81(\pm 0.03) \times E_{s}$$
[17]

The few alkoxyamines not described by this equation are related to compounds subjected to intramolecular hydrogen bonding, which increase the k_d value.^{149,159} It is also interesting to note that the steric effect is far more important than the polar effect.

3.10.3.1.3 The recombination rate constant k_c

Contrary to the k_d value, the recombination rate constant k_c has been less studied. This is due to (1) the difficulty to perform experimental measurement as long as use of a laser flash photolysis (LFP) apparatus is required,^{211,212} (2) the difficulty to gain access to a wide range of alkyl radicals since specific radical initiator has to be designed,²¹¹ and (3) the fact that k_c values can only vary within 2 or 3 orders of magnitude $(10^5-10^8 \,\mathrm{L\,mol^{-1}\,s^{-1}})$.¹⁸² For these reasons, it was not considered as a main parameter to be tuned. Nevertheless, the polymerization of styrene mediated with nitroxides 12 and 13 was studied.¹²⁵ It was shown that varying k_c led to a drastic increase of the polymerization rate, even though k_d values were similar. If the k_c value is low enough, a loss of control and livingness occurs.

The most important study on k_c was performed by the group of Fischer.²¹¹ In particular, they confirmed only a slight variation of k_c with temperature as expected for a recombination of two radicals. More importantly, it was

shown that most of the temperature-dependence studies exhibit a non-Arrhenius behavior. In certain cases, such as the recombination of methacrylic alkyl radicals and SG1, the k_c value could even decrease with an increase of the temperature.²¹¹ This behavior depends on the congestion around the radical center for both the alkyl fragment and the nitroxide moiety.

3.10.3.1.3(i) Influence of the alkyl fragment

Due to the low number of alkyl radical structures measured so far, only one quantitative approach is available, which allows the various effects involved in the recombination reaction of alkyl radicals with nitroxides to be rationalized.²¹³ The log k_c versus BDE(C–H) plots of alkyl radicals showed a linear correlation.^{182,213} Furthermore, all regressions representing the different nitroxides intersected at the higher BDE(C–H) value (i.e., close to the BDE of methane at $3.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$), which corresponds to the diffusion-controlled rate constant.

The direct measurement of the recombination rate constant was only performed with model alkyl radicals due to the lack of suitable macroinitiors for LFP experiments. In this case, the influence of the polymer chain on the recombination rate constant has been investigated essentially by indirect methods; either by simulation²¹⁴ or from the determination of K.¹²⁵ K can be extracted from the slope of the $\ln([M]_0/[M])$ versus time plot,²¹⁵ calculated from ESR analyses,^{154,162} or measured by automatic continuous online monitoring of polymerization reactions (ACOMP).²¹⁶ The values of k_c obtained by the above-mentioned methods cannot be considered of very high accuracy due to imprecisions imparted by the determination of K and by the chain-length dependence for $k_{\rm d}$. Guillaneuf et al.²¹⁷ proposed a direct determination of the recombination rate constant between macroradicals and nitroxides by a method called radical nitroxide recombination-pulsed lamp polymerization-size-exclusion chromatography (RNR-PLP-SEC). This method uses a single-pulse PLP approach in combination with the analysis of the SEC molar mass distribution. The molar masses are used to determine k_{cr} similarly to the traditional method applied in the determination of the chain-transfer rate constants (i.e., the Mayo method and the full chain-length distribution method).

Contrary to the dissociation rate constant, the recombination rate constant exhibits a very high chain-length dependence where k_c for the macroradical is lower than k_c for the model radical. For instance, k_c for styryl radical and SG1 is $4.6 \times 10^6 \text{ Lmol}^{-1} \text{ s}^{-1}$ at $120 \,^{\circ}\text{C}$,²¹¹ whereas a 10-fold decrease was observed for the polystyryl radical ($5.3 \times 10^5 \text{ Lmol}^{-1} \text{ s}^{-1}$ at $120 \,^{\circ}\text{C}$).²¹⁷ The same trend was found for acrylate/SG1 system.^{211,216} In the case of poly(methyl methacrylate) (PMMA) macroradicals and SG1, the k_c value decreased by 2 orders of magnitude compared to the model radical.²⁰⁶ This result was assigned to a strong penultimate effect which also increased the dissociation rate constant but to a lower extent.^{206,207}

3.10.3.1.3(ii) Influence of the nitroxide fragment

Studies establishing a relationship between the structure of the nitroxide and the k_c value, and involving polar, steric, and stabilization effects are very scarce. Using experimental data,^{182,218–220} it was assumed that the main parameters involved in the recombination reaction were the stabilization (σ_L) and the congestion around the aminoxyl moiety (E_s).

The following bi-parameter correlation was then proposed¹⁸² (eqn [18]).

$$\log k_{\rm c}({\rm M}^{-1}~{\rm s}^{-1}) = 10.35~(\pm 0.11)~+~0.47~(\pm 0.17) \times \sigma_L \\ +~0.43~(\pm 0.02) \times E_{\rm s,tot} \qquad [18]$$

with $E_{s,tot}$ the total steric constant taking into account the two groups attached to the nitrogen. Here, only the four α , α' -substituents of the aminoxyl function have to be taken into account for the steric demand. In the case of acyclic nitroxides, one methyl of the *tert*-butyl group linked to the nitrogen and the β -hydrogen are located in the same plane as the aminoxyl function and do not interfere with the recombination.

As expected, the parameters for stabilization and steric effects are positive, in good agreement with the decrease of the k_c value with the increase in both the stabilization and the bulkiness of the aminoxyl radical. It is shown that the major effect is due to the congestion around the aminoxyl moiety (~90%) with a lower contribution of the stabilization effect (~10%). The $k_{c,0}$ parameter has a value ($2.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, eqn [18]), typical of the diffusion-controlled rate constant that should correspond to the scavenging of alkyl radicals by the hypothetically more reactive dimethylaminoxyl radical. These studies showed that only the four α, α' -substituents flanking the aminoxyl function governed the steric hindrance around the radical center. As a consequence, the k_c value is independent of the type of nitroxide, provided they have the same substituents and the same stabilization effect.¹⁸²

3.10.3.1.4 Kinetics enhancement

One of the main problems of reversible termination processes such as NMP is related to the longer polymerization time compared to conventional radical polymerization processes. This is due to the low concentration of propagating radicals, required to prevent/minimize self-termination events, as well as the slow accumulation of nitroxide due to the PRE.

Much effort has then been made to enhance the rate of NMP and this can be achieved by different manners. The group of Georges^{17,221} showed that organic acids such as camphorsulfonic acid²²¹ (CSA) as well as 2-fluoro-1-methylpyridinium *p*-toluene-sulfonate¹⁷ were able to increase the rate of styrene polymerization mediated by TEMPO. Strong acids such as CSA are known to react with TEMPO, thus decreasing the amount of the free nitroxide in the medium.²²² It was also reported that the recombination rate constant between model alkyl radical and TEMPO decreased in the presence of acid, due to a strong increase in the medium polarity.²²³ However, these additives caused the broadening of the molar mass distribution, particularly at the beginning of the polymerization.

Using a similar approach, the strong acids were replaced by efficient nitroxide-reducing agents such as ascorbic acid and reducing sugar compounds.^{224,225} Various α -hydroxy ketones and aldehydes, able to form such structures, were then investigated and the best combination was a glyceraldehyde dimer/ pyridine mixture.²²⁶

Another approach was developed simultaneously by Fukuda²²⁷ and Matyjaszewski²²⁸ research groups. They used long half-life time radical initiators, such as *tert*-butyl hydroperoxide or dicumyl peroxide, to decrease the concentration of the free nitroxide in the medium and enhance the polymerization rate while keeping low PDIs. This approach was investigated on a theoretical basis by Souaille and Fischer.¹⁷⁵ They found that the living character of the resulting polymer and the control of the molar mass distribution are not significantly altered if the external initiation rate is below 1% of the initial dissociation rate. This beneficial effect is not directly due to the formation of additional growing chains but due to the control of the concentrations of both radical species. In this case, up to a 10-fold increase in the polymerization rate can be observed.

Another way to accelerate the polymerization kinetics would be to weaken the NO-C bond. Some acylating agents such as acetic anhydride (Ac₂O) were successfully employed for TEMPO-mediated polymerization.²²⁹ A controlled PS-TEMPO at 125 °C in 5 h with $M_{\rm p}$ up to 150 000 g mol⁻¹ and a PDI close to 1.4 was obtained. The acceleration feature was assigned to a reversible acylation reaction between the lone electron pair on the alkoxyamine nitrogen and the acyl group. The coordination of this acyl group to the nitrogen atom would induce a partial positive charge and result in a polarization of the NO-C bond. In contrast, Goto *et al.*²³⁰ determined the k_d value of a PS-TEMPO adduct in the presence of Ac₂O and did not detect any acceleration effect on the dissociation rate constant. They also proved that this effect was not related to an enhancement of the thermal polymerization. Interestingly, no degradation of TEMPO was witnessed at 110 °C in the presence of Ac₂O over a period of 15 h.230 Eventually, it was mentioned a possible coordination of the nitroxide with the anhydride, in good agreement with a previous study.231

Considering these results, different compounds such as acetylacetone or malonitrile have been tested as potential accelerating agents with TEMPO.²³² Hydrogen bonding between the two methylene protons and both the O and N atoms of the nitroxide or the alkoxyamine was proposed. Lansalot *et al.*¹⁶⁰ showed that the structure of the nitroxide directly influenced the effect of Ac₂O since the addition of Ac₂O on SG1-mediated polymerization did not lead to any rate enhancement. Supported by calculations of solvent-accessible surfaces, they also concluded that only the oxygen of the nitroxide could be accessible to additives, certainly conducting to a weak dipole–dipole interaction and a decrease of the instantaneous nitroxide concentration in the reaction medium. This result also explained the nitroxide structure dependency of the polymerization rate enhancement.

Chang and Studer²³³ developed a different approach to enhance the kinetics of TEMPO-mediated polymerization. Due to the well-known nitroxide interchange between macroalkoxyamines upon polymerization, a combination of TEMPO and a highly active nitroxide such as nitroxides 11, 16, or 17 was successfully proposed. For nitroxide additives with equilibrium constant values larger than *K* of PS-TEMPO by 3 orders of magnitude, an increase of the conversion by about a factor of 2 can be achieved. Significant increase of the polymerization rate was obtained with only 25% of the alkoxyamine additive with respect to the initial styryl-TEMPO. This result could be important since efficient alkoxyamines are more expensive than styryl-TEMPO and combining the two nitroxides could have industrial applications.

3.10.3.2 Range of Monomers for NMP

NMP has been employed so far for a vast number of different monomers, leading to homopolymers and copolymer architectures covering a wide spectrum of properties. Due to the very large number of articles, the following part intends to present only the main achievements.

3.10.3.2.1 Homopolymerization 3.10.3.2.1(i) Styrene and derivatives

Among the monomers exhibiting a controlled radical polymerization via NMP, styrene has probably been the most studied in terms of mechanism, kinetics, and potential side reactions. A large number of stable nitroxides have been tested and appeared to be quite efficient to lead to well-defined PSs, with good control over molar mass, molar mass distribution, and chain-end structure with an excellent ability for reinitiation, toward block copolymers.⁴ With most cyclic nitroxides the polymerization is rather slow and requires high temperatures (typically above 100 °C), but these features could be improved with either the use of acyclic nitroxides such as DBNO (Table 2, 27),²³⁴ TIPNO (Table 2, 29),^{33,134} and SG1 (Table 3, 52) 154,235 or by playing with the steric hindrance of TEMPO derivatives.¹²⁴ In the same way, the polymerization of styrene derivatives (i.e., styrene substituted on the aromatic ring) was performed with success using the same nitroxides. Those monomers were, for instance, para-substituted styrenes (F, Cl, Br, CH₃, OCH₃, CF₃, CH₂Cl), which did not behave very differently from styrene.^{236–238} Among them, an important derivative is chloromethylstyrene (CMS), also called vinylbenzyl chloride, which is a very interesting monomer allowing a variety of post-polymerization modifications.²³⁹⁻²⁴² The NMP led to well-defined homopolymers and block copolymers, 243,244 even though side reactions such as chain transfer were observed, due to the presence of the reactive chloromethyl group.²⁴⁵ Other substituted styrenes of interest are 4-acetoxystyrene, 4-tertbutoxystyrene, or even p-(1-methylcyclohexyloxy)styrene, the polymer of which is a precursor for poly(p-hydroxystyrene), also called poly(4-vinylphenol). The corresponding polymers were prepared via NMP, in particular block copolymers exhibiting phase separation properties.²⁴⁶⁻²⁴⁸

Fluorinated styrenic polymers have been prepared via radical polymerization using TEMPO or SG1 as mediators, for a potential application in the design of amphiphilic block copolymers used as stabilizers in supercritical carbon dioxide dispersion polymerization.^{249,250}

Other styrene derivatives were also considered as functional monomers for a multitude of potential applications. Among the possible aromatic substituting groups one may count: mesogens for liquid-crystalline copolymers, 251-253 luminescent phenylenevinylene units,²⁵⁴ alkyne groups,²⁵⁵ dimethyl phosphonate,²⁵⁶ and phtalimide as a precursor for aminomethyl group.²⁵⁷ Water-soluble styrene derivatives (the most important one being SS) are of particular interest for the design of amphiphilic block copolymers, in particular when they can be polymerized directly, without the need for a hydrophobic precursor. TEMPO (Table 1, 1) was first used as a mediator, mainly in organic solvent such as ethylene glycol and allowed well-defined homopolymers and derived amphiphilic block copolymers to be synthesized.²⁵⁸⁻²⁶⁰ Water-soluble nitroxides based on 1,1,3,3-tetramethylisoindolin-2-oxyl and 1,1,3,3tetraethylisoindolin-2-oxyl with an ionic group on the aromatic ring (either a quaternary ammonium or a sulfonate substituent) were used for the polymerization directly in water at temperatures above 100 °C.130 A water-soluble

carboxy derivative of TIPNO (Table 2, 37b) and the corresponding alkoxyamine allowed the polymerization of SS to be successfully achieved at temperatures below 100 °C and to lead to well-defined polymers, providing the first example of NMP in homogeneous aqueous solution below the boiling point of water.¹⁴⁵ With SG1 as a mediator, the aqueous phase polymerization temperature could also be decreased below 100 °C, leading to the same controlled behavior of the system.²⁶¹ Another water-soluble derivative of styrene is sodium 4-styrene carboxylate, the polymerization of which was controlled by TEMPO as described in an early report.²⁵⁸

Neutral, water-soluble styrenic monomers that have been polymerized in the presence of nitroxides are, for instance, those that bear a sugar moiety (see Section 3.10.4.4.1 for details) as a ring substituent leading to glycopolymers^{262–266} or styrenic macromonomers of poly(ethylene oxide).²⁶⁷

3.10.3.2.1(ii) Vinylpyridines

In addition to styrene, the other monomers that have been particularly well studied in TEMPO-mediated radical polymerization are 4-vinylpyridine (4-VP),^{268–271} 2-vinylpyridine (2-VP),^{272,273} and to a lesser extent 3-vinylpyridine (3-VP).^{274,275} The NMP led to a good control over the polymer characteristics and well-defined architectures could be easily produced, such as amphiphilic block or graft copolymers.^{276–280} Not only TEMPO was used as a stable radical mediator but also SG1, which led to well-controlled polymerization systems either in solution²⁸¹ or in emulsion initiated by a water-soluble poly (acrylic acid) (PAA) macroinitiator.²⁸²

3.10.3.2.1(iii) Acrylic esters

The TEMPO-mediated homopolymerization of *n*BA was tested in different conditions, but the problems arising from the too strong alkoxyamine C-ON bond made the synthesis of welldefined living polymers rather difficult.^{224-226,283} Other cyclic nitroxides²⁸⁴ or sterically hindered TEMPO analogs^{124,125} gave better results in terms of polymerization time and living character of the chains. The best results were however found with the acyclic nitroxides TIPNO, 33 SG1, 154, 285, 286 and TIPNO derivatives.144,287 Similarly, other acrylic esters were tested, with the same results as with nBA in terms of polymerization kinetics and control over molar masses. For instance, tertbutyl acrylate (tBA) is often used as protected acrylic acid (AA) to synthesize amphiphilic copolymers.^{288–291} In addition, 1,1,2,2-tetrahydroperfluorodecyl acrylate,²⁹² 2-hydroxyethyl acrylate (HEA),²⁹³ 2-hydropropyl acrylate,²⁹⁴ N-acryloylmorpholine,²⁹⁴ 2-(acryloyloxy)ethylbenzyldimethylammonium chloride,²⁶¹ poly(ethylene glycol) acrylate,²⁹⁵ 2-(dimethylamino)ethyl acrylate, 296,297 and finally trimethylsilyl propargyl acrylate²⁹⁸ have been studied, most of the time with a good success in term of control over the polymer characteristics.

3.10.3.2.1(iv) Acrylonitrile and acrylic acid

The NMP of acrylonitrile has seldom been studied in homopolymerization but more often in copolymerization, essentially with styrene since the resulting copolymer is of high importance for industrial applications. The controlled homopolymerization initiated by a TIPNO-based alkoxyamine showed good control until high molar masses.³³ However, as studied with SG1, the living character of the chains was not very good.²⁹⁹ The nitroxide-mediated homopolymerization of AA under its nonprotected form was performed in 1,4-dioxane solution at 120 °C and was initiated by an SG1-based alkoxyamine. The results showed a good control over the polymerization and the chain-end structure toward moderate molar mass polymers.^{300,301} When high molar masses were targeted, chain transfer to the solvent and to the polymer had a nonnegligible effect on the structural quality. Those living PAA macroalkoxyamines found applications in the synthesis of amphiphilic diblock copolymers, either in solution³⁰² or in aqueous emulsion.^{303–306} They were also employed as stabilizers/ compatibilizers of carbon nanotubes/polymer composites.³⁰⁷

3.10.3.2.1(v) Acrylamide, N-substituted and N,N-disubstituted acrylamides

The NMP of acrylamide was studied by NMP using SG1 as the nitroxide and a reasonable quality of control with possibility of extension toward diblock copolymers chain was observed.^{308,309} Among the N-substituted acrylamides, the most common one is certainly N-isopropylacrylamide (NIPAAm), but very few works have however been performed via NMP so far.³¹⁰ Another N-substituted acrylamide, tert-butylacrylamide, was polymerized using SG1 as a mediator. Good control over the polymer was observed when low molar mass chains were targeted; at higher molar masses, broader molar mass distributions were obtained, assigned to chain transfer to the monomer.³¹¹ In comparison, N,N-dimethylacrylamide (DMAAm) and to a lesser extent N,N-diethylacrylamide (DEAAm) received a greater interest. The former one leads to a fully water-soluble polymer, whereas PDEAAm exhibits a low critical solution temperature in the same range as that of PNIPAAm. With TEMPO, the DMAAm homopolymerization results were not fully encouraging since rather poor control was observed, that is, broad molar mass distributions for low molar mass polymers and block copolymers.^{277,278,312,313} Better results in terms of homopolymer structure and livingness were actually achieved with SG1.^{261,281,294,314,315} The polymerization of DEAAm was studied in the presence of SG1 as a mediator, using PAA-based macroalkoxyamines as initiators. The systems led to amphiphilic block copolymers formed directly in an aqueous dispersion and to self-stabilized nanogels.282

3.10.3.2.1(vi) Dienes

The NMP of conjugated diene monomers such as butadiene and more importantly isoprene was studied from the early times of the technique by both the groups of Keoshkerian *et al.*²²⁵ for isoprene and Pradel *et al.*^{316,317} for butadiene, in both cases with TEMPO. A detailed study was published quite recently for isoprene as a monomer and showed that the optimum temperature was 145 °C with both TEMPO and 4oxo-TEMPO (**Table 1**, **4**) as mediators, although side reactions were observed.³¹⁸ Well-defined homopolymers and copolymer architectures based on either butadiene or isoprene could be achieved using TIPNO, demonstrating the ability of the technique to provide high molar mass polydienes with low PDIs.^{319–321} The controlled radical copolymerization of chloroprene or isoprene with dimethyl 1,3-butadiene-1-phosphonate was later investigated in the presence of TEMPO.³²²

3.10.3.2.1(vii) Methacrylic esters

To date, only the DPAIO nitroxide was able to control efficiently the homopolymerization of MMA.^{181,196} Acyclic aromatic nitroxides mimicking the DPAIO structure were also prepared and tested for the polymerization of MMA.^{323,324} Such compounds allowed the preparation of PMMA with a controlled character at low to moderate conversion (<45%).

For other nitroxides, in particular TEMPO and other cyclic ones, side reaction of β -hydrogen transfer was shown to totally impede the achievement of a controlled polymerization and led to 100% of dead chains, all with a vinylidene-type terminal unsaturation.^{133,176,194,325} However, this difficulty did not prevent the synthesis of block copolymers, providing the first block was well controlled (i.e., PS) and the methacrylate monomer was polymerized in a second step.^{325,326} With SG1, the situation was more contrasted and actually depended strongly on the concentration of free nitroxide in the system: extensive self-terminations of the propagating radicals at low SG1 concentration.^{327,328} In consequence, appropriate experimental conditions could not be found for the controlled homopolymerization of methacrylic esters.

3.10.3.2.1(viii) Cyclic ketene acetals

Radical ring-opening polymerization has been essentially developed by Bailey *et al.* in the mid-80s.^{329,330} With appropriate monomers such as cyclic ketene acetals, the method leads to polyesters, while keeping all the advantages of a free-radical polymerization process. With NMP, however, results are very scarce and only TEMPO was used so far in the polymerization of 2-methylene-1,3-dioxepane initiated by di-*tert*-butyl peroxide at 125 °C.³³¹

3.10.3.2.2 Random copolymerization

3.10.3.2.2(i) Kinetic and theoretical studies

The nitroxide-mediated copolymerization was far less studied than the homopolymerization although a large number of polymers produced via a radical polymerization mechanism are actually random copolymers.³³² Early kinetic and mechanistic studies were published by Zaremski *et al.* for the TEMPO-mediated copolymerization of styrene with various comonomers.^{188,333–335} They discussed various regimes depending on the ability or disability of the second monomer to undergo a controlled/living NMP and determined experimentally the activation–deactivation equilibrium constants for many of those systems.

In a more recent study, Charleux *et al.*³³⁶ studied the theoretical features of the activation–deactivation equilibrium in nitroxide-mediated copolymerization and applied it to the SG1-mediated copolymerization of methyl methacrylate with a low percentage of styrene (typically in the 4–9 mol.% range). They actually demonstrated that the system exhibited all the characteristics of a living/controlled polymerization, which was explained by the following features: (1) the overall concentration of propagating radicals was strongly reduced by the copolymerization effect and the irreversible termination reactions undergone by the MMA/SG1 system were hence slowed down; (2) isolated styrene subunits were incorporated into the chains and the terminal one promoted the reversible deactivation by the SG1 nitroxide; and (3) the MMA penultimate unit effect enhanced deactivation of the so-formed styryl-SG1
alkoxyamine, which then exhibited a reduced dissociation temperature with respect to styrene homopolymerization (**Box 2**).^{208,337} Consequently, the polymerization could be performed efficiently in the 70–90 °C temperature range. This technique was later expanded to a series of methacrylate monomers such as methacrylic acid (MAA),³³⁸ poly(ethylene glycol) methyl ether methacrylate (MePEGMA),³³⁹ ethyl (EMA) and *n*-butyl methacrylate (*n*BMA),³⁴⁰ *tert*-butyl methacrylate (*t*BMA),³⁴¹ glycidyl methacrylate (GMA),³⁴⁰ and methacryloyl galactose (AcGalEMA).³⁴² The same results as with styrene were obtained with acrylonitrile, however, with a lower polymerization rate, most probably due to the stronger acrylonitrile–SG1 alkoxyamine bond.³⁴³

The MMA/S nitroxide-mediated copolymerization system was further studied on a theoretical basis using kinetic Monte Carlo simulations, under batch or forced-gradient conditions. The effect of the deactivation reaction on the segment length and length distribution was studied and it was concluded that the theory used for classical radical copolymerization does not always hold in CLRP.^{344–346}

Box 2

NMP of Methacrylic Esters with a Very Small Amount of a Comonomer

By J. Nicolas, University Paris-Sud

Even though the second generation of nitroxides (SG1, TIPNO, etc.) permitted the broadening of the range of monomers to be controlled, they still failed to yield well-defined and living polymers with methacrylic esters such as MMA. This was explained by the too high activation–deactivation equilibrium constant, K, which led to a high concentration of propagating radicals. This increases the occurrence of irreversible terminations (both homotermination between propagating radicals and β -hydrogen transfer from the propagating radical to the nitroxide).

However, a significant breakthrough has been recently witnessed with the discovery that, only a very small amount (4.4–8.8 mol.%) of a suitable comonomer (either styrene or acrylonitrile) during the SG1-mediated polymerization of methacrylic esters initiated by alkoxyamine **71** (**Table 4**) allowed all the criteria of a controlled/ living system to be fulfilled (high monomer conversion, high initiator efficiency, linear evolution of M_n , low PDI, and high living chain fraction).³³⁶ In such a system, the small amount of comonomer drastically decreases the overall concentration of propagating radicals via a decrease of the average activation–deactivation equilibrium constant, <*K*>, and allows the preferential formation of macroalkoxyamines with a methacrylic ester-comonomer-SG1 terminal sequence able to dissociate at low temperature (typically in the 70–90 °C range).²⁰⁸



Predicted values of the average activation–deactivation equilibrium constant, <K>, for the copolymerization of MMA with nBA or S or AN at 90 °C as a function of the molar fraction of comonomer, f.

This approach was believed to be universal as it has been successfully applied to numerous methacrylates such as MMA, MAA, EMA, *n*BMA, *k*BMA, AcGalEMA, and MePEGMA.^{208,338–340,342,347}



Universal feature of the SG1-mediated polymerization of methacrylic esters with styrene or acrylonitrile as a comonomer and formation of methacrylic ester–comonomer–SG1 terminal sequence.

Besides, the so-formed copolymers being living, with high crossover efficiency toward block copolymers, it also appeared to be an efficient route for the synthesis of water-soluble macroalkoxyamines employed for surfactant-free emulsion polymerization of MMA at temperatures below 90 °C. ^{348–350}

Beyond these achievements, this strategy allowed the design of methacrylic ester-rich copolymers while still taking advantage of the versatility of the SG1 nitroxide toward other vinylic monomers.

3.10.3.2.2(ii) Reactivity ratios

Despite the recent theoretical analysis reported above, the reactivity ratios were determined experimentally for various systems and did not show significant differences with those found in classical radical copolymerization. In those systems, the polymerizations were essentially carried out in controlled/ living conditions either because both comonomers were easily controlled or because the composition was such that the major comonomer exhibited controlled NMP with the selected nitroxide. Many examples are based on styrene with a variety of methacrylate and acrylate comonomers, mostly in the presence of TEMPO or SG1.^{341,347,351-364}

3.10.3.2.2(iii) Living random and gradient copolymers

As a consequence of a low (or nonexisting) difference in reacand ratios between NMP tivity classical radical copolymerization, the same compositional drift is observed. Nevertheless, the fast initiation rate and the simultaneous growth of all chains at a similar rate of monomer incorporation leads to a much narrower composition distribution,³⁵⁵ with better defined properties of the so-formed copolymers. With a significant difference of reactivity of the comonomers, the composition drift results in a compositional gradient along the chains, conducting to copolymers with new, almost unexplored properties. A broad variety of the studied copolymers were based on styrene as a comonomer, ideally to ensure a good control over the polymerization, especially when TEMPO was used as a mediator. One of the most studied systems in term of properties of the formed gradient copolymers such as T_{σ} and phase separation was the styrene/acetoxystyrene (leading to poly(styrene-co-hydroxystyrene) gradient copolymers after deprotection) by Gray et al., 365 Kim et al., 366,368 and Mok et al.^{367,369}

Another system of great interest was the copolymerization of styrene and acrylonitrile, which finds important applications in industry. The control was essentially ensured by TEMPO,^{359,370,371} particularly at the azeotropic composition at which no composition drift is expected.³⁷² Suspension copolymerization was considered with the same success as in bulk.³⁷³

Although the homopolymerization of methacrylate monomers cannot be controlled by the most classical nitroxides used, the TEMPO-, TIPNO-, and SG1-mediated copolymerizations were shown to work quite well, in conditions where relatively low amounts of the methacrylate comonomer were used.^{121,374–376}

The random and gradient nitroxide-mediated copolymerizations were also applied as a tool to synthesize amphiphilic copolymers and study their self-assembling properties in aqueous solution or their stabilizing efficiency in emulsion or miniemulsion polymerization. This was, for instance, the case for styrene and neopentyl *p*-styrenesulfonate (leading to styrene sulfonic acid after deprotection)³⁷⁷ along with styrene and AA.^{357,378-381}

Another route toward potentially amphiphilic copolymers is the copolymerization of styrene with maleic anhydride, ^{382–385} which has the particularity to lead to poly(styrene-*co*-maleic anhydride) alternate copolymers and ultimately to poly (styrene-*co*-maleic anhydride)-*b*-polystyrene block copolymers after complete depletion in maleic anhydride. Maleimide comonomers were similarly copolymerized with styrene such as *N*-alkylmaleimide or *N*-phenylmaleimide,^{386–388} *N*-benzylmaleimide, and *N*-cyclohexylmaleimide.³⁸⁹ Dialkyl fumarates were also studied.³⁹⁰

Finally, the copolymerization of styrene with either 2-VP²⁷³ or vinylcarbazole^{391,392} were performed, with TEMPO as a nitroxide mediator.

Non-styrenic monomers were copolymerized in the presence of SG1 such as the DMAAm/*n*BA couple leading to gradient copolymers upon controlled addition of DMAAm.^{393,394} 2-VP and acrylonitrile were also copolymerized using either TEMPO or SG1 as a mediator with the aim of forming block copolymers with styrene.³⁹⁵ Vinyl chloride, although its polymerization is not controlled via NMP, could be incorporated into a variety of random copolymers prepared via suspension copolymerization.³⁹⁶

3.10.3.3 Polymerizations in Aqueous Dispersed Media

Polymerizations in dispersed media represent an attractive set of processes exhibiting a unique combination of interesting features and properties. Among them, radical polymerization in aqueous dispersed media (emulsion, dispersion, etc.) and in supercritical carbon dioxide (scCO₂) have been widely investigated, the former being one of the most important industrial processes for the production of synthetic polymers.^{397,398} However, even though CLRP techniques are now well understood in homogeneous media, their transposition in dispersed media, especially in aqueous emulsion, is far less straightforward and still remains an active research field.³⁹⁹⁻⁴⁰⁵ This is mainly due to the dispersed feature of these systems, leading to different loci of polymerization, where the main difficulty is both to obtain stable latex particles and to fulfill all the criteria of CLRP. NMP has been extensively studied in heterogeneous polymerization media such as aqueous emulsion, miniemulsion, dispersion, precipitation, microemulsion, and in scCO₂.⁴⁰³ In the following part, only aqueous emulsion and miniemulsion NMP will be reviewed.

3.10.3.3.1 Aqueous miniemulsion polymerization

In a miniemulsion process, the starting monomer phase (Figure 15, right) is divided into submicronic droplets by a high shear device (ultrasonicator or microfluidizer).406,407 Therefore, the droplets become small enough so that they can compete for the radical entry and become the primary locus of polymerization, hence acting as bulk nanoreactors. This allows the complex nucleation step existing in conventional emulsion polymerization to be avoided, thus permitting the use of the same reagents as in bulk. In general, a miniemulsion polymerization requires the addition of a hydrophobe, such hexadecane, to suppress Ostwald ripening.406,407 as Interestingly, this role can be fulfilled by using a nitroxide-terminated macroinitiator (for instance. PS-TEMPO), thus avoiding the use of hexadecane. 406,408,409 The addition of a small amount of high molar mass polymer that enhanced droplet nucleation and stabilization has also been reported.407,410,411

Both oil- and water-soluble initiators have been investigated in miniemulsion NMP with TEMPO and SG1. Bicomponent systems were the first to be applied as they only required the addition of a nitroxide to a classical radical initiator for the establishment of the activation-deactivation equilibrium.



Figure 15 Initial state of aqueous emulsion (left) and miniemulsion polymerization (right). M = monomer; R[•] = radical initiator.

However, an important breakthrough came from the development of SG1-based, water-soluble alkoxyamines, which represented a crucial step toward true NMP in emulsion.⁴⁰²

3.10.3.3.1(i) Oil-soluble bicomponent initiating system

The first report concerned the use of BPO–TEMPO for the polymerization of styrene at 125 °C with CSA as a rate accelerant.⁴¹² A good control was shown for M_n up to 40 000 g mol⁻¹ with PDIs in the 1.14–1.6 range. Stable latex at 20 wt.% solids were obtained but with large diameters and rather broad particle size distributions. Analogous bulk polymerization proceeded faster, which is explained by the monomer segregation in droplets and diffusion of active species to the aqueous phase. It was also noted that TEMPO offered a better control than TEMPO-OH regarding the evolution of $M_{n\nu}$ especially at the onset of the polymerization, whereas the kinetics were not significantly affected whatever the nitroxide.^{413,414}

The use of SG1 allowed the miniemulsion polymerization of styrene to proceed at temperatures below 100 °C.⁴¹⁵ Even though only 60% monomer conversion was obtained after 24 h, probably due to the PRE and a negligible rate of thermal autoinitiation of styrene at such temperatures, polymers exhibited rather low PDIs.

3.10.3.3.1(ii) Water-soluble bicomponent initiating system

In this situation, the polymerization starts in the aqueous phase and conducts the formation of oligoradicals and oligomeric alkoxyamines that enter the monomer droplets, hence becoming the primary locus of polymerization.

Macleod *et al.*⁴¹⁶ reported very fast polymerizations and low PDIs by selecting TEMPO and potassium persulfate (KPS) for the polymerization of styrene at 135 °C, even though a large proportion of chains were eventually dead. Interestingly, when TEMPO was replaced by the more hydrophilic TEMPO-OH, evolution of M_n with conversion was affected and a poor control in the early stages of the polymerization was noticed, likely due to the lack of free nitroxide in the organic phase.⁴¹³ This highlighted the crucial importance of the aqueous phase kinetics and the partition coefficient of the nitroxides on the outcome of the miniemulsion polymerization.⁴¹⁷

The use of $K_2S_2O_8/Na_2S_2O_5$ redox initiating system in conjunction with SG1 allowed the polymerization rate of styrene to be enhanced compared to its counterpart with AIBN at

90 °C.^{415,418} An optimal [SG1]₀/[KPS]₀ ratio of 1.2 was found to be the best compromise regarding a fast polymerization and a good quality of control. Following an induction period necessary to the *in situ* formation of SG1-based alkoxyamines, styrene conversion reached 90% in 8 h with molar masses in good agreement with the predicted values and PDIs in the 1.5–2.0 range.

3.10.3.3.1(iii) Oil-soluble monocomponent initiating system

Both molecular and macromolecular oil-soluble alkoxyamines have been successfully employed in miniemulsion polymerization. The polymerization of styrene proceeded at 125 °C using a PS-TEMPO macroinitiator $(M_n = 7050 \text{ g mol}^{-1})$ in the presence of hexadecane and Dowfax 8390.419-421 However, thermal autoinitiation of styrene led to high PDIs and lower molar masses than predicted. Surprisingly, a similar macroalkoxyamine prepared in situ led to high monomer conversion and narrow molar mass distributions (PDI = 1.15),⁴²² which was contradictory to conclusions from a mathematical model developed by Ma et al.423 predicting a decrease of the living fraction with monomer conversion together with an increase of the PDI at high conversion. Chain extensions with nBA from PS-TEMPO⁴²² or PS-TIPNO-OH⁴²⁴ macroinitiators turned out to be an efficient route to PnBA-b-PS diblock copolymer latexes. Importantly, the use of PS-TEMPO macroinitiators also permitted a high conversion in a short period of time to be achieved and avoided the use of a volatile co-stabilizer.409 Nearly complete conversions were achieved within 2-3 h while still exhibiting low PDIs and high degrees of livingness. Even though a lower polymerization temperature (i.e., 100 °C) could be reached, PDIs were slightly higher (ca. 1.4-1.6) than those obtained under classical experimental conditions.⁴⁰⁸ Cross-linking NMP in miniemulsion of styrene with 1% DVB at 125 °C was also reported. 425,426

Molecular alkoxyamines based on TEMPO and derivatives^{423,424,427} or SG1^{164,285,355,428} also received great interest regarding miniemulsion NMP. For the polymerization of styrene initiated by the styryl-TEMPO alkoxyamine, adequate experimental conditions led to narrow molar mass distributions (PDI ~ 1.3) and high monomer conversions.⁴²⁷ With *n*BA at 135 °C upon the addition of ascorbic acid, the miniemulsion polymerization conducted to rather high PDIs compared to previous results with the TIPNO-OH nitroxide.⁴²⁴ The more versatile SG1-based oil-soluble alkoxyamine (MONAMS) allowed better results to be obtained as well-defined PnBA homopolymers²⁸⁵ and gradient copolymers³⁵⁵ with styrene were obtained at solids content up to 45 wt.%. A highly living PnBA-SG1 macroinitiator led to stable PnBA-*b*-P(*n*BA-*co*-S) block copolymer latex.¹⁶⁴

3.10.3.3.1(iv) Water-soluble monocomponent initiating system

Nicolas et al.¹⁶⁶ took advantage of the water solubility of the BlocBuilder alkoxyamine to report the first example of a water-soluble monocomponent initiating system in miniemulsion NMP. Indeed, when turned into its carboxylate salt form, this alkoxyamine is fully water-soluble and can readily initiate polymerization in the aqueous phase. The authors polymerized *n*BA and styrene in a controlled fashion at 20 wt.% solids at 112 and 120 °C, respectively. Only with styrene was the initiating efficiency lower than expected due to highly pronounced PRE leading to a very slow chain growth in the aqueous phase. The addition of a very small amount of methyl acrylate (MA), acting here as an entry rate enhancer due to appropriate copolymerization conditions, allowed a perfect match between predicted and experimental molar masses to be obtained. All latexes exhibited excellent colloidal stability. Due to its negative charge, average diameters $(D_z = 260 - 310 \text{ nm})$ were significantly lower than those obtained with the MONAMS alkoxyamine under identical experimental conditions.

3.10.3.3.2 Aqueous emulsion polymerization

The initial state of a typical *ab initio* emulsion polymerization is mainly composed of large droplets (>1 μ m) of hydrophobic monomer(s) and of a large number of monomer-swollen micelles (Figure 15, left).³⁹⁷ In contrast to miniemulsion, the emulsion process requires the use of water-soluble radical initiators. Latex particles are then obtained via a complex nucleation mechanism where the polymerization takes place in small particles supplied with monomer via its diffusion through the aqueous phase from the large droplets.

3.10.3.3.2(i) Bicomponent initiating system

First attempts to perform NMP in true emulsion systems were rather unsuccessful and met with limited success due to colloidal instability and/or poor control, mainly assigned to nucleation of the large droplets of monomer and nitroxide partitioning.³⁹⁹

Among TEMPO and TEMPO derivatives under KPS initiation at 130 °C, only amino-TEMPO led to stable latexes stabilized by SDS with good control/livingness.⁴²⁹ Similarly at 120 °C, acetoxy-TEMPO also gave satisfying results,⁴³⁰ which also highlighted the strong influence of the partitioning characteristics of the nitroxide over the control/stability in *ab initio* emulsion NMP. With K₂S₂O₈/Na₂S₂O₅ and SG1 at 90 °C, the polymerization exhibited a rather good control even though a few percent of coagulum was noticed.⁴¹⁵

Optimized concentration of nitroxide in the polymerization loci⁴³¹ while preventing thermal initiation in monomer droplets was achieved by the use of a combination of TEMPO and 4-stearoyl-TEMPO that exhibit different water solubility.⁴³² The polymerization of styrene at 135 °C with sodium dodecylbenzenesulphonate as a surfactant yielded coagulum-free stable latex (D_z = 45 nm) with excellent control/livingness. A two-step nitroxide-mediated surfactant-free emulsion polymerization of styrene was also successfully carried out using KPS and the nitroxide SG1.⁴³³ A seed was prepared from polymerization of a small fraction of styrene (1.5%) followed by addition of the remaining amount. After a long induction period, due to the formation of SG1-capped styrene oligomers in the aqueous phase, the polymerization conducted to good colloidal stability and livingness, but rather broad molar mass distribution (PDI>1.7).

3.10.3.3.2(ii) Molecular alkoxyamines

All successful results with molecular alkoxyamines concerned seeded systems in which the complex nucleation step is circumvented. The first example resembled a miniemulsion process and used a PS latex allowed to swell with styrene and an oil-soluble, TEMPO-based alkoxyamine.⁴³⁴ Although the polymerization proceeded at 125 °C with some control/ livingness, PDIs were around 1.5 due to thermal initiation of styrene.

A significant breakthrough has been witnessed with the use of water-soluble, SG1-based alkoxyamines (Figure 16) via a simple two-step emulsion process, as reported by Charleux and Nicolas⁴⁰² and Nicolas et al.⁴³⁵ The first step consisted in the synthesis of low solids content seed latexes containing living PnBA oligomers by ab initio batch emulsion polymerization under microemulsion-like conditions from alkoxyamine 72,⁴⁰² hence preventing the formation of large droplets of monomer. A second load of monomer (either S or nBA) is then added in 'one shot'435 or in a continuous fashion436 in order to target higher solids content by efficient chain extension. Polymerizations exhibited fast kinetics together with controlled molar masses up to 35 000 g mol⁻¹ and low PDIs. Besides, this simple process allowed 16 wt.% solid latexes to be obtained with good colloidal properties and neither coagulum nor destabilization over time (final concentrations of surfactant were as low as \sim 2–4 wt.% with respect to the monomer). However, particle size distributions were rather broad with average diameters in the 260-660 nm range, depending on the initial concentration of surfactant. When *n*BA and S were consecutively added, a stable 26 wt.% PnBA-b-PS diblock copolymer latex was obtained.

Nicolas *et al.*⁴³⁷ reported the synthesis of a novel difunctional, water-soluble alkoxyamine based on SG1 (DIAMA-Na, **73**) that permitted to both narrow the particle size distribution and to gain access to ABA triblock copolymer latexes. This alkoxyamine was prepared by intermolecular radical 1,2-addition of BlocBuilder onto tri(ethylene glycol) diacrylate (see Section 3.10.4.1.1 for details).⁴³⁸ Final latexes exhibited good control over polymer chains and a marked decrease in average diameter and narrower particle size distribution compared to analoguous latexes with the BlocBuilder alkoxyamine, which was assigned to the double negative charge of the neutralized DIAMA. A PS-*b*-PnBA-*b*-PS triblock copolymer latex was also obtained by sequential polymerization of *n*BA and S from a SG1-*Pn*BA-SG1 seed.

3.10.3.3.2(iii) Macromolecular alkoxyamines

In a single polymerization step, Delaittre *et al.*³⁰⁵ synthesized amphiphilic diblock copolymer nanoparticles obtained from surfactant-free polymerization of S or *n*BA initiated by SG1-terminated poly(sodium acrylate) (PNaA-SG1) macroalkoxyamines. *Ab initio* emulsion NMP of styrene and *n*BA were successfully performed at 120 °C at 20 wt.% solids. The final



Figure 16 Two-step SG1-mediated emulsion polymerization initiated with monofunctional (BlocBuilder salt, 72) or difunctional (DIAMA-Na, 73) water-soluble SG1-based alkoxyamines. Synthesis of the living seed latex (a) followed by its chain extension after 'one shot' or continuous addition of monomer (b).

particle diameters were less than 100 nm and exhibited a spectacularly narrow particle size distribution. The resulting particles were pH-sensitive; at pH > 7, the shell was a stretched polyelectrolyte brush that effectively stabilized the particles, whereas, at pH = 4, the hairy layer collapsed onto the particle surface, resulting in unstable particles.³⁰⁶

This approach was further extended to P(MAA-*co*-S)-SG1 macroalkoxyamines employed for the emulsion copolymerization of MMA with a low percentage of styrene at temperatures below 90 °C.³⁴⁸ Fast polymerizations led to well-controlled polymers and high initiating efficiencies due to the high dissociation rate constant of the macroalkoxyamines. Self-assembly of the formed amphiphilic block copolymers led to small particles ($D_z < 100 \text{ nm}$). Besides, PEG-based macroalkoxyamines obtained from terpolymerization of MAA, MePEGMA and a few percent of S were involved in the synthesis of PEG-coated, amphiphilic diblock copolymer latexes.³⁵⁰

Alternatively, SS can also act as an efficient comonomer for the polymerization of MAA in dimethylsulfoxide solution at 76 °C.³⁴⁹ The resulting P(MANa-*co*-SS)-SG1 macroalkoxyamine was shown to be particularly well suited for the *ab initio*, batch emulsion polymerization of MMA with a small amount of S. Latexes were stable and exhibited small average diameters in the 29–43 nm range.

3.10.4 Advanced Architectures and Materials by NMP

3.10.4.1 Chain-End Functionalized Polymers from NMP

Due to the high chain-end fidelity observed for NMP, various chain-end functionalized (co)polymers have been prepared so far where α - and ω -functionalization pathways can be distinguished.

3.10.4.1.1 Alpha-functional polymers

The α -functionalization of polymer chains can be readily performed by using an appropriate initiator, bearing the functionalized fragment on the alkyl moiety (**Table 4**). Gigmes *et al.*¹⁸² prepared a large number of alkoxyamines with various functionalized alkyl moieties for structurereactivity relationships studies but only a few of them were used for polymerization purpose.

As already discussed in Section 3.10.2.2.2, functionalized 1-phenylethyl fragments represent the great majority of the synthesized alkoxyamines, whatever the nitroxide structure. The group of Hawker prepared various alkoxyamines and in particular one bearing a benzyl chloride moiety (74 and 75) from 4-vinylbenzylchloride.⁸⁶ Replacement of the chloride by other functional groups opened access to a wide selection of functionalized initiators. For instance, alkoxyamine 75 can be readily converted into the highly nucleophilic

aminomethyl-substituted alkoxyamine (78) by nucleophilic substitution with sodium azide (77) followed by a reduction step with lithium aluminum hydride.⁸⁶ The chlorine atom was also replaced, with difficulty though, by an hydroxy function (76) via reaction of KOAc in the presence of N-(2-hydroxypropyl)methacrylamide followed by hydrolysis in ethanolic NaOH with 18-crown-6.439 The synthetic pathway leading to alkoxyamine 76 was further optimized by Bothe and Schmidt-Naake⁸⁸ using a preformed 4-vinylbenzyl alcohol. In this way, the Braslau⁴⁴⁰ research group reported a facile preparation of the benzyl alcohol derivatives 79, whose synthesis was easier than for compound 76. They also prepared a carboxylic acid-functionalized alkoxyamine 80 protected by a tert-butyl group, which could be easily removed by post-polymerization treatment with TFA.440 Thiols (81)441 and alkyne (82)⁴⁴² groups were also inserted onto TIPNO-based alkoxyamines. The structures 75-82 were then post-functionalized to prepare alkoxyamines bearing a ligand (terpidine),⁴⁴³ a chromophore,^{439,444} or a vinyl group.⁴⁴⁵

The functional group can also be inserted on another carbon of the alkyl moiety. The groups of Hawker,⁷¹ Braslau,¹⁰⁶ and Priddy⁴⁴⁶ prepared alkoxyamines **83**, **84**, and **85**, respectively, in which hydroxy and chlorine functionalities were linked to the methyl group close to the aminoxyl function instead of being in para-position of the phenyl ring.

The group of Tordo^{165,449} prepared the alkoxyamine 71, commercialized by Arkema under the trademark BlocBuilder MA.⁴⁴⁷ The introduction of a carboxylic acid group represented a breakthrough in NMP, in both homogeneous and aqueous dispersed media, since its salt is water-soluble.⁴⁰² The coupling of this alkoxyamine with alcohols was investigated and it was shown that the combination of a high steric hindrance and a high dissociation rate constant prevented efficient coupling reactions.⁴⁴⁹ In contrast, the coupling of alkoxyamine 71 with amine-containing compounds was achieved either by preparing the activated ester derivative, MAMA-NHS (86),⁴⁴⁸ or by using a suitable coupling agent, that is, benzotriazol-1-yl-oxytripyrrolidinophosphonium hexafluorophosphate (PyBOP).⁴⁵⁰

A very efficient method for preparing functionalized alkoxyamines was recently proposed and this method relied on the low BDE of the BlocBuilder alkoxyamine (71) to perform quantitative intermolecular radical 1,2-addition onto various olefins (Figure 17).⁴³⁸ In the case of activated olefins, the challenge consists in avoiding a multiple monomer addition. However with alkoxyamine 71, the resulting alkoxyamine after addition bears a less stabilized, bulky secondary radical moiety compared to the 1-carboxy-1-methyl ethyl radical moiety of the starting alkoxyamine, which prevents further addition.

This reaction was successfully performed at 100 °C in solution with various olefins such as S,⁴³⁸ nBA,⁴³⁸ HEA (Figure 17, 87),⁴³⁸ AA,⁴³⁸ 4-VP,⁴⁴⁹ SS,⁴⁴⁹ and *N*-acryloylglucosamine.⁴⁴⁹ The intermolecular radical 1,2-addition is also useful to prepare di- or triblock copolymers by the reaction of multifunctionalized olefins such as butanediol diacrylate⁴³⁷ or pentaerythrithol tri- or tetraacrylate.⁴³⁸

3.10.4.1.2 Omega-functional polymers

Contrary to ATRP and RAFT techniques,¹⁸ the removal or the transformation of NMP (co)polymers ω -end-groups has not been extensively studied. Two distinct solutions can be considered: (1) a radical pathway where functionalization occurred after decomposition of the (macro)alkoxyamine, and (2) a nonradical route in which the (macro)alkoxyamine is reacted directly. An illustration of end-group transformations achieved so far for NMP is given in Figure 18.

Concerning the removal of the nitroxide moiety, the easiest way is to heat up the macroalkoxyamine in the presence of an hydrogen donor compound such as a thiol.¹ In particular, it was shown that thiophenol was a very efficient hydrogen donor agent for such a purpose.^{197,343,451}

The first example of functionalization was reported by Solomon et al.¹ They reduced the TEMPO to an hydroxy end-group using a mixture of Zn/acetic acid. Malz et al.452 extended this approach on the TEMPO moiety with different reducing agents such as LiAlH₄ and they also showed that the TEMPO end-group could be oxidized at room temperature to a ketone moiety by the reaction with mCPBA. With TIPNO chain ends, O'Bryan and Braslau⁴⁵³ developed a single-electron oxidation using ceric ammonium nitrate to form secondary benzylic cations. These cations are then trapped by various reactants (including the solvent) to prepare the corresponding alcohol, ether, or amide chain-end functionalized polymers. However, these methods failed for SG1-based alkoxyamines,454 certainly due to a poor accessibility of the aminoxyl function deriving from a higher steric hindrance of the SG1 compared to TEMPO or TIPNO nitroxides.¹⁶⁰

Harth *et al.*⁴⁵⁵ took advantage of a radical approach to functionalize (macro)alkoxyamines. They used a nonself-polymerizable monomer (maleimide or maleic anhydride) as a radical trap and then succeeded in preventing multiple radical additions. This step is followed *in situ* by an elimination of the TIPNO nitroxide. Various other radical traps



Figure 17 Mechanism of the intermolecular radical 1,2-addition.



Figure 18 Various functionalized ω-end-groups accessible for NMP polymers.

were investigated. For instance, functionalized or nonfunctionalized tetraethylthiuram disulfide compounds were used with PS-TEMPO,⁴⁵⁶ whereas benzyl enol ether and ethanesulfonylazide were employed for TIPNO-based polymers.457,458 The latter was also used by Guillaneuf et al.454 who also investigated the use of dioxygen, combined with an in situ reduction of the formed macrohydroperoxide with triphenylphosphine to prepare hydro-terminated PS. An halogen functionalization was also performed by a mild radical bromination reaction using ethyl 2-bromo-isobutyrate as bromine transfer agent.⁴⁵⁴ The transformation of the nitroxide moiety into a bromine end-group opens the door to reinitiation/polymerization under ATRP conditions and associated chemical post-modifications. Similarly, a technique was developed to exchange the nitroxide functionality by a RAFT agent called ESARA (exchange of substituents between (macro)alkoxyamines and (macro)RAFT agents).459

Another method to introduce ω-end-groups is to exchange the nitroxide moiety with another nitroxide bearing a functional group. The groups of Turro, 460 Scaiano, 461 and Hawker^{128,462} studied the nitroxide exchange between TEMPO-terminated PS and 4-substituted TEMPO derivatives. A large excess of free nitroxide was necessary to achieve complete functionalization, due to the similar reactivity of the two nitroxides in the reaction medium. Besides, this method yields ω -functionalized polymers still with a labile end-group that could be detrimental regarding certain applications. Guillaneuf et al.454 optimized this method by using an exchange between two nitroxides exhibiting different reactivities (TEMPO replacing the SG1 with only 2 equiv. of TEMPO). They also combined this approach with a method already developed by the groups of Rizzardo¹ and Pionteck,⁴⁵² in order to obtain hydroxyl- and keto-functionalized polymer with no alkoxyamine labile group from PS-SG1 precursors.

3.10.4.2 Diblock and Triblock Copolymers by NMP

3.10.4.2.1 General trends

The chain-end fidelity inherent to the NMP process was widely applied to the synthesis of various macromolecular architectures such as diblock or triblock copolymers. Not only may these architectures be prepared with a similar degree of control to other CLRP methods, but NMP also provided easier routes to block copolymers, not directly accessible using existing CLRP techniques. A typical example is the direct polymerization of MAA under SG1 control,^{300,338} in contrast to ATRP where *tert*butyl (meth)acrylate should be polymerized and subsequently deprotected.

Examples related to the synthesis of linear AB diblock copolymers prepared by NMP are gathered in **Table 5**, whereas **Tables 6** and 7 presents triblock copolymers obtained from difunctional alkoxyamines (ABA-type copolymer) or monofunctional ones (ABC-type copolymers), respectively. For the sake of simplicity, we only report achievements dealing with pure polymer blocks (i.e., blocks being composed of one type of monomer) and not copolymers with blocks synthesized by nitroxide-mediated random copolymerization.

The most widely applied synthetic pathway for block copolymer is the sequential polymerization of different monomers (**Table 5**). After polymerization of the first monomer, the resulting macroinitiator could be either used *in situ* or purified/isolated prior to further chain extension, the latter option being usually the most preferred one for an optimum purity of the second block. Alternatively, three other approaches have been also investigated for block copolymers: (1) the coupling of a functionalized alkoxyamine with a telechelic or monofunctional polymer to yield a macroinitiator; (2) a double-headed initiator bearing an alkoxyamine moiety and an initiating group for another polymerization method (see Section

Monomer A	Monomer B	Nitroxide	References
		1, 27	463–465
	OAc	2b	129
	Br		
		52	377
	0=S=0		
		1	256

Table 5 Structure of monomers and nitroxides employed in the synthesis of linear AB diblock copolymers by NMP



Table 5(Continued)

Monomer A	Monomer B	Nitroxide	References
	Aco OAc Aco OAc	1	263
	COO(CH ₂) ₄ O-COO-	1	468
		1	469
		1	469
	Fe O	1	470
		1	265



Table 5	Continued
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Monomer A	Monomer B	Nitroxide	References
		27	475
		1	312, 313
		29	319, 471
		1	313
		1	313
		1	313
		1	313, 326



|--|

Monomer A	Monomer B	Nitroxide	References
SO ₃ ⁻ Na ⁺	ОН	1	478
SO3 ⁻ Na ⁺		52	261
SO ₃ ¬Na ⁺		6	479
SO3 ⁻ Na ⁺		1	478
SO ₃ ¬Na ⁺	COONa	1	478
SO ₃ ⁻ Na ⁺	N	1	478



Monomer A	Monomer B	Nitroxide	References
		29	484
OAc			
	Si		
		1	485
Т ОАС	COO(CH ₂) ₆ OCOOOMe		
		29	467
 OAc	Si Si		
		29	467
 OAC	SiSi		
		29	486
OAc	O Si		



Table 5 (Continued)

Monomer A	Monomer B	Nitroxide	References
		1	257
		29	467
O=S=O		52	377
		29	486



Table 5(Continued)





Table 5 (Continued)

Monomer A	Monomer B	Nitroxide	References
↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓	$ \begin{array}{c} \begin{array}{c} \begin{array}{c} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \begin{array}{c} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \begin{array}{c} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \begin{array}{c} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \begin{array}{c} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \begin{array}{c} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \begin{array}{c} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \begin{array}{c} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \begin{array}{c} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \begin{array}{c} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \begin{array}{c} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \begin{array}{c} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \begin{array}{c} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \begin{array}{c} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \begin{array}{c} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \begin{array}{c} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \begin{array}{c} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \begin{array}{c} \\ \\ \\ \end{array} \\ \\ \end{array} \\ \\ \begin{array}{c} \\ \\ \\ \end{array} \\ \\ \end{array} \\ \\ \begin{array}{c} \\ \\ \\ \end{array} \\ \\ \end{array} \\ \\ \begin{array}{c} \\ \\ \\ \end{array} \\ \\ \end{array} \\ \\ \begin{array}{c} \\ \\ \\ \end{array} \\ \\ \end{array} \\ \\ \begin{array}{c} \\ \\ \\ \end{array} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \begin{array}{c} \\ \\ \\ \end{array} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \begin{array}{c} \\ \\ \\ \end{array} \\ \\ \\ \\ \end{array} \\ \\ \\ \\ \\ \end{array} \\ \\ \\ \\ \\ \\ \end{array} \\$	29	490, 491
	R = H, t Bu	29	492
	o iPr o iPr	29	492



	inued
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Table 5 (Continued)			
Monomer A	Monomer B	Nitroxide	References
		29	494
		29	495
$ \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$		29	494
COO(CH ₂) ₁₀ COO-COOCH ₃	0-COO(CH ₂) ₁₀ CH ₃	29	496

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Table 5(Continued)





Table 5	(Continued)
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Monomer A	Monomer B	Nitroxide	References
		52	295
		29	33
		52	296
D NMe ₂		52	296
		52	511
		52	261



Monomer A	Monomer B	Nitroxide	References
		2b	513
	\rightarrow		
		29	319
		29	505
N O			
		1	514
		29	515

CS-TEMPO, 2,2,6,6-tetramethyl-4-[d-(+)-10-camphorsulfonyl]-1-piperidinyloxy; TEIOAI, 1,1,3,3-tetraethylisoindolin-2-oxyl-5-trimethylammonium iodide; TEIOSNa, sodium 1,1,3,3-tetraethylisoindolin-2-oxyl-5-sulfonate; F-TIPNO, 2,2,5-trimethyl-4-fluorophenyl-3-azahexane-3-oxyl; PROXYL, 2,2',5-trimethyl-5'-phenylpyrrolidinyl-1-oxyl.

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Central monomer	Outer monomer	Nitroxide	References	Central monomer	Outer monomer	Nitroxide	References
		1	516			29, 39	146, 517, 518
		52	296			52, 29	287, 437, 519
		29	517			39	518
		39	518			52	296

Table 6 Structure of monomers and nitroxides employed in the synthesis of linear ABA triblock copolymers by NMP from difunctional alkoxyamines or bis-nitroxides

Table 6(Continued)



Monomer A	Monomer B	Monomer C	Nitroxide	References
			1, 52, 38	144, 524, 525
			38	144
			1	466
HO			1	526

 Table 7
 Structure of monomers and nitroxides employed in the synthesis of linear ABC triblock copolymers by NMP from monofunctional alkoxyamine

3.10.4.3.1 for details); and (3) the termination of a polymerization by a functionalized alkoxyamine.⁴

Whereas diblock copolymers were mainly prepared by sequential polymerizations of two different monomers, triblock copolymers were generally obtained by divergent chain growth from a difunctional alkoxyamine (Table 6). However, a few examples report consecutive polymerization of three different monomers from monofunctional initiators (Table 7). TEMPO and TEMPO-like nitroxides were almost exclusively employed for the polymerization of styrenic derivatives. The versatility of TIPNO and SG1 nitroxides allowed greater flexibility regarding the range of monomer that can be controlled. Consequently, they have been intensively employed for the design of a myriad of block copolymers.

3.10.4.2.2 Monomer sequence

NMP has proven to have great flexibility regarding the sequential polymerization of various monomers. However, similarly to anionic polymerization, blocking efficiency may depend on the sequence of block synthesis when designing specific block copolymers. The most famous example is the preparation of *PnBA-b*-PS block copolymer. This particular order (i.e., first *nBA* then S) gives quantitative reinitiation and very low PDIs. However, the reverse strategy, which consisted in the chain extension by *nBA* from a PS macroinitiator, usually lead to a significant amount of dead chains and large PDIs due to unfavorable kinetic parameters. This was illustrated with TEMPO, TIPNO, and SG1 both in homogeneous and aqueous dispersed media.^{33,435,437,472} However, well-defined PS-*b*-P*n*BA were obtained from a PS macroinitiator terminated by nitroxide **38**, but with the help of a high amount of free nitroxide (*ca.* 16–20%).¹⁴⁴

Monomer sequence is also important when methacrylic esters^{208,520} or acrylonitrile²⁹⁹ are involved. It is well known that homopolymerization of MMA failed to be controlled by common nitroxides, which closes the route to PMMA macroinitiators. In contrast, controlled polyacrylonitrile (PAN) homopolymers can be obtained under SG1 control but chain extension leads to bimodal molar mass distributions, even with large excess of nitroxide. Nevertheless, starting from PnBA-SG1 macroinitiators allowed PMMA- or PAN-based block copolymers to be designed.

3.10.4.2.3 Microphase separation/nanostructuration

A direct application of block copolymers is related to nanostructured materials. Microphase-separated block copolymers comprising two or more incompatible polymer blocks are indeed of high interest as they combine the properties of different homopolymers at the nanometer scale.⁵²⁷ With this view, Huang *et al.*⁵²⁸ prepared a surface-active perfluorodecanoyl-terminated P(S-*co*-MMA) random copolymer via the esterification reaction of the P(S-*co*-MMA) block with an excess of perfluorodecanoyl chloride. For films confined between two continuous neutral surfaces, the orientation of the lamellar microdomains was observed to be perpendicular to the film surfaces throughout the entire film thickness.⁵²⁸

It was shown that high molar mass, polydisperse acrylic PnBA/PMMA diblock and triblock copolymers prepared by SG1-mediated polymerization were shown to self-assemble into various nanostructures despite substantial molecular disorder.⁵²⁰ Lamellae are observed around 55–65 vol.% PMMA, while perfectly symmetrical copolymers adopt a curved interface concave toward PMMA and form cylinders or cylindrical micelles with poor lattice order. This was assigned to unbalanced polydispersity between the two blocks arising from the lack of control over polymerization of PMMA under the synthesis conditions used.

Nicolas et al.^{500,529} reported the preparation of nanostructured diblock and triblock copolymer particles comprising a PnBA first/central block and PS or PMMA second/outer blocks by NMP in miniemulsion or ab initio emulsion polymerization. Monofunctional and difunctional SG1-based alkoxyamines were used as initiators and sequential monomer additions were performed without any removal of unreacted monomer. Self-assembly of the obtained block copolymers was investigated both after drying the latex at room temperature as well as after different thermal treatments. Transmission electronic microscopy and atomic force microscopy analyses revealed the occurrence of 'onion-like' lamellar microphases directly inside the latex particles for high enough copolymer molar masses and irrespective of molar mass distribution. This particular organization evolved toward more classical block copolymer phase morphologies upon solvent casting and/or thermal annealing of latex films.

3.10.4.2.4 Self-assembly in aqueous solution

Amphiphilic block copolymers able to self-assemble are of high interest as they can be employed as macrosurfactants, viscosity modifiers, colloidal aggregates for biomedical purposes, and so on.⁵³⁰ In recent years, due to their robustness and efficiency, CLRP techniques have been extensively exploited in the design of amphiphilic block copolymers able to form a wide range of colloidal objects such as nanoparticles or micelles.^{531,532}

In the field of NMP, self-assembly in aqueous solutions of amphiphilic block copolymers based on styrene derivatives, ^{259,377,471,478,479,533,534} acrylates, ^{302,475,506,510,535} acrylamides, ^{278,536} or even sugar moieties³⁴² have been investigated.

An interesting class of colloidal aggregates, originating from the group of Wooley, is the family of PAA-based cross-linked block copolymer micelles.⁵³² Core–shell nanoassemblies were obtained from block copolymer designed by TIPNO-mediated polymerization. The usual strategy was to perform sequential polymerization of *t*BA and of a hydrophobic monomer (generally styrene derivatives or isoprene), the *tert*-butyl groups being further removed to yield amphiphilic block copolymers. Due to the presence of many functionalities (carboxylic acid, alkoxyamine, etc.), the corresponding micelles were successfully stabilized by cross-linking, core-, and/or shell-functionalized and decorated with molecules of interest,^{507,537–541} thus representing a very versatile colloidal platform.

As seen in Section 3.10.3.3.2, the self-assembly can also occur *in situ* during the surfactant-free polymerization of a hydrophobic monomer initiated with water-soluble (macro) alkoxyamines in aqueous dispersed media such as emulsion^{303–306,348–350} or dispersion.²⁸²

3.10.4.3 Complex Macromolecular Architectures

3.10.4.3.1 Combination of NMP and other polymerization methods

It is well known that other polymerization methods (controlled radical, ionic, coordination, etc.) also allow a high level of control over molar mass, low polydispersities, end-group fidelity, and molecular architecture to be achieved. Due to their own specificity, it was therefore of high interest to combine them with NMP in order to design various block copolymers with unique properties due to structurally different blocks. The synergy induced by the rich variety of microstructures in bulk and in solution permitted to employ these block copolymers as compatibilizers, impact modifiers, surface modifiers, coating materials, antistatic agents, adhesives, drug delivery devices, and information storage. Two main synthetic routes have been developed so far for the combination of different polymerization methods (Figure 19).

The first route employs heterofunctional initiators that allow the combination of mechanistically distinct polymerization reactions without the need for intermediate transformation and protection steps.^{542,543} This has been



Figure 19 The different methods to prepare block copolymer by the combination of NMP and other polymerization processes: Use of a heterofunctional initiator (a) or an end-group transformation pathway (b).

thoroughly reviewed by Bernaerts and Du Prez.⁵⁴⁴ The second route consists of a post-polymerization modification of the chain end, by which the polymerization mechanism could be changed. This approach has been reviewed by Yagci and Tasdelen.⁵⁴⁵ As the exhaustive description of this topic would be beyond the scope of this chapter, the reader is referred to the above-cited reviews for more details.

3.10.4.3.2 Cyclic polymers

Cyclic polymers have attracted considerable attention due to the unique properties deriving from the topological constraints of their particular architecture.^{546–550} The classical way to prepare such structures is based on the intramolecular cyclization of a linear polymer precursor, either α, α' -difunctional or α, ω -heterodifunctional. Whereas the former method is usually suitable for the coupling between a dicarbanionic polymer and a difunctional electrophile, the latter can be easily adapted to NMP since telechelic polymers exhibiting reactive end-groups can be prepared. Lepoittevin et al.⁵⁵¹ were the first to prepare macrocyclic PSs with controlled dimensions and narrow distributions using α-carboxyl-ω-hydroxy-heterodifunctional PS as a linear precursor. The polymerization was initiated by the 4,4'-azobis(4-cyanovaleric acid) and controlled by 4hydroxy-TEMPO (Table 1, 2a). The cyclization was performed by esterification in dilute solution (to ensure intramolecular cyclization reactions rather than intermolecular condensations) using 1-methyl-2-chloropyridinium iodide as a catalyst. The cyclization product was well characterized using different analytical techniques such as infrared spectroscopy, SEC, liquid chromatography at the critical condition, and matrix-assisted laser desorption/ionization-time of flight. This study led to cyclic polymers with two weak bonds, the alkoxyamine bond, which is thermolabile, and the ester function, which is chemically sensitive. To overcome the potential dissociation of the alkoxyamine bond and hydrolysis of the ester group, O'Bryan et al.⁴⁵⁸ reported the synthesis of azide-alkyne telechelic linear polymers prepared by a combination of NMP and post-functionalization. Cyclization of these precursors was achieved via a copper-catalyzed intramolecular azide-alkyne cycloaddition (CuAAC, the so-called click chemistry)⁵⁵² under high-dilution conditions.

However, the cyclization usually gives a mixture of linear and cyclic polymers that are difficult to separate. The synthesis of cyclic polymers from cyclic alkoxyamine by ring-expansion polymerization (Figure 20) can represent a suitable alternative to the end-to-end cyclization approach. For that purpose, Ruehl *et al.*⁵⁵³ prepared 5-membered and 17-membered cyclic alkoxyamines based on TIPNO to generate macrocyclic PSs. ESR analyses showed that, unlike the 17-membered cyclic alkoxyamine, the stability of the 5-membered ring prevents the alkoxyamine cleaveage into a nitroxide and an alkyl radical.

Cyclic polymers were obtained as a mixture of monocyclic polymer (in which a single alkoxyamine moiety is incorporated into the polymer chain) and oligomeric cyclic polymers (comprising several alkoxyamine bonds). Identical results were also obtained from a similar alkoxyamine tethered via azide/alkyne click chemistry.⁵⁵⁴ The generation of such an oligomeric cyclic polymer was assigned to radical ring-crossover reactions, originating from nitroxide exchange. Maeda et al.555 had already taken advantage of this phenomenon by investigating the 'dynamic covalent bonds' feature of alkoxyamines. In particular, a simple heating of a cyclic alkoxyamine compound (condensation of TEMPO-based diol alkoxyamine and adipoyl chloride) afforded the corresponding macrocycle by intermolecular radical crossover reaction.556 The obtained poly (alkoxyamine) could also depolymerize to the unimer by the same process under high-dilution conditions.

3.10.4.3.3 Star polymers

Star polymers exhibit interesting properties, especially their lower bulk and solution viscosities compared to linear analogues of the same molar mass. In addition, these architectures contain a higher amount of chain-end functionalities, which may be of high importance regarding many applications. Star polymers are usually prepared from CLRP by two different methods: (1) the 'core-first' method, and (2) the 'arm-first' method.⁵⁵⁷

3.10.4.3.3(i) The core-first approach

The core-first approach has the advantage that well-defined star polymers with a constant number of arms and identical arm lengths can be prepared, which is crucial for the study of structure–property relationship. In the case of NMP, this route requires the synthesis of multifunctional alkoxyamines.⁵⁵⁷ The first example was reported by Hawker⁵⁵⁸ using a tri-functionalized alkoxyamine based on TEMPO. Well-defined PS star polymers were obtained. A variety of star polymers were also prepared using multifunctional (3, 6, or 12 arms) TEMPO-based alkoxyamines.^{559–566} The core of the star



Oligomeric polymer

Figure 20 Synthesis of macrocycles by nitroxide-mediated ring-expansion polymerization.

polymer was either a mesitylene,⁵⁶⁵ a cyclodextrin,⁵⁶¹ a porphyrin,⁵⁶⁰ a dendrimer,⁵⁵⁹ or a polyhedral oligomeric silsesquioxane fragment.⁵⁶⁶ With the use of multifunctional SG1-based alkoxyamines, star polymers containing a *PnBA* block were synthesized.⁵⁶⁷ Multifunctional, TIPNO-based alkoxyamines were also designed and employed in the synthesis of 6- and 12-arm star polymers based on S, MA, DMAAm, and isoprene.^{568,569} Recently, octafunctional alkoxyamines were synthesized by derivatization of resorcinarene with TEMPO or a SG1 analogue (**Table 3**, **54**).¹⁵⁸

A significant improvement was proposed by Dufils *et al.*⁴³⁸ who developed a straightforward, one-step method to prepare multifunctional SG1-based aloxyamine via intermolecular radical 1,2-addition of the BlocBuilder alkoxyamine onto commercially available, multifunctional olefins. This conducted to 3- and 4-arms, well-defined star polymers.

3.10.4.3.3(ii) The 'arm-first' approach

The 'arm-first' approach involves the coupling of a preformed linear polymer with a multifunctional coupling agent such as divinylbenzene (DVB). This technique results in a star structure with a network core due to the coupling agent and a shell of the preformed linear polymer.⁵⁵⁷ The advantage of this approach relies on its simplicity since no organic synthetic step is needed. Nevertheless, the resulting star polymers do not exhibit a constant arm number and this leads to the formation of star polymers with high polydispersities. The groups of Fukuda^{570,571} and Abrol et al.⁵⁷² reported the NMP of styrene derivatives and 4,4-divinylbiphenyl to produce a slightly cross-linked homogeneous material. Later, the Long⁵⁷³ and Hadjichristidis⁵⁷⁴ research groups used PS-TEMPO to prepare well-defined PS star structures. Kaga et al.575 performed similar experiments with DVB and various vinyl saccharides to obtain star-shaped polymers having a glycoconjugated core exhibiting good encapsulation properties. Bosman et al.576 used a PS-TIPNO and combinatorial techniques to prepare a library of well-defined macromolecules with three-dimensional architecture. Complex star architectures, from a wide range of block and random copolymers with various end-group functionalities, were successfully synthesized. These materials were active as supramolecular hosts for the encapsulation of a variety of guests and as scaffolds for catalytic sites, which can be located at either the periphery or in the core of the stars.⁴³⁹

3.10.4.3.4 Grafted and comb polymers

Branched polymers are macromolecular structures composed of a main polymer chain (backbone) to which one or more side chains (branches) are covalently attached. When the backbone and the branches are of the same chemical nature, these architectures are called 'comb' polymers, whereas the term 'graft' polymers is used when backbone and branches differ from their chemical nature and/or composition.⁵⁵⁷ So far, three methods have been developed for the synthesis of randomly branched grafted (co)polymers: (1) the 'grafting to' or 'grafting onto'; (2) the 'grafting from'; and (3) the 'grafting through', also called the macromonomer method.⁵⁵⁷

3.10.4.3.4(i) The 'grafting to' method

The 'grafting to' method is based on the coupling of end-reactive branches with functional groups randomly distributed along the polymer backbone. In this case, the NMP is used to prepare the backbone by copolymerization of a mixture of traditional and reactive/functional monomers. For instance, Tsoukatos *et al.*⁵⁷⁷ prepared a PS-*g*-PI copolymer from the reaction of polyisoprene macroanions onto a P(S-*co*-CMS). Higaki *et al.*⁵⁷⁸ used the 'dynamic covalent bonds' approach⁵⁵⁵ to prepare grafted copolymers. A polymethacrylate with pending TEMPO-based alkoxyamine moieties was first prepared by ATRP at 50 °C followed by a radical crossover reaction of alkoxyamine units between the side chains and a PS-TEMPO to afford the corresponding grafted polymer.⁵⁷⁸ Interestingly, the starting materials can be recovered simply by raising the temperature again with an excess amount of alkoxyamine derivatives.

3.10.4.3.4(ii) The 'grafting from' method

The 'grafting from' method consists in the generation of initiating sites along the polymer backbone, able to initiate the polymerization of a second load of monomer.

The first route to introduce initiating sites relies on the copolymerization of an alkoxyamine-functionalized monomer based on styrene, acrylate, or methacrylate derivatives.445,558 Functionalized polyolefins were also obtained from an octene-substituted alkoxyamine employed in the copolymerization with propylene or 4-methylpentene using a cationic metallocene catalyst.⁵⁷⁹ Zhang et al.⁵⁸⁰ also prepared an alkoxyamine-functionalized monomer with an acyloxyl alkyl moiety. Controlled grafted polymerization of styrene was achieved, even though the location of the bond breaking events remained uncertain due to the release of alkoxyl and aminyl radicals.⁵⁸¹ Appelt and Schmidt-Naake⁵⁸² have synthesized 'inverted' alkoxyamine-based monomers where the double bond is linked to a polymerizable nitroxide (4-acryloyloxy-2,2,6,6-tetramethylpiperidine-N-oxyl). In this case, the grafting occurred by an insertion mechanism where the nitroxide moieties are localized along the backbone.

In the second method, the alkoxyamine-functionalized backbone is prepared by a chemical modification of a preformed polymer. Abbasian and Entezami⁵⁸³ prepared alkoxyamine-functionalized poly(vinyl chloride) (PVC) in a three-step procedure. PVC was first arylated with toluene by Friedel-Crafts acylation followed by a bromination step using N-bromosuccinimide. The bromine atom was finally reacted via nucleophilic substitution by the TEMPO hydroxylamine anion. PVC-g-PS was finally obtained after TEMPO-mediated polymerization of styrene. А TEMPO-functionalized isotactic poly(1-butene) macroinitiator was synthesized by Jo et al.584 who used a rhodium-catalyzed activation of the alkane C-H bonds and subsequent transformations of the boronate ester group into an hydroxyl pendant group. This reactive moiety was then used to attach a TEMPO-based alkoxyamine bearing another hydroxy function by an ether linkage. A method to prepare PE-g-PS from a poly(ethylene-co-m,p--methylstyrene) obtained by metallocene-catalyzed polymerization was also reported.585 The macroalkoxyasynthesized after bromination mine was with N-bromosuccinimide followed by a nucleophilic reaction with the TEMPO hydroxylamine anion.

Another method to achieve alkoxyamine-functionalized polymer backbones is to generate alkyl macroradicals by hydrogen abstraction followed by their trapping by free nitroxide. Sun
*et al.*⁵⁸⁶ generated alkyl radical on a poly(2-(dimethylamino) ethyl methacrylate) by hydrogen abstraction under UV (sensitized by benzophenone). Another possibility is to react the polymer with alkoxyl radicals (usually *tert*-butoxyl) resulting from the decomposition of peroxides. The grafting mechanism on polybutadiene using a mixture of peroxides and 4-oxo-TEMPO (**Table 1**, **4**) was also investigated.^{587,588} It was shown that alkoxyamine-functionalized polybutadiene can be generated by heating the polymer precursor in the presence of just nitroxide at low temperature, without initiator. This was explained by the hydrogen abstraction ability of TEMPO at 110–120 °C, or its tendency to undergo addition to double bonds.

Eventually, alkyl radicals can be randomly produced along the polymer chain after its exposure to irradiations (electron beam or ⁶⁰Co γ -ray irradiation). This was demonstrated with a *N*-phthaloylchitosan (the soluble intermediate for the modification of chitosan) followed by the grafting of either S or SS.^{589,590} The structure and/or the location of the aminoxyl function was, however, unclear. Holmberg *et al.*⁵⁹¹ irradiated poly(vinylidene fluoride) (PVDF) in the presence of TEMPO. The macroinitiator was then used to graft styrene or a styrene/ *N*-phenylmaleimide mixture onto the PVDF membranes. Such a result was surprising since the alkoxyamine formed should be very stable and not prone to decomposition.

Interestingly, alkyl radicals can be generated along the polymer backbone in the presence of monomer and nitroxide via a bimolecular process. The preparation of polypropylene (PP) functionalized by hydroperoxide by means of γ -irradiation was reported.^{592–594} The resulting macroperoxide was then heated up to 125 °C in the presence of styrene or a styrene/butyl methacrylate mixture to produce the desired PP-g-PS or PP-g-P(S-co-BMA), respectively. Daly *et al.*⁵⁹⁵ and Daly and Evenson⁵⁹⁶ used esters of *N*-hydroxypyridine-2-thione or Barton esters to produce radicals on a polymer backbone under UV irradiation. This was successfully applied to poly (arylene ether sulfone)⁵⁹⁶ or hydroxypropyl cellulose backbones.⁵⁹⁵

3.10.4.3.4(iii) The 'grafting through' method

The last approach for the synthesis of graft copolymers is called the 'grafting through' or the macromonomer method. A macromonomer is an oligomeric or a polymeric chain bearing a polymerizable end-group, its copolymerization with another monomer yielding graft copolymers.⁵⁵⁷ The advantage of such a method is that branches can be synthesized from other polymerization techniques. In particular, Hawker et al.⁵⁹⁷ reported the preparation of well-defined PS grafted with polycaprolactone, polylactide, poly(ethylene oxide), or polyethylene using TEMPO-mediated polymerization. The analysis of the graft systems revealed that the macromonomer was incorporated as expected, depending on the reactivity ratio, while analysis of the backbone after cleavage of the branches showed that its molar mass was controlled by the initiator/monomer molar ratio. Ryan et al.³⁶⁴ showed that macromonomers prepared by addition fragmentation chain transfer, to form acrylic and styrenic polymers bearing ω-2-carboalkoxy-2-propenyl end-groups ($CH_2=C(CO_2R)CH_2=: R=Me_1$, Et, Ph), could be copolymerized with styrene in the presence of the SG1 nitroxide. They also determined the reactivity ratios and revealed a pronounced gradient structure, with the number of branches

per main chain decreasing gradually with the increase of monomer conversion.

3.10.4.3.5 Hyperbranched polymers

Hyperbranched polymers belong to a class of synthetic tree-like macromolecules called dendritic polymers. Hyperbranched polymers are polymers with densely branched structures and a large number of end-groups. Dendritic polymers include dendrimers⁵⁹⁸ that have completely branched star-like topologies and hyperbranched polymers that have imperfectly branched or irregular structures. From a practical point of view, if the branching density is equal to 1, a dendrimer is obtained, whereas when the branching density is lower and the branches are randomly distributed along the macromolecular structure, a hyperbranched polymer is formed.⁵⁵⁷ The group of Frechet⁵⁹⁹ reported the use of a dendritic initiator (a polyether dendron functionalized in the core by an alkoxyamine moiety) to prepare hybrid dendritic-linear block copolymers with well-controlled molar masses and low polydispersities. Recently, Lang et al.⁶⁰⁰ prepared a semiconductor hybrid diblock copolymer comprised of p-type dendritic and n-type linear blocks by NMP. The dendron, which contained triphenylamine (TPA) moieties, was functionalized by a TIPNO-based alkoxyamine, allowed the polymerization of perylene bisimide acrylate to be perfomed. UV-visible spectroscopy showed that the photoluminescence was completely quenched, indicating the occurrence of charge transfer between perylene bisimide blocks and TPA segments.

In 1995, Frechet et al.⁶⁰¹ developed a new technique to prepare hyperbranched polymer from vinyl monomers. This method was based on the polymerization of inimers (=INItiator + monoMER) and was called self-condensing vinyl polymerization. This approach was combined with NMP to prepare relatively well-defined hyperbranched polymers.⁶⁰² The presence of bound nitroxide functionalities at the chain ends of the hyperbranched structure affords interesting opportunities for the preparation of alternate molecular architectures such as hyperbranched stars. In this process, the living chain end is used to initiate the polymerization of vinyl monomers, such as styrene.⁶⁰² Importantly, these inimers are similar to monomer containing alkoxyamine fragments, also called polymerizable alkoxyamines (see Section 3.10.4.3.4 for details). Nevertheless, the main difference relies on the polymerization mode. If the alkoxyamine is stable enough during the first polymerization step, only grafted or comb polymers can be obtained. However, if the alkoxyamine can be dissociated, hyperbranched polymers are prepared. Li et al.⁶⁰³ synthesized a nitroxide functionalized with a double bond and used it for the polymerization of styrene at 120 °C. This led to hyperbranched PS with labile NO-C bonds attached to every grafting point. The branched structure can be further broken by heating up the polymer in the presence of a trap or a hydrogen donor.

3.10.4.4 Biomaterials

Due to high robustness, flexibility and rather mild experimental conditions as well as the possibility to insert varied functional groups within the polymer chains, CLRP techniques have been employed recently in the design of glycopolymers and polymer–peptide bioconjugates.^{604–608} Several important examples in this field have been reported so far for NMP.

3.10.4.4.1 Glycopolymers

Synthetic glycopolymers have been exclusively prepared using sugar moieties bearing a polymerizable function (also termed glycomonomer, see Table 8), styrenic, 262-266,609-611 acrylate, 475,535 or methacrylate. 342 Polymerizations of $N-(p-vinylbenzyl)-[O-\beta-D-galactopyranosyl-(1 \rightarrow 4)]-D-gluco$ namide (VLA, G1 with R=H) and its protected counterpart **G1** with R = Ac) were performed (Ac-VLA, in dimethylformamide (DMF) at 90 °C with 2-(benzoyloxy)-1-(phenylethyl)-DBN (BS-DBN) as the alkoxyamine in the presence of dicumyl peroxide.²⁶² Whereas VLA gave poor results, the polymerization of Ac-VLA led to predictible $M_{\rm p}$ s in the 2-40 kDa range and very low PDIs. A lipophilic DBN-based alkoxyamine (1-(4-N,N-dioctadecylcarbamoylphenyl) ethyl-DBN, DODA-PE-DBN) also yielded good control with Ac-VLA.⁶¹¹ The resulting glycolipids were further mixed with a phospholipid to form stable liposomes, at the surface of which galactose residues specifically recognized RCA lectin. This approach was also applied to an acrylate-containing glycomonomer, 3-O-acryloyl-1,2:5,6-di-O-isopropylidene-α-D-glucofuranoside (AIpGlc, G2), with the BS-DBN alkoxyamine in p-xylene at 100 °C.475 Predicted molar masses and PDIs in the 1.2-1.6 range were obtained. Eventually, a PS-DBN was chain-extended to yield a well-defined PS-b-PAIpGlc block copolymer.

The polymerization of a wide range of sugar-functionalized styrene was also controlled by TEMPO-based molecular alkoxvamines^{264–266,609} and macroalkoxyamines.^{263,265,610} Chen and Wulff^{265,266} employed the styryl-TIPNO for the bulk or solution polymerization at 130 °C of protected glycomonomers G3-6. For bulk experiments, linear evolutions of molar masses were obtained together with PDIs below 1.5, except for glycomonomer G6 where the PDI was unexpectedly high.²⁶⁶ The monomer to alkoxyamine molar ratio was then varied in order to target different molar masses. The solution polymerization of G3 in diphenyl ether at 50 wt.% gave narrower molar mass distributions, even though the polymerization rate was lower. Access to a small library of diblock copolymers was also investigated by chain-extension experiments with styrene of TEMPO-terminated glycopolymers obtained from glycomonomers G3-6, even though PDIs significantly increased due to the presence of dead glycopolymer chains. Miura et al.⁶⁰⁹ used **BPO-TEMPO** with protected glycomonomer G1. Polymerizations were conducted in 40 wt.% DMF at 130 °C and gave low PDIs (<1.4) and high monomer conversions. The affinities of the glycopolymers toward lectins were shown to depend on the degree of polymerization; the higher the DP, the stronger the affinity.

Well-defined diblock copolymers were also successfully obtained by polymerization of protected glycomonomer G3,²⁶⁵ G7,²⁶³ and $G8^{263}$ from low molar mass TEMPO-terminated PS and subsequent deprotection. Interestingly, when DVB was used as a cross-linking agent upon chain extension with glycomonomer G7 or G8, core-glycoconjugated star-shaped PS architectures were obtained.⁶¹⁰ From a difunctional TEMPO-based alkoxyamine, polymerization of glycomonomer G7 at 125 °C for 5 h followed by chain extension afforded the corresponding triblock

copolymers.²⁶⁴ Complete deacetylation restored the poly (4-vinylbenzyl glucoside) block.

Due to their versatility, SG1 and TIPNO were involved in the polymerization of acrylate- and methacrylate-based glycomonomers. For instance, Hawker et al. successfully controlled the polymerization of glycomonomer G9 in DMF at 105 °C with a TIPNO-based alkoxyamine functionalized with a lipogroup.535 philic *N*,*N*-di(octadecyl) amine These lipo-glycopolymers were shown to be surface-active and to form stable Langmuir films with accurate control over the molecular area. Well-defined poly(2-(β -D-galactosyloxy)ethyl methacrylate-co-styrene)-b-polystyrene (P(GalEMA-co-S)-b-PS) amphiphilic block copolymers were obtained from SG1-mediated polymerization of glycomonomer G10, using either P(AcGalEMA-co-S)-SG1 or PS-SG1 macroinitiators, followed by deacetylation of AcGalEMA moieties.342 The self-assembling ability of PS-b-P(GalEMA-co-S) amphiphilic glycopolymers was then exploited to obtain micellar structures and honeycomb-structured porous films of intact biofunctionality.

3.10.4.4.2 Bioconjugates

3.10.4.4.2(i) Conjugation to preformed peptides/proteins

Studies concerning the synthesis of bioconjugates by NMP only concerned small-sized peptides.^{606,608} Becker et al.^{508,509} used a combination of solid-phase peptide synthesis (SPPS) and surface-initiated NMP for the construction of the entire bioconjugate on Wang's resin. This was illustrated by the derivatization of the protein transduction domain (PTD) of the human immunodeficiency virus (HIV) Tat protein⁵⁰⁹ and the antimicrobial peptide tritroticin (VRRFPWWWPFLRR),⁵⁰⁸ by a fluorine-labeled TIPNO-based alkoxyamine for sequential NMP at 135 °C of tBA and MA (or S). It afforded well-defined PTD-poly(acrylic acid)-*b*-poly(methyl acrylate) (PTD-PAA-b-PMA) and tritrpticin-poly(acrylic acid)-b-polystyrene (tritrpticin-PAA-b-PS) hybrid block copolymers. Upon self-assembly, micelles decorated with tritrpticin exhibited an enhancement of the antimicrobial activity against Staphylococcus aureus and Escherichia coli when compared to free tritrpticin. Similarly, Trimaille et al.450 prepared an SG1-functionalized peptide (SG1-GGGWIKVAV) by SPPS and by direct coupling with the BlocBuilder alkoxyamine and the terminal amine group of the peptide in the presence of a coupling agent (Figure 21). Surface-initiated NMP of styrene was then performed to yield, after further cleavage from the support, the resulting peptide-PS bioconjugates.

The design of a PEGylation system based on NHS-functional comb-shaped polymethacrylates with PEG side chains was applied to the conjugation of a neuroprotective peptide and to lysozyme as a model protein.⁶¹² However, a tunable reactivity toward lysozyme was observed depending on the nature of the alkoxyamine used. Whereas copolymers deriving from alkoxyamine 71 led to partial coupling to lysozyme, quantitative conjugation to the latter was obtained from similar copolymers exhibiting a less sterically hindered NHS extremity.

3.10.4.4.2(ii) Combination of NMP and NCA polymerization

Another strategy to construct polymer–peptide bioconjugates is to combine the polymerization of α -amino-acid-*N*-carboxyanhydrides (NCA) with NMP.^{606,608} NCA

Table 8 Structure of glycomonomers polymerized by NMP



(Continued)







Figure 21 Synthesis of SG1-functionalized peptides as precursors for polymer-peptide conjugates.



Figure 22 Structure of functionalized alkoxyamines for NCA and NMP polymerizations.

polymerization proceeds by a ring-opening mechanism and is initiated by nucleophiles or bases such as primary amines or alkoxides.^{613–617}

Steig *et al.*⁶¹⁸ developed difunctional TIPNO-based initiators (**Figure 22**, **88**) where ring-opening polymerization (ROP) of β -benzyl-L-glutamate-*N*-carboxyanhydrides (BLG-NCA) was performed, followed by the NMP of styrene via a one-pot process to afford well-defined poly(γ -benzyl-L-glutamate)-*b*-polystyrene (PBLG-*b*-PS) low PDI bioconjugates in the 73–150 kDa range. Knoop *et al.*⁶¹⁹ reported the use of a dual initiator containing a primary amine and a TIPNO group (Table 4, 78) for sequential ROP of BLG-NCA in DMF at 0 °C and styrene by TIPNO-mediated polymerization at 120 °C. High structural degree of control was obtained, either from a two-step process (i.e., from a purified PBLG-TIPNO macroinitiator), or by a one-pot process, owing to a high compatibility of both polymerization techniques.

3.10.5 Conclusions and Perspectives

CLRP is one of the most rapidly developing areas in polymer science. Among the various existing techniques, NMP was the first to be proposed. Even though comparison between CLRP techniques in order to extract the ideal candidate is extremely complex, Braunecker and Matyjaszewski⁶²⁰ recently proposed a polar-type chart whereby performance of the different methods (NMP, ATRP, and RAFT) in different areas are reported (synthesis of high/low molar mass polymers, end-functional polymers, block copolymers, the range of polymerizable

monomers, the synthesis of various hybrid materials, environmental issues, and the polymerization in aqueous media).

NMP has the main advantage that purely organic systems and functional (including acidic) monomers can be used, the latter being used without protecting chemistry. In addition, it has the advantage of being governed only by a thermal process and does not require any transition metal catalysts or bimolecular exchange with sulfur-based compounds. All CLRP techniques have now rather similar efficiencies for the preparation of hybrid materials as well as the possibility to be performed in (aqueous) dispersed media. Even though, due to potential toxicological issues and environmental concerns, a great deal of effort is being devoted to developing ATRP-based processes with lower amounts of catalyst (the so-called ARGET and ICAR processes) or efficient RAFT end-group removal pathways, NMP is perhaps the CLRP of choice, especially regarding potential biomedical applications. For instance, the BlocBuilder MA alkoxyamine (71), commercially developed by Arkema, exhibits a very high lethal dose 50 (LD50) of about 2000 g kg^{-1,621} Although one might argue that the toxicity of the controlling agent is different from the one of the polymer, the group of Davis⁶²² recently reported in vitro cytotoxicity studies of various RAFT-synthesized water-soluble polymers, where it was shown that their cytoxicity depended on the cell type and on the nature of the RAFT end-group. Chenal et al.⁶²³ did a similar study with SG1-based polymers and demonstrated the innocuousness of SG1-terminated copolymers even at very high doses, without any purification other than a simple precipitation. As well as this, the same authors showed no cytotoxic effect coming from the nitroxide SG1 in case of a quantitative release from a SG1-terminated polymer.623

However, the main limitation of NMP is related to the range of monomers that can be controlled. Whereas nonconjugated monomers such as vinyl acetate (VAc) and *N*-vinyl pyrrolidone (NVP) cannot be homopolymerized, recent findings reported that methacrylic esters can be controlled by the DPAIO nitroxide¹⁸¹ or by the copolymerization with a low amount of either styrene²⁰⁸ or acrylonitrile.³⁴³ Second, the use of relatively high temperatures are generally required even though drastic improvements have been witnessed as actual NMP systems can be successfully performed in the 70–90 °C range.

These limitations may explain the lower amount of publications devoted to NMP compared to ATRP and RAFT. Nevertheless, the situation from an industrial point of view is rather different, mainly due to the difficulty of preparing moderators in large scales and/or to the need of end-groups removal steps. Destarac⁶²⁴ recently proposed a very interesting overview of the industrial development of CLRP processes where he reported that several products from NMP have been commercialized by Ciba and Arkema.

Following on from these state of the art developments, what could be the future of NMP? First, there is a need for new nitroxides able to extend the range of polymerizable monomers and to perform homopolymerization of methacrylic esters. Further works should be dedicated to improve the control of methacrylate derivatives since this family of monomers is important due to the combination of their physical properties and the various functionalized structures that are already commercially available. Second, the control of VAc and NVP would be crucial to have access to hydrophilic polymers that could degrade under environmental and in vivo conditions as well as exhibiting the ability to resist nonspecific protein adsorption in biological environments.

These new nitroxides could also bring interesting advances regarding the relatively high temperatures that are generally required, by accelerating the kinetics and then lowering the polymerization temperature. As for RAFT polymerization, 625 switchable nitroxides or alkoxyamines whose properties could change with an external stimulus could lead to a breakthrough regarding block copolymer synthesis. A good example in this field is given by the groups of Gigmes and Lalevee, 136,138,139 who have shown by nitroxide-mediated photopolymerization (see Box 1) that the dissociation properties of the alkoxyamine could be tuned by varying the light intensity.

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Nitroxide-Mediated Polymerization

343

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1923

323

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Nitroxide-Mediated Polymerization

347

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Biographical Sketches



Julien Nicolas graduated from the Ecole Supérieure de Chimie Organique et Minérale (ESCOM) (Cergy-Pontoise, France), in 2001. He completed his PhD in 2005 under the supervision of Prof. Bernadette Charleux at the University of Pierre and Marie Curie (Paris), where he studied nitroxide-mediated polymerization (NMP) in homogeneous and aqueous dispersed media. He then joined the group of Prof. David M. Haddleton at the University of Warwick (United Kingdom) for a postdoctoral fellowship to design polymer–protein bioconjugates by controlled/living radical polymerization (CLRP). In 2007, he was appointed permanent CNRS researcher in the group of Prof. Patrick Couvreur, University Paris-Sud (France), where his current research activities are focused on the CLRP and on the synthesis of novel (bio)polymers and nanoparticles for drug delivery purposes.



Yohann Guillaneuf graduated from the Ecole Nationale Supérieure des Industries Chimiques (ENSIC) (Nancy, France), in 2002. He completed his PhD in 2006 under the supervision of Prof. Denis Bertin at the University of Provence (Marseille, France), where he studied the kinetics of nitroxide-mediated polymerization (NMP). He then joined the group of Prof. Robert G. Gilbert at the Key Centre for Polymer Colloids (KCPC) (University of Sydney, Australia) for a postdoctoral fellowship on the synthesis of amphiphilic copolymers by RAFT polymerization. Then, he moved with Prof. Robert G. Gilbert to the University of Queensland (Brisbane, Australia) to work on the characterization of polysaccharides. In 2008, he came back to the University of Provence to work with Dr. Didier Gigmes on nitroxide-mediated photopolymerization (NMP²). In 2010, he was appointed permanent CNRS researcher in the group of Dr. Didier Gigmes (University of Provence, France), where his current research activities are focused on the mechanisms of NMP and the development of both NMP² and controlled radical ring-opening polymerization method based on nitroxide (NMrROP).



Denis Bertin got his education in 1993 at the National Engineer School of Chemistry in Montpellier, France. In 1997, he obtained a PhD in material science under the guidance of Prof. Bernard Boutevin (Montpellier, France). He started his career in Elf-Atochem Company (Serquigny, France), where he was in charge of the material process service. In 1999, he joined the University of Provence (Marseille, France) as an associate professor. He obtained his Habilitation in 2003 at the University of Provence and became a full professor of this university in the same year. His research interests are focused on controlled radical polymerization and the design of complex polymer architectures for applications in the field of health, environment, and energy. In 2004, along with Dr. Didier Gigmes, he created the team Chimie Radicalaire Organique et Polymère de Spécialité (CROPS) in the Laboratoire Chimie Provence. Since January 2008 he has been the vice-director of the Laboratoire Chimie Provence and since June 2008 he has been the Dean of Science of the University of Provence.



Didier Gigmes got his education in chemistry at the University Paul Cezanne (Marseille, France). In 1998, he received a PhD in organic chemistry under the guidance of Prof. Paul Tordo (Marseille, France). Then he completed a first postdoctoral fellowship at Elf-Atochem, North America in Pennsylvania (USA) under the supervision of Dr. Gary Silverman. Then, he came back to France to work as a postdoctoral fellow under the supervision of Prof. Paul Tordo in Marseille. In 2001, he obtained a position of researcher at CNRS to develop the nitroxide-mediated polymerization (NMP). In 2004, he was the co-founder with Pr. Denis Bertin of the team Chimie Radicalaire Organique et Polymère de Spécialité (CROPS) that belongs to the Laboratoire Chimie Provence. In 2008, he defended his Habilitation at the University of Provence, and since June 2008, he has been the group leader of the team CROPS. In October 2010, he has appointed Research Director at the CNRS. During the past few years he has been working on the development of NMP and especially the design of a highly efficient SG1-based alkoxyamine, which currently belongs to the most efficient alkoxyamines known to conduct NMP. After a significant contribution to the comprehension of the mechanisms involved in NMP, one of his main concerns is now to promote NMP in material science for various applications such as biomaterials, environment, and energy.



Bernadette Charleux graduated from the Institut de Chimie et Physique Industrielles of Lyon (France) in 1987. In 1991, she received a PhD degree from the University Claude Bernard in Lyon (France), under the supervision of Dr. Christian Pichot at the joint research unit CNRS–BioMérieux. She was working on the elaboration of functionalized latex particles for medical diagnostic applications. She then spent 6 months at the CNRS center of Thiais (France), working in the area of conducting polymers. During that period she got a permanent CNRS researcher position to work in the field of cationic polymerization in the group of Prof. Jean-Pierre Vairon, at the Laboratoire de Chimie des Polymères at the University Pierre and Marie Curie (Paris, France). She received the Habilitation in 2000 and was appointed full professor in 2001. Her current research activities are based on many aspects of controlled/living radical polymerization (CLRP) with, in particular, its application to aqueous dispersed systems.

3.11 Organometallic-Mediated Radical Polymerization

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3.11.1	Introduction: Discovery of OMRP	351
3.11.2	Mechanistic Interplays	352
3.11.3	Tuning the Metal–Carbon Bond Strength	353
3.11.4	Interplay of Dissociative and Associative Processes	354
3.11.5	'Clean' OMRP-RT Processes	358
3.11.5.1	Titanium Systems	358
3.11.5.2	Vanadium Systems	359
3.11.5.3	Chromium Systems	359
3.11.5.4	Molybdenum Systems	360
3.11.5.5	Iron Systems	361
3.11.5.6	Cobalt Systems	361
3.11.6	OMRP-RT versus CCT	365
3.11.7	Interplay of OMRP-RT and ATRP	367
3.11.8	Metal Elimination and Recycling	372
3.11.9	Conclusions and Perspectives	373
References		373

3.11.1 Introduction: Discovery of OMRP

Organometallic-Mediated Radical Polymerization (OMRP) refers to a controlled radical polymerization method whereby the active radical chain is reversibly trapped by a transition metal complex with the direct formation of a metal-carbon bond (see Figure 1). Thus, this is a 'reversible deactivation' method where the dormant state is an organometallic system and the controllability of the chain growth rests on the 'persistent radical effect',¹ as for other kinds of 'stable free-radical polymerization' (SFRP), notably 'nitroxide-mediated polymerization' (NMP, Chapter 3.10) and for 'atom transfer radical polymerization' (ATRP, chapters 3.12 and 3.13). Interest in this technique lies in the potential, given the modular effect of the metal coordination sphere on the homolytic metalcarbon bond strength in the $P_n - Mt^{x+1}/L_v$ dormant species, to achieve controlled growth for monomers that are associated to more reactive radicals and the results obtained so far are promising. Severe limitations are the need to use stoichiometric amounts of the metal complex (one molecule per chain) and permanence of the latter as chain end in the isolated polymer, requiring posttreatment if metal-free polymers are sought. However, metal removal, recovery, and recycling are possible in principle (see Section 3.11.8).

The terms 'stable free-radical' or 'persistent radical' are actually not always appropriate for this technique, because the metal complex that moderates the active radical concentration does not necessarily have radical character (one unpaired electron, $S = \frac{1}{2}$) and the organometallic dormant species is not always diamagnetic. The moderator may also possess any other spin state (including zero), yielding a stable dormant species with a spin multiplicity of different parity. For instance, spin singlet (S = 0) Os^{II} complexes yield spin doublet ($S = \frac{1}{2}$) alkylosmium(III) dormant species,² while spin quartet (S = 3/2) Co^{II} complexes yield spin singlet alkylcobalt(III) dormant species.³ For this reason, use of the generic SFRP acronym is not appropriate. The term CMRP (for Cobalt-Mediated Radical Polymerization, recently reviewed⁴) only pertains to the use of cobalt and is not specific for the reversible deactivation mechanism (*vide infra*). The term OMRP covers all metals.⁵ The use of this acronym was initially limited to the reversible deactivation mechanism outlined in **Figure 1**. However, it has recently been shown that organometallic compounds may also act as transfer agents for the controlled radical polymerization that follows the degenerative transfer principle, as outlined later in Section 3.11.4. In this chapter, both these two controlled polymerization methods, which may in certain cases interplay, will be outlined. When addressing each specific mechanism, an additional qualifier will be added to the acronym, OMRP-RT for reversible termination and OMRP-DT for degenerative transfer, whereas the OMRP term will be used in a more general situation.

The first reported controlled polymerization based on the OMRP-RT principle appears to have been presented by Minoura in a series of articles starting in 1978, where the redox initiating system BPO/Cr²⁺ was used for the polymerization of vinyl monomers.⁶⁻¹⁰ Not only were the kinetics different than in free-radical polymerization (very low reaction orders in Cr²⁺ and BPO), but also the polymerization was observed to continue after all Cr²⁺ had been converted by the peroxide to Cr³⁺ and the degree of polymerization was found to increase with monomer conversion at low temperatures (< 30 °C). These studies included the report of a block copolymer (PMMA-b-PAN). Polydispersity indexes were not reported for these studies. Minoura formulated the mechanistic hypothesis of the formation of a 'metal complex with the free radical' and stated that "the recombination of free radicals formed by the dissociation of the complexed radicals competes with a disproportionation of free radicals". However, these studies did not have a great impact in the polymer community, being cited only a handful of times before 1994. A few subsequent contributions reported the application of similar conditions to other metals but well-controlled polymerizations were not found.11-14



Figure 1 Free energy profile of the OMRP equilibrium (Mt = metal, L = ligand, M = monomer).



Figure 2 Cobalt complexes used in the first reports of OMRP.

The area started to boom after 1994, by which time awareness of controlled radical polymerization methods was rising, when the well-controlled polymerization of acrylates was reported almost simultaneously by the groups of Harwood and Wayland using organocobalt(III) compounds based on glyoxime (cobaloximes) and porphyrins as initiators (Figure 2).^{15,16} While II is a thermal initiator, I needs photochemical activation of the Co-C bond. Both families of cobalt complexes had previously been used as models for the study of the fragile Co^{III}-carbon bond in vitamin B12. The reactivity of these families of compounds with radicals was therefore well known, notably some of them had been found quite efficient as chain transfer catalysts in radical polymerization.¹⁷ The first report of a controlled polymerization by the OMRP-DT method is much more recent, again from the Wayland group using a cobalt porphyrin system such as II as transfer agent.¹⁸

3.11.2 Mechanistic Interplays

It is not possible to fully appreciate the achievements, limitations, and potential of OMRP without first highlighting the complexity of one-electron transition metal reactivity, because metal complexes can react with radical chains in several different ways,19 each one of them potentially interfering, competing, or interplaying with OMRP. The most relevant possibilities are schematically summarized in Figure 3.⁵ Starting with the simpler case where halogens or other transferable atoms or groups X are not present in the system, the metal complex Mt^{x}/L_{y} employed to moderate the radical concentration in the OMRP-RT equilibrium may also abstract an H atom, leading to an intermediate hydride complex L_v/Mt^{x+1}-H and ultimately start a new chain, in 'chain transfer catalysis' (CCT, Chapter 3.09). The dichotomy of these two processes - radical annihilation to form the organometallic dormant species on one side and H atom transfer on the other side is delicately controlled by the metal coordination sphere (L_{ν}) in a way that is not yet completely understood, and the simultaneous presence of these two phenomena is frequently observed (see Section 3.11.6). If excess radical initiator - beyond 1 equiv. relative to Mt^{x}/L_{y} – is present and if the coordination sphere of the resulting $R-Mt^{x+1}/L_{\nu}$ allows it, continuous radical injection into solution may lead to a rapid associative and degenerate radical exchange, OMRP-DT. Degenerate transfer polymerization may also be carried out with many other transfer agents, as shown in Chapters 3.06-3.08. The associative (OMRP-DT) and dissociative (OMRP-RT) equilibria have also been shown to interplay for specific systems (see Section 3.11.4). Obviously, OMRP-DT cannot take place unless excess radicals are present. Conversely, excess radicals in principle reduce not only the dissociation from the dormant species but also the impact of CCT through a reduction of the Mt^{x}/L_{y} concentration. For close to stoichiometric conditions between Mt^{x}/L_{y} and R[•], however, all three processes can in principle interplay.

If, in addition, transferable groups X are present (the most common case being that of halogen atoms), then an additional interplay may be installed between OMRP-RT and ATRP equilibria. In essence, the active radical concentration can be moderated simultaneously by Mt^x/L_γ to yield the OMRP dormant species (R– Mt^{x+1}/L_γ) and by L_γ/Mt^{x+1} –X to yield the ATRP dormant species (R–X) and Mt^x/L_γ , their relative importance covering the entire spectrum between pure ATRP and pure OMRP. Thus, OMRP trapping may not only assist an ATRP process by reducing the concentration of the chain carrier



Figure 3 Interplay of different one-electron processes involving transition metal complexes and radical polymer chains (metal-bonded ligands are not shown).

radicals but may also interfere with it by trapping the radicals irreversibly and stop the polymerization. In the latter case, starting from Mt^x/L_γ and an ATRP initiator R–X, the outcome is an irreversible one-electron oxidative addition. All scenarios are possible and this area has been reviewed.⁵

3.11.3 Tuning the Metal–Carbon Bond Strength

Leaving aside for the moment OMRP-DT and CCT, it is useful to briefly examine the energetic profile of the reaction coordinate for the one-electron oxidative addition (see Figure 4). The enthalpy of the ATRP activation equilibrium can be expressed as the difference between two homolytic bond-dissociation enthalpies (BDEs): the R-X bond being broken and the Mt^{x+1} -X bond being formed. Control will be ensured when this BDE difference is placed in a suitable range, not too low (otherwise too many radicals would be produced leading to too many terminations) and not too high (not enough radicals to sustain polymerization). The entropic effect should not be very important for this equilibrium, since the same number of molecules are present on each side. Once the active radicals are produced, the Mt^{x}/L_{y} species can install the OMRP-RT equilibrium, the enthalpy of which is equal to the Mt^{x+1} -R BDE. In this case, a positive entropy term for the dissociation process will render ΔG smaller than ΔH . Electronic effects affect only the ΔH term, not the ΔS term, and reflect directly on ΔG .

Stabilized radicals (such as those of the polystyrene or polyacrylate growing chains), are associated to relatively weak bonds (i.e., BDE(R–X) and BDE(Mt^{x+1}–R) are relatively small). Many metal systems have been found to ensure a reasonable control by ATRP for these monomers, showing that ΔH (ATRP) is located in a suitable range. For these systems, OMRP trapping was shown to be either too unfavorable (BDE(Mt^{x+1}–R) too small) or to contribute to reversibly deactivate the growing chains (see Section 3.11.7). Thus, ATRP and OMRP-RT cooperate in the latter case. More reactive radicals such as those of the poly(vinyl acetate), poly(vinyl chloride), or polyethylene



Figure 4 Energy profile, on an enthalpy scale, of a one-electron oxidative addition reaction.

chains, on the other hand, yield stronger bonds by 10 kcal mol⁻¹ or more,^{20,21} increasing both $\Delta H(\text{ATRP})$ and $\Delta H(OMRP-RT)$. Therefore, the same metal complexes that control the ATRP of styrene and acrylates give slower activation (or none whatsoever) for vinyl acetate, vinyl chloride, or ethylene. In order to promote the ATRP activation, it is therefore necessary to select a more reactive metal complex, capable of giving stronger bonds, thus lowering $\Delta H(ATRP)$. However, $\Delta H(\text{OMRP-RT})$ keeps increasing (Figure 4). The inevitable conclusion is that ATRP of an unreactive monomer (associated to a reactive radical) is always likely to be associated with OMRP trapping, reversible or irreversible. These considerations help illustrate why OMRP-RT has an advantage and greater potential over other controlled radical polymerization strategies, and particularly over ATRP, for controlling monomers that lead to reactive radical chains.

Tuning $\Delta H(OMRP-RT)$ requires modulation of only one bond strength, that of the $L_{\nu}/Mt^{x+1}-R$ bond, which can be envisaged through modification of Mt and L_w while interplay with ATRP can be eliminated by eliminating transferable atoms such as halogens from the system. A rough calculation can give estimates for the suitable range of ΔH (OMRP-RT). Targeting polymers with $X_n \sim 100$ and $\geq 90\%$ of living chains, the free radicals should have at least a 99.9% probability to extend the chain relative to terminations $(0.999^{100} = 0.905)$, meaning that the rate of propagation should be >1000 times the rate of termination. From the relationship $v_{\rm D}/v_{\rm t} = (k_{\rm p}/k_{\rm t})[{\rm M}]/[{\rm R}^{\bullet}]$ and a typical [M]~10 M for bulk polymerizations, we derive $[R^{\bullet}] < 10^{-3} (k_{\rm p}/k_{\rm f})$. The rate constants for propagation and termination are of course monomer-dependent and a great variability is reported for many of them depending on conditions (T, solvent) and on the method used for the determination.²² Taking high and low limits for this ratio as 10^{-3} and 10^{-7} gives a radical concentration $< 10^{-6}$ or 10^{-10} , respectively, to be established by the OMRP-RT pseudo-equilibrium. Considering < 10% terminations before the persistent radical effect sets in, the equilibrium $[Mt^{x}/L_{y}]/$ $[R-Mt^{x+1}/L_{\nu}]$ ratio would be <0.1, giving K<10⁻⁷ or 10⁻¹¹ in the two extreme cases. This leads to $\Delta G_{\text{OMRP}} > 10 \text{ kcal mol}^{-1}$ for high (k_p/k_t) monomers or >15 kcal mol⁻¹ for low (k_p/k_t) monomers for polymerizations carried out at room temperature (at 120 °C, these lower estimates become 13 and 20 kcal mol^{-1} , respectively). Since the OMRP-RT activation process generates two active species from one dormant, $\Delta S(OMRP-RT)$ is expected to be as much as 30 EU, or $T\Delta S \sim 9 \text{ kcal mol}^{-1}$ at r.t. (or ~12 at 120 °C), leading to the estimation of ΔH (OMRP-RT) > 19 for high (k_p/k_t) monomers or >24 kcal mol⁻¹ for low $(k_{\rm p}/k_{\rm t})$ monomers for a r.t. polymerization (>25 and >32 kcal mol⁻¹ for a polymerization carried out at 120 °C). More stringent conditions are required to make higher X_n macromolecules, and stronger bonds will obviously ensure better control for the same $X_{n'}$ but at the same time slow down the polymerization process.

Searching for a Mt^x/L_γ complex that leads to a suitable OMRP-RT equilibrium with a reactive radical, it is best to engineer it without easily transferable groups in the coordination sphere and to carry out the polymerization under pure OMRP-RT conditions (no use of X– Mt^{x+1}/L_γ trapping species or R–X initiators; use of classical initiator sources such as AIBN or a stable organometallic complex R– Mt^{x+1}/L_γ). Under these conditions, there will be no interference of ATRP-type equilibria.



Figure 5 OMRP activation–deactivation equilibrium for the $CpCr^{II}(nacnac^{Ar,Ar})$ system.

Table 1Calculated bond dissociation enthalpies (in
kcal mol⁻¹) and bond lengths (in Å) for the Cr^{III} -R bond in
compounds $CpCr(nacnac^{Ar,Ar})(R)$ (see Figure 5)^a

	Ar = Ph		Ar = Xyl	
R	BDE	Cr–C	BDE	Cr–C
CH(Me)Ph CH ₂ Ph CH(Me)OOCMe	11.8 20.8 28.4	2.173 2.136 2.109	2.0 13.3 19.7	2.197 2.146 2.124

 $^a\mathrm{DFT}$ calculations using the B3LYP functional and the 6-31G ** basis set. 21

There may still be, however, interplay with OMRP-DT if excess radicals are present and with CCT under any circumstance.

A recently explored system (CpCr^{II}(nacnac^{Ar,Ar})) (Figure 5) was used to calculate the Cr^{III}–R BDE for various R[•] and aryl substituents. The calculated values, reported in Table 1, clearly show how the bond strength is affected by the radical nature (CH(Me)Ph (model of PS radical) < CH₂Ph < CH(Me) OOCCH₃ (model of PVAc radical)) and by the aryl group size (Xyl < Ph). The optimized Cr^{III}–C distance shows an inverse correlation with the bond strength.²¹

The steric activation strategy for the weakening of Mt^{x+1} –C bonds, however, has limitations because the additional steric bulk in the coordination sphere also creates an extra radical trapping barrier, slowing down deactivation and worsening the chain growth control, as shown by some experimental results that will be detailed in later sections. The best design of a suitable mediator for the OMRP-RT of unreactive monomers should therefore be oriented toward the use of relatively unencumbering ligands in combination with metals that afford homolytically weak bonds with alkyl groups. As the BDE of Mt^{x+1}-C bonds increases on going down a group of transition metals, the most promising metals are therefore those of the first transition series (3d metals like Ti, V, Cr, etc.). Heavier transition metals may be more suitable in principle to control the polymerization of more reactive monomers, although in those cases the ATRP strategy appears more attractive.

3.11.4 Interplay of Dissociative and Associative Processes

As outlined in Section 3.11.2, excess radicals relative to the amount needed to convert Mt^{x}/L_{y} into R-Mt^{x+1}/L_y may trigger an associative and degenerate radical exchange process, leading to controlled polymerization by degenerative transfer. This phenomenon cannot occur, however, for just any metal complex. The prerequisites are a vacant coordination site to accommodate the incoming radical chain and a suitable electronic configuration at the metal center to establish an incipient bonding interaction with the incoming radical at the transition state level. The only system where this phenomenon has been highlighted so far is five-coordinate Co^{III}, such as the phorphyrin complex II (Figure 2) and related systems. This electronic configuration and coordination geometry fulfill the two above-mentioned criteria, because the metal complex is coordinatively unsaturated with a square pyramidal geometry, related to an octahedral geometry with a vacant axial site and the metal has a 16-electron configuration with a low-energy metal-based empty orbital directed toward the vacant site and therefore ready to accommodate the entering radical. In a fully associative two-step mechanism, the intermediate adduct would formally be a 17-electron octahedral Co^{IV} complex. Such an intermediate has neither been isolated nor spectroscopically detected. Thus, the exchange is more likely a one-step associative interchange mechanism where addition of one radical chain entails expulsion of the other one via a three-center three-electron transition state as shown in Figure 6, as also validated by a theoretical study.²³

Wayland was first to report the occurrence of this mechanism, for the polymerization of methyl acrylate mediated by complex Co^{II}(TMP),^{18,24,25} which is also capable of controlling the polymerization of the same monomer by reversible termination, though more slowly.^{16,26} A good illustration of this principle is presented in Figure 7. When the amount of V-70 initiator used (V-70 is a trade name for 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile)) is such that the total amount of primary radicals injected into solution is 0.8 per cobalt, a slow polymerization takes place by OMRP-RT because Co^{II} (TMP) is not completely converted into PMA-Co^{III}(TMP) and latent radical can only be generated by the dissociative equilibrium. When the amount of primary radicals is greater, on the other hand, faster polymerization occurs by OMRP-DT, but only after an induction time needed to convert all Co^{II} to PMA-Co^{III}. The rate of polymerization after that time is governed by the rate of radical generation from the initiator, like in free-radical polymerization. After all initiator is consumed (6-7 times the half life, which is 11 min under these conditions) the polymerization does not stop but rather continues at a slower rate, because it becomes governed again by reversible



Figure 6 Associative radical exchange for a square pyramidal alkyl cobalt(III) complex.



Figure 7 Time evolution of $\ln([MA]_0/[MA])$ for the methyl acrylate polymerization initiated by V-70 in benzene at 333 K ($[MA]_0 = 2.5 \text{ M}$, $[Co^{II}(TMP)] = 1.2 \times 10^{-3} \text{ M}$), R*/Co^{II} = 0.80 (1), 1.2 (2), and 2.0 (3). Reprinted with permission from Wayland, B. B.; Peng, C.-H.; Fu, X.; *et al. Macromolecules* 2006, *39*, 8219.²⁵ Copyright 2006 American Chemical Society.

termination. The chain growth is well controlled in all cases (trace 1: 47% conversion after 62 h, $M_n = 9.91 \times 10^4$ with $M_w/M_n = 1.11$; trace 2: 54% conversion after 150 min, $M_n = 9.5 \times 10^4$ with $M_w/M_n = 1.06$; trace 3: 69% conversion after 105 min, $M_n = 11.6 \times 10^4$ with $M_w/M_n = 1.06$), with M_n increasing linearly with monomer conversion.²⁵ A quantitative mechanistic analysis based on ¹H NMR observations places the rate of radical exchange for the PMA[•] chains and PMA–Co^{III} (TMP) as ~7 × 10⁵ M⁻¹.²⁷

Interestingly, when using the sterically less demanding tetra-(*p*-methoxyphenyl)porphyrin derivative (III, Figure 8) in the OMRP-RT of acrylates (total $\mathbb{R}^{\bullet}/\mathrm{Co}^{II} = 0.9$), the resulting polymer grows only up to a maximum $X_n \sim 200$, indicating the intervention of CCT. However, use of excess radicals leads to a controlled polymer growth by OMRP-DT, because under these conditions the Co^{II} is maintained at sufficiently low concentrations such that the β -H atom transfer is effectively guenched.²⁵

The above studies were later extended to the controlled polymerization of AA in water at 333 K to produce well-controlled PAA chains by use of the water-soluble Co^{II} complex **IV** with the tetra(3,5-disulfonatomesityl)porphyrin ligand. For instance, a 81.6% conversion in 30 min, including

an induction period of 13 min, led to a PAA with an M_n of 232 000 (theory 212 000) and an M_w/M_n of 1.20.²⁸ The control is again ensured by interplay of degenerate transfer and reversible termination, because polymerization continues at a slower rate after all initiator is exhausted. Like for the MA polymerization described above, the AA polymerization is also controlled by a complex with the sterically less demanding tetra(4-sulfonatophenyl)porphyrin ligand (V), but only under degenerate transfer conditions where excess radical ensures a low concentration of the Co^{II} chain transfer catalyst.

The growing radical chains generated by vinyl acetate form stronger bonds with the cobalt porphyrin system, thus the dissociative pathway is essentially shut down and polymerization occurs only in the presence of excess radicals by OMRP-DT. In this case M_n deviates toward lower values from theory as conversion increases,²⁹ indicating that the PVAc⁺ chains have a greater propensity than the PMA⁺ chains to undergo CCT, even under conditions where the Co^{II} concentration is kept low by excess radicals. Block copolymers of methyl acrylate and vinyl acetate could also be obtained by first initiating MA polymerization with AIBN at 333 K in the presence of Co^{II}(TMP) to yield a PMA-Co^{III}(TMP) intermediate with $M_n = 30\,000$ and $M_w/M_n = 1.11$, then removing the acrylate monomer and



Figure 8 Additional porphyrin ligands used in cobalt-mediated radical polymerization.



Figure 9 Cobalt(II) bis(β -diketonates) used in cobalt-mediated radical polymerization.

adding vinyl acetate until obtaining a PMA-*b*-PVAc with $M_{\rm n} = 85\,000$ and $M_{\rm w}/M_{\rm n} = 1.21.^{29}$ The AIBN half life at 333 K is much longer than the reaction time of 2 h to form the PMA block, thus AIBN remains present in solution to initiate the VAc polymerization for the second block by OMRP-DT.

In 2005, Jérôme et al. reported a very efficient and well-controlled radical polymerization of VAc in the presence of Co(acac)₂ (acac = acetylacetonate), VI (Figure 9), with V-70 as radical initiator in bulk, using a V-70/Co ratio of 6.5.30 Polymers with $M_{\rm p}$ up to 10^5 were obtained with $M_{\rm w}/M_{\rm n}$ = 1.33, although narrower distributions (down to 1.11) were obtained for smaller M_n . On the other hand, no control could be achieved with this system for nBuA and a subsequent contribution from the Matyjaszewski group revealed an increasing control for the generation of VAc-stat-nBuA copolymer chains as the proportion of VAc increased.³¹ The resulting Co(acac)₂-capped chains were then further chain-end functionalized leading to a variety of new polymers.^{32,33} The polymerization can also be carried out using peroxides (lauroyl or benzoyl), reduced in situ by part of Co (acac)₂ or by an external sacrificial reducing agent (citric or ascorbic acid), as radical source at 30 °C.³⁴ The initial Jérôme contributions formulated the hypothesis of a control by

reversible termination, the strongest indicator being that the polymerization could be successfully resumed after isolating oligomers at low conversion, repeatedly precipitating them in heptane, and adding new monomer. Under these conditions no more V-70 initiator is present to generate new radicals. However, the presence of long induction times and the very rapid polymerization, approaching the rate of free-radical polymerization while remaining controlled in the presence of such large excess of radical initiator, were not explained.

The rationalization of these observations was provided later by Poli and Matyjaszewski.³ In essence, the PVAc[•] chain forms a strong PVAc-Co(acac)₂ bond, too strong to dissociate significantly and sustain OMRP-RT when operating in bulk monomer and the polymerization takes place only by the degenerative transfer mechanism after the initial induction time, just like for Wayland's porphyrin system. The two dormant species, R-Co^{III}(porphyrin) and R-Co^{III}(acac)₂, are isostructural and isoelectronic. However, in the presence of ligands with sufficient binding capacity, the acetylacetonate system can more readily saturate its coordination sphere as shown in Figure 10. The pentacoordinated PVAc-Co^{III}(acac)₂ species (VIII) can be stabilized by addition of the ligand L to generate the six-coordinate complex PVAc-Co^{III}(acac)₂(L) (IX). However, L can also add to Co^{II}(acac)₂ to generate five-coordinate $Co^{II}(acac)_2(L)$ and then six-coordinate $Co^{II}(acac)_2(L)_2$. Ligand binding globally favors the Co^{II} system, shifting the Co-PVAc bond breaking equilibrium toward the active radical chain and opening up the possibility of OMRP-RT, with a polymerization rate that depends on the L concentration and binding strength. At the same time, since ligand exchange is rapid for octahedral Co^{II} but slow for octahedral Co^{III} (a kinetically inert system), ligand addition to the Co^{III} dormant species blocks the possibility of associative radical exchange and shuts down the



Figure 10 Ligand addition equilibria in the Co(acac)₂-mediated polymerization of VAc.

OMRP-DT. The chain extension experiment that initially led Jérôme *et al.* to propose the OMRP-RT mechanism is triggered by the coordination of water, originating from incompletely dried solvents, to the vacant site of the isolated oligomer–Co^{III} (acac)₂ chain end. This proposition was later confirmed by a Poli–Jérôme collaboration (see also Section 3.11.5).³⁵ A more detailed experimental and theoretical investigation of the nature of the PVAc–Co^{III}(acac)₂ dormant chain in the absence of coordinating ligands indicates chelation by the carbonyl function of the metal-bonded VAc unit, to form a five-membered ring (system **X**), estimated to provide an additional ~3 kcal mol⁻¹ stabilization to the system. Hence, the PVAc[•] dissociation equilibrium is further retarded when operating in bulk monomer, because the latter does not have sufficient coordinating power to act itself as monodentate ligand.

Several examples of chain-extension experiments and block copolymer syntheses carried out in the absence of donor ligands have been reported for PVAc-Co(acac)₂ macroinitiators prepared under degenerate transfer conditions^{30,36} (block copolymer syntheses carried out in the deliberate presence of donor ligands will be discussed separately in Section 3.11.5.3). As mentioned above, these are probably triggered by adventitious water if the residual external radical source is no longer present. Among the most intriguing cases are the syntheses of PVAc-b-(PVAc-co-PO), PVAc-b-(PVAc-co-PE), and PVAc-b-PO. In the first two cases, octene or ethylene were added to the PVAc-Co(acac)₂ obtained at low conversion, resulting in a slow down of polymerization kinetics and copolymers with low polydispersity and low olefin incorporation relative to the comonomer feed. Tailing of the distribution at the low $M_{\rm n}$ side suggests terminations, presumably by degradative chain transfer with formation of stable allyl radicals in the case of octene, whereas in the case of ethylene the polymerization stopped after small ethylene consumption (DP of 141 and 17 for VAc and E according to ¹H NMR).³⁷ In these cases, it is not clear whether any external radical source was still present after the olefin addition, sustaining an OMRP-DT mechanism. For the PVAc-b-PO synthesis, on the other hand, the PVAc-Co (acac)₂ macroinitiator was isolated and redissolved in tolueneoctene to yield octene polymerization without induction time by OMRP, which stopped after about 14% conversion. Hydrolysis of this polymer gave PVOH-b-PO, which could aggregate to polymeric micelles in water-DMF mixtures.³⁷ It seems possible that the polymerization stops because of the formation of stronger (acac)₂Co-CH₂CH(*n*Hex)(polymer)

bonds, which cannot be reactivated even upon coordination of donor molecules.

Although the simple Co(acac)₂ system traps the growing PVAc chains irreversibly (in the absence of sufficiently strong ligands). increasing the steric bulk of the β -diketonate ligand labilizes the Co^{III}-PVAc bond and favors again interplay of the two OMRP mechanisms. As shown in Figure 11, VAc polymerization in the presence of $Co(acac)_2$ and $Co(tmhd)_2$ (tmhd = 2,2,6,6tetramethylheptane-3,5-dionate), VII (Figure 9), gives essentially the same results during the induction period and up to approximately. 6 half-lives of the V-70 initiator, as predicted for DTP processes with equally efficient transfer agents. However, when no new radicals are injected into solution to sustain degenerate transfer and the system comes back to the reversible termination regime, the process mediated by Co(acac)₂ essentially stops, whereas that mediated by Co(tmhd)₂ continues with a first-order monomer consumption, as expected for OMRP-RT. The effective polymerization rate constants in the RT regime were estimated as $< 1.4 \times 10^{-4} \text{ h}^{-1}$ and $5.1 \times 10^{-3} \text{ h}^{-1}$ for the two mediators under the conditions outlined in Figure 11, an acceleration factor of >35 on going from the acac to the tmhd system, which parallels the calculated weakening of the Co^{III}-C bond by approximateyl 1.4 kcal mol^{-1.38} A stagnation of the $M_{\rm p}$ values at high conversions for the Co(tmhd)₂ system, when sufficient amounts of the Co^{II} complex are regenerated by the inevitable termination processes, suggests that CCT also interplays. The final outcome is a poorer degree of control by Co(tmhd)₂ relative to Co(acac)₂.

In addition to steric effects as shown above, electronic effects have also been probed for the bis(β-diketonate) systems of Co^{II} . The electron-poorer compounds $Co(acacF_3)_2$ and $Co(acacF_6)_2$ (XI and XII in Figure 12), related to VI by replacement of one or two CH₃ groups of acac with CF₃ groups, were tested in the VAc polymerization in the presence of 1 equiv. V-70 at 30 °C in bulk monomer. These are conditions in which VI operates by degenerate transfer. Compound XI also led to a controlled polymerization after an induction time, whereas compound XII yielded polymerization immediately, signalling a reversible radical trapping mechanism. However, the controlling ability of this compound was poor with $M_{\rm n}$ much greater than theory and broad MWD, in agreement with slow trapping.³¹ Compound XI proved superior for the polymerization of vinyl chloroacetate (VClOAc), albeit with relatively broad MWD $(M_w/M_n = 1.7-1.9)$, whereas PNVP and random VAc-NVP copolymers were better controlled by VI, with control improving with the proportion of VAc.³⁹ The characteristics of



Figure 11 Conversion vs. time for the vinyl acetate polymerization mediated by Co(acac)₂ (filled diamond) or Co(tmhd)₂ (filled square), in toluene (50% v/v) at 30 °C. VAc/V-70/Co = 500:2:1.³⁸



Figure 12 Fluorinated bis(β -diketonates) and bis(β -ketoiminates) of cobalt(II) used in cobalt-mediated radical polymerization.

all these polymerization processes (fast polymerization after an induction time) seem consistent with a degenerate transfer mechanism, although a contribution from OMRP-RT is possible.

Another briefly studied isoelectronic system consists of replacing an oxygen atom of the β -diketonato ligand with an NAr group, giving β -ketoiminato ligands (systems XIII). These new ligands are at the same time bulkier and electronically more donating. The steric bulk tends to weaken the Co^{III}– PVAc bond, but the better donor power has the opposite effect through the stabilization of the higher oxidation state.⁴⁰ All processes previously observed for the β -diketonato systems (OMRP-DT, OMRP-RT, and CCT) are also observed here, but the major effect of the greater bulk appears to be a slowing down of radical trapping, leading to poorer control. The steric effect also disfavors the addition of neutral donors relative to the smaller β -diketonato systems (Figure 10), leading to essentially identical results for the polymerizations conducted either in the presence or in the absence of coordinating ligands.

3.11.5 'Clean' OMRP-RT Processes

A degenerative transfer process, as already stated above, cannot take place if the OMRP dormant species, the metal complex $R-Mt^{x+1}/L_{\gamma}$, has no suitable vacant site to accept the incoming radical or if its electronic configuration does not allow the new bond to be established. In this case, any amount of excess radicals should in principle produce polymer by free-radical polymerization. The systems that interplay with degenerate transfer in the presence of excess radicals, described in Section 3.11.4, can also function as 'clean' mediators of OMRP-RT when (1) the polymerization is started using a substoichiometric amount of radical initiator relative to Mt^x/L_{γ} ; (2) donor ligands block the coordination site where excess radicals need to dock to trigger the degenerative transfer process; or (3) the higher oxidation state organometallic complex $R-Mt^{x+1}/L_{\gamma}$ is used as initiator in the absence of external radical sources. Efficient initiation from an organometallic $R-Mt^{x+1}/L_{\gamma}$ requires careful choice of R in such a way that the initiator $R-Mt^{x+1}$ bond is not stronger than the bond subsequently formed in the dormant polymer chain. This section is organized by metal type, from left to right of the transition series.

3.11.5.1 Titanium Systems

The only system based on titanium that appears to control radical polymerization, introduced by Asandei, is based on the half-sandwich titanocene system, $Cp_2Ti^{IV}Cl_2$, after *in situ* reduction to $[Cp_2Ti^{III}Cl]_2$ by Zn.⁴¹ Based on previous knowledge on the radical ring opening of epoxides by compound $Cp_2Ti^{III}Cl$ (**XIV**), which is in equilibrium with its dimer $[Cp_2Ti^{III}Cl]_2$, and subsequent applications in organic synthesis which included evidence that latent radicals are trapped by a second equivalent of $Cp_2Ti^{III}Cl$ in the absence of substrate, this system was successfully applied to the controlled polymerization of styrene (Figure 13).⁴² The radical ring opening of substituted epoxides yields a mixture of isomeric primary and



Figure 13 Initiation and control of radical polymerization by the Cp₂TiCl/epoxide system.

secondary C-centered radicals, with the secondary radical being typically favored. The proposed mechanism is consistent with the need to use a Ti^{III}/epoxide ratio of 2:1 or higher for best results, and with the known low Ti^{IV}–C BDE. Initiator efficiencies depend on the Ti/epoxide, epoxide/styrene, Zn/Cp₂Ti^{IV}Cl₂ ratios, and on temperature. Screening of various related titanium sources, which include the half-sandwich YTi^{IV}Cl₃ compounds (Y = Cp, Cp*, indenyl) and scorpionate analogues, a variety of substituted metallocenes L₂Ti^{IV}X₂ (L = Cp*, RCp with R = Et, *i*Pr, or *t*Bu, indenyl; X = F, Cl, Br, Me, CO) and the phthalocyanine derivative PCTi^{IV}Cl₂, revealed that the best reagent is in fact the least expensive and commercially available Cp₂Ti^{IV}Cl₂, ^{43,44} while Zn was found to be the best reducing agent, especially in the form of nanoparticles.⁴⁵

Aldehydes, peroxides, and alkyl halides are also efficient initiators.^{41,46} Single-electron transfer (SET) reduction of aldehydes by XIV generates primary Cp₂ClTi^{IV}-OCHR[•] radicals, which then initiate the polymerization with greater initiator efficiencies than the epoxides, presumably because of a lower propensity for deoxygenation side reactions.⁴⁷ Peroxides operate through a redox process, rather than by thermal decomposition, the best results being obtained when at least two Ti^{III} ions per peroxide are used. One Ti^{III} ion is consumed in the redox initiation and the second one provides control in the reversible termination of the growing chains.⁴⁸ Alkyl halides R-X undergo halogen atom transfer to yield Cp₂Ti^{IV}ClX and R[•], but the resulting growing polymer chain is controlled by trapping by a second Cp2Ti^{III}Cl molecule to yield an organometallic dormant chain rather than by reverse halogen atom transfer. Thus, the process is controlled by OMRP-RT and not by ATRP, contrary to the suggestion of other authors.⁴⁹⁻⁵¹ It could indeed be considered as a system where ATRP and OMRP-RT interplay (Section 3.11.7), except that the atom transfer step is irreversible and thus provides no contribution to the regulation of the radical concentration. DFT studies indeed show that the reactions leading from $Cp_2Ti^{IV}Cl_2$ and R^{\bullet} (R=CH(Me)Ph or C(Me_2)COOMe) to $Cp_2Ti^{III}Cl + R-Cl$ are endothermic by 6.9 or 8.7 kcal mol⁻¹, whereas those leading from Cp2Ti^{III}Cl and R[•] to Cp2Ti^{IV}Cl(R) are exothermic by -16.7 or -16.6 kcal mol⁻¹, respectively.⁵²

The XIV system seems unique among transition metal complexes in its ability to control the polymerization of a diene monomer, isoprene.⁵³ A linear dependence of M_n on conversion, first-order kinetics and moderate polydispersities (1.4–1.6) up to high conversion (>50%) were observed for epoxide/Cp₂Ti^{IV}Cl₂/Zn = 1/3/6–1/4/8 at 90–110 °C. Random and block copolymers with styrene could also be obtained.

3.11.5.2 Vanadium Systems

Use of this metal in OMRP (or indeed in any CRP) is very recent. Shaver has reported that the polymerization of VAc is well controlled (M_n linearly growing with conversion, M_w / $M_n \sim 1.3$) when initiated by AIBN in the temperature range 70-120 °C, in the presence of complex [BIMPY]VCl₃, XV (Figure 14).^{54,55} A good match between observed and calculated molecular weights was observed at low conversions (up to c. 30%), whereas inconsistent results obtained at higher conversions were attributed to the complex decomposition. The occurrence of an OMRP mechanism with the VII/VIII couple, rather than an ATRP or an OMRP with a V^{III}/V^{IV} couple, was suggested experimentally by the generation of one macromolecule per molecule of AIBN initiator, by the absence of Cl-capped functionalities, by the presence of the metal as chain end (NMR, XPS, EPR, removal by reaction with thiols or methanolysis), and supported theoretically by DFT calculations. This system has also been extended to the polymerization of other vinyl esters (vinyl proprionate, vinyl pivalate, vinyl benzoate) with comparable results, whereas the polymerization of styrene, MMA, and AN did not result in any suitable control. One notable point about this controlling system, at variance with all others investigated so far for VAc, is its good performance at high temperatures, where a more readily available thermal initiator such as AIBN may be used.

3.11.5.3 Chromium Systems

After the Minoura studies mentioned in Section 3.11.1, Grishin has disclosed the moderating effect of tricarbonyl(arene)chromium complexes where the η^6 -arene ligand is



Figure 14 Proposed mechanism of action for the OMRP of VAc in the presence of the vanadium complex XV.



Figure 15 Vinylarenes used in tricarbonyl(arene)chromium-mediated polymerization and proposed mechanism of action.

vinyl-substituted, like those shown in **Figure 15**, for instance, **XVI** for arene = styrene, in the radical polymerization of acrylic monomers and styrene in a series of papers starting in 2003.^{56–}

⁵⁹ The mechanism of action is proposed to involve radical addition to the vinylarene ligand to yield a stabilized radical **XVII**, which is not incorporated in the polymer chain (i.e., does not add to monomer) but is capable of moderating the polymer growth. Whether the dormant chain involves a direct bond between chromium and the polymer chain, however, is not clear. It is also not clear why these systems do not seem to promote β-H abstraction processes, contrary to the related cyclopentadienyl systems that will be discussed later in Section 3.11.6. These polymerizations are initiated by AIBN at 50–70 °C and result in linear growth of M_n with conversion, although the polymers produced have relatively broad MWD ($M_w/M_n > 1.6$).

More recently, Poli and Smith have presented evidence of VAc-controlled polymerization initiated by V-70 in the presence of complexes CpCr(nacanac^{Ar,Ar}) (Ar = Xyl, XVIII; Dipp, XIX; Figure 16).^{21,60} As shown in the initial report, the experiment carried out in the presence of XVIII at 50 °C led to a < 15% conversion before polymerization stopped, while that carried out in the presence of XIX at 30 °C proceeded to 70% conversion in 40 h. Although the level of control was poor (M_n = 67 000 vs. targeted 30 000 at 70% conversion, M_w/M_n = 1.8), the molecular weight increased with conversion suggesting the intervention of a reversible termination process (Figure 5). The substoichiometric amount of V-70 and the absence of an induction time rule out an OMRP-DT mechanism.

This evidence was initially taken to suggest a dramatic Cr–C bond labilization by the bulkier Dipp substituents, implying irreversible radical trapping by the less encumbered nacnac^{Xyl,Xyl} system, and DFT calculations indeed confirmed a

strong weakening effect upon the size increase of the phenyl ring ortho-substituents, as discussed in Section 3.11.3 (Table 1). More recently, the organometallic CpCr(nacnac^{Xyl,Xyl})(Np) derivative (XX) has become available. Its use as thermal initiator for the VAc polymerization indicated a rather slow but sustained polymerization at room temperature, in contradiction with the above interpretation, yielding polymers with targeted M_n and relatively low M_w/M_n (<1.5). The apparent polymerization rate constant decreased and stabilized to a new low value after approximately 150 h but polymerization did not stop, which was interpreted as the result of occasional head-to-head addition, leading to a stronger Cr-C bond that is less easily reactivated (Figure 17). The polymerization stopped completely, however, upon raising the temperature to 50 °C or higher, accompanied by a color change of the solution from purple to orange. This is caused by the formation of the acetate complex CpCr(nacnac^{Xyl,Xyl})(OAc), which is not able to regenerate radicals, explaining the initial result of the XVIII/V-70 experiment at 50 °C.61

3.11.5.4 Molybdenum Systems

Poli has reported the controlled polymerization of styrene at 100 °C in bulk initiated by thermal decomposition of AIBN for the half-sandwich complexes CpMo^{III}Cl₂L₂ (**XXI–XXIII**) shown in Figure 18.⁶² An ATRP/OMRP-RT/CCT interplay, which was observed when using organic halide initiators, will be addressed later in Section 3.11.7. Under OMRP-RT conditions, controlled polymerization was observed for all systems with linear growth of M_n as a function of conversion, without any indication of CCT, although the M_w/M_n values are relatively high (1.3–1.7).

Since the latent PS[•] radicals were also shown to be quenched by halogen atom transfer from Mo^{IV} halides such



Figure 16 Structures of CpCr(nacnac^{Ar,Ar}) complexes used in OMRP of VAc.



Figure 17 Apparent polymerization rate constant and rationalization for the VAc polymerization initiated by CpCr(nacnac^{XyI,XyI})(Np).



Figure 18 Half-sandwich molybdenum compounds used in the OMRP of styrene.

as CpMo^{IV}Cl₃L₂ (see Section 3.11.7), it is conceivable that they could also abstract a Cl atom from the OMRP dormant species, CpMo^{IV}Cl₂L₂(PS), to engage in an ATRP-controlled polymerization. This, however, seems ruled out by the absence of Cl chain ends from the PS obtained under these conditions (whereas halogen-terminated polymer chains are obtained under ATRP conditions). Possibly, the putative ATRP spin trap is extremely bulky since it contains the dormant chain as a ligand and is unlikely to react rapidly with another bulky macroradical. The alternative possibility of Cl[•] transfer from the CpMo^{III}Cl₂L₂ complex is excluded by the greater strength of the Mo^{III}–Cl bond, as also suggested by DFT calculations.

3.11.5.5 Iron Systems

In spite of the relevance of Fe^{III}–C bond homolysis in organic transformations and the extensive use of Fe^{II} complexes as ATRP catalysts (see Chapter 3.13), only one report appears to be available on the use of iron as OMRP trapping agent without the intervention of other one-electron processes. This deals with the use of various macrocyclic Fe^{II} complexes in AIBN-initiated styrene polymerization. At 80 °C, a linear

dependence of $M_{\rm n}$ versus conversion and low $M_{\rm w}/M_{\rm n}$ (<1.5) were observed.^{63,64} Other reports on the implication of Fe complexes in radical polymerization through reversible formation of Fe–C bonds, although with the intervention of chain transfer, are discussed in Sections 3.11.6 and 3.11.7. Given the low toxicity and low cost of iron, further development in this area seems warranted.

3.11.5.6 Cobalt Systems

This is the most studied metal for OMRP, leading to the controlled polymerization of the widest range of monomers. Complex VI in combination with V-70, as already discussed in Section 3.11.4, was shown to provide excellent control and fast rates for the VAc polymerization also under suspension conditions,⁶⁵ yielding PVAc with targeted M_n and low M_w/M_n up to very high M_n (10⁵) and high monomer conversions. The massive amount of water provides OMRP-RT activation (**Figure 10**) and shuts down degenerate transfer, as demonstrated in later contributions,^{3,35} and the Co^{II} complex partition with the water phase contributes to speeding up the polymerization without negatively affecting the controlling ability.

Complex Co^{II}(TMP) and V-70 (under conditions of generation of <1 radical per Co atom) promote the OMRP-RT of MA at 60 °C, although the polymer growth is much slower than under the OMRP-DT regime.^{25,66} The neopentyl compound II and an analogous compound where the neopentyl group is replaced with CH(COOCH₃)CH₃ provide very effective initiating systems for the generation of PMA and PMA-*b*-PBA (M_w/M_n < 1.3). The steric requirements of these TMP-based systems effectively prohibit β -H transfer processes leading to CCT.¹⁶ The steric repulsion between the TMP ligand and the *t*Bu group of the neopentyl ligand is also crucial for weakening the Co–C bond with the primary and nonstabilized neopentyl radical. The pseudo-equilibrium constant for the homolytic bond cleavage in PMA–Co^{III}(TMP), K= $(1.15 \pm 0.10) \times 10^{-10}$ at 333 K, was determined from the observed polymerization rate using the experimental determination of the [Co^{II}(TMP)]/[PMA–Co^{III}(TMP)] ratio and independent knowledge of the propagation rate constant.²⁷ The analogous constant for the pseudo-equilibrium of dissociation of PVAc–Co^{III}(TMP) could not be determined because the extent of dissociation was too small to give measurable polymerization rates, but could be estimated as <10⁻¹².

Effective porphyrin-based organometallic initiators for the MA polymerization were produced for TMP and for its octabromo derivative, Br_8TMP , by reacting the corresponding porphyrinato Co^{II} complexes with V-70 in the presence of small amounts of MA (MA/Co ~ 30–50).⁶⁷ The resulting compounds (XXIII and XXIV in Figure 19) gave rise, in the absence of any external radical source, to well-controlled polymerizations of MA to very high molecular weights (M_n up to 5 × 10⁵ with M_w/M_n down to 1.1). The bromine-containing system XXIV gave a substantially greater rate of polymerization (>30 times higher than XXIII), due to the steric labilization of the Co–PMA bond. From a variable-temperature study, the (TMP) Co–PMA BDE was estimated as 24 kcal mol⁻¹.

When using the 1,3-bis(2-pyridylimino)isoindolatocobalt (II) complexes XXVI and XXVII (Figure 20),⁶⁸ excellent control for the polymerization of MA was reported. However, a slight excess of radicals relative to cobalt was used in this case $([MA]/[V-70]/[Co^{II}] = 600:1:1; f = 0.53$ in benzene solution at 60 °C) and a detailed kinetic analysis was not presented, thus it is unclear whether or not degenerate transfer contributes to the process. Whereas the methanol adducts (complexes XXVIIa-k) gave M_n greater than theory, broader polydispersities and induction times, which were attributed to the need to displace the methanol ligand from the coordination sphere, polymerizations carried out in the presence of the solvent-free complexes XXVI (only c, j and k were reported) were well controlled ($M_w/M_n < 1.13$ at >60% conversion) with M_n in close agreement with theory.

For the acetylacetonate system VI, a well-defined organometallic compound is not available to serve as initiator, but a suitable initiating system was produced by thermally decomposing V-70 in VAc in the presence of a large excess of VI. Since trapping of PVAc[•]-type radicals by this compound is irreversible in the absence of donor ligands, the initially formed $R_0(VAc)_n^{\bullet}$ radicals [$R_0 = Me_2(MeO)CCH_2C(CN)(CH_3)$] produced a mixture of VI-capped short oligomers, $R_0(VAc)_nCo(acac)_2$ (n < 4)³⁵ (XXVIII, Figure 21), which proved an excellent thermal initiator,

Br

Br



Figure 19 PMA macroinitiators capped with Co(TMP) (XXIV) and Co(Br₈TMP) (XXV).



Figure 20 1,3-Bis(2-pyridylimino)isoindolatocobalt(II) complexes used in the OMRP of MA.



Figure 21 Generation of a short-chain organometallic initiator from Co(acac)₂.

once activated by donor ligands, for the OMRP-RT of VAc, AN, and NVP. One notable advantage of this initiation method is the possibility of operating at low temperatures, whereas the alternative use of (VI + V-70) requires at least 30 °C to ensure a reasonable rate of radical generation.

For instance, the bulk polymerization of VAc in the presence of pyridine (1 equiv.) and with a VAc/XXVIII ratio of 238 yielded a 61% conversion in 30 h at 30 °C, with M_n = 17 000 ($M_{n,th}$ = 12 300) and M_w/M_n = 1.10.³⁵ The kinetic scheme and predicted rate law are summarized in Figure 22, which also reports relevant results for polymerizations carried out in the presence of a variable concentration of water or with the same concentration of different donor molecules. The increased apparent rate constant upon increasing [H₂O] (Figure 22(b)) is consistent with the R_p expression, while the different rate constants witnessed for the different L reflect a different ability



$$R_{p} = k_{p} \frac{k_{a}[R-Co^{III}][L]}{k_{d}[Co^{II}]} [VAc]$$



Figure 22 (a) Kinetic scheme and rate law for the OMRP of VAc initiated by **XVIII**. (b) First-order plot, M_n , and M_w/M_n for the bulk polymerization in the presence of a variable amount of water: $[VAC]_0/[XXVIII]_0 = 358$, $[H_2O]_0/[XXVIII]_0 = 30$ (filled triangle), 60 (filled square), 120 (filled diamond). (c) First-order plot, M_n and M_w/M_n for the bulk polymerization in the presence of different donor molecules ($[XXVIII]_0/[VAC]_0) = 1/60/358$, (filled square) L = DMF, (filled diamond) L = DMSO, (filled triangle) L = H₂O. The dotted lines represent the theoretical dependence of the molar mass vs. conversion. Reproduced with permission from Debuigne, A.; Poli, R.; Jérôme, R.; *et al. ACS Symp. Ser.* **2009**, *1024*, 131.⁶⁹ Copyright 2009 American Chemical Society.

to displace the activation pre-equilibrium $(k_a[R-Co^{III}]/k_d[Co^{II}])$ term in the rate law).⁶⁹ DFT calculations on the pre-equilibrium step yield relative activation enthalpies in excellent qualitative agreement with the relative reactivity order: easier activation for water (6.0 kcal mol⁻¹) intermediate for DMSO $(7.1 \text{ kcal mol}^{-1})$ and less facile for DMF (10.8 kcal mol⁻¹). The PVAc dissociation from the L-free dormant species, on the other hand, would cost $13.0 \text{ kcal mol}^{-1}$, rationalizing the low polymerization rate under these conditions (Section 3.11.4).⁶⁹ The chain extension of a PVAc-Co (acac)₂ macroinitiator (structurally identical to XXVIII but with greater n) is also very effective under miniemulsion conditions, yielding stable latexes with targeted $M_{\rm p}$ up to 10⁵ and low polydispersities.⁷⁰ High conversions were already observed during ultrasonication at 0 °C, and further chain extension was then observed at 30 °C. As in the above-mentioned suspension conditions, the presence of water ensures OMRP-RT activation and shuts down OMRP-DT.

Compound XXVIII also proved a good thermal initiator for the controlled polymerization of AN and NVP, but only when this was carried out in a donor solvent such as DMF or DMSO. For AN, the best results were obtained in DMSO at 0 °C ([AN]/ [XXVIII] = 752 and DMSO/AN: 50/50 v/v), with polymers having lower M_w/M_n (< 1.2) and M_n closer to theory relative to the experiment carried out at 30 °C. A DFT study has rationalized the benefit of ligand coordination for the monomer switching process: the bond of ligand-free PVAc-Co^{III}(acac)₂ is stronger than that of ligand-free PAN-Co(acac)₂, yielding slow activation. On the other hand, the bond dissociation energies are leveled for the ligand adducts PVAc-Co^{III}(acac)₂(DMSO) and PAN-Co^{III}(acac)₂(DMSO).⁷¹ Based on this principle, well-defined block copolymers of type PVAc-b-PAN have also been obtained, later transformed to the new polymers PVOH-b-PAN and PVOH-b-PAA by selective or complete methanolysis, respectively.⁷² Well-defined PVAc-b-PNVP polymers, only mildly affected by a slow initiation problem $(M_w/M_n \sim 1.4 \text{ vs. } 1.1-1.2 \text{ for the macroinitiator})$, and the PVOH-*b*-PNVP product of subsequent methanolysis were also obtained by initiating NVP polymerization with a PVAc–Co (acac)₂ macroinitiator under reversible termination conditions (absence of external radical source) in anisole/toluene solution.⁷³ In this case, the monomer itself is sufficiently coordinating and presumably activates the macroinitiator through the formation of a PVAc–Co(acac)₂(NVP) adduct (Figure 10).

Somewhat surprisingly, addition of isoprene to a PAN-Co^{III} (acac)₂(DMSO) dormant chain did not yield controlled growth of a polyisoprene block, but rather an efficient coupling of the PAN radical chains, after addition to one isoprene monomer per radical, to generate mid-chain functionalized symmetrical PAN- I_{n2} -PAN polymers. The efficiency is close to 100%, even for relatively high $M_{\rm p}$ polymers (up to 25 000).⁷⁴ DFT calculations have once again helped rationalize this observation.⁷⁵ As shown in Figure 23, Co(acac)₂ binds the [•]CH(Me)CN radical (model of the PAN[•] chain) more strongly than the [•]CH₂CH=CHCH₃ radical (model of the allyl radical of the PAN-I[•] chain). Further addition of DMSO to vield an electronically saturated adduct further differentiates the two dormant chains in terms of stability. Activation by Co^{III}-C bond cleavage yields Co^{II}(acac)₂(DMSO), which is then further stabilized by a second DMSO molecule (cf. Figure 10). The model of the dormant PAN-Co^{III}(acac)₂(DMSO) chain is thus sufficiently stable relative to the free radical and Co^{II}(acac)₂ (DMSO)₂ to ensure a persistent radical effect and controlled growth, whereas the model of the putative PAN-I-Co^{III}(acac)₂ (DMSO) dormant chain is not sufficiently stabilized. Therefore, following activation of PAN-Co^{III}(acac)₂(DMSO) and isoprene addition, the PAN-I[•] radicals are not efficiently trapped and their concentration dramatically increases, leading to coupling. Further work has shown that a wide variety of



Co(acac)₂(CH(CN)CH₃)(DMSO)

Figure 23 Energetic scheme for the interaction of Co(acac)₂ with models of the PAN* and PAN-I* radical chains from DFT calculations.

dienes, including functionalized ones, can be used for this radical coupling process and that the coupling process is also quite efficient (>90%) for PVAc-Co(acac)₂(DMSO) and slightly less efficient (75–80%) for PNVP-Co(acac)₂(NVP) dormant chains.^{75,76} Mid-chain functionalized triblock copolymers have also been prepared by diene addition to PVAc-*b*-PNVP-Co(acac)₂(NVP). NMR and MALDI-TOF analyses confirm the predominant presence of two diene units in the polymer chains, with detection also of small amounts of families containing three and more diene molecules but no visible fractions with one or zero diene molecules.

3.11.6 OMRP-RT versus CCT

The ability of transition metal compounds, mostly having radical character, to abstract H atoms from organic radicals has been appreciated since the 1970s. For instance, Pt^{II}(H)I(PEt₃)₂ is a by-product of the oxidative addition of *i*PrI to Pt(PEt₃)₃, which takes place by a radical pathway through I[•] transfer with generation of the (PEt₃)₃Pt^II and *i*Pr[•] radicals (propene, propane, and 2,3-dimethylbutane are also formed).⁷⁷ Direct evidence for reversible Mt^{x+1} -C bond formation (OMRP trapping) with the chain-carrying radicals has been presented for several efficient CCT catalysts based on Co^{II,78-80} Both processes, illustrated schematically in Figure 24, have the same first-order dependence on the metal complex and on the radical chain, thus their competition is not affected by concentration. The relative preference for these two pathways is affected by the nature of the metal, by its coordination sphere, and by the nature of the radical chain. For the Co^{II} catalysts, both steps have been shown



Figure 24 Competitive OMRP trapping and β -H atom transfer for a Mt[×]/L_y chain-carrying radical pair.

to occur at diffusion-controlled or close to diffusion-controlled rate, indicating that the activation energies are extremely low.¹⁷ When controlled chain growth is sought, the intervention of any amount of CCT is unwanted, whereas when CCT is the desired process, the intervention of reversible OMRP trapping only has the effect of slowing down the polymerization but does not affect the catalyst ability to moderate the polymer molecular weight. For less active catalysis such as the porphyrin derivatives, a significant isotope effect $k_{\rm H}/k_{\rm D}$ of 3.5 for the H[•] transfer process was observed, suggesting a direct H atom transfer instead of a β -H elimination from the OMRP dormant species.⁸¹ This conclusion may not be general for all chain transfer catalysts, however (*vide infra*).

Empirical rules for catalytic activity have been offered for Co^{II} complexes with macrocyclic ligands, arguably the most developed family of chain transfer catalysts, such as the crucial importance of a core of four N atoms, macrocycle planarity, π conjugation in the macrocyclic ligand and steric effects, and the moderate electronic effect of equatorial ligand substituents.¹⁷ Thus, it is possible to convert effective CCT catalysts to species suitable for OMRP by incorporating special substituents into the design of the equatorial ligand. Poor CCT catalysts are potentially good candidates for OMRP, if the factor limiting the CCT is formation of a stable metal alkyl species (i.e., if the Mt^{x+1}–C bond has a suitable strength). However, as already mentioned in Section 3.11.2, how the CCT/OMRP-RT interplay depends on molecular parameters in general is not completely clear at this point.

Most investigations related to H[•] abstractions from growing polymer chains have been carried out on Co^{II} systems. Porphyrin complexes were the first ones found to promote CCT,^{82,83} although cobaloximes have later received most of the attention.^{17,84} Within the porphyrin systems, the aptitude toward OMRP trapping or β-H atom transfer seems very sensitive to the porphyrin steric bulk, more encumbered systems apparently disfavoring CCT to a greater extent than Co-C bond formation.⁸⁵ Thus, complexes with TMP (as in II) and complex IV lead to controlled growth while complexes with less substituted rings lead to CCT. The tendency toward H atom transfer from β -H atom-containing radicals is signalled by the details of the interaction of Mt^x/L_v complexes with cyanoalkyl radicals generated from initiators such as AIBN or V-70. The different possible reactions are summarized in Figure 25. The primary radical can add a monomer to generate a new radical, which is then trapped by Mt^{x}/L_{y} to yield the OMRP dormant species XXIX. The possibility that the primary radical is trapped



Figure 25 General mechanism of the reaction of cyanoalkyl radicals with metal complexes and olefin monomers.

directly to yield the organometallic product XXX is usually not observed because of the stabilized nature of this radical and the resulting weakness of the Mt^{x+1}–C bond. Alternatively, the β -H atom transfer process leads to a hydride intermediate, usually not observed, which then transfers the H atom to a monomer followed by trapping of the new reactive radical to yield XXXI. Mechanistic studies by ¹H NMR on the reaction with Co^{II}(porphyrin) complexes in the presence of a variety of alkenes, including MA or VAc, have shown the initial formation of CH₂=C(CN)R and product XXXI as the predominant species.^{23,86–88} The reaction with other complexes that are much less prone to CCT, on the other hand, for instance, VI or XXIV,^{35,68} give no sign of species such as XXXI or polymers containing such function as chain end, by ¹H NMR or MALDI-TOF MS analyses.

A DFT study on the reaction of the model $[Co^{II}(por)]$ system (por = porphyrinato) with the $(CH_3)_2(CN)C^{\bullet}$ and $CH_3(OAc)$ CH^{\bullet} radicals addresses the BDE of the resulting Co^{III} organometallic adducts and the energetics of the H atom transfer reaction from $(CH_3)_2(CN)C^{\bullet}$ to $[Co^{II}(por)]$ and from $[Co^{III}(H)(por)]$ to VAc, in good agreement with the experimental data.⁸⁹ The effect of the porphyrin structure on the competitive radical trapping and H atom transfer barriers, however, remains to be analyzed.

Interesting systems that appear to promote both OMRP-RT and CCT have been described by Milani⁹⁰ and Baird⁹¹ for the polymerization of acrylonitrile. The dibenzyl complexes XXXII (Figure 26) polymerizes AN in the dark at 20 °C with excellent productivities (up to $38.4 \text{ kg P}(\text{g Co})^{-1}$ in 72 h), provided that no radical trap is present, without the addition of an external radical source.90 Addition of hydroquinone monomethylether drastically reduces the productivity, suggesting radical characteristics. No polymerization occurred when using XXXII with R = Me, in agreement with the expected greater resistance of the Co^{III}-CH₃ bond toward homolytic cleavage. No effect on the $M_{\rm n}$ (around 6 × 10⁴) by the reaction time and by the complex concentration was noted, while the average number of chains per complex molecule increased with time (up to 35), demonstrating the chain transfer catalytic nature of the process. The isolated polymers showed monomodal MWD when obtained in THF solution and trimodal when obtained in bulk monomer, suggesting the presence of various metallic species with a different catalytic activity in bulk monomer and a single site in THF.

The Fe complex XXXIII, isoelectronic with XXXII, gives excellent conversions of AN, after an induction period, in 3 h at room temperature in the absence of a cocatalyst.⁹¹ Similarly, high activities were also observed when using the Fe^{II}(bipy)₂Cl₂/ AlEt₃ combination, presumably generating XXXIII in situ, whereas lower (but not zero) activities were obtained for Fe^{II}(bipy)₂Me₂ or Fe^{II}(bipy)₂Cl₂/AlMe₃. The activity was lowest in toluene solution, average in bulk AN, and highest in DFM, and the resulting polymers had very narrow MWD $(M_w/M_p = 1.02 - 1.05)$ and low M_w (750-800), with the generation of up to 35 polymer chains per catalyst molecule. The mechanism of action of this system is controversial. The initial proposition of a coordination/insertion mechanism by Yamamoto⁹² is in conflict with the absence of activity for ethylene polymerization in the presence of MAO or $B(C_6F_5)_3$ activators. Jordan, on the other hand, proposed an anionic mechanism on the basis of the observed chain branching pattern.⁹³ Evidence considered consistent with the radical mechanism is the ability to copolymerize AN and styrene but not to homopolymerize styrene,⁹¹ whereas the inability to incorporate VCl in copolymers with AN was taken as negative evidence.93 This system also induces the homopolymerization of other polar monomers such as MVK, MA, MMA, and VAc.⁹² There is agreement on the reason for the induction period, necessary for the elimination of ethylene and ethane and formation of a hydride active species. The alternative mechanistic interpretations consider AN coordination and insertion into the Fe-H bond, or formation of a cyanoethyl complex that is more susceptible to Fe-C homolytic bond cleavage, or hydride transfer to AN.

Continuing on iron chemistry, a series of styrene polymerization studies reported by Gibson have revealed the action of the α -diimine complexes Fe^{II}Cl₂(R'N=CR"CR"=NR'), XXXIV, as either chain transfer catalysts or as mediators for controlled chain growth as a function of the spin state of the related Fe^{III}Cl₃(R'N=CR"CR"=NR') complexes XXXV.^{94–96} The polymerizations were carried out under ATRP conditions (organic halide initiator) and will thus be analyzed more in detail in Section 3.11.7. Of relevance to this section, however, the mechanism leading to chain transfer has been proposed to involve β-H elimination from the OMRP resting state XXXVI, leading to XXXVII, rather than direct H[•] transfer from the chain carrier radical to the chain transfer catalyst (see Figure 27). Mechanistic studies have involved the low-temperature *in situ* generation of the putative alkyl iron(III) species XXXVI by



Figure 26 Cobalt and iron systems promoting the OMRP and CCT of AN.



Figure 27 Interplay of ATRP, OMRP-RT, and CCT in styrene polymerization with α -diimine complexes of iron.

alkylation of Fe^{III}Cl₃(RN=CR'CR'=NR). Alkyl derivatives obtained from high-spin (S = 5/2) trichloride precursors, which favor controlled polymer growth by ATRP, are unstable above –78 °C, whereas those obtained from intermediate-spin (S = 3/2) precursors, which favor CCT, are stable up to –30 °C.⁹⁵ Thus, Gibson formulated the proposal that the greater 'carbophilicity' of the intermediate-spin complexes favors radical trapping, leading to the OMRP dormant species and ultimately to CCT, whereas the high-spin systems do not have sufficient affinity to form a bond with the chain carrier radicals and therefore do not promote CCT.

Norton has thoroughly investigated half-sandwich chromium carbonyl derivatives, inspired by literature reports of a radical pathway for the hydrogenation of certain unsaturated substrates by low-valent hydride complexes (Figure 28), that is, anthracene/HCo^I(CO)₄,⁹⁷ α -methylstyrene/HMt^{x+1}L_n (Mt^{x+1}L_n = Mn^I(CO)₅,⁹⁸ or CpM^{II}(CO)₃ with M = Mo or W⁹⁹), and styrene/HCo^I(CO)₄.¹⁰⁰ Note that the initial equilibrium corresponds to the β-H atom transfer process in CCT¹⁰¹ and that all above-mentioned substrates lead to highly stabilized radicals.

Use of metal complexes with weaker Mt^{x+1} –H bonds (i.e., leading to a more stabilized metal-based radical) led to chain transfer catalytic activity in MMA polymerization.¹⁰² The pentaphenylcyclopentadienyl compound (C₅Ph₅)Cr^I(CO)₃, XXXVIIIa, is a stable radical (no tendency to form dimer XLa) and the corresponding hydride complex (C₅Ph₅)Cr^{II}(CO)₃H, XXXIXa, is also available (Figure 29). The reaction of XXXIXa with a large excess of MMA produces low- M_n PMMA, rather than hydrogenated MMA. The same process is initiated by thermal AIBN



Figure 28 Radical mechanism for the hydrogenation of olefins.

decomposition in the presence of XXXVIIIa; M_n^{-1} increased proportionally with XXXVIIIa according to the Mayo equation, yielding a transfer constant $C \sim 1000$, that is, comparable with that of many Co^{II} catalysts. A subsequent investigation¹⁰³ has revealed greater transfer constants for less hindered complexes (see Figure 29), for example, 6300 for the Cp* complex XXXVIIIb (which is also a stable radical in solution, although it crystallizes as the dimer XLb) and 25000 for the Cp complex XXXVIIIc (which dimerizes extensively). A steric bulk increase by CO substitution with phosphine or phosphite ligands L, yielding the stable mononuclear complexes XXXVIIId-g, on the other hand, showed a negative effect on C. Note, however, that the displacement of the H[•] transfer equilibrium toward XXXIX lowers the effective concentration of the transfer agent and vields values of *C* from the slope of the Mayo plot that underestimate the true transfer constant.¹⁰⁴ Greater values of k_{reinit} for less hindered systems (e.g., $1.74(8) \times 10^3$, $2.61(5) \times 10^3$, and $14(3) \times 10^3 \,\mathrm{M^{-1} \, s^{-1}}$ at 323 K for **a**, **b**, and **c**, respectively) were determined on the basis of H/D exchange kinetics using MMA- d_{5} , while similar experiments with styrene- d_8 showed no substantial steric hindrance effect and ΔG (50 °C) values of +11 and +10 kcal mol⁻¹ were derived for the H[•] transfer process from XXXIXa to MMA and styrene, respectively.¹⁰⁵

A temperature-dependent study showed a decrease of $k_{\rm tr}$ to MMA in bulk monomer with increasing temperature (1.6×10^6 and $0.79 \times 10^{6} \text{ M}^{-1} \text{ s}^{-1}$ at 60.4 and 80.2 °C, respectively), explained by the competition with Cr^{II}-PMMA bond formation (see Figure 29), the homolytic bond dissociation energy of which was estimated as $< 10 \text{ kcal mol}^{-1}$.¹⁰⁶ Mt^{x+1}–C bond formation should be an even greater issue when the chain-carrying radical is secondary, as in the polymerization of styrene, and the greater CCT efficiency for monomers leading to tertiary chain-carrying radicals such as MMA may be attributed at least in part to this factor. Thus, the above results show that steric hindrance decreases the effectiveness as a chain transfer catalyst, but also discourages OMRP trapping. The criteria that emerge for optimizing a chain transfer catalyst are (1) stability at the polymerization temperature, (2) sufficient steric crowing to discourage its own dimerization and the formation of metal-carbon bonds with the chain-carrying radicals (OMRP trapping), and (3) thermoneutrality for the H[•] transfer process (~equivalent BDE for the Mt^{x+1}-H and C-H bonds). Note, however, that too much steric crowding ultimately slows down H[•] transfer and decreases the catalytic activity.

In terms of the influence of the olefin structure, CCT activity is especially high for methacrylates and styrene, while acrylates tend to yield more efficient OMRP trapping by cobalt complexes.¹⁷ A study of H[•] transfer from CpCr(CO)₃H to a variety of olefins yields the rate constants and relative rates are shown in **Figure 30**,¹⁰⁷ but no equivalent information is apparently available on the catalytically more relevant H[•] transfer from the chain-carrying radical to the transfer agent, which is usually the rate-determining step in CCT.

3.11.7 Interplay of OMRP-RT and ATRP

As discussed in Section 3.11.2, OMRP trapping is always possible in principle when a polymerization is carried out under ATRP conditions (Figure 4), that is, upon initiating the polymerization by a halogenated organic compound R_0 -X and a



Figure 29 A few half-sandwich Cr compounds used in CCT. C(MMA) is the transfer constant to MMA (in bulk monomer) at 70 °C, as determined by a Mayo analysis. From Tang, L.; Norton, J. *Macromolecules* 2004, *37*, 241.¹⁰³



Figure 30 Rate constants for H[•] transfer from CpCr(CO)₃H to various olefins at 323 K.

low-valent metal catalyst Mt^{x}/L_{y} , or by a conventional source of primary radicals R_{0}^{\bullet} and the oxidized metal complex, $X-Mt^{x+1}/L_{y}$ – so-called 'reverse ATRP' conditions. The question of how much OMRP-RT contributes to the control of the polymer chain growth, however, is not systematically addressed when testing the performance of new ATRP catalysts. The limiting situations are no OMRP-RT contribution at all, namely the polymerization occurs by a pure ATRP mechanism, and a dominant (but still reversible) OMRP trapping, yielding a system that operates essentially by a pure OMRP-RT mechanism. The ultimate extreme of strong Mt^{x+1} –R bonds will not be considered because it leads to irreversible trapping and no polymerization (stoichiometric one-electron oxidative addition, see Section 3.11.3).

Matjyaszewski has tested the ATRP catalysts CuBr/dNbpy and CuOTf/dTbpy (OTf = trifluoromethanesulfonate; dNbpy = 4,4'-di-5-nonyl-2,2'-bipyridine; dTbpy = 4,4'-di-tertbutyl-2,2'-bipyridine) as potential OMRP trapping agents.¹⁰⁸ Radical polymerizations in the presence of these compounds were carried out with initiation by thermal decomposition of AIBN. For styrene, no effect was observed, but the rate of the MA polymerization was significantly reduced, although with no notable regulating effect on the molecular weight and MWD. These results indicate that significant reversible OMRP trapping indeed takes place during the ATRP of MA and not in the case of styrene, but control is always ensured by the ATRP trapping process.

Since the strength of the Cu^{II}–C bond depends not only on the Cu^{II} ancillary ligands but also on the nature of the polymer chain, a greater importance of OMRP trapping is anticipated for more reactive radical chain carriers, for instance, PVAc or PVCl. It should be noted that no stable Cu^{II}-alkyl complex has so far been described, all attempts at generating them lead to the release of radicals.¹⁰⁹⁻¹¹² It has been stated that Cu^I catalysts do not promote the ATRP of VAc, presumably due to the relatively strong PVAc-Cl bond.¹¹³ However, a recent report shows a relatively well-controlled VAc polymerization under ATRP conditions in bulk monomer at 70 °C using Cu^IX/tPy (X = Cl, Br; tPy = 2,2':6',2''-terpyridine) with the ethyl 2-bromoisobutyrate initiator (VAc/initiator/catalyst = 150:1:1; 80% conversion in 10 h, $M_n = 13300$ ($M_{n,th} = 10320$), $M_{\rm w}/M_{\rm p}$ = 1.69).¹¹⁴ The performance of this system was attributed to the high activity of the Cu^IX/tPy complex, whereas the known slow deactivation of tPy complexes of Cu^{II} would apparently not constitute a problem for the more reactive PVAc[•] chains. However, the possibility of OMRP trapping as a contributor to chain growth regulation may also be worth consideration, though the isolated polymer contained only halogen-terminated chains (as verified by ¹H and ¹³C NMR analysis). A series of reports by Percec has also shown the ability of certain Cu¹ compounds to control the polymerization of VCl.^{115,116} This process has been interpreted on the basis of an SET mechanism,^{117–119} which has however been heavily criticized.¹²⁰ The contribution of a reversible OMRP trapping, which has not yet been considered, may possibly rationalize the phenomenon.

The first evidence of constructive interplay between ATRP and OMRP-RT was shown by Poli for styrene polymerization with the CpMo^{III}Cl₂L₂ complexes shown in Figure 18.⁶² In addition to OMRP-RT as already discussed in Section 3.11.5.3, the phosphine derivatives XXI and XXII mediate the controlled polymerization of styrene under ATRP conditions (at 80 °C in bulk monomer with initiation by bromoethylbenzene). Since the ATRP equilibrium is displaced toward the Mo^{III} catalyst, the latter is available in large concentrations to engage in OMRP trapping, which is independently shown to ensure an efficient persistent radical effect as discussed in Section 3.11.5.3. Consequently, the two trapping mechanisms positively cooperate. The ATRP trapping, however, is dominant because the resulting polymer is shown to have halogenated chain ends, with both Cl and Br functionalities being revealed by a MALDI-TOF MS analysis.

For the related η^4 -butadiene complex XXIII, although controlled growth is observed under OMRP-RT conditions (see Section 3.11.5.3), low- M_n polymers were obtained without evolution of M_n with conversion under ATRP conditions, indicating the occurrence of CCT.⁶² This happens because a high concentration of the Mo^{III} chain transfer catalyst is present only when operating under ATRP conditions, whereas the majority of the metal system during the OMRP-RT experiment is present as the organometallic Mo^{IV} dormant species. The ligand effect on the performance under ATRP conditions (pseudo-living growth for XXI and XXII, CCT for XXIII) can be interpreted on steric grounds as in the case of the porphyrinato cobalt(II) family: H[•] transfer is discouraged to a greater extent than reversible radical trapping by the more sterically hindered phosphine derivatives. However, it is not clear whether for this system CCT occurs by direct H[•] transfer, like for the porphyrinato Co^{II} system, or by β -H elimination after OMRP trapping, as proposed for the Fe^{II} systems described in **Figure 27**. If Mo^{IV}–PS bond formation precedes β -H elimination, a coordination site in the electronically saturated dormant species must become available by ligand dissociation (e.g., rearrangement of the butadiene ligand from η^4 to η^2 or the cyclopentadienyl ligand from η^5 to η^3).

Other Mo complexes have shown a similar behavior. Half-sandwich complexes with α -diimine ligands (type XLI, Figure 31) behave similarly to the related phosphine and butadiene complexes of Figure 18, with good control for styrene polymerization by ATRP (initiation by 1-bromoethytlbenzene) by XLIa-d and reasonable control by OMRP-RT for XLc (initiation by AIBN at 100 °C, with linearly growing $M_{\rm n}$ up to 30% conversion and $M_w/M_n \sim 1.6$).¹²¹ In combination with the Al (OiPr)₃ cocatalyst, compound XLId was also shown effective for the ATRP of acrylates initiated by ethyl 2-iodopropionate (yielding PMA, PBA, and PMA-b-PS polymers), but the initiator efficiency factor was anomalously low (as low as 0.55), without apparent intervention of extensive terminations at the outset of the polymerization.¹²² On the other hand, complex XLId did not lead to any polymerization of MA under OMRP-RT conditions (initiation by AIBN), demonstrating that the primary radicals and the short PMA[•] chains are trapped irreversibly by XLId. The reason for the low initiator efficiency in ATRP could. therefore, be explained by the occurrence of ATRP activation and irreversible OMRP trapping, leading to one-electron oxidative addition which, given the 1:1 Mo^{III}/initiator stoichiometry, consumes all of the catalyst and only 50% of the initiator. Under ATRP condition, the polymerization must,



Figure 31 Other Mo^{III} complexes used in ATRP and OMRP-RT.

therefore, be controlled by a Mo^{IV}/Mo^V couple, namely one or both of the one-electron oxidative addition products.¹²³ In agreement with this interpretation, an experiment conducted with a Mo^{III}/initiator stoichiometry of 1:0.5 did not lead to any polymerization, but the subsequent addition of one more equivalent of initiator led to ATRP with 100% initiator efficiency (relative to the subsequently added equivalent). The ability of Mo^{IV}/Mo^V couples to mediate ATRP was later demonstrated for complexes $Mo^{IV}OX_2(PMe_3)_3$ (X = Cl, I).¹²⁴ Changing the halogen atom from Cl to I (going from XLId to XLIe) rendered the OMRP deactivation reversible again. Hence, complex XLIe gave rise to the ATRP of styrene and MA with high initiator efficiencies and also to the OMRP of both monomers, though with poor control under the latter conditions.¹²³ Complexes XLII, on the other hand, gave rise to excellent control in the ATRP of styrene, but OMRP trapping was shown to contribute only to a minor extent to ensure a persistent radical effect.125,126

The same behavior reported for the Mo^{III} complexes XXI and XXII was also observed by Matyjaszewski for the osmium compounds $Os^{II}Cl_2(PPh_3)_3$ (XLIII) and $Cp^*Os^{II}Br(PiPr_3)_2$ (XLIV) (Figure 32).^{2,127} Complex XLIII ensures good control by ATRP in the bulk polymerization of styrene, MMA, and BA at





100 °C, with first-order kinetics and targeted M_n being observed in all cases ($M_w/M_n = 1.11$ at 90% for Sty, 1.63 at 73% for BA, 1.62 at 80% for MMA). The same compound also gave a controlled polymer growth for styrene with initiation by thermal decomposition of AIBN, either in bulk or in DMF. The polydispersity indexes are high (e.g., 2.81 at 71% conversion for the bulk experiment) because a significant number of low- M_n dead chains are generated at the beginning of the reaction, but M_n increased with conversion over 48 h, well beyond the time needed to fully decompose the initiator.² It was later shown that a PS with a much lower M_w/M_n of 1.3 resulted when radicals were generated much more slowly by monomer thermal self-initiation.¹²⁷

Chain-end analysis did not reveal any Cl chain ends for the PS obtained under OMRP-RT conditions, whereas virtually all chains were Cl-terminated when produced under ATRP conditions (virtually all could be successfully extended by Cu-catalyzed ATRP). This result, similar to that of the Mo^{III} systems XXI and XXII, indicates that ATRP trapping is dominant in the presence of OMRP-RT. A DFT calculation on model $Mt^{II}Cl_2(PH_3)_3$ systems (Mt = Ru, Os) gives results in qualitative agreement with the experiment and also predicts a similar ΔH_{ATRP} for the Ru and Os system, whereas $\Delta H(OMRP-RT)$ is much smaller for Ru (see Figure 33). Considering that $\Delta S(\text{OMRP-RT}) >> 0$, thus $\Delta G(\text{OMRP-RT}) < \Delta H(\text{OMRP-RT})$, whereas $\Delta S(ATRP) \sim 0$ and $\Delta G(ATRP) \sim \Delta H(ATRP)$, ATRP trapping should be more favorable for both metals. These results also suggest that the ATRP of styrene catalyzed by RuCl₂(PPh₃)₃ should take place under an essentially pure ATRP control, even though a slight contribution of OMRP trapping cannot be excluded.¹²⁷ Complex XLIV also provides control for styrene under ATRP conditions $(M_w/M_n \sim 1.05)$, although complications related to the coordination chemistry gave only limited monomer conversions. Like for complex XLIII, linear growth of Mn was obtained under OMRP-RT conditions, but M_w/M_n was uncontrolled.



Figure 33 Energetics (values in kcal mol⁻¹) from DFT calculations¹²⁷ for the ATRP and OMRP trapping equilibria involving the Ph(CH₃)CH[•] model radical of PS[•] and the indicated complexes of Os (bold solid lines) and Ru (thin dashed lines).

The iron system of Figure 27 is another case where ATRP activation interplays with OMRP trapping, even though the latter is only an entry for CCT, as proposed by Gibson, for those systems for which XXXV has an intermediate spin state. OMRP-RT does not seem to provide a pathway for controlled chain growth for this system (see Section 3.11.6). Bulk polymerizations of styrene initiated by 1-chloroethylbenzene lead to controlled polymer growth for complexes A with R' = alkyl and R" = H (for which XXXV has S = 5/2), with generation of Cl-terminated polymer chains. Complexes with R' = aryl (for which XXXV has S = 3/2), on the other hand, led to slower polymerizations and generation of vinyl-terminated polymer chains with low $M_{\rm p}$ which did not increase with conversion.⁹⁴ For complexes with R' = cyclohexyl and R'' = aryl group, the presence of electron withdrawing para-substituents on R" gave CCT, but an increasingly electron-donating nature of the substituent gave an increased tendency for pseudo-living growth (see Figure 34). The polymerization rate and polymer $M_{\rm n}$ correlate with the Hammet σ parameter of the phenyl substituent.⁹⁶ Interplay of ATRP and CCT, *via* a proposed formation of the OMRP dormant species, has also been shown for the same family of Fe complexes in the polymerization of MA, MMA, and *p*-methoxystyrene.¹²⁸

Finally, ATRP and OMRP-RT were also shown to interplay for the half-sandwich Cr^{II} complexes XVIII and XIX of **Figure 16**. As outlined in Section 3.11.5.2, these complexes are able to trap PVAc[•] growing chains to generate the OMRP dormant species. Knowledge that Cr^{II} is a strong reducing agent and that the conversion of Cr^{II} -X compounds to Cr^{II} requires strong reductants such as Zn led to the anticipation that XVIII and XIX should be capable to abstract a Cl atom from Cl-terminated PVAc. Indeed, this was shown to occur.¹²⁹ VAc polymerization initiated by methyl 2-chloropropionate in bulk monomer at 50 °C gave rise to sustained polymerization initially. However, the initiator efficiencies were low (<0.2), the polydispersity indexes were high (1.6–1.8), and



Figure 34 Trend of M_n vs. conversion for the bulk styrene polymerization at 120 °C initiated by 1-chloroethylbenzene in the presence of FeCl₂(CyN=CR"=NCy) (R" = p-MePh, filled square; p-MeOPh, filled cicle; p-Me₂NPh, filled diamond). The straight line corresponds to the theoretical molecular weight for living growth. Reprinted with permission from Allan, L. E. N.; Shaver, M. P.; White, A. J. P.; Gibson, V. C. *Inorg. Chem.* **2007**, *46*, 8963.⁹⁶ Copyright 2007 American Chemical Society.



Figure 35 Relative energies (in kcal mol⁻¹) for the ATRP and OMRP trapping of the model (CH_3COO)(CH_3) CH^* radical of the PVAc* growing chain by half-sandwich Cr systems, according to a computational study by the QM/MM (B3LYP/UFF) method. From Champouret, Y.; MacLeod, K. C.; Smith, K. M.; Poli, R. *Organometallics* **2010**, *29*, 3125.⁶¹

the polymerizations stopped after low conversions (~15% for XVIII, ~25% for XIX). This phenomenon was attributed to the dominance of the OMRP trapping and to the known (see Section 3.11.5.2) decomposition of the OMRP dormant species by acetate transfer, as confirmed by the color change from purple of the OMRP dormant species to orange of the deactivated Cr^{III} acetate complex. Identical results were also obtained under reverse ATRP conditions, initiating the polymerization by decomposition of V-70 at 50 °C in the presence of complex CpCr^{III}(nacnac^{Xyl,Xyl})Cl. The OMRP trapping Cr^{II} complex (XVIII) is not initially present in this case, but is generated initially by the ATRP trapping process, and then polymerization continues under OMRP-RT control until irreversible deactivation. The DFT calculations (Figure 35) confirm that OMRP trapping is more favorable in this case and reveal, as expected, that the ATRP equilibrium is less affected than the OMRP-RT equilibrium by the steric hindrance of the aryl substituent.

3.11.8 Metal Elimination and Recycling

The major drawback of OMRP (by both reversible termination and degenerate transfer) is the covalent linking of the metal complexes as chain ends in the isolated polymer. In addition to the inherent cost associated to the stoichiometric use of one molecule of metal complex per macromolecule, most if not all the ensuing practical applications would also require a complete metal removal. A general strategy for the removal of the metal complex, also allowing the recovery and recycling of the metal species, has been presented by Jérôme for the particular case of the CMRP of VAc. It was first shown that the PVAc-Co^{III} $(acac)_2$ chain terminus can be modified by the reactions with TEMPO or thiols, releasing the metal from the macromolecules.32 The reaction with TEMPO was later exploited after grafting the cobalt complex on a solid support (see Figure 36). Since the Co^{II} complex is not oxidized by TEMPO, the supported complex can be reused in a subsequent



Figure 36 General strategy for polymer release and regeneration of the Co^{II} complex in cobalt-mediated radical polymerization of VAc (the nature of the PVAc–Co^{III} dormant species is more likely a ligand adduct, like **IX**, or a chelated species, like **X**, depending on conditions, see **Figure 10** and related discussion in Section 3.11.5.5).
polymerization run. Two types of supports, silica and Merrifiel resin, have been tested with comparable results as shown in Figure 36. The reaction of the acac-modified support with excess Co(acac)₂ ensures that all cobalt centers are bonded to only one surface-grafted acetylacetonato ligand. Application of this strategy allowed the generation of TEMPO-terminated PVAc with M_n proportional to conversion and narrow MWD $(M_w/M_n \le 1.40)$, although only a fraction of the supported Co centers was shown to lead to polymer chains (37% for silica, 25% for the Merrifield resin). After the thermal treatment with TEMPO and purification, the recycled support was used again for a second and then again for a third VAc polymerization, leading to new batches of PVAc, although the initiator efficiency decreased by approximately 30% after each recycle. This decrease was attributed to either cobalt leaching or to oxidation during the purification steps.¹³⁰ Since the Co^{III}-PVAc bond is stronger than most other putative Co^{III}-polymer bonds,³ the strategy promises to be of wide applicability.

3.11.9 Conclusions and Perspectives

In the last 15 years, OMRP has proven a robust and reliable method for controlling the polymerization of a variety of monomers. Its advantage, relative to other controlled radical polymerization methods, is in the flexibility of the metal complex, via optimization of the metal and coordination sphere, making the Mt^{x+1}-C bond strength suitable in principle for controlling any monomer. The technique has been successfully applied so far to the polymerization and copolymerization of acrylates, methacrylates, acrylonitrile, styrenics, isoprene, vinyl acetate, and N-vinyl pyrrolidone. Understanding the coordination chemistry of the regulating metal complex has allowed the optimization of monomer switching between two monomers of very different reactivity, to yield PVAc-b-PAN in Co(acac)2mediated polymerization. Achieving control for the polymerization of other challenging monomers (for instance, fluorinated olefins, α -olefins) is within realistic possibilities. One major disadvantage of OMRP, as we have outlined in this chapter, is its intimate interplay with other one-electron processes implicating the transition metal complex. In terms of the production of targeted molecular weights, the major interplay to worry about is with chain transfer catalysis. A full understanding of how the metal and ligands nature orient the system toward reversible radical trapping (OMRP-RT) or H[•] transfer (CCT) will aid the design of new metal complexes for the controlled polymerization of a desired monomer. Another great disadvantage of OMRP is the need of a stoichiometric amount of metal complex (one molecule per chain), thus research oriented toward the use of nonexpensive and nontoxic (or less toxic) metals such as Fe and Cu, which have not yet been extensively investigated within this context, and toward the metal anchoring on a recyclable solid support should lead to further major advances.

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Biographical Sketch



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3.12 Copper-Mediated Atom Transfer Radical Polymerization

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3.12.2ATRP Equilibrium379312.3.1Reverse ATRP380312.3.1Reverse ATRP381312.3.2Simultaneous Reverse and Normal Initiation381312.3.3Activators Generated by Electron Transfer ATRP381312.3.4Activator Regenerated by Electron Transfer ATRP381312.3.5Initiators for Continuous Activator Regeneration382312.3.6ATRP With Akyl Pseudohaldes382312.3.7Electrochemical Control Over an ATRP384312.4Removal of Copper385312.5.1Electrochemical Control Over an ATRP385312.5.2AttRP Themodynamics and Kinetics385312.5.1Equilibrium Constants in ATRP385312.5.2Activation Red Constants in ATRP386312.5.4Inner Sphere Electron Transfer391312.6.6Components/Phenomenology/Process391312.6.6Solvent Effects and Selection of a Catalyst for Polymerization in Homogeneous Aqueous Media393312.6.6Solvent Effects and Selection of a Catalyst for Polymerization in Homogeneous Aqueous Media393312.6.6.1Minemuision397312.6.6.2Dispersion397312.6.6.3Readive surfactants396312.6.6.4Atoditives393312.6.6.5Dispersion397312.6.6.5Dispersion397312.6.6.5Dispersion397312.6.6.5Dispersion397312.6.6.5Dispersion397<	3.12.1	Introduction	378
3.12.3Initiating an ATRP380312.3.1Reverse ATRP381312.3.2Simultaneous Reverse and Normal Initiation381312.3.3Activators Regenerated by Electron Transfer ATRP381312.3.4Activator Regenerated by Electron Transfer ATRP381312.3.5Initiators for Continuous Activator Regeneration382312.3.6ATRP with Aky Pseudohaldes382312.3.7Electrochemical Control Over an ATRP384312.5.1Equilibrium Constants in ATRP385312.5.2ATRP with Aky Pseudohaldes385312.5.3Ratical Nature of the Propagating Species389312.5.4Inner Sphere Electron Transfer versus Outer Sphere Electron Transfer390312.6.1Moromers391312.6.2Initiators391312.6.3Solvent Effects and Selection of a Catalyst for Polymerization in Homogeneous Aqueous Media393312.6.6ATRP in Biphasic Aqueous Systems395312.6.6Microemuision397312.6.6Microemuision397312.6.6Interse miniemulsion397312.6.6Interse miniemulsion397312.7.7Control over Polymer Composition397312.7.1Control over Polymer Composition397312.7.2Homogolymers397312.7.3Linear copolymers397312.7.4Tracleity Control400312.7.5Grafting trimation397312.7.6Interse miniemulsion397<	3.12.2	ATRP Equilibrium	379
312.3.1 Reverse ATRP 380 312.3.2 Simultaneous Reverse and Normal Initiation 381 312.3.3 Activators Generated by Electron Transfer ATRP 381 312.3.4 Activator Regenerated by Electron Transfer ATRP 381 312.3.5 Initiators for Continuous Activator Regeneration 382 312.3.6 ATRP with Akyl Pseudohalides 382 312.3.7 Electrochemical Control Over an ATRP 384 312.4 Removal of Copper 385 312.5.1 Equilibrium Constants in ATRP 385 312.5.4 Inner Sphere Electron Transfer Versus Outer Sphere Electron Transfer 399 312.5.4 Inner Sphere Electron Transfer Versus Outer Sphere Electron Transfer 391 312.6.1 Monomers 391 312.6.2 Initiators 391 312.6.3 Ligands 393 312.6.4 Additives 393 312.6.5 Solvent Effects and Selection of a Catalyst for Polymerization in Homogeneous Aqueous Media 393 312.6.6.1 Minemulsion 395 312.6.6.1 Minemulsion 395 312.6.6.2 Minemulsion 395 312.6.6.3 Indexemulsion 397 312.6.6.4 A True emulsion system 397 <	3.12.3	Initiating an ATRP	380
312.3.2Simultaneous Reverse and Normal Inflation381312.3.3Activator Regenerated by Electron Transfer ATRP381312.3.4Activator Regenerated by Electron Transfer ATRP381312.3.5Initiators for Continuus Activator Regeneration382312.3.6ATRP with Alkyl Pseudohalides382312.3.7Electrochemical Control Over an ATRP384312.5.1Removal of Copper385312.5.1ATRP hermodynamics and Kinetics385312.5.2Activation Rate Constants in ATRP387312.5.3Ratical Nature of the Progagating Species389312.5.4Inner Sphere Electron Transfer versus Outer Sphere Electron Transfer390312.6.1Monomers391312.6.2Ligands393312.6.3Ligands393312.6.4Additives393312.6.5Solvent Effects and Selection of a Catalyst for Polymerization in Homogeneous Aqueous Media393312.6.6ATRP in Biphasic Aqueous Systems396312.6.6.1Minicreenuision397312.6.6.2Micreenuision397312.6.6.3Reactive system397312.6.6Inverse minemulsion397312.6.6Inverse minemulsion397312.6.6Inverse minemulsion397312.6.6Inverse minemulsion397312.7.1Control decy Opymers397312.7.2Homogolymers397312.7.3Linear acopolymers397312.7.4Gradin	3.12.3.1	Reverse ATRP	380
312.3.3 Activators Generated by Electron Transfer ATRP 381 312.3.4 Activator Regenerated by Electron Transfer ATRP 381 312.3.5 Initiators for Continuous Activator Regeneration 382 312.3.6 ATRP with Alvy Pseudohaldes 382 312.3.7 Electrochemical Control Over an ATRP 384 312.4 Removal of Copper 385 312.5.1 Equilibrium Constants in ATRP 385 312.5.2 Activation Rate Constants in ATRP 387 312.5.4 Inner Sphere Electron Transfer versus Outer Sphere Electron Transfer 390 312.6.5 Components/Phenomenology/Process 391 312.6.6 Inner Sphere Electron Transfer versus Outer Sphere Electron Transfer 393 312.6.6 Additives 393 312.6.6 Additives 393 312.6.6 Additives 393 312.6.6 Atria The Braisic Aqueous Systems 395 312.6.6 Atrice inabiaison system 397 312.6.6 Micromutsion 397 312.6.6 Micromutsion 397 312.6.6 Nueneuusion 397	3.12.3.2	Simultaneous Reverse and Normal Initiation	381
312.3.4 Activator Regenerated by Electron Transfer ATEP 381 312.3.5 Initiators for Continuous Activator Regeneration 382 312.3.7 Electrochemical Control Over an ATEP 384 312.3.7 Electrochemical Control Over an ATEP 385 312.5.1 ATEP Thermodynamics and Kinetics 385 312.5.1 Equilibritum Constants in ATEP 385 312.5.2 Activation Rate Constants in ATEP 386 312.5.3 Radical Nature of the Propagating Species 389 312.6.4 Inner Sphere Electron Transfer versus Outer Sphere Electron Transfer 390 312.6.6 Components/Phenomenology/Process 393 312.6.6 Initiators 393 312.6.6 ATEP in Biphasic Aqueous Systems 393 312.6.6 ATEP in Biphasic Aqueous Systems 395 312.6.6.1 Miniernalision 396 312.6.6.2 Microenalision 397 312.6.6.3 Reservice surfactants 396 312.6.6.4 AtTWe enulsion system 397 312.6.6.5 Dispersion 397 312.6.6.6 TIPER controleener Polymer Compositio	3.12.3.3	Activators Generated by Electron Transfer ATRP	381
312.3.5Initiators for Continuous Activator Regeneration382312.3.6ATRP with Allyl Pseudohaldes382312.3.7Electrochemical Control Over an ATRP384312.4Removal of Copper385312.5.1Equilibrium Constants in ATRP385312.5.1Equilibrium Constants in ATRP387312.5.3Radical Mature of the Propagating Species389312.5.4Inner Sphere Electron Transfer versus Outer Sphere Electron Transfer390312.6.5Components/Phenomenology/Process391312.6.1Monomers393312.6.3Ligands393312.6.4Additives393312.6.5Solvent Effects and Selection of a Catalyst for Polymerization in Homogeneous Aqueous Media393312.6.6ATRP in Biphasic Aqueous Systems396312.6.6ATRP in Biphasic Aqueous Systems396312.6.6ATRP in Biphasic Aqueous Systems397312.6.6Inverse miniamulsion397312.6.6Inverse miniamulsion397312.6.6Inverse miniamulsion397312.7.1Control over Polymer Composition397312.7.2Homopolymers398312.7.3Linear copolymers398312.7.4Homopolymers398312.7.5Linear copolymers400312.7.4Homopolymers398312.7.5Linear Segmented Copolymers401312.8.1Graft- and CompoShaped (Co)polymers400312.8.2Hortworks/G	3.12.3.4	Activator Regenerated by Electron Transfer ATRP	381
312.3.6ATRP with Alkyl Pseudohalides382312.3.7Electrochemical Control Over an ATRP384312.4Removal of Copper385312.5.5ATRP Thermodynamics and Kinetics385312.5.1Equilibrium Constants in ATRP385312.5.2Activation Rate Constants in ATRP385312.5.3Radical Nature of the Propagating Species389312.6.4Inner Sphere Electron Transfer versus Outer Sphere Electron Transfer391312.6.1Monomers391312.6.2Initiators391312.6.3Ligands393312.6.4Additives393312.6.6ATRP in Biphasic Aqueous Systems395312.6.6ATRP in Biphasic Aqueous Systems396312.6.6.1Microemulsion396312.6.6.2Microemulsion397312.6.6.3Reactive surfactants397312.6.6.4At true emulsion system397312.6.6.5Dispersion397312.6.6.6Inverse miniemulsion397312.6.7Control over Polymer Composition397312.7.7Control over Polymers398312.7.1Linar Segmented Copolymers398312.7.3(Colpolymers with Controlled MW398312.7.4Linar Segmented Copolymers400312.7.5Linar Segmented Copolymers401312.8.1Grafting timoly402312.8.1Grafting timoly402312.8.2Brush Macronlecular brushes404 <td>3.12.3.5</td> <td>Initiators for Continuous Activator Regeneration</td> <td>382</td>	3.12.3.5	Initiators for Continuous Activator Regeneration	382
312.3.7Electrochemical Control Over an ATRP334312.4Removal of Copper385312.5.1Equilibrium Control over an ATRP385312.5.2ATRP Thermodynamics and Kinetics385312.5.3Radical Nature of the Propagating Species389312.5.4Inner Sphere Electron Transfer versus Outer Sphere Electron Transfer390312.6.6Components/Phenomenology/Process391312.6.1Monomers391312.6.2Initiators391312.6.3Ligands393312.6.4Additives393312.6.5Solvent Effects and Selection of a Catalyst for Polymerization in Homogeneous Aqueous Media393312.6.6ATRP in Biphasic Aqueous Systems395312.6.6.1Miniemulsion396312.6.6.2Microemulsion396312.6.6.3Reactive surfactants396312.6.6.4A true emulsion397312.6.6.5Dispersion397312.6.6Inverse miniemulsion397312.7.7Control over Polymers393312.7.1Control over Polymers398312.7.2Homopolymers398312.7.3.1Linear copolymers397312.7.4Control over Polymer Controlled MW398312.7.5Linear copolymers397312.7.6Linear copolymers398312.7.7Control over Polymer Controlled MW398312.7.7Control over Polymer Statistical and gradient398312.7.4 </td <td>3.12.3.6</td> <td>ATRP with Alkyl Pseudohalides</td> <td>382</td>	3.12.3.6	ATRP with Alkyl Pseudohalides	382
3.12.4Removal of Copper3853.12.5ATRP Thermodynamics and Kinetics3853.12.5.1Equilibrium Constants in ATRP3853.12.5.2Activation Rate Constants in ATRP3873.12.5.3Radical Nature of the Propagating Species3893.12.5.4Inner Sphere Electron Transfer versus Outer Sphere Electron Transfer3903.12.6.1Monomers3913.12.6.2Initiators3913.12.6.3Ligands3933.12.6.4Additives3933.12.6.6ATRP in Biphasic Aqueous Systems3933.12.6.6ATRP in Biphasic Aqueous Systems3953.12.6.6.1Miniemulsion3953.12.6.6Minemulsion3963.12.6.6A Ture' enulsion system3973.12.6.6Dispersion3973.12.6.6Inverse miniemulsion3973.12.7.1Well-Defined Copolymers3983.12.7.3(Colpolymers3983.12.7.4TatcatoyOpymers3983.12.7.4TatcatoyOpymers4003.12.7.4TatcatoyOpymers4003.12.7.4Farth and Comb-Shaped (Co)polymers4013.12.8.1Grafting from'4023.12.8.2Brush Macromolecular brushes4043.12.8.3(Hyper)branched Copolymers4013.12.7.4TatcatoyOpymers4013.12.7.5Linear Segmented Copolymers4023.12.7.4Grafting from'4023.12.7.5Linear Segmented Cop	3.12.3.7	Electrochemical Control Over an ATRP	384
3.12.5.ATRP Thermodynamics and Kinetics3853.12.5.1Equilibrium Constants in ATRP3853.12.5.2Activation Rate Constants in ATRP3873.12.5.3Radical Nature of the Propagating Species3893.12.5.4Inner Sphere Electron Transfer versus Outer Sphere Electron Transfer3903.12.6.1Components/Phenomenology/Process3913.12.6.2Initiators3913.12.6.3Ligands3933.12.6.4Additives3933.12.6.5Solvent Effects and Selection of a Catalyst for Polymerization in Homogeneous Aqueous Media3933.12.6.6ATRP in Biphasic Aqueous Systems3953.12.6.6.1Miniemulsion3963.12.6.6.2Minoremulsion3963.12.6.6.3Reactive sufactantis3963.12.6.6.4A true emulsion3973.12.6.6.6Inverse miniemulsion3973.12.7.1Well-Defined Copolymers3973.12.7.2Homopolymers3973.12.7.4Homopolymers3983.12.7.5Linear copolymers: statistical and gradient3983.12.7.4Tacticity Control4003.12.7.5Linear Segmented Copolymers4013.12.8.1Graft- and Como-Shaped (Co)polymers4023.12.8.1Graft- and Como-Shaped (Co)polymers4023.12.8.3(Hyper)branched Copolymers4043.12.8.4Site Copolymers Ming architecture4043.12.8.5Networks/Geis404 <trr>3.12.8.4<td>3.12.4</td><td>Removal of Copper</td><td>385</td></trr>	3.12.4	Removal of Copper	385
3.12.5.1Equilibrium Constants in ATRP3853.12.5.2Activation Rate Constants in ATRP3873.12.5.3Radical Nature of the Propagating Species3893.12.5.4Inner Sphere Electron Transfer versus Outer Sphere Electron Transfer3903.12.6.4Monomers3913.12.6.5Ligands3933.12.6.6Ligands3933.12.6.6Additives3933.12.6.6Additives3933.12.6.6ATRP in Biphasic Aqueous Systems3953.12.6.6Microemulsion3963.12.6.6.3Reactive surfactants3963.12.6.6A True emulsion3973.12.6.6Dispersion3973.12.6.6Dispersion3973.12.6.6Inverse miniemulsion3973.12.6.6Dispersion3973.12.7.7Control over Polymer Composition3973.12.7.1Well-Defined Copolymers3983.12.7.3(Colpolymers vit Controlled WW3983.12.7.4Tacticity Control4003.12.7.4Tacticity Control4003.12.8.1Grafting from4013.12.8.1Grafting from4023.12.8.2Brush Macromolecular busines4043.12.8.3(Hyper)branched Copolymers4013.12.7.4Tacticity Control4003.12.7.5Linear Segmented Copolymers4013.12.7.4Grafting from4023.12.7.5Linear Segmented Copolymers404 <t< td=""><td>3.12.5</td><td>ATRP Thermodynamics and Kinetics</td><td>385</td></t<>	3.12.5	ATRP Thermodynamics and Kinetics	385
312.5.2Activation Rate Constants in ATRP387312.5.3Radical Nature of the Propagating Species389312.5.4Inner Sphere Electron Transfer versus Outer Sphere Electron Transfer390312.6.1Components/Phenomenology/Process391312.6.2Initiators391312.6.3Ligands393312.6.4Additives393312.6.5Solvent Effects and Selection of a Catalyst for Polymerization in Homogeneous Aqueous Media393312.6.6Miniemulsion395312.6.6.1Miniemulsion395312.6.6.2Microemulsion396312.6.6.3Reactive suffactants396312.6.6.4A 'true' emulsion system397312.6.6.5Dispersion397312.6.6.6Inverse miniemulsion397312.7.7Control over Polymer Composition397312.7.1Veli-Defined Copolymers398312.7.3Linear copolymers statistical and gradient398312.7.3Linear copolymers400312.7.4Tatcicity Control400312.7.5Linear Segmented Copolymers401312.8.1'Grafting through'402312.8.2Brush Macromolecular bushes404312.8.3(Hyper)branched Copolymers401312.8.4Couplymers with varying architecture404312.8.5Networks/Gels403312.8.6Star Coopolymers with varying architecture404312.8.7Hubber Couplymers406 <td>3.12.5.1</td> <td>Equilibrium Constants in ATRP</td> <td>385</td>	3.12.5.1	Equilibrium Constants in ATRP	385
3.12.5.3Radical Nature of the Propagating Species3893.12.5.4Inner Sphere Elector Transfer versus Outer Sphere Electron Transfer3903.12.6.1Monomers3913.12.6.2Initiators3913.12.6.3Ligands3933.12.6.4Additives3933.12.6.5Solvent Effects and Selection of a Catalyst for Polymerization in Homogeneous Aqueous Media3933.12.6.6ATRP in Biphasic Aqueous Systems3953.12.6.6ATRP in Biphasic Aqueous Systems3953.12.6.6.3Reactive surfactantis3963.12.6.6.4A true enulsion3973.12.6.6.5Dispersion3973.12.6.6.6Inverse minismulsion3973.12.6.6.5Dispersion3973.12.7.1Well-Defined Gopolymers3973.12.7.3(Colpolymer Somposition3973.12.7.4Tatchtly Control MW3983.12.7.5Linear Segmented Cooplymers3983.12.7.4Tatchtly Control4003.12.7.5Linear Segmented Cooplymers4013.12.7.4Tatchtly Control4003.12.7.5Linear Segmented Cooplymers4013.12.8.1Graft- and Complymers4013.12.8.2Brush Macromolecular brushes4043.12.8.3(Hyper)branched Cooplymers4063.12.8.4Core list4063.12.8.5Networks/Gels4063.12.8.4Star Cooplymers4063.12.8.5Networks/Gels40	3.12.5.2	Activation Rate Constants in ATRP	387
3.12.5.4Inner Sphere Electron Transfer3903.12.6Components/Phenomenology/Process3913.12.6.1Monomers3913.12.6.2Initiators3913.12.6.3Ligands3933.12.6.4Additives3933.12.6.5Solvent Effects and Selection of a Catalyst for Polymerization in Homogeneous Aqueous Media3933.12.6.6ATRP in Biphasic Aqueous Systems3953.12.6.6.1Minemulsion3963.12.6.6.2Micromulsion3963.12.6.6.3Reactive surfactants3963.12.6.6.4A true 'emulsion system3973.12.6.6.5Dispersion3973.12.6.6.6Inverse minemulsion3973.12.7.7Control over Polymer Composition3973.12.7.1Weil-Defined Copolymers3983.12.7.2Homopolymers3983.12.7.3Linear copolymers3983.12.7.4Tacticty Control4003.12.7.5Linear copolymers4003.12.7.5Linear copolymers4003.12.7.5Linear copolymers4013.12.8.1Grafting from'4023.12.8.2Brush Macromolecules4043.12.8.3(Hyper)branched Copolymers4013.12.8.4Grafting from'4023.12.7.5Linear segmented Copolymers4013.12.8.1Grafting from'4023.12.8.2Brush Macromolecules4043.12.8.3(Hyper)branched Copolymers406 </td <td>3.12.5.3</td> <td>Radical Nature of the Propagating Species</td> <td>389</td>	3.12.5.3	Radical Nature of the Propagating Species	389
3.12.6Components/Phenomenology/Process3913.12.6.1Monomers3913.12.6.2Initiators3913.12.6.3Ligands3933.12.6.4Additives3933.12.6.5Solvent Effects and Selection of a Catalyst for Polymerization in Homogeneous Aqueous Media3933.12.6.6ATRP in Biphasic Aqueous Systems3953.12.6.6ATRP in Biphasic Aqueous Systems3953.12.6.6.1Minemulsion3953.12.6.6.2Micoemulsion3963.12.6.6.3Reactive surfactants3963.12.6.6.4A true' enulsion system3973.12.6.6.5Dispersion3973.12.6.6.6Inverse miniemulsion3973.12.7.1Vell-Defined Copolymers3983.12.7.3(Co)polymers with Controlled MW3983.12.7.3Control over Polymer Composition3983.12.7.4Tacticity Control4003.12.7.5Linear copolymers3983.12.7.4Tacticity Control4003.12.7.5Linear Segmented Copolymers4013.12.8.1Graft- and Comb-Shaped (Co)polymers4013.12.8.2Brush Macromolecules4043.12.8.3(Hyper)branchecular brushes4043.12.8.4Star Copolymers with varing architecture4043.12.8.2Brush topolymers4063.12.8.3(Hyper)branched Copolymers4063.12.8.4Star Copolymers with varing architecture4063.12.8.5Ne	3.12.5.4	Inner Sphere Electron Transfer versus Outer Sphere Electron Transfer	390
3.12.6.1Monomers3913.12.6.2Initiators3913.12.6.3Ligands3933.12.6.4Additives3933.12.6.5Solvent Effects and Selection of a Catalyst for Polymerization in Homogeneous Aqueous Media3933.12.6.6ATRP in Biphasic Aqueous Systems3953.12.6.6ATRP in Biphasic Aqueous Systems3953.12.6.6Minemulsion3963.12.6.6.1Minemulsion3963.12.6.6.2Microenulsion3973.12.6.6.4A true' emulsion system3973.12.6.6.5Dispersion3973.12.6.6Inverse miniemulsion3973.12.7.1Control over Polymer Composition3973.12.7.2Homopolymers3983.12.7.3(Co)polymers with Controlled MW3983.12.7.3Linear Copolymers4003.12.7.4Tacticity Control4003.12.7.4Tacticity Control4003.12.8.1Graft- and Comb-Shaped (Co)polymers4013.12.8.1Graft- and Comb-Shaped (Co)polymers4013.12.8.2Brush Macromolecules4043.12.8.3Grafta frond4023.12.8.4Star Copolymers with varying architecture4043.12.8.4Star Copolymers4063.12.8.4Star Copolymers4063.12.8.4Star Copolymers4063.12.8.5Network/Gels4063.12.8.4Star Copolymers4063.12.8.5Network/Gels406	3.12.6	Components/Phenomenology/Process	391
3.12.6.2Initiators3913.12.6.3Ligands3933.12.6.4Additives3933.12.6.5Solvent Effects and Selection of a Catalyst for Polymerization in Homogeneous Aqueous Media3933.12.6.6ATRP in Biphasic Aqueous Systems3953.12.6.6.1Miniemulsion3953.12.6.6.2Microemulsion3963.12.6.6.4A 'true' emulsion system3973.12.6.6.5Dispersion3973.12.6.6.6Inverse miniemulsion3973.12.7.7Control over Polymer Composition3973.12.7.1Well-Defined Copolymers3983.12.7.3(Co)polymers with Controlled MW3983.12.7.4Homopolymers3983.12.7.5Linear copolymers4003.12.7.4Tacticity Control4003.12.7.5Linear segmented Copolymers4003.12.7.4Faching trom'4023.12.8.1Graft- and Comb-Shaped (Co)polymers4013.12.8.1Grafting through'4023.12.8.1Grafting through'4023.12.8.1Grafting through'4023.12.8.2Brush thacromolecules4043.12.8.4Star Copolymers4063.12.8.4Star Copolymers4063.12.8.5Networks/Gels4063.12.8.4Star Copolymers4063.12.8.5Networks/Gels4063.12.8.4Star Copolymers4063.12.8.5Networks/Gels4063.12	3.12.6.1	Monomers	391
3.12.6.3Ligands3933.12.6.4Additives3933.12.6.5Solvent Effects and Selection of a Catalyst for Polymerization in Homogeneous Aqueous Media3933.12.6.6ATRP in Biphasic Aqueous Systems3953.12.6.6.1Miniemulsion3963.12.6.6.2Microemulsion3963.12.6.6.3Reactive surfactants3963.12.6.6.4A 'true' emulsion system3973.12.6.6.5Dispersion3973.12.6.6.6Inverse miniemulsion3973.12.7.7Control over Polymer Composition3973.12.7.1Well-Defined Copolymers3983.12.7.2Homopolymers3983.12.7.3Linear copolymers3983.12.7.4Tacticity Control4003.12.7.5Linear copolymers4003.12.7.4Tacticity Control4003.12.7.5Linear Segmented Copolymers4013.12.8Polymer Topology4013.12.8.1Grafting from'4023.12.8.1Grafting from'4023.12.8.1.3'Grafting from'4023.12.8.4Star Copolymers4043.12.8.4Star Copolymers4063.12.8.4Star Copolymers4063.12.8.4Star Copolymers4063.12.8.4Star Copolymers4063.12.8.4Star Copolymers4063.12.8.5Networks/Gels4063.12.8.4Star Copolymers4063.12.8.5Networks/Gels<	3.12.6.2	Initiators	391
3.12.6.4Additives3333.12.6.5Solvent Effects and Selection of a Catalyst for Polymerization in Homogeneous Aqueous Media3333.12.6.6ATRP in Biphasic Aqueous Systems3953.12.6.6Microemulsion3953.12.6.6.1Microemulsion3963.12.6.6.2Microemulsion system3973.12.6.6.3Reactive surfactants3963.12.6.6.4A True' emulsion ysstem3973.12.6.6.5Dispersion3973.12.6.6.6Inverse miniemulsion3973.12.7.7Control over Polymer Composition3973.12.7.1Well-Defined Copolymers3983.12.7.3(Co)polymers statistical and gradient3983.12.7.3(Co)polymers statistical and gradient3983.12.7.4Tacticity Control4003.12.7.5Linear copolymers4003.12.7.6Linear copolymers4003.12.7.7Cohyper Topology4013.12.7.8Polymer Topology4013.12.8.1Graft- and Comb-Shaped (Co)polymers4013.12.8.1Grafting from'4023.12.8.2Brush Macromolecular brushes4043.12.8.3(Hyper)branched Copolymers4063.12.8.4Star Copolymers4063.12.8.4Star Copolymers4063.12.8.4Star Copolymers4063.12.8.5Networks/Gels4063.12.8.4Star Copolymers4063.12.8.5Networks/Gels4083.1	3.12.6.3	Ligands	393
3.12.6.5 Solvent Effects and Selection of a Catalyst for Polymerization in Homogeneous Aqueous Media 393 3.12.6.6 ATRP in Biphasic Aqueous Systems 395 3.12.6.6.1 Miniemulsion 395 3.12.6.6.2 Microemulsion system 396 3.12.6.6.3 Reactive surfactants 396 3.12.6.6.4 A 'true' emulsion system 397 3.12.6.6.5 Dispersion 397 3.12.6.6.6 Inverse miniemulsion 397 3.12.7.7 Control over Polymer Composition 397 3.12.7.7 Homopolymers 397 3.12.7.8 Homopolymers 398 3.12.7.3 Linear copolymers 398 3.12.7.4 Hoinpolymers 398 3.12.7.5 Linear Segmented Copolymers 400 3.12.7.6 Polymer Topology 401 3.12.8 Polymer Topology 401 3.12.8.1 Graft- and Comb-Shaped (Co)polymers 401 3.12.8.1 Grafting from' 402 3.12.8.2 Brush Macromolecular brushes 404 3.12.8.1 'Grating frong in arbitecture 404<	3.12.6.4	Additives	393
3.12.6.6 ATRP in Biphasic Aqueous Systems 395 3.12.6.6.1 Miniemulsion 396 3.12.6.6.2 Microemulsion 396 3.12.6.6.3 Reactive surfactants 396 3.12.6.6.4 A 'true' emulsion system 397 3.12.6.6.5 Dispersion 397 3.12.6.6.6 Inverse miniemulsion 397 3.12.7.7 Control over Polymer Composition 397 3.12.7.1 Well-Defined Copolymers 398 3.12.7.2 Homopolymers 398 3.12.7.3 (Co)polymers with Controlled MW 398 3.12.7.4 Linear copolymers 400 3.12.7.5 Linear copolymers 400 3.12.7.4 Tacticity Control 400 3.12.7.5 Linear Segmented Copolymers 401 3.12.8.1 Grafting from' 402 3.12.8.1 Grafting trough' 402 3.12.8.1 Grafting trough' 402 3.12.8.2 Brush Macromolecular brushes 404 3.12.8.2 Brush Macromolecular brushes 404 3.12.8.3 (Farting t	3.12.6.5	Solvent Effects and Selection of a Catalyst for Polymerization in Homogeneous Aqueous Media	393
3.126.6.1 Minemulsion 395 3.126.6.2 Microemulsion 396 3.126.6.3 Reactive surfactants 396 3.126.6.4 A 'true' emulsion system 397 3.126.6.5 Dispersion 397 3.126.6.6 Inverse miniemulsion 397 3.12.7 Control over Polymer Composition 397 3.12.7.1 Well-Defined Copolymers 398 3.12.7.3 (Co)polymers with Controlled MW 398 3.12.7.3 Linear copolymers 398 3.12.7.4 Tacticity Control 400 3.12.7.5 Linear copolymers 400 3.12.7.5 Linear Segmented Copolymers 400 3.12.8.1 Grafting from' 402 3.12.8.1 Grafting from' 402 3.12.8.1 Grafting through' 402 3.12.8.2 Brush Macromoleculars 404 3.12.8.3 Grafting through' 402 3.12.8.4 Star Copolymers 406 3.12.8.5 Networks/Gels 406 3.12.8.4 Star Copolymers 406	3.12.6.6	ATRP in Biphasic Aqueous Systems	395
3.12.6.6.2 Microemulsion 396 3.12.6.6.3 Reactive surfactants 396 3.12.6.6.4 A 'true' emulsion system 397 3.12.6.6.5 Dispersion 397 3.12.6.6.6 Inverse miniemulsion 397 3.12.7.7 Control over Polymer Composition 397 3.12.7.1 Well-Defined Copolymers 398 3.12.7.2 Homopolymers 398 3.12.7.3 (Co)polymers with Controlled MW 398 3.12.7.4 Tacticity Control 398 3.12.7.5 Linear copolymers: statistical and gradient 398 3.12.7.4 Tacticity Control 400 3.12.7.5 Linear Segmented Copolymers 400 3.12.7.4 Tacticity Control 400 3.12.7.4 Grafting from' 402 3.12.8.1 Grafting from' 402 3.12.8.2 Brush Macromolecular brushes 404 3.12.8.1.2 'Grafting from' 402 3.12.8.2 Brush Macromolecular brushes 404 3.12.8.3 'Grafting through' 402 3.12.8.4	3.12.6.6.1	Miniemulsion	395
3.12.6.6.3 Reactive surfactants 396 3.12.6.6.5 Dispersion 397 3.12.6.6.5 Dispersion 397 3.12.6.6.6 Inverse miniemulsion 397 3.12.7.1 Well-Defined Copolymers 398 3.12.7.2 Homopolymers 398 3.12.7.3 (Co)polymers with Controlled MW 398 3.12.7.4 Linear copolymers. statistical and gradient 398 3.12.7.5 Linear copolymers 400 3.12.7.4 Tacticity Control 400 3.12.7.5 Linear segmented Copolymers 400 3.12.7.6 Polymer Topology 401 3.12.7.5 Linear Segmented Copolymers 400 3.12.8 Polymer Topology 401 3.12.8.1 Graft- and Comb-Shaped (Co)polymers 401 3.12.8.2 Brush Macromolecules 404 3.12.8.2 Brush Macromolecules 404 3.12.8.2 Brush Macromolecules 404 3.12.8.2 Brush Macromolecules 404 3.12.8.4 Star Copolymers 406 3.12.8.5 Networ	3.12.6.6.2	Microemulsion	396
3.12.6.6.4 A True emulsion system 397 3.12.6.6.5 Dispersion 397 3.12.6.6.6 Inverse miniemulsion 397 3.12.7.1 Control over Polymer Composition 397 3.12.7.1 Well-Defined Copolymers 398 3.12.7.3 (Co)polymers with Controlled MW 398 3.12.7.3.1 Linear copolymers: statistical and gradient 398 3.12.7.3.2 Alternating copolymers 400 3.12.7.4 Tacticity Control 400 3.12.7.5 Linear Segmented Copolymers 400 3.12.7.4 Tacticity Control 400 3.12.7.5 Linear Segmented Copolymers 400 3.12.7.6 Grading trough 401 3.12.8 Polymer Topology 401 3.12.8.1 Grading through 402 3.12.8.1 Grading through 402 3.12.8.1 Grading through 402 3.12.8.2 Brush Macromolecules 404 3.12.8.3 Grading through 402 3.12.8.4 Star Copolymers with varying architecture 404 3.12.	3.12.6.6.3	Reactive surfactants	396
3.12.6.6.5 Dispersion 397 3.12.6.6.6 Inverse miniemulsion 397 3.12.7 Control over Polymer Composition 397 3.12.7.1 Well-Defined Copolymers 398 3.12.7.2 Homopolymers with Controlled MW 398 3.12.7.3.1 Linear copolymers: statistical and gradient 398 3.12.7.3.2 Alternating copolymers 400 3.12.7.4 Tacticity Control 400 3.12.7.5 Linear copolymers 400 3.12.7.4 Tacticity Control 400 3.12.7.5 Linear Segmented Copolymers 400 3.12.8.1 Graft- and Comb-Shaped (Co)polymers 401 3.12.8.1 Graft- and Comb-Shaped (Co)polymers 401 3.12.8.1 Grafting troi 402 3.12.8.2 Brush Macromolecules 404 3.12.8.2 Brush Macromolecules brushes 404 3.12.8.2 Brush copolymers with varying architecture 404 3.12.8.2 Brush copolymers 406 3.12.8.4 Star Copolymers 406 3.12.8.2 Brush copolymers 406	3.12.6.6.4	A 'true' emulsion system	397
3.12.6.6.6Inverse minimulsion3973.12.7.1Veil-Defined Copolymers3973.12.7.2Homopolymers3983.12.7.3(Co)polymers with Controlled MW3983.12.7.3.1Linear copolymers: statistical and gradient3983.12.7.4Tacticity Control4003.12.7.5Linear copolymers4003.12.7.6Linear Segmented Copolymers4003.12.7.7Tacticity Control4003.12.7.8Polymer Topology4013.12.8Polymer Topology4013.12.8.1Grafting from'4023.12.8.1.2'Grafting from'4023.12.8.2Brush Macromolecules4043.12.8.2Brush Macromolecules4043.12.8.2Brush copolymers4063.12.8.4Star Copolymers4063.12.8.4Star Copolymers4063.12.8.4Star Copolymers4063.12.8.4Star Copolymers4063.12.8.5Networks/Gels4083.12.8.5Networks/Gels4083.12.9Site-Specific Functional Monomers4013.12.9.1Polymerization of Functional Monomers4103.12.9.2Postpolymerization of Incorporated Monomer Units4113.12.9.3Use of Functional ATRP Initiators411	3.12.6.6.5	Dispersion	397
3.12.7Control over Polymer Composition3973.12.7.1Well-Defined Copolymers3983.12.7.2Homopolymers3983.12.7.3(Co)polymers with Controlled MW3983.12.7.3.1Linear copolymers: statistical and gradient3983.12.7.4Tacticity Control4003.12.7.5Linear copolymers4003.12.7.4Tacticity Control4003.12.7.5Linear Segmented Copolymers4013.12.8Polymer Topology4013.12.8.1Graft- and Comb-Shaped (Co)polymers4023.12.8.1.2'Grafting from'4023.12.8.1.3'Grafting frough'4033.12.8.2Brush Macromolecules4043.12.8.2Brush Macromolecules4043.12.8.2Brush copolymers with varying architecture4063.12.8.3(Hyper)branched Copolymers4063.12.8.4Star Copolymers4063.12.8.4Coupling onto4063.12.8.4Coupling onto4063.12.8.4Star Copolymers4063.12.8.4Star Copolymers4063.12.8.4Star Copolymers4063.12.8.5Networks/Gels4083.12.8.4Star Copolymers4063.12.8.5Networks/Gels4083.12.9Site-Specific Functional Monomers4103.12.9.1Polymerization of Functional Monomers4103.12.9.2Postpolymerization for Incorporated Monomer Units41103.12.9.3 </td <td>3.12.6.6.6</td> <td>Inverse miniemulsion</td> <td>397</td>	3.12.6.6.6	Inverse miniemulsion	397
3.12.7.1Well-Defined Copolymers3973.12.7.2Homopolymers3983.12.7.3(Co)polymers with Controlled MW3983.12.7.3.1Linear copolymers: statistical and gradient3983.12.7.3.2Alternating copolymers4003.12.7.4Tacticity Control4003.12.7.5Linear Segmented Copolymers4003.12.8Polymer Topology4013.12.8.1Graft- and Comb-Shaped (Co)polymers4013.12.8.1.1'Grafting from'4023.12.8.2Brush Macromolecules4043.12.8.2Brush Macromolecules4043.12.8.2Brush Macromolecules4043.12.8.3(Hyper)branched Copolymers4063.12.8.4Star Copolymers4063.12.8.4Star Copolymers4063.12.8.4Coupling onto4063.12.8.5Networks/Gels4063.12.8.5Networks/Gels4083.12.9Site-Specific Functionality4103.12.9.1Polymerization of Incorporated Monomer Units4103.12.9.2Postpolymerization of Incorporated Monomer Units411	3.12.7	Control over Polymer Composition	397
3.12.7.2Hompoprimers3983.12.7.3(Co)polymers with Controlled MW3983.12.7.3.1Linear copolymers: statistical and gradient3983.12.7.3.2Alternating copolymers4003.12.7.4Tacticity Control4003.12.7.5Linear Segmented Copolymers4003.12.8Polymer Topology4013.12.8.1Graft- and Comb-Shaped (Co)polymers4013.12.8.1'Grafting from'4023.12.8.1.2'Grafting through'4023.12.8.1.3'Grafting to'4033.12.8.2Brush Macromolecules4043.12.8.2Brush Macromolecules4043.12.8.3(Hyper)branched Copolymers4043.12.8.4Star Copolymers with varying architecture4043.12.8.3(Hyper)branched Copolymers4063.12.8.4Star Copolymers4063.12.8.4Coupling onto4063.12.8.5Networks/Gels4063.12.8.5Networks/Gels4083.12.9Site-Specific Functionality4103.12.9.1Polymerization of Functional Monomers4103.12.9.2Postpolymerization of Incorporated Monomer Units4113.12.9.3Use of Functional ATRP Initiators411	3.12.7.1	Weil-Defined Copolymers	397
3.12.7.3(Co)polymers with Controlled MW3983.12.7.3.1Linear copolymers: statistical and gradient3983.12.7.3.2Alternating copolymers4003.12.7.3.2Alternating copolymers4003.12.7.4Tacticity Control4003.12.7.5Linear Segmented Copolymers4003.12.8.1Graft- and Comb-Shaped (Co)polymers4013.12.8.1.1'Grafting from'4023.12.8.1.2'Grafting through'4023.12.8.1.3'Grafting through'4033.12.8.2Brush Macromolecules4043.12.8.2Brush Macromolecules4043.12.8.2Brush copolymers with varying architecture4043.12.8.3(Hyper)branched Copolymers4063.12.8.4Star Copolymers4063.12.8.3Coupling onto4063.12.8.4Star Copolymers4063.12.8.4Star Copolymers4063.12.8.4Star Copolymers4063.12.8.4Coupling onto4063.12.8.4Star Copolymers4063.12.8.4Networks/Gels4083.12.8.5Networks/Gels4083.12.9Site-Specific Functional Monomers4103.12.9.1Polymerization of Functional Monomers4103.12.9.2Postpolymerization of Incorporated Monomer Units4113.12.9.3Use of Functional ATRP Initiators411	3.12.7.2	Homopolymers	398
3.12.7.3.1Enter copolymers3983.12.7.3.2Alternating copolymers4003.12.7.4Tacticity Control4003.12.7.5Linear Segmented Copolymers4003.12.8Polymer Topology4013.12.8.1Graft- and Comb-Shaped (Co)polymers4013.12.8.1Grafting from'4023.12.8.1.3'Grafting trough'4023.12.8.2Brush Macromolecules4033.12.8.2Brush Macromolecules4043.12.8.2Brush Macromolecules4043.12.8.2Brush copolymers with varying architecture4043.12.8.2Brush copolymers4063.12.8.3(Hyper)branched Copolymers4063.12.8.4Star Copolymers4063.12.8.4Coupling onto4063.12.8.4.1Core first4063.12.8.5Networks/Gels4083.12.8.5Networks/Gels4083.12.9Site-Specific Functional Monomers4103.12.9.1Polymerization of Incorporated Monomer Units4103.12.9.3Use of Functional ATRP Initiators411	3.12.7.3	(Co)polymers with Controlled NW	398
3.12.7.3.2Atternating copolymers4003.12.7.4Tacticity Control4003.12.7.5Linear Segmented Copolymers4013.12.8Polymer Topology4013.12.8.1Graft- and Comb-Shaped (Co)polymers4013.12.8.1.2'Gratting from'4023.12.8.1.3'Gratting through'4023.12.8.2Brush Macromolecules4033.12.8.2Brush Macromolecules4043.12.8.2Brush copolymers with varying architecture4043.12.8.2Brush copolymers4063.12.8.4Star Copolymers4063.12.8.4Core first4063.12.8.4Coupling onto4063.12.8.5Networks/Gels4083.12.8.5Networks/Gels4083.12.9.1Polymerization of Functional Monomers4103.12.9.2Postpolymerization of Incorporated Monomer Units4103.12.9.3Use of Functional ATRP Initiators411	3.12.7.3.1	Linear copolymers: statistical and gradient	398
3.12.7.4Tablety Control4003.12.7.5Linear Segmented Copolymers4003.12.8Polymer Topology4013.12.8.1Graft- and Comb-Shaped (Co)polymers4013.12.8.1'Grafting from'4023.12.8.1.2'Grafting through'4023.12.8.2Brush Macromolecules4043.12.8.2Brush Macromolecules4043.12.8.2Brush copolymers with varying architecture4043.12.8.3(Hyper)branched Copolymers4063.12.8.4Star Copolymers4063.12.8.4Star Copolymers4063.12.8.4Coupling onto4063.12.8.5Networks/Gels4063.12.8.5Networks/Gels4063.12.8.5Networks/Gels4063.12.9Site-Specific Functional Monomers4103.12.9.1Polymerization of Functional Monomers4103.12.9.3Use of Functional ATRP Initiators411	3.12.7.3.2	Alternating copolymers	400
3.12.7.5Entreat segmented Copolymers4003.12.8Polymer Topology4013.12.8.1Graft- and Comb-Shaped (Co)polymers4023.12.8.1.1'Grafting from'4023.12.8.1.2'Grafting through'4033.12.8.2Brush Macromolecules4043.12.8.2Brush Macromolecules brushes4043.12.8.2Brush copolymers with varying architecture4043.12.8.3(Hyper)branched Copolymers4063.12.8.4Star Copolymers4063.12.8.4Core first4063.12.8.4.1Core first4063.12.8.4.3Arm first4063.12.8.5Networks/Gels4083.12.9Site-Specific Functional Monomers4103.12.9.1Polymerization of Incorporated Monomer Units4103.12.9.3Use of Functional ATRP Initiators411	3.12.7.4	Tacticity Control	400
3.12.0Polymer Toppugy4013.12.8.1Graft- and Comb-Shaped (Co)polymers4013.12.8.1.1'Grafting from'4023.12.8.1.2'Grafting through'4023.12.8.1.3'Grafting to'4033.12.8.2Brush Macromolecules4043.12.8.2.1Linear macromolecular brushes4043.12.8.2.2Brush copolymers with varying architecture4043.12.8.3(Hyper)branched Copolymers4063.12.8.4Star Copolymers4063.12.8.4Coupling onto4063.12.8.5Networks/Gels4083.12.8.5Networks/Gels4083.12.9.1Polymerization of Functional Monomers4103.12.9.2Postpolymerization Modification of Incorporated Monomer Units411	3.12.7.3 2 12 0	Linear Segmented Copolymers	400
3.12.8.1'Grafting from'4013.12.8.1.1'Grafting from'4023.12.8.1.2'Grafting through'4033.12.8.2Brush Macromolecules4043.12.8.2Brush Macromolecular brushes4043.12.8.2Brush copolymers with varying architecture4043.12.8.3(Hyper)branched Copolymers4063.12.8.4Star Copolymers4063.12.8.4Star Copolymers4063.12.8.4.1Core first4063.12.8.4.2Coupling onto4063.12.8.5Networks/Gels4083.12.9.1Polymerization of Functional Monomers4103.12.9.2Postpolymerization Modification of Incorporated Monomer Units4103.12.9.3Use of Functional ATRP Initiators411	3.12.0 2.10.0.1	Graft, and Comb-Shaped (Co)polymore	401
3.12.0.1.1Grafting from4023.12.8.1.2'Grafting through'4033.12.8.1.3'Grafting to'4033.12.8.2Brush Macromolecules4043.12.8.2Brush copolymers with varying architecture4043.12.8.2Brush copolymers with varying architecture4043.12.8.3(Hyper)branched Copolymers4063.12.8.4Star Copolymers4063.12.8.4.1Core first4063.12.8.4.2Coupling onto4063.12.8.4.3Arm first4063.12.8.5Networks/Gels4083.12.9Site-Specific Functionality4103.12.9.1Polymerization of Functional Monomers4103.12.9.2Postpolymerization Modification of Incorporated Monomer Units411	3.12.0.1 2.12.0.1	Crafting from'	401
3.12.8.1.2Grating through4023.12.8.1.3'Grating to'4033.12.8.2Brush Macromolecules4043.12.8.2.1Linear macromolecular brushes4043.12.8.2.2Brush copolymers with varying architecture4043.12.8.3(Hyper)branched Copolymers4063.12.8.4Star Copolymers4063.12.8.4.1Core first4063.12.8.4.2Coupling onto4063.12.8.4.3Arm first4063.12.8.4.3Arm first4063.12.8.5Networks/Gels4083.12.9Site-Specific Functionality4103.12.9.1Polymerization of Functional Monomers4103.12.9.2Postpolymerization Modification of Incorporated Monomer Units411	3.12.0.1.1	Grafting through'	402
3.12.8.13Grading to4003.12.8.2Brush Macromolecules4043.12.8.2.1Linear macromolecular brushes4043.12.8.2Brush copolymers with varying architecture4043.12.8.3(Hyper)branched Copolymers4063.12.8.4Star Copolymers4063.12.8.4.1Core first4063.12.8.4.2Coupling onto4063.12.8.4.3Arm first4063.12.8.5Networks/Gels4083.12.9Site-Specific Functionality4103.12.9.1Polymerization of Functional Monomers4103.12.9.2Postpolymerization Modification of Incorporated Monomer Units411	3.12.0.1.2	Grafting to'	402
3.12.8.2Linear macromoleculars4043.12.8.2.1Linear macromolecular brushes4043.12.8.2.2Brush copolymers with varying architecture4043.12.8.3(Hyper)branched Copolymers4063.12.8.4Star Copolymers4063.12.8.4.1Core first4063.12.8.4.2Coupling onto4063.12.8.4.3Arm first4063.12.8.5Networks/Gels4083.12.9Site-Specific Functionality4103.12.9.1Polymerization of Functional Monomers4103.12.9.2Postpolymerization Modification of Incorporated Monomer Units4113.12.9.3Use of Functional ATRP Initiators411	3 12 8 2	Brush Macromolecules	403
3.12.8.2.1Enda indeformetodial brasils4043.12.8.2.2Brush copolymers with varying architecture4043.12.8.3(Hyper)branched Copolymers4063.12.8.4Star Copolymers4063.12.8.4.1Core first4063.12.8.4.2Coupling onto4063.12.8.4.3Arm first4063.12.8.5Networks/Gels4083.12.9Site-Specific Functionality4103.12.9.1Polymerization of Functional Monomers4103.12.9.2Postpolymerization Modification of Incorporated Monomer Units4103.12.9.3Use of Functional ATRP Initiators411	3 12 8 2 1		404
3.12.8.3(Hyper)branched Copolymers4063.12.8.4Star Copolymers4063.12.8.4.1Core first4063.12.8.4.2Coupling onto4063.12.8.4.3Arm first4063.12.8.5Networks/Gels4083.12.9Site-Specific Functionality4103.12.9.1Polymerization of Functional Monomers4103.12.9.2Postpolymerization Modification of Incorporated Monomer Units4103.12.9.3Use of Functional ATRP Initiators411	3 12 8 2 2	Rrush conclumers with varving architecture	404
3.12.8.4Star Copolymers4063.12.8.4Core first4063.12.8.4.1Core first4063.12.8.4.2Coupling onto4063.12.8.4.3Arm first4063.12.8.5Networks/Gels4083.12.9Site-Specific Functionality4103.12.9.1Polymerization of Functional Monomers4103.12.9.2Postpolymerization Modification of Incorporated Monomer Units4103.12.9.3Use of Functional ATRP Initiators411	3 12 8 3	(Hyner)branched Conolymers	406
3.12.8.4Core first4063.12.8.4.2Coupling onto4063.12.8.4.3Arm first4063.12.8.5Networks/Gels4083.12.9Site-Specific Functionality4103.12.9.1Polymerization of Functional Monomers4103.12.9.2Postpolymerization Modification of Incorporated Monomer Units4103.12.9.3Use of Functional ATRP Initiators411	3 12 8 4	Star Conolymers	406
3.12.8.1.1Coupling onto4063.12.8.4.2Coupling onto4063.12.8.4.3Arm first4063.12.8.5Networks/Gels408 3.12.9 Site-Specific Functionality4103.12.9.1Polymerization of Functional Monomers4103.12.9.2Postpolymerization Modification of Incorporated Monomer Units4103.12.9.3Use of Functional ATRP Initiators411	3 12 8 4 1	Core first	406
3.12.8.4.3Arm first4063.12.8.5Networks/Gels408 3.12.9 Site-Specific Functionality4103.12.9.1Polymerization of Functional Monomers4103.12.9.2Postpolymerization Modification of Incorporated Monomer Units4103.12.9.3Use of Functional ATRP Initiators411	3.12.8.4.2	Coupling onto	406
3.12.8.5Networks/Gels4083.12.9Site-Specific Functionality4103.12.9.1Polymerization of Functional Monomers4103.12.9.2Postpolymerization Modification of Incorporated Monomer Units4103.12.9.3Use of Functional ATRP Initiators411	3.12.8.4.3	Arm first	406
3.12.9Site-Specific Functionality4103.12.9.1Polymerization of Functional Monomers4103.12.9.2Postpolymerization Modification of Incorporated Monomer Units4103.12.9.3Use of Functional ATRP Initiators411	3.12.8.5	Networks/Gels	408
3.12.9.1Polymerization of Functional Monomers4103.12.9.2Postpolymerization Modification of Incorporated Monomer Units4103.12.9.3Use of Functional ATRP Initiators411	3.12.9	Site-Specific Functionality	410
3.12.9.2Postpolymerization Modification of Incorporated Monomer Units4103.12.9.3Use of Functional ATRP Initiators411	3.12.9.1	Polymerization of Functional Monomers	410
3.12.9.3 Use of Functional ATRP Initiators 411	3.12.9.2	Postpolymerization Modification of Incorporated Monomer Units	410
	3.12.9.3	Use of Functional ATRP Initiators	411

3.12.9.4 3.12.10 3.12.10.1 3.12.10.2 3.12.10.2.1	End-Group Transformation Hybrid Materials Segmented Copolymers by Mechanistic Transformation Brushes Attached to Surfaces Flat surfaces	411 412 412 413 413
3.12.10.2.2	Brushes tethered to spherical particles	414
3.12.10.2.3 3.12.10.3 3.12.10.4	Brushes from concave surfaces Carbon Nanostructures Bioconiugates	415 415 416
3.12.11	Applications	416
3.12.11.1	Thermoplastic Elastomers	417
3.12.11.2	Supersoft Elastomers	417
3.12.11.3	Surfactants and Dispersants	417
3.12.11.4	Functional Flat Surfaces	418
3.12.11.5	Conducting Polymers	419
3.12.11.6	Biorelated Applications	419
3.12.11.6.1	Antibacterial surfaces	419
3.12.11.6.2	Drug delivery	420
3.12.11.7	Other Industrial Applications	420
3.12.12	Conclusions	421
References		421

3.12.1 Introduction

The development of controlled radical polymerization (CRP), and even more specifically copper-mediated atom transfer radical polymerization (ATRP), is based on an understanding and integration of chemistry developed over the past 70 years in the fields of organic chemistry, coordination chemistry, conventional radical polymerization (RP), and living ionic polymerizations, augmented by electrochemistry and inorganic and computational chemistry that came together in the mid-1990s.¹⁻¹⁸ ATRP is mechanistically related to transition metal-mediated atom transfer radical addition (ATRA) reactions and indeed this relationship was the reason this transition metal-mediated CRP process was named ATRP.^{19,20} ATRP can be viewed as a very special case of an ATRA, Scheme 1. In contrast to ATRA reactions, which focus on defining conditions for addition of a single unsaturated molecule to a molecule containing a radically transferable atom or group (R-X), ATRP requires reactivation of the first formed alkyl halide adduct with the unsaturated compound (monomer) and the further reaction of the intermittently formed radical with additional monomer units (propagation).

The 'livingness' of this polymerization process, assuming that conditions have been selected that provide fast efficient initiation, where the rate of initiation is at least comparable with the rate of propagation, can be ascertained from a linear first-order kinetic plot, accompanied by a linear increase in polymer molecular weight (MW) with conversion.¹⁹ The number-average degree of polymerization (DP_n) is determined by the ratio of concentration of reacted monomer to molar concentration of the initially introduced initiator, that is, DP_n = Δ [M]/[RX]₀.

Copper-based ATRP is a particularly successful CRP that has attracted commercial interest²¹ because of its easy experimental setup; use of readily accessible and inexpensive catalyst complexes formed with commercially available aliphatic amines, imines, or pyridine-based ligands; and simple commercially available or easily prepared alkyl halide, (pseudo)halide initiators, macroinitiators,²²⁻²⁴ or functionalized solid surfaces.^{25,26}

Historically, the development and use of copper-based catalysts^{19,27} for ATRP has predominately been conducted with a halogen as the transferable atom and a (partially) soluble copper catalyst complex with N-based ligands.²⁸⁻³¹ This body of work forms the foundation for most of the observations, discussions, and conclusions presented in this chapter. Other transition metals have been examined and continue to be examined by many researchers throughout the world,³²⁻⁴¹ and that work is summarized in Chapter 3.13. Other transferable atoms or groups have also been explored.41-48 Nevertheless, copper has proven by far to be the transition metal most often used, as determined by the successful application of a spectrum of copper complexes as catalysts for the ATRP of a broad range of radically copolymerizable monomers in diverse media by many academic49-60 and industrial research groups.^{61–69}

ATRP has emerged as one of the most powerful synthetic techniques for the preparation of functional materials in polymer science since it allows the synthesis of polymers with predetermined MW, narrow molecular weight distribution (MWD), as well as desired composition and molecular architecture.^{41,48,49,70–72} Copolymers prepared by ATRP retain high chain end functionality, which allows them to serve as macro-initiators in the synthesis of block copolymers⁷² or participate in various postpolymerization modifications to prepare telechelic copolymers with functionality selected for specific end use applications.^{73–75} A variety of organic/inorganic nano-composites,²⁶ bioconjugates,^{76–83} and other complex nanostructured materials^{84,85} have also been synthesized by this technique.

In order to conduct a successful ATRP, the transition metal complex should be at least partially soluble in the reaction medium but reactions can be run under homogeneous or heterogeneous conditions. The former generally provides a narrower MWD since the concentration of activator and



Scheme 1 Mechanism of metal complex-mediated ATRA and ATRP reactions (Cf. Scheme 2 for a discussion of the terms used in this scheme).

deactivator can be controlled more precisely.^{70,71} Reaction temperatures typically range from room temperature to 150 °C, but can be correspondingly altered. Higher temperatures are generally beneficial because temperature increases the rate constant of propagation to a greater degree than that of termination,^{86–88} although the contribution of side reactions can increase.^{89,90} The reaction can be run under vacuum or pressure.^{91–93} Reactions can be conducted not only in the presence of moisture but also in the presence of water under homogeneous⁹⁴ or heterogeneous (microemulsion, miniemulsion, emulsion, and suspension) conditions.^{95–98} Reactions have been conducted in ionic liquids^{99–102} and in supercritical carbon dioxide.^{103–105}

Mechanistic studies provide the fundamental foundation required to develop a comprehension of the critical parameters for an ATRP.¹⁰⁶ The studies generated the knowledge required to develop more environmentally benign ATRP procedures^{107–110} and remain crucial to any future developments in ATRP, since they generate the kinetic data that provide the underpinnings for chemical engineers to scale up the processes to industrial-scale production of specialty materials.

Indeed, because copper-based ATRP was the first robust CRP process, and reversible addition fragmentation transfer (RAFT) polymerization processes and second-generation mediators for nitroxide-mediated polymerization (NMP) capable of controlled polymerization of acrylates were not developed until later than 1995, many materials initially prepared by copper-based ATRP are materials that were prepared for the first time by any CRP process.^{20,111}

3.12.2 ATRP Equilibrium

The general scheme depicting the mechanism of ATRP is shown in **Scheme 2**. For clarity, in most of the schematics describing an ATRP, charges and counterions have been omitted.

Most ATRP reactions require the addition,²⁰ or *in situ* formation,¹¹²⁻¹¹⁴ of four essential components required for an ATRP reaction:

$$P_{n} - X + Mt^{m}/L - \frac{k_{act}}{k_{deact}} + \frac{P_{n}^{*} + X - Mt^{m+1}/L}{(k_{p})} - \frac{k_{t}}{k_{t}} + \frac{P_{n} - P_{n}}{P_{n} - P_{n}}$$

Scheme 2 Representation of the ATRP equilibrium (Note: $k_{act} \ll k_{deact}$).

- 1. a molecule, which is called a (macro)initiator P_n -X, with at least one transferable atom or group, frequently a halogen where X = Cl or Br;
- a transition metal compound, Mt^(m), that can undergo a one-electron redox reaction (in this chapter we focus predominately on the use of copper);
- 3. a ligand, L, that forms a complex with the transition metal to modify catalyst solubility, stability, and activity; and
- 4. one or more radically (co)polymerizable monomers.

Other language has been used to describe this process. Indeed many authors have intermittently used other names/abbreviations for reactions utilizing the same components to 'clarify' specific aspects of the reaction.^{39,41,115–119} This multiplicity of nomenclature may have created confusion as to the fundamental similarity, or indeed identical nature of the reactions being discussed. A recent recommendation by IUPAC¹²⁰ clarifies this position by recommending that specific reversible-deactivation radical polymerizations (RDRPs) should adopt terminology consistent with that in IUPAC documents, specifically that the controlled RDRP procedures in which the deactivation of the radicals involves catalyzed reversible atom transfer or reversible group transfer usually, though not exclusively, by transition metal complexes be named atom transfer radical polymerization, ATRP.¹²⁰

The basic principles underlying all controlled radical-based polymerization processes, using the direct addition or *in situ* formation of the four reagents, P_n –X, $Mt^{(m)}/L$, X– $Mt^{(m+1)}/L$, and radically copolymerizable monomers, are the same resulting in the formation of the identical copolymers irrespective of the name given to the reaction.^{20,111,121}

The ATRP process involves polymerization of radically (co) polymerizable monomers by a procedure requiring formation of a dynamic equilibrium requiring 'activation' (k_{act}) of a

dormant alkyl (pseudo)halide initiator with a transition metal complex in a lower oxidation state comprising a ligand and 'deactivation' (k_{deact}) of the growing polymer chain end by reaction of the active propagating radical with the transition metal complex in the higher oxidation state, comprising a radically transferable atom or group.

Mechanistically, ATRP is based on an inner sphere electron transfer (ISET) process, which involves a homolytic reversible (pseudo)halogen transfer between a dormant species (P_n-X) and a transition metal complex (Mt^m/L) , resulting in the formation of propagating radicals (P_n^*) and the metal complex in the higher oxidation state (i.e., $X-Mt^{m+1}/L$). Radicals react reversibly with the oxidized metal complexes, $X-Mt^{n+1}/L$, in a deactivation reaction to reform a dormant species, which can contain additional monomer units, and the transition metal complex (Mt^m/L) in the lower oxidation state, that is, the activator. Polymer chains grow by the addition of monomers to the periodically generated radicals in a manner similar to a conventional RP, with the rate constant of propagation $(k_{\rm p})$. Termination reactions, occurring at diffusion-controlled reaction rates (k_t) , also occur in ATRP (as in any RP), mainly through radical coupling and disproportionation, thereby increasing the concentration of the higher oxidation state transition metal complex, $X-Mt^{n+1}/L$, in the reaction medium. The higher oxidation state transition metal complex, $X-Mt^{n+1}/L$, is the equivalent of the persistent radical in an ATRP. In fact, ATRP achieves control through the persistent radical effect.^{5,122,123}

In 'classic' ATRP reactions this excess of deactivator was primarily generated by early termination reactions between activated initiator radicals. This 'waste' of initiator can be reduced by deliberate addition, or *in situ* formation, of a low molar fraction of the X–Mtⁿ⁺¹ species. For example, the addition of a small amount of Cu^{II} halides to the feedstock (<10% of all Cu species) in a standard copper-based ATRP leads to better controlled polymerizations, with decreased polymerization rates, as a consequence of instantaneous control and increased initiation efficiency due to an increased rate of deactivation.^{70,71,124,125}

The rate of polymerization is ultimately governed by the position of the ATRP equilibrium, as illustrated in eqn [1] for a particular monomer, M.

$$R_{\rm p} = k_{\rm p} K_{\rm ATRP} \frac{[\rm RX][\rm Cu'L]}{[\rm X - \rm Cu'^{\rm I}L]} [\rm M]$$
^[1]

Quantifying K_{ATRP} , for a given catalyst, therefore provides an excellent measure of the catalyst's true activity in a polymerization reaction.^{123,126} The nature of the ligand, L, dramatically affects the values of both rate constants, k_{act}^{127} and $k_{\text{deacv}}^{106,126}$ and therefore their ratio, K_{ATRP} .

Equation [2] illustrates how the dispersity (M_w/M_n) of a polymer prepared by an ATRP, in the absence of chain termination and transfer reactions, relates to the concentration of initiator (RX) and deactivator (X–Cu^{II}/L), the rate constants of propagation (k_p) and deactivation (k_{deact}), and monomer conversion (p).¹²⁸

$$\frac{M_{\rm w}}{M_{\rm n}} = 1 + \left(\frac{k_{\rm p}([RX]_0 - [RX]]}{k_{\rm deact}[{\rm X} - {\rm Cu}^{\rm II}/{\rm L}]}\right) \left(\frac{2}{p} - 1\right)$$
[2]

Thus, for the same monomer, a catalyst that deactivates the growing chains faster, smaller k_p/k_{deact} , will produce polymers

with a narrower MWD, a smaller M_w/M_n value. This value can also be decreased by increasing the concentration of deactivator, although at the cost of slower rates of polymerization.

All ATRP reactions utilize transfer of a radically transferable atom or group from an initiator or dormant species to a lower oxidation state transition metal complex in a reaction involving homolytic bond cleavage to form an active propagating species. This active species can incorporate one or more monomer units prior to being deactivated by reverse transfer of the atom or group from the higher oxidation state transition metal complex to reform a dormant species. In some systems, several activation/deactivation steps may occur before one monomer unit is added. In contrast to initiators used in standard RPs, all fragments of an ATRP initiator are incorporated into the final macromolecule.

3.12.3 Initiating an ATRP

A successful ATRP should meet several criteria in order to be considered a 'controlled' RP process. The initiator should be consumed early in the reaction and the rate of initiation should be at least comparable with the rate of propagation, which leads to predictable MW for the propagating polymer chains. The degree of polymerization (DP) should be equal to the moles of monomer converted to polymer over the initial concentration of initiator added to the reaction: $DP = \Delta[M]/[I]_0$.

Second, the number of monomer units added during each activation cycle should be small, if one desires to prepare a polymer with a low M_w/M_n ratio.

There are presently several ways to set up the ATRP equilibrium, shown in Scheme 2, and they will now be addressed in greater detail.

In 1995, it was established that the ATRP equilibrium can be approached from both sides:

- a standard or 'normal' ATRP starting with R–X/Mtⁿ (an ATRP initiator (R–X) and a catalyst with the transition metal in a lower oxidation state (Mtⁿ)),^{19,27} which has been used as the exemplary procedure in the discussion below Scheme 2 and
- a 'reverse' ATRP which starts by addition of the transition metal compound in its higher oxidation state, X–Mtⁿ⁺¹, which is then converted to the activator (Mtⁿ) by reaction with a standard free radical initiator.¹²⁹

In a standard ATRP reaction, a solution of the lower oxidation state copper complex is added to the reaction medium or formed *in situ* from a Cu^{I} salt and an N-containing ligand. This can present a problem if active catalyst complexes are formed because the readily oxidized activator complex can react with oxygen, present in the system as an impurity, and be quickly deactivated. However, this spontaneous oxidation could increase the efficiency of initiation from R–X since termination reactions required to form the equivalent of the 'persistent radical' could be avoided or reduced.⁷¹

3.12.3.1 Reverse ATRP

In the initial example of a 'reverse' ATRP, **Scheme 3**, ^{20,129} both the ATRP initiator and reduced 'activator' catalyst complex were formed by reaction with radicals generated by decomposition



Scheme 3 'Reverse' ATRP procedure showing formation of Cu(I) activator and dormant initiator from radicals formed from an added free radical initiator, AIBN.

of conventional free radical initiators, such as azobis(isobutyronitrile) (AIBN)¹³⁰ or benzoyl peroxide (BPO),¹³⁰ in the presence of higher oxidation state transition metal complexes. The schematic shows the manner in which the activator and ATRP initiator are formed in a 'classic reverse' ATRP activation procedure.

The initially formed radicals react with the higher oxidation state transition metal to form an ATRP activator and an ATRP initiator, or start a polymerization that is quickly deactivated by reaction with the higher oxidation state transition metal to form a dormant chain and an ATRP activator. Thereafter, the reaction proceeds as a normal ATRP.

A variation of a reverse ATRP was developed using Cu(0) to provide the ability to start with stable active Cu(II) catalyst precursors (cf. Section 3.12.3.4 on activator regenerated by electron transfer (ARGET) ATRP). This allows for a simple experimental setup without problems associated with oxidation of a readily oxidized Cu(I) complex.^{112,113} Reduction of the higher oxidation state transition metal with Cu(0), in any solid state, occurs quickly in most cases to form the Cu(I) catalysts. This simple procedure to initiate an ATRP was used subsequently by Percec when examining RP of butyl methacrylate initiated with sulfonyl chlorides.¹³¹

3.12.3.2 Simultaneous Reverse and Normal Initiation

An improved 'reverse' ATRP was developed to take advantage of the ability to use more active catalyst complexes, that is, more readily oxidized complexes,^{132,133} without increasing the concentration of copper in the reaction. This procedure was called a simultaneous reverse and normal initiation procedure (SR&NI), since the activator and a small fraction of the initiating chains were formed in a 'reverse' ATRP reaction, while the majority of the growing chains were initiated from the added normal ATRP initiator molecule. A limitation of SR&NI clarified after development of 2D chromatography is the presence of a small fraction of polymer chains initiated by the added free radical initiator.¹³³

3.12.3.3 Activators Generated by Electron Transfer ATRP

SR&NI evolved into activators generated by electron transfer (AGET) where an ATRP initiator is added to the reaction as a separate compound along with the higher oxidation state catalyst precursor for an active ATRP catalyst complex. The



Scheme 4 Reagents added to reaction for AGET initiation mechanism.

added deactivator can be activated by various reducing agents^{56,132,134–137} including Mt^{0,112,113} The added reducing agents are selected so that they reduce the deactivator to the activator in a reaction that does not form a radical or any additional initiating species. The reducing agents reduce the higher oxidation state transition metal complex, X–Mt^{*m*+1}/L, to the Mt^{*m*}/L activator *in situ* through a nonradical-forming reaction.¹¹² The reagents initially added to an AGET ATRP reaction are shown in red in Scheme 4.

Note that, as with SR&NI, the formation, or addition, of Mt⁰ in any form to the reaction medium does not change the mechanism but only the manner of attaining the equilibrium conditions and the rate of polymerization.^{138,139} However, it should be noted that Mt⁰ can act as a supplemental initiator and may increase the absolute concentration of catalyst in the reaction medium. Other transition metals have been used to reduce the concentration of the deactivator in ARGET ATRP including metallic zinc, magnesium, and iron.¹⁴⁰

When the implications of the convenient AGET procedure for initiating an ATRP were considered, it was recognized that it should be possible to use the reducing agents to constantly regenerate the ATRP activator from Cu(II) species, irreversibly formed during inevitable radical/radical termination processes, without directly or indirectly producing initiating species that generate new chains.¹⁰⁸ This new procedure, ARGET ATRP, is not just another way to initiate an ATRP but can be considered as a new way to run a CRP.

3.12.3.4 Activator Regenerated by Electron Transfer ATRP

ARGET ATRP is a 'green' procedure that uses ppm of the catalyst in the presence of the appropriate reducing agents such as FDA-approved tin(II) 2-ethylhexanoate $(Sn(EH)_2)$, glucose,^{108,141} ascorbic acid,¹⁴² phenol,⁵⁶ hydrazine and phenylhydrazine,^{109,143} excess inexpensive ligands,¹⁴⁴ or selected nitrogen-containing monomers.¹³⁶ Cu⁰ also works as a reducing agent in an ARGET ATRP¹³⁹ but it increases the level of transition metal halides (CuX and CuX₂) in the reaction system due to continuous reduction of Cu^{II} formed by unavoidable termination reactions: (Cu⁰ + Cu^{II} = 2Cu^I).

Since the reducing agents allow starting an ATRP with the oxidatively stable Cu^{II} species, the reducing/reactivating cycle can be employed to eliminate air or other radical traps in the system. For example, styrene was polymerized by the addition of 5 ppm of CuCl₂/tris[2-(dimethylamino)ethyl]amine (Me₆TREN) and 500 ppm of Sn(EH)₂ to the reaction mixture, resulting in preparation of a polystyrene (PS) with M_n = 12 500 ($M_{n,th}$ = 12 600) and M_w/M_n = 1.28 without removal of inhibitors or deoxygenation.¹⁰⁸

ARGET ATRP has also been applied to polymerization from surfaces, even in the presence of limited amounts of air, **Figure 1**. The repetitive reduction/oxidation cycle between the reducing agent and transition metal consumes all oxygen in the reactor.¹⁴⁵

Generally, in an ARGET system it is desirable to add an excess of the ligand compared with the amount required to form the transition metal complex. This may be necessary to compensate for competitive complexation of the low amount of added transition metal with monomer/solvent/reducing agent that are all present in significant molar excess compared with the transition metal. In fact, it has been determined that the ARGET procedure can be driven based solely on addition of excess ligand, ligand substitute,^{137,146} or a nitrogen-containing monomer.¹³⁶ (Meth)acrylates have been controllably polymerized by heterogeneous ARGET ATRP with equimolar equivalents of ligand and copper levels as low as 6.5 ppm.¹⁴⁷

Another advantage of ARGET ATRP is that catalyst-induced side reactions are reduced to a significant degree. Therefore, it is now possible to drive an ATRP reaction to higher conversion and prepare copolymers with higher MW while retaining chain end functionality.^{148,149} This has been confirmed by successful chain extension of macromolecules formed using this initiation/continuous reactivation system.¹⁵⁰

3.12.3.5 Initiators for Continuous Activator Regeneration

The concept of initiators for continuous activator regeneration (ICAR) could simplistically be considered a 'reverse' ARGET ATRP. In ICAR ATRP, a source of organic free radicals is employed to continuously regenerate the Cu^I activator that is otherwise consumed in termination reactions when catalysts are used at very low concentrations. With this technique, controlled synthesis of PS and poly(meth)acrylates ($M_w/M_p < 1.2$) can be conducted with catalyst concentrations between 5 and 50 ppm, levels at which removal or recycling of the catalyst complex would be unnecessary for many applications. The reaction is driven to completion with low concentrations of added standard free radical initiators.¹⁰⁹ Computer simulations confirmed that the rate of polymerization in ICAR is governed by the rate of decomposition of the added free radical initiator, as in RAFT, while the degree of control and the rate of deactivation and MWD are controlled by K_{ATRP} , as in ATRP.^{109,123,150,151}

Note that components of RAFT and ICAR ATRP are quite similar. In addition to (co)monomers and radical initiators (AIBN), RAFT includes alkyl dithioesters (often made from alkyl bromides) and ICAR, the same alkyl bromides, and ppm amounts of Cu catalyst.

These similarities remove the clear distinction between the three classic CRP systems (NMP, RAFT, and ATRP), particularly since ATRP can be conducted with an expanding range of radically transferable groups, initially exemplified by the use of azide⁴³ and thiocyanates^{42,44} as transferable groups, but now expanded to include alkyl pseudohalides (APH) based on dithioesters, xanthates, dithiocarbonates, or trithiocarbonates.^{46,152–154}

3.12.3.6 ATRP with Alkyl Pseudohalides

ATRP of styrene and methyl methacrylate (MMA) was successfully conducted with various alkyl diethyldithiocarbamate (DC) initiators in the presence of copper catalysts with nitrogen-based ligands, **Scheme 5**.¹⁵⁴ Well-controlled polymers with narrow MWD were achieved, $M_w/M_n < 1.1$ (St) and $M_w/M_n < 1.2$ (MMA).

When conducting an ATRP with an initiator containing an APH with the pseudohalogen (PH) acting as the transferable group, some selection of the initiator/APH has to occur. If an



Figure 1 'Grafting from' a flat silicon substrate in the presence of air. Reprinted from Matyjaszewski, K.; Dong, H.; Jakubowski, W.; *et al. Langmuir* **2007**, *23*, 4528–4531,¹⁴⁵ with permission from the ACS.

Scheme 5 ATRP with dithiocarbamates as the radically transferable (pseudo)halogen groups.

appropriate selection is made,⁴⁶ the polymerization rate follows first-order kinetics with respect to monomer conversion, and the MW of the polymers increases linearly up to high conversion. The results of ¹H NMR analysis of low molar mass model compounds and chain extension from the macroinitiators confirmed that well-defined PS bearing an PH as the active chain end was obtained via ATRP of St with end-group containing a degenerative transfer agent as the radically transferable group. Ligand structure and ligand/copper ratio also affected the degree of control attained in the polymerization. The activation rate constants and equilibrium constants for ATRP with initiators containing an PH as the radically transferable group and copper complexes were determined. The results of cyclic voltammetry with the Cu^{II}DC₂ complex indicated that it has more negative reduction potential and, consequently, higher (pseudo)halidophilicity than complexes formed by Cu^{II}Br₂ or Cu^{II}Cl₂ with the same ligand, Me₆TREN.⁴⁷

An advantage of initiating an ATRP with an PH as the transferable group, over conducting a standard RAFT polymerization, is that no new chains are formed by added radical initiators and higher MW copolymers can be prepared. A similar process also allowed preparation of copolymers with vinyl acetate.¹⁵⁵ The procedure also provides the possibility to conduct both ATRP and RAFT reactions concurrently¹⁵⁴ or sequentially^{155,156} with ATRP initiators containing pseudo-halide as one of the transferable groups.

In the case of concurrent ATRP/RAFT, overall control is provided by a dual mediating system where activation/deactivation is conducted by ATRP in conjunction with degenerative exchange by RAFT. A concurrent ATRP/RAFT process with cumyl dithiobenzoate acting as the initiator/dormant species for ATRP and also as the chain transfer agent for RAFT was successfully demonstrated in well-controlled polymerizations of both styrene and MMA. The polymerizations displayed first-order kinetics with respect to monomer conversion, and polymer MW increased linearly up to high conversion.¹⁵⁷ This was extended to a dual concurrent ATRP/RAFT of methyl acrvlate (MA) in a procedure requiring coinitiation by alkyl halides.¹⁵⁸ The presence and relative concentration of the APH and alkyl halide affected the MWD at low monomer conversion and rate of polymerization. An increase in the concentration of APH resulted in lower Mw/Mn values but decreased rates of polymerization. In summary, it is possible to achieve a well-controlled polymerization of MA at various DPs in new dual concurrent ATRP/RAFT with ARGET levels of copper catalyst. Increasing the relative amount of APH affords polymers with narrow MWD even at early stages of monomer conversion.

As Figure 2 illustrates, purer block copolymers were obtained by the concurrent CRP method than by RAFT alone, demonstrating that the overall level of control in an ATRP with an initiator containing a degenerative transfer agent as the radically transferable group provides a more controlled polymerization process in comparison with conventional RAFT polymerization. Increasing the amount of CuBr/ligand added to the reaction resulted in faster polymerization. The rate could be further increased by adding Cu⁰ to the reaction medium to reduce the concentration of Cu^{II} formed by termination reactions.48 Note that the contributions of both RAFT and ATRP depend on the performance of the initiator with pseudohalogen as the radically transferable group and the activity of the copper/ligand catalyst complex. Indeed, photoirradiated ATRP has been conducted with an alkyl dithiocarbamate as transferable group at ambient temperature.¹⁵⁹ The polymerization was photocontrollable, that is, polymerization proceeded mainly under UV irradiation at room temperature while maintaining controlled M_n and low M_w/M_n throughout the procedure. The current technique may find use in a variety of practical applications where thermally unstable monomers are used and the procedure is suitable for micropatterning.



Figure 2 Successful preparation of a block copolymer with narrower MWD by Cu-activated RAFT. Reprinted from Kwak, Y.; Nicolay, R.; Matyjaszewski, K. *Macromolecules* **2008**, *41*, 6602–6604, ¹⁵⁴ with permission from the ACS.

3.12.3.7 Electrochemical Control Over an ATRP

When one considers the status of ATRP at the end of 2010, after exemplification of ARGET and ICAR ATRP¹⁰⁹ and a 'true' emulsion ATRP process,⁹⁷ one could ask what targets remain to be improved in order to make ATRP more industrially compatible? The answers include, as always, reducing costs, eliminating/reducing reagents, defining conditions that allow simplified reaction conditions, for example, low levels of O₂ permissible, and if possible providing additional degrees of polymerization control. So what's next?

It is a new procedure for continuously controlling the ratio of activator to deactivator by electrochemical procedures. Electrochemical methods offer multiple readily adjustable parameters, for example, applied current, potential, and total charge passed, to manipulate polymerization rates by selective targeting of the desired concentration of the redox-active catalytic species. As discussed below, cyclic voltammetric (CV) studies of copper complexes suitable for catalyzing ATRP have been used for over a decade to measure the activity of copper-based catalyst complexes in an ATRP.^{29,160} In the CV studies it was found that the $E_{1/2}$ value for the redox couple Cu^I/Cu^{II} strongly depends on the nature of the ligand and the halogen.¹²⁷ However, application of a continuous electrochemical stimulus (i.e., electrolysis), which can be uniquely paired with ATRP owing to its inherent redox-active catalytic system, had been generally overlooked.

The proposed mechanism of ATRP mediated through electrochemical control over the ratio of Cu^I/Cu^{II} and (re)generation of activators is shown in **Scheme 6**.

Essentially, a targeted fraction of the air-stable Cu^{II}Br₂/Me₆TREN catalyst complexes can be electrochemically reduced to Cu^IBr/Me₆TREN activators to invoke or trigger a controlled polymerization. In the absence of mass transport limitations, the rate of reduction is dictated by the applied potential (E_{app}), allowing one to finely tune the polymerization rate by balancing the ratio of Cu^{II}:Cu^{II}.¹⁶¹ Figure 3(a) shows how the rate of an ATRP was controlled by changing the applied potential (E_{app}) with the more negative potential which induces a faster reduction of Cu^{II}Br₂/Me₆TREN and an increase in [Cu^{IB}r/Me₆TREN]/[Cu^{II}Br₂/Me₆TREN] ratio resulting in the faster rate. Figure 3(b) shows that the MW of the polymer formed in the three reactions increased linearly with conversion and narrow MWDs were attained.

Further to this point of electrochemical control over an ATRP, electrochemical methods allow a lower oxidation state catalyst (Cu¹Br/Me₆TREN) to be reverted back to its original higher oxidation state, by simply shifting E_{app} to more positive values, thus providing a means to rapidly



Scheme 6 Schematic of proposed mechanism for electrochemical control over an ATRP.



Figure 3 (a) Monomer conversion with respect to time. (b) Number-average MW (M_n) and M_w/M_n with respect to conversion as a function of applied potential. Reprinted from Magenau, A. J. D.; Strandwitz, N. C.; Gennaro, A.; Matyjaszewski, K. *Science* **2011**, *332*, 81–84,¹⁶¹ with permission from the AAAS.



Figure 4 (a) Conversion (solid circles) and applied potential (dashed line) with respect to time and (b) number-average MW (M_n) and M_w/M_n with respect to conversion. Reprinted from Magenau, A. J. D.; Strandwitz, N. C.; Gennaro, A.; Matyjaszewski, K. *Science* **2011**, *332*, 81–84, ¹⁶¹ with permission from the AAAS.

deactivate an ongoing polymerization and thereby control temperature exotherms. In Figure 4(a) toggling between 'on' and 'off' states is represented by changes of the applied E_{app} values to -0.69 and -0.40 V versus Ag⁺/Ag, respectively, in polymerizations conducted in 50% (v/v) MA in acetonitrile (MeCN) at 25 °C with a total reaction volume of approximately 12 ml. Figure 4(a) clearly shows that the polymerization reaction stopped soon after changing E_{app} and started again when E_{app} was reduced. Figure 4(b) shows that the MW of the formed polymer increased regularly with conversion and that there was no change in 'livingness' of the formed polymer during the enforced dormancy. This procedure for electrochemically mediated ATRP has been given the abbreviation *e*-ATRP.

As we transition to copper removal it should be noted that electrodeposition can be used to remove copper from an ATRP. 162

3.12.4 Removal of Copper

One disadvantage of the 'early' ATRP procedures was associated with the relatively high concentration of catalyst; often an equimolar concentration of initiator and catalyst was present. This high concentration of catalyst was required to overcome the effects of radical termination reactions in the presence of relatively low-activity catalysts.¹³⁸ Purification of the product was reviewed in detail by Shen et al.¹⁶³ Purification methods included passing the polymer solution through a column filled with silica or neutral alumina,¹⁶⁴ stirring with an ion exchange resin,165 clay,166,167 precipitation of the polymer into a nonsolvent, 168, 169 or the use of a heterogeneous catalyst that is easily isolated after polymerization.¹⁷⁰⁻¹⁸⁰ The development of higher activity catalysts and polymerization procedures involving continuous regeneration of the deactivator formed by termination reactions have reduced the amount of copper that has to be removed down to ppm levels.

ARGET and ICAR ATRP are industrially relevant, as they can be conducted in the presence of limited amounts of air and the final products obtained from these techniques are essentially colorless.^{145,181} However, for certain applications, for example, electronic and biomedical, or if one desires a pure white solid product, it may be important to further reduce the catalyst concentration to below 1 ppm levels.¹⁸² The techniques developed earlier still work. However, the electrochemically controlled ATRP could easily facilitate the electrodeposition of Cu to remove it from an ATRP.¹⁶²

3.12.5 ATRP Thermodynamics and Kinetics

Determination of equilibrium constants and rate constants is crucial in order to understand the kinetics of an ATRP. Experimentally, the values of k_{actv} k_{deactv} and K_{ATRP} can be determined by direct analysis of the polymerization mixture, by, for example, EPR, NMR, GC, GPC, and IR or by the study of low MW model compounds. Furthermore, while some side reactions, for example, thermal initiation of monomer, elimination reactions, transfer reactions, degradation of the catalyst, and some physical parameters (e.g., viscosity and inhomogeneity), may have an important effect on the kinetics of an ATRP, the influence of these parameters may also be investigated by model studies or by computer simulation.^{183–187}

3.12.5.1 Equilibrium Constants in ATRP

The ATRP equilibrium was shown in **Scheme 2**. One approach to developing a deeper understanding of the overall ATRP equilibrium is to examine the reactions that 'formally' contribute to the overall equilibrium:

$$K_{\text{ATRP}} = rac{k_{ ext{act}}}{k_{ ext{deact}}} = K_{ ext{BH}} K_{ ext{ET}} K_{ ext{EA}} K_{ ext{X}}$$

The ATRP equilibrium (K_{ATRP} in Scheme 7) can be expressed as a combination of several formally contributing reversible reactions. The ATRP equilibrium can be defined as the product of the equilibrium constants describing homolytic bond dissociation of R–X and Cu^{II}–X, that is, the halogenophilicity of the initiator and deactivator. Thus, K_{BH} describes equilibrium

(a)
$$Mt^{z}L_{n} + P - X - XMt^{z+1}L_{n} + P'$$

$$K_{\text{ATRP}} = K_{\text{BH}} K_{\text{Halo}}$$

(b) P-X
$$\underset{K_{BH}}{\longleftarrow} P^{\bullet} + X^{\bullet}$$

$$Mt^{2}L_{n} + X^{\bullet} \underset{K_{Halo}}{\longleftarrow} XMt^{z+1}L_{n}$$
(c) $Mt^{z}L_{n} \underset{K_{EA}}{\longleftarrow} Mt^{z+1}L_{n} + e^{\ominus}$
 $X^{\bullet} + e^{\ominus} \underset{K_{EA}}{\longleftarrow} X^{\ominus}$
 $X^{\ominus} + Mt^{z+1}L_{n} \underset{K_{act}}{\longleftarrow} XMt^{z+1}L_{n}$

Scheme 7 Equilibria formally contributing to the overall ATRP equilibrium.

k_{deac}

 $RX \Leftrightarrow R^{\bullet} + X^{\bullet}$ and K_{HALO} describes equilibrium X–Cu (II) $\Leftrightarrow X^{\bullet} + Cu(I)$. The term 'halogenophilicity' (K_{HALO}) refers to the formation of a Cu^{II}–X bond from Cu^I and a halogen atom X[•], whereas halidophilicity (K_{Halido}) refers to the formation of Cu^{II}–X from Cu^{II} and a halide anion X⁻. Therefore,

 K_{HALO} can be expressed as the product of the equilibrium constants for the electron transfer between metal complexes (K_{ET}), the electron affinity of the halogen (K_{EA}), and the equilibrium constant for the heterolytic cleavage of the Mt^{*n*+1}–X</sub> bond ($K_{\text{X}}=K_{Halido}$), which measures the 'halidophilicity' of the deactivator.¹⁸⁸ This means that the activity of a catalyst in an ATRP reaction depends not only on the redox potential but also on the halidophilicity of the transition metal complex. For complexes that have similar halidophilicity, the redox potential can be used as a very good measure of catalyst activity in an ATRP.¹⁸⁹

The K_{ATRP} values should correlate with the bond dissociation energy (BDE) of the initiators or low MW dormant chain end surrogates. The relationship between initiator structure and K_{ATRP} was examined for a series of halogen-based initiators with the same catalyst complex, tris[(2-pyridyl)methyl]amine (TPMA), as ligand, in MeCN solvent at 22 °C. The results are shown in Figure 5. It can be concluded that for a given catalytic system in the same solvent, where $K_{\rm ET}$, $K_{\rm EA}$, and $K_{\rm X}$ are essentially constant, K_{ATRP} depends upon the energy required for alkyl halide bond homolysis, or K_{BH}. Indeed, when the alkyl halide bond dissociation energies were calculated for a series of ATRP monomers/initiators, they were found to correlate well with measured values of K_{ATRP} .^{45,190} Differences between the equilibrium constants measured for a selection of alkyl halides, selected to provide information on growing chain ends, exceed a hundred thousand.



Figure 5 Relationship between K_{ATRP} and structure of alkyl halide initiators, measured with $Cu^1X/TPMA$ (X = Cl or Br) as catalyst with MeCN as solvent at 22 °C: 3°: red, 2°: blue, 1°: black; R–Br: solid, R–Cl: open, R–I: bottom-half solid; Amide: \checkmark , Phenyl: \bigstar , Ester: \Box , Nitrile: \circ , Phenyl-ester: \diamond , Allyl: \bigstar . Reprinted from Tang, W.; Kwak, Y.; Braunecker, W.; *et al. J. Am. Chem. Soc.* **2008**, *130*, 10702–10713, ¹⁰⁶ with permission from the ACS.

The equilibrium constants increase with degree of substitution of the initiator, primary (black entries) < secondary (blue) < tertiary (red), and with the leaving atom/group, for example, for methyl 2-halopropionates, chloro:bromo:iodo, iodide (bottom half-filled) < chloride (open) < bromide (filled) and the presence of radical stabilizing groups for secondary initiators –COOR (squares) < – Ph (triangles) <–CN (circles) ≪ joint –Ph and R–COOEt groups (diamonds).

The most active initiator is EBPA (a mixed benzyl-ester initiator), which is \sim 20 000 times more active than PEBr and 300 000 times more active than MBrP. This is due to the synergistic stabilization effect of the phenyl and carboxyethyl groups. EBPA is an efficient initiator for monomers with large equilibrium constants, such as acrylonitrile (AN) and MMA.

The equilibrium constants for copper-based ATRP were determined for a wide range of nitrogen-based ligands and initiators in MeCN at 22 °C. Values of K_{ATRP} were measured with CuBr/L complexes and EBriB (constant K_{BH} and K_{EA}). The results displayed a linear correlation between K_{ATRP} and $E_{1/2}$ (i.e., K_{ET}) for the series of Cu¹ complexes formed with the different ligands, **Figure 6**.^{190–192} The correlation should be linear when K_{BH} , K_{EA} , and K_{Halido} are constant and the majority of the complexes investigated showed good quasi-reversibility under these conditions as judged by their relatively low ΔE_p values.

CV data were also recorded for 14 Cu catalysts in MeCN with the noncoordinating counterion CF₃SO₃. The poorer correlation between logarithmic values of K_{ATRP} for CuBr/L complexes and values of E_{V_2} of Cu^{II}(CF₃SO₃)₂/L suggests that the values for K_{Halido} for the complexes are different. The Cu^{II}Br₂/L complexes are more reducing than their Cu^{II}(CF₃SO₃)₂/L analogues, and the difference in measured E_{V_2} values allows the calculation of apparent halidophilicities of the complexes. For some complexes with tetradentate ligands, where Cu^{II} is coordinatively saturated and Br⁻ serves as the counterion, the difference in E_{V_2} values, 240 mV, corresponds to an apparent halidophilicity of ~10⁴ M⁻¹ in MeCN. This value is consistent with typical values measured in aprotic



Figure 6 Relationship between K_{ATRP} and redox potential for various copper complexes. Reprinted from Braunecker, W. A.; Tsarevsky, N. V.; Gennaro, A.; Matyjaszewski, K. *Macromolecules* **2009**, *42*, 6348–6360,¹⁸⁹ with permission from the ACS.

solvents (10^4-10^5 M^{-1}).¹⁹³ An examination of the structure of the ligands shows that the general order of Cu complex activity for ligands is tetradentate (cyclic-bridged)>tetradentate (branched)>tetradentate (cyclic)>tetradentate (linear)> tridentate>bidentate ligands. The nature of nitrogen atoms in ligands also plays a significant role in the activity of the Cu complexes and follows the order pyridine≥aliphatic amine> imine.^{106,127} Apparently, steric effects around the Cu center are very important, as K_{ATRP} for Me₆TREN is 100 000 times larger than that for tris[2-(diethylamino)ethyl]amine (Et₆TREN).¹⁹⁴ Figure 7 shows how K_{ATRP} varies with ligand structure.

The effects of an added solvent on radical-based reactions are generally quite small but it has been observed that the rates of copper-based ATRP reactions increase in the presence of polar solvents^{195,196} and water.¹¹⁷

The solvent dependency of K_{ATRP} was also examined¹⁸⁹ in terms of Kamlet–Taft parameters for 11 solvents and then extrapolated to cover catalyst activity in a total of 28 solvents, including water. The log(K_{ATRP}) values measured in this work for Cu¹Br/1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) + MBriB are plotted against values predicted by the Kamlet–Taft relationship; the line representing values predicted by the Kamlet–Taft relationship is shown in **Figure 8**.¹⁸⁹ Predicted values of K_{ATRP} for 16 organic solvents and water are also provided, based on these solvent-independent coefficients and the appropriate solvatochromic parameters.

As can be seen in Figure 8, the use of multivariable linear regression has allowed the extrapolation of ATRP catalyst activity to cover complexes that span nearly 7 orders of magnitude in activity, from 10^{-11} in fluoroalcohols to nearly 10^{-4} in water. In general, K_{ATRP} ranges between 10^{-9} and 10^{-10} in aromatic hydrocarbons; between 10^{-8} and 10^{-19} in ethers, ketones, and nitriles; is $\sim 10^{-8}$ in most alcohols; and is between 10^{-7} and 10^{-8} for amides. The main reason for higher values of K_{ATRP} in more polar solvents could be related to better solvation of more polar Cu^{II} complexes than less polar Cu^I species.

It was proposed that calculations could also be used to predict equilibrium constants for less reactive monomers. Knowing K_{BH} as well as the rate constants of propagation for a given monomer, the rates of polymerization could be calculated for different monomers in ATRP under comparable conditions, same catalyst, and constant K_{ET} , K_{EA} , and K_X . For example, if the ATRP of AN reached 90% conversion in 1 s, MA would require 2 h, styrene 22 h, and vinyl acetate 30 years under the same conditions.¹⁹⁰ This calculation merely serves to demonstrate the necessity of choosing an appropriate catalyst and appropriate reaction conditions for each monomer.

A novel approach toward screening of ATRP catalysts by electrospray ionization mass spectroscopy (ESI_MS) was recently developed. The ESI_MS methodology allows for the rapid assay of ATRP catalyst performance without prior polymerization experiments.^{197,198}

3.12.5.2 Activation Rate Constants in ATRP

Activation rate constants (k_{act}) for a specific ATRP reaction are typically determined from model studies in which the transition metal complex is reacted with a model alkyl halide in the presence of a radical trapping agent, such as 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) or SG1.¹²⁶ This works for every catalyst complex, even less active complexes based on



Figure 7 Effect of ligand structure on *K*_{ATRP} for a series of copper-based catalysts. Reprinted from Tang, W.; Kwak, Y.; Braunecker, W.; *et al. J. Am. Chem. Soc.* **2008**, *130*, 10702–10713,¹⁰⁶ with permission from the ACS.



Figure 8 Experimental vs. Kamlet–Taft predicted K_{ATRP} . Reprinted from Braunecker, W. A.; Tsarevsky, N. V.; Gennaro, A.; Matyjaszewski, K. *Macromolecules* **2009**, *42*, 6348–6360, ¹⁸⁹ with permission from the ACS.

pyridinimine ligands¹⁹⁹ and higher activity Me₆TREN systems.^{106,187,200} The rates are typically determined by monitoring formation of Cu^{II}X/L_n or the rate of disappearance of the alkyl halide in the presence of excess activator (Cu^IX/L_n) and excess TEMPO, which traps radicals faster than Cu^{II}X₂/L_n deactivates them (Scheme 8).¹²⁶

$$Cu^{I}X/L + R-X \xrightarrow{k_{act}} Cu^{II}X_{2}/L + R^{\bullet}$$

Scheme 8 Measurement of k_{act} by trapping with TEMPO.

Under such conditions, the activation rate constant can be kinetically isolated from the deactivation rate constant, as given by eqn [3]:

$$\ln([RX]_0/[RX]_t) = k_{act} [Cu^I X/L]_0 t$$
[3]

The values were also determined for some polymeric systems using GPC techniques and the results displayed similar kinetics.^{127,201} Other techniques include NMR,²⁰² HPLC,²⁰³ and stop-flow.¹⁸⁷

Conventional GC or GPC methods are limited in measuring rate constants with the maximum upper limit of $\sim 1 \text{ M}^{-1} \text{ s}^{-1}$. This limitation prompted a study of the stop-flow technique for measuring very fast activation rate constants for model systems in copper-mediated ATRP.^{86,187} The mixing time, ca. 1 ms, and speed of data collection, one full spectrum ca. every 1 ms for

diode-array UV-visible spectrophotometers, allow the measurement of pseudo-first-order rate constants up to ca. $1 \times 10^2 \text{ s}^{-1}$, $t_{1/2} = \text{ca.} 5 \text{ ms}$ and second-order rate constants up to ca. $1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. The stop-flow technique allowed determination of activation rate constants which were not previously accessible, thereby opening up a new way to systematically determine activation rate constants and activation parameters for highly active ATRP complexes. Indeed the activity of catalyst complexes formed with a broad spectrum of ligands has been determined and covers a wide range.^{106,127}

Figure 9(a) shows the correlation of activation rate constants (k_{act}) and deactivation rate constants (k_{deact}) with equilibrium constants (K_{ATRP}) for various Cu^IBr/ligands with EtBriB at 22 °C in MeCN.^{127,199} The equilibrium constant increases as a consequence of an increase in k_{act} accompanied by a decrease in k_{deact} . The ideal catalyst for ARGET and ICAR would have a large value for K_{ATRP} and k_{deact} .

Figure 9(b) shows the trend with various initiators in the presence of a Cu^I/TPMA catalyst complex at 22 °C in MeCN.^{45,199} The figure shows that more reactive dormant species generate less reactive radicals and lower k_{deact} ; however k_{deact} is less dependent on K_{ATRP} for initiators than for ligands.

A study focusing on the effect of temperature on the activation rate constant, k_{actr} provides additional insight into the mechanism of activation.⁸⁶

3.12.5.3 Radical Nature of the Propagating Species

The existence of a radical, (P_n^{\bullet}) , has been proposed in copper-mediated ATRP and is based on several experimental observations,^{204–206} which are discussed below in greater detail.

There is abundant evidence that ATRP operates via a radical mechanism including chemoselectivity,²⁰⁴ cross-propagation kinetics,⁵¹ and kinetic isotope effects,²⁰⁶ which are similar to the values seen for conventional RPs. However, the specific nature of a CRP with intermittent activation and deactivation

can result in some deviation in cross-propagation kinetics from those seen in a standard RP. 204,207,208

- The reactivity ratios, which are very sensitive to the nature of the active centers, are nearly identical to those reported for conventional radical copolymerization of the same monomers but are different from those observed for anionic, group transfer, and cationic systems.^{51,209–213}
- Regioselectivity and stereoselectivity are similar to those for a conventional RP. All the polymers formed by ATRP have regular head-to-tail structures with the dormant species of the typical secondary/tertiary alkyl halide structures, as evidenced by NMR.^{210,214} In addition, polymers prepared by ATRP have similar tacticity to polymers prepared by conventional free radical processes.^{27,215}
- A racemization study using optically active alkyl halides also supports the intermediacy of a radical.²¹⁶
- The polymerization is initially retarded by the presence of a small amount of oxygen or the presence of 'true radical inhibitors', such as galvinoxyl and TEMPO that directly react with a growing radical and inhibit chain growth by terminating the reaction.²¹⁶
- On the other hand, antioxidants, such as substituted phenols, used to prevent *in situ* formation of peroxides which can subsequently initiate polymerization of (meth)acrylates increased the rate of an ATRP reaction.²¹⁷ This was later recognized to occur by the antioxidant acting to reduce the concentration of the deactivator, X–Mt^{m+1}.⁵⁶
- ATRP can be carried out in the presence of water^{218,219} or other protogenic reagents and is tolerant of a variety of functionalities on the comonomers, just as in the case of standard RP reactions.
- Cross-exchange between different halogens²²⁰ and different polymerization systems (thermal and ATRP or nitroxide mediated and ATRP) demonstrates they have the same intermediates and supports a common radical mechanism.²²¹ An



Figure 9 (a) Ligands 1: Cyclam-B, 2: Me₆TREN, 3: TPMA, 4: BPED, 5: TPEDA, 6: PMDETA, 7: BPMPA, 8: dNbpy, 9: HMTETA, 10: bpy, 11: N4[3,2,3], 12: N4[2,3,2]. (b) Initiators 1: MCIAc, 2: BzCI, 3: PECI, 4: MCIP, 5: EtCliB, 6: BzBr, 7: CIAN, 8: PEBr, 9: MBrP, 10: CIPN, 11: EtBriB, 12: BrPN, 13: EBPA. Reprinted from Tang, W.; Kwak, Y.; Braunecker, W.; *et al. J. Am. Chem. Soc.* **2008**, *130*, 10702–10713, ¹⁰⁶ with permission from the ACS.

equimolar mixture of initiators for NMP and ATRP leads to the preparation of PS with a unimodal MWD.²²²

- ATRP is converted into a system which displays conventional RP characteristics upon the addition of octanethiol as a chain transfer reagent.²⁰⁵ Chain transfer in *n*-butyl acrylate (*n*BA) polymerization also resembles the conventional radical process.²²³ However, some differences between all CRP processes and conventional RP are observed²²⁴ and can be explained by the coexistence of various competing equilibria.²⁰⁷
- If a 'classic' ATRP reaction is driven to high levels of monomer conversion, a doubling of the MW, or cross-linking in multi-functional initiator systems, has been observed as a result of induced radical-radical termination reactions.^{225–227}
- EPR studies have revealed the presence of $X M_t^{m+1}$ species resulting from the persistent radical effect in ATRP reactions.^{228–233}
- Propagating free radicals have been observed directly by EPR in the polymerization of dimethacrylates.²³⁴

So the process is a radical-based procedure.

The question then becomes how are the radicals generated and how do they react?

3.12.5.4 Inner Sphere Electron Transfer versus Outer Sphere Electron Transfer

Mechanistically, atom transfer processes can occur via the outer sphere electron transfer (OSET) and ISET or atom transfer passing through a Cu–X–C transition state, which is formally also a single electron transfer (SET) process. OSET can proceed via a stepwise manner with radical anion intermediates or in a concerted process with simultaneous dissociation of alkyl halide to a radical and anion. According to Marcus analysis of electron transfer processes, OSET should have an energy barrier ~18 kcal mol⁻¹ higher than what was experimentally measured, that is, OSET should be ~10¹⁰ times slower than ISET (Figure 10).¹⁸⁸

The differences are much greater than any computational or experimental errors and it can be concluded that an ATRP occurs via a copper-catalyzed concerted homolytic dissociation of the alkyl halide. In addition, the one-step dissociative electron transfer to form a radical and an anion is energetically more favorable than the two-step process via the radical anion intermediates.

Despite the significant amount of work on the role of Cu^0 and the effect of polar solvents on the kinetics of an ATRP,^{109,113,139,235} there has been a continuing effort expended on proposing that the changes in activity observed in the presence of Cu^0 in polar solvents indicate a change in mechanism^{118,119,236} rather than merely reflecting a change in reaction conditions.^{139,188} As discussed before, Cu(0) is one of several possible reducing agents in the ATRP process. However, an alternative mechanistic proposal for ATRP in the presence of Cu(0) was presented and named SET-LRP (living radical polymerization).^{118,143,236–238} This mechanism was postulated for polymerization of MA in DMSO in the presence of copper(0) and Me₆TREN, a ligand that forms a very active ATRP complex.²³⁹ The proposed mechanistic scheme relies on the



Figure 10 Comparison of the free energies during an ISET and concerted OSET process for the reaction of bromoacetonitrile with Cu¹/TPMA catalyst in MeCN at 25 °C. Reprinted from Lin, C. Y.; Coote, M. L.; Gennaro, A.; Matyjaszewski, K. *J. Am. Chem. Soc.* 2008, *130*, 12762–12774, ¹⁸⁸ with permission from the ACS.

OSET from copper zero to alkyl halide to form Cu(I) species and radical anions. The resulting Cu(I) species was assumed to 'instantaneously' disproportionate back to Cu(0) and Cu(II) species. Intermediate radical anions were proposed to cleave to form propagating radicals and anions that associate with Cu(II) species. Growing radicals were postulated to be trapped exclusively by Cu(II) species to form the dormant species and a Cu(I) complex that would not activate the dormant species but should again 'instantaneously' disproportionate.

Detailed kinetic and mechanistic studies show that alkyl halides react preferentially with the soluble Cu(I)/Me₆TREN complex, due to its very high ATRP activity rather than with solid Cu(0) that has relatively small surface area. Cu(0) serves as the reducing agent and comproportionates with Cu(II) formed as a 'persistent radical' in the radical termination process, but it also slowly reacts directly with alkyl halides and acts as a supplemental activator. Only ~10% of CuBr/Me₆TREN disproportionates in DMSO, even less in mixtures containing monomer, MA.

Disproportionation/comproportionation is relatively slow rather than 'instantaneous'. Therefore, disproportionation is only partial and, in most systems, comproportionation dominates. Cu(I) is always present in the system and is the predominant activator. The faster rate of polymerization in DMSO is due to a larger ATRP equilibrium constant in DMSO than in other solvents.¹⁸⁹ Moreover, OSET process is much slower than the ISET process, due to very slow electron transfer to alkyl halides.¹³⁹ Thus the proposed SET-LRP mechanism is not possible, since it violates the principle of microscopic reversibility.^{139,240}

These conclusions have recently been confirmed in an independent article with one of the corresponding authors, being the author of the initial paper proposing SET-LRP.^{236,241} Both experimental and quantum-chemically calculated data show that dissociative electron transfer to alkyl halides, those commonly used as initiators in CRP, does not produce intermediate radical anions. It was postulated by the SET mechanism that reductive cleavage of these compounds follows a concerted mechanism in which electron transfer and bond breaking occur in a single step. On the basis of quantum-chemically calculated data, C-X bond dissociation during the activation step of SET-LRP cannot be classified as being either homolytic or heterolytic because injection of one electron in RX produces an ion-radical adduct without a covalent bond between carbon and the bromide anion. In contrast, if activation of R-X by Cu^I complexes in ATRP occurs via atom transfer, the process may be considered as a metal-catalyzed homolytic C-X bond dissociation.

3.12.6 Components/Phenomenology/Process

3.12.6.1 Monomers

There are still some limitations to the range of monomers that can be homopolymerized in an ATRP. The limitation is related to the requirement for repeated reactivation of the dormant species by the transition metal complex. With the current spectrum of catalysts there should be an α-stabilizing substituent adjacent to the transferable atom or group in order that the dormant chain end be reactivated. The initial range of monomers that could be polymerized by ATRP included styrenes,¹⁹ (meth)acrylates,²⁷ meth(acrylamides),^{242,243} and AN.²⁴⁴⁻²⁴⁸ ATRP was then expanded to include several functional monomers including 4-vinyl pyridine, 249-252 monomers containing an -OH group, such as 2-hydroxyethyl acrylate (HEA)⁹⁴ and 2-hydroxyethyl methacrylate (HEMA),^{57,253,254} glycidyl (meth)acrylate, 246,254-256 and precursors of ionic monomers²⁵⁷ including dimethylaminoethyl methacrylate (DMAEMA),^{258–260} 2-(trimethylammonium)ethyl methacrylate trifluoromethanesulfonate, and 2-(dimethylethylammonium) ethyl methacrylate bromide.²⁶¹

Glycidyl acrylate²⁵⁷ has been copolymerized by ATRP yielding well-defined polymers containing the reactive glycidyl group, which can be used as a precursor for other functional groups.²⁵⁶ Water-soluble monomers (both neutral and ionic) can be polymerized in controlled fashion by ATRP directly in protic (aqueous) media.¹³⁸ Some examples of monomers, including those with polar groups that have been polymerized by ATRP, are shown in **Scheme 9**.

Simple alkenes have been copolymerized by ATRP with polar monomers.^{262–264} Recent improvements in catalysis and expansion of suitable transferable atoms or groups have allowed ATRP of vinyl pyrrolidone,²⁶⁵ vinyl acetate,²⁶⁶ and vinyl chloride.²³⁷

The major differences between the polymers prepared by ATRP and prior art polymers prepared by a conventional radical polymerization (RP) are the additional degrees of control over architecture, MW, MWD, and telechelic functionality provided by CRP.

In addition to low MW monomers, a broad range of macromonomers have been copolymerized with low MW monomers to form graft copolymers^{208,267,268} and even homopolymerized to form bottle brush polymers.^{269–272}

3.12.6.2 Initiators

The procedure for 'normal' initiation of an ATRP reaction employs an initiator molecule, R–X, either a small molecule, a



Scheme 9 Examples of monomers, and a few functional methacrylates, that have been polymerized by ATRP.

macromolecule, or a functionalized surface of any topology, with one or more radically transferable atoms or groups,²⁷³ most often an alkyl (pseudo)halide. This R-X molecule has been called the initiator, even though in contrast to standard RP initiators, this molecule is an inherently thermally stable entity and is incorporated in its entirety into the final polymer. The added initiator, R-X, can be a monofunctional initiator or a multifunctional initiator, that is, it can possess more than one functional -X group, capable of providing a site for chain growth.²⁰ The rate of polymerization is first order with respect to the concentration of R-X. The best results have been obtained when X has been either chlorine or bromine but iodine has also been successful with acrylates, vinyl acetate, and vinyl chloride, and it provides for the possibility of a controlled degenerative transfer polymerization. 44,266,274-276 One or more functions can be combined in a single molecule, for example, an initiator and a monomer, which directly form a (hyper)branched structure when (co)polymerized,²⁷⁷ or the role of solvent and (pseudo) ligand, which acts to stabilize the catalyst complex.²⁶¹

The primary advantage of a 'normal ATRP initiation' procedure is that it provides great freedom for the choice of both initiator and catalyst complex. The most active catalyst can be selected, provided all reagents are pure and oxygen free, resulting in lower levels of transition metal and other impurities in the final product. However, care has to be taken in selecting the appropriate initiator, catalyst, and reaction conditions since activation rate constants k_{act} for a variety of initiators can vary by a factor of 1 million,⁴⁵ Figure 11. Therefore, selection of the appropriate radically transferable atom or group on the initiator and transition metal complex is important to provide control over the efficiency of the initiation reaction.²⁷⁸ The activation rate constants are highest for tertiary alkyl halides and lowest for primary alkyl halides. The activity of alkyl bromides is several times larger than that of the analogous alkyl chlorides in reactions mediated by the same catalyst complex. This is related to the higher BDE or lower K_{BH} of the C–Cl bond, Scheme 7. However, the magnitude of this difference is mitigated by the higher halogenophilicity of copper to chlorine compared with bromine, K_{Halo} .¹⁰⁶ This observation has been successfully used in 'halogen exchange' processes that can significantly improve initiation and cross-propagation efficiency.^{220,279–281}

Polymers prepared by other polymerization processes can be functionalized at the termini or along the backbone and incorporated into an ATRP as a macroinitiator,^{22,282–284} leading to the preparation of well-defined block and graft copolymers comprising a broader range of monomers. Simultaneous use of both a macroinitiator and a macromonomer improves incorporation of phase-separable macromonomers into the graft polymer.²⁰⁸

Molecules with initiating functionality can be attached to any type of polymer, or a solid surface,²⁸⁵ either a particle,^{25,286} a flat surface,²⁸⁷ a fiber,²⁸⁸ or a porous material.^{289,290}

A functional initiator may carry a second noninitiating functionality, in addition to a radically transferable atom or group, to yield hetero-telechelic materials.²⁹¹ Since ATRP is a radical-based process, many functional groups can be tolerated in the initiator molecule including hydroxy, epoxy, amino, amido, cyano, and azido and many other functional groups can be incorporated in a protected form. Therefore, the added initiator can also be used to introduce additional functionality into the α -chain end or within the 'core' of a multiarmed star or composite material, see Sections 3.12.8 and 3.12.10 (Scheme 10).



Figure 11 Variation of k_{act} based on structure of initiator (alkyl group and transferable atom). Reprinted from Tang, W.; Matyjaszewski, K. *Macromolecules* **2007**, *40*, 1858–1863,⁴⁵ with permission from the ACS.



Scheme 10 Organic/inorganic composite structures: ATRP from tethered initiators.

3.12.6.3 Ligands

Recent reviews on the structural aspects of copper-catalyzed ATRP^{28,40,292,293} provide some background on the fundamentals of transition metal-catalyzed atom transfer reactions, including ATRA and ATRP. The reviews focus on the structure of a Cu catalyst complex formed with bidentate, tridentate, and tetradentate nitrogen ligands. The primary role of the ligand added to an ATRP is to solubilize the Cu salts and to tune the Cu catalyst activity to optimally conduct a well-controlled polymerization. Nitrogen-based ligands generally work well for Cu-mediated ATRP. The choice of ligand greatly influences the effectiveness of the catalyst in a specific polymerization reaction. One complex at the same concentration does not work for every (co)polymerization since catalyst activity spans several orders of magnitude. A broad series of ligands forming catalyst complexes with an expansive range of activity are discussed in the context of how structure affects catalyst activity in addition to solvent and temperature, including those listed below with their common abbreviations.

Ligand	Abbreviation
2,2'-Bipyridine	bpy
4,4'-Di(5-nonyl)-2,2'-bipyridine	dNbpy
2,2':6',2" -Terpyridine	tpy
4,4',4" -Tris(5-nonyl)-2,2' :6',2"-terpyridine	tNtpy
Diethylenetriamine	DETA
N, N, N', N'-tetramethylethylenediamine	TMEDA
Triethylenetetramine	TETA
N,N-bis(2-pyridylmethyl)amine	BPMA
<i>N</i> -propyl(2-pyridyl)methanimine	NPrPMI
<i>N</i> , <i>N</i> , <i>N</i> '', <i>N</i> ''-pentamethyldiethylenetriamine	PMDETA
<i>N</i> , <i>N</i> -bis(2-pyridylmethyl)octylamine	BPMOA
1,1,4,7,10,10-Hexamethyltriethylenetetramine	HMTETA
Tris[2-aminoethyl]amine	TREN
Tris[2-(dimethylamino)ethyl]amine	Me ₆ TREN
Tris[(2-pyridyl)methyl]amine	TPMA
1,4,8,11-Tetraaza-1,4,8,11- tetramethylcyclotetradecane	Me ₄ Cyclam
<i>N.N.N'</i> .N'-tetrakis(2-pyridylmethyl)ethylenediamine	TPEN
1,4,8,11-Tetraazacyclotetradecane	Cyclam

Some structures of ligands frequently used for ATRP are shown in Scheme 11.

Depending on the type of amine ligand, the complexes are either neutral (triamines) or ionic (2,2'-bipyridine (bpy) and tetramines). The counterions in the case of the ionic complexes were either a bromide anion (1,4,8,11-tetraaza-1,4,8,11-tetramethylcyclotetradecane (Me₄Cyclam) and HMTETA) or the linear [Cu¹Br₂]⁻ anion (4,4'-di(5-nonyl)-2,2'-bipyridine (dNbpy)). The halide anions can interact with Cu¹ cationic species and reduce its activity.²⁸ No direct correlation was found between the length of the Cu^{II}-Br bond and the deactivation rate constant in an ATRP,²⁸ which suggests that other parameters such as the entropy for the structural reorganization between the Cu^{II} and Cu^{II} complexes might play an important role in determining the overall activity of the catalyst in ATRP.²⁹²

As discussed in the kinetics section, the ratio of activity for the Cu^I/ligands catalyst complexes and initiators each spans 7 orders of magnitude. General order of activity of the Cu complex formed with specific types of ligands is 1,4,8,11-Tetraazacyclotetradecane (Cyclam)-B>N4-branched>N4-linear>N3>N2. Ethylene is a better linkage than propylene for coordinating nitrogen in the ligand. Anionically charged ligands form stable and active neutral Cu complexes but their deactivation rate constants are low.^{194,294} Because of the high stability of the Cu^I and Cu^{II} complexes with TPMA this catalyst is particularly suitable for ARGET and ICAR ATRP reactions.¹⁸⁹

3.12.6.4 Additives

A number of reagents that would not be considered essential for the creation of an ATRP equilibrium have been added to ATRP reactions in order to modify the kinetics of the ATRP. In addition to the various reducing agents, including sugars, Sn^{II}, or Cu⁰, initially added to activate and reactivate the Cu^{II} complex in AGET and ARGET initiating systems, one can include addition of many specific reagents (also mild reducing agents) to modify K_{ATRP} , including solvents or additives like tertiary amines,¹⁴⁶ pyridine,²⁹⁵ malononitrile,²⁹⁶ phenol,²⁹⁷ antioxidants,¹¹⁸ water,²⁹⁸ inorganic halides,²⁶¹ and nanoclay^{167,299,300} that increase the rate of an ATRP.

3.12.6.5 Solvent Effects and Selection of a Catalyst for Polymerization in Homogeneous Aqueous Media

The performance of copper-based ATRP catalysts can be predicted based on the stability constants of the Cu^{II} and Cu^{II}



Scheme 11 Examples of classes of N-based ligands suitable for preparing copper-based catalyst complexes for ATRP.

complexes with the chosen ligand L, β^{II} and β^{I} , respectively.³⁰¹ A high β^{II}/β^{I} ratio is required for high catalytic activity.³⁰¹ Both β^{II} and β^{I} should be large in order to prevent catalyst deactivation through competitive coordination of monomer and/or polymer that are present in large molar excess. More halidophilic Cu^{II}–L complexes provide more active catalyst complexes and better control over the polymerization due to the fact that there is a sufficient concentration of deactivator present in the system.³⁰²

If the ATRP is to be carried out in aqueous media, in addition to the above requirements, the ratio $\beta^{II}/(\beta^I)^2[L]$ should be considered to account for potential disproportionation of the Cu^I complex.²⁶¹ Acidic monomers may be polymerized if the ligands meet all outlined requirements and are as weakly basic as possible. Cu^I complexes are generally unstable in aqueous media and tend to disproportionate. For instance, the disproportionation of noncomplexed Cu^I in water is characterized by an equilibrium constant as large as $K_{disp} = 10^{6}.^{303}$ Addition of excess ligand L, or a ligand substitute, can significantly affect the equilibrium and the new equilibrium constant is determined by the stabilization of Cu^{II} relative to Cu^I upon coordination with L, eqn [4].

$$K_{\rm disp}^* = \frac{1 + \beta^{\rm II}[L]}{(1 + \beta^{\rm I}[L])^2} K_{\rm disp} \approx \frac{\beta^{\rm II}}{(\beta^{\rm I})^2[L]} K_{\rm disp}$$
[4]

For ligands forming 1:1 complexes with copper ions, the activity of the catalyst is proportional to β^{II}/β^{I} , whereas the tendency of the Cu^I complex to disproportionate in aqueous solution depends on the ratio $\beta^{II}/(\beta^{I})^{2}[L]$.³⁰¹ Thus, a map can be constructed that can be used to select a ligand for aqueous ATRP that forms an active catalyst complex yet remains stable toward disproportionation. Various redox processes related to ATRP and the Cu^I disproportionation reaction, including the effect of both ligand and solvent, were reviewed.^{189,304} The

value of K_{ATRP} can vary by a factor of 80 based solely on solvent effects.¹⁸⁹ The analysis clearly answers the solvent affect questions raised early in the development of ATRP.¹⁹⁵

Figure 12 illustrates that while the $Cu^{I}/N, N, N', N''$, N''-pentamethyldiethylenetriamine (PMDETA) complex is active, it disproportionates in aqueous ATRP. On the other hand, ligands such as bpy, HMTETA, and TPMA can be used in aqueous media, although with rather different activities. If necessary, catalyst disproportionation in water can be suppressed by using an appropriate cosolvent or by addition of a pseudoligand that will stabilize Cu^{I} versus Cu^{II} , such as pyridine, which allows



Figure 12 Correlation between ATRP catalytic activity and tendency for disproportionation for several Cu¹ complexes. Reprinted from Tsarevsky, N. V.; Matyjaszewski, K. *Chem. Rev.* **2007**, *107*, 2270–2299,¹³⁸ with permission from the ACS.

aqueous ATRP of ionic monomers such as sodium 4-styrenesulfonate and 2-(N,N,N-trialkylammonium)ethyl methacrylate salts to be conducted.^{138,302,304}

3.12.6.6 ATRP in Biphasic Aqueous Systems

Water is an inexpensive environmentally friendly solvent with high thermal capacity. It is an attractive medium for exothermic radical copolymerization reactions, particularly since both solution polymerization of water-soluble monomers and biphasic polymerization of hydrophobic monomers in latexes have found direct industrial-scale applications in various practical fields. It is possible to prepare polymer lattices and solid particles with a wide range of sizes, from nanometers to millimeters, by employing the full spectrum of aqueous dispersed media: suspension, dispersion, emulsion, miniemulsion, microemulsion, and inverse miniemulsion systems.98 One advantage of biphasic media for the preparation of polymers from initiators containing multiple initiation sites is that there is a further segregation of the low concentration of active radicals through compartmentalization,³⁰⁵⁻³⁰⁹ which reduces the formation of macroscopic cross-linked gels.

Selection of a suitable ligand is a critical first step in order to conduct a controlled ATRP in any biphasic aqueous system. The choice of surfactant is also important for all heterogeneous systems. However, ligand selection remains of primary importance, since the ligand determines the solubility of the metal complex in the monomer phase and partitioning of the metal complexes between the different phases. The earliest work directed at conducting an ATRP in an emulsion system required relatively low solids content and high surfactant levels, 13% solids, and over 10 wt.% surfactant based on monomer^{218,310} for production of stable latexes. However, by moving to a miniemulsion process and using reverse initiation,^{311,312} it was possible to increase the solids content of the system to 30% and significantly reduce the level of surfactant, to 2 wt.%

surfactant based on monomer, in addition to starting with an oxidatively stable catalyst complex. The critical requirement is selection of an appropriate ligand shown in (Scheme 12); dNbpy, BPMODA, 4,4',4"-tris(5-nonyl)-2,2':6',2"-terpyridine (tNtpy) and EHA₆TREN are sufficiently hydrophobic ligands to retain an adequate concentration of Cu^{II} in the monomer droplets dispersed in a miniemulsion polymerization. These ligands provide controlled polymerizations, while complexes formed with bpy, PMDETA, and Me₆TREN allow migration of Cu^{II} to the aqueous phase and control is lost.^{311,313,314}

Suitable commercially available surfactants include CTAB, Brij 98, and Tween 80, whereas poly(ethylene glycol) (PEG) 100, PEG 4600, Brij 97, and Tween 20 provided less stable emulsions.

3.12.6.6.1 Miniemulsion

While reverse initiation simplified setting up a miniemulsion ATRP, it limited the range of materials that could be prepared and the catalysts that could be employed in the reaction. In a reverse initiation procedure one cannot independently adjust catalyst level and $DP_{target'}$ since formation of both the lower oxidation state catalyst complex and the ATRP initiator depends on the amount of standard free radical initiator added to the reaction. Therefore, a new initiation system was developed, SR&NI,¹³² that involved addition of both an ATRP initiator and a free radical initiator. SR&NI allowed the preparation of block and star copolymers in a miniemulsion with low levels of an active catalyst and low levels of surfactant.133,311 The use of SR&NI provided stable latexes with high solids content. As shown in the 2D chromatography plot in Figure 13(a), only 4.5% of linear homopolystyrene was present in the final polymer when a tri-arm poly(methyl acrylate) macroinitiator was chain extended by styrene in an SR&NI miniemulsion process.¹³³ The homopolymer results from the use of a free radical initiator to activate the catalyst complex which simultaneously generated a monofunctional initiator.



Scheme 12 Suitability of ligands for (mini)emulsion ATRP.



Figure 13 2D chromatography plots of star block copolymers prepared by SR&NI (a) and AGET initiation (b) procedures, respectively. Conditions for each polymerization are reported in Reference 95. **Figure 13(a)** reprinted from Min, K.; Gao, H.; Matyjaszewski, K. *J. Am. Chem. Soc.* **2005**, *127*, 3825–3830, ⁹⁵ with permission from the ACS.

This particular 2D chromatography plot, **Figure 13(a)**, provided the incentive to work on a further improvement in the procedures used for initiation of an ATRP and directly led to the development of AGET ATRP.^{95,133} In an AGET ATRP miniemulsion polymerization process, a water-soluble reducing agent is used to activate the catalyst and control the fraction of deactivator present in the suspending medium. The other 2D chromatography plot, **Figure 13(b)**, shows the final result of an AGET ATRP using the same tri-arm macroinitiator. No homopolymer can be detected. The amount and addition rate of the reducing agent affect the polymerization rate and the level of control attained in the polymerization. However, as the image shows, when the appropriate selection is made, no homopolymer and no coupling product are detected.

A further advantage of AGET ATRP is that by adding an excess of reducing agent, the reaction can be successfully carried out in the presence of small amounts of air,¹³⁵ thereby simplifying setup procedures.

3.12.6.6.2 Microemulsion

Copper-based ATRP was recently expanded to microemulsion polymerization systems.⁹⁶ The proper selection of ligand and surfactant remains the key to success. A hydrophobic ligand is preferred for mini- and microemulsion and selection of a nonionic surfactant with a suitable hydrophilic–lipophilic balance (HLB) value results in good colloidal stability and good control. As shown in **Figure 14**, AGET initiation provided copolymers with narrow MWD, $M_w/M_n = 1.28$, and narrow particle size distribution. Ascorbic acid was selected as the reducing agent since it is soluble in the aqueous phase, ensuring rapid reduction of any Cu(II) species that migrates to the aqueous phase or is present at the interphase. Control is better in an AGET system because all reagents are present in the dispersed droplets before activation occurs.

3.12.6.6.3 Reactive surfactants

One of the limitations associated with conducting a CRP in miniemulsion or microemulsion systems is the requirement for high levels of surfactants that could contaminate the final high-value nanoparticles (NPs). This has been overcome by



Figure 14 GPC traces of polymers prepared in microemulsion by FRP and ATRP using different procedures for initiation/activation of the reaction. Reprinted from Min, K.; Matyjaszewski, K. *Macromolecules* **2005**, *38*, 8131–8134, ⁹⁶ with permission from the ACS.

the preparation and use of reactive surfactants that can act as initiators for the subsequent ATRP.³¹⁴⁻³¹⁶ In the latter referamphiphilic block copolymers poly(ethylene ence, oxide)-b-polystyrene (PEO-PS-Br) with various MWs were synthesized using a PEO homopolymer (PEO-Br) macroinitiator. Initially AB block copolymers were used as macroinitiators and stabilizers (reactive surfactants) for AGET ATRP of nBA, in miniemulsion either with or without ethyl 2-bromoisobutyrate (EBiB) as coinitiator. Under both conditions, the reactions were well controlled and stable latexes were formed. In the presence of EBiB, the amount of surfactant required to form a stable emulsion can be reduced to 1.7-4 wt.% versus monomer. Because of the covalent linking of the surfactants to polymer chains, no free surfactant is left in the reaction system on completion of the polymerization. Since the surfactant is tethered to the latex particle, the possibility of migration during subsequent film formation was avoided. This procedure has been expanded by introducing the concept of a dual reactive

surfactant, wherein the α -functionality on the surfactant provides a convenient peripheral functional group for postreaction functionalization of the formed latex particles.³¹⁶

A similar approach has been employed in RAFT procedures.³¹⁷

3.12.6.6.4 A 'true' emulsion system

The expansion of dispersed media ATRP to microemulsion provided the critical step required for development of a process for addition of pure monomer to the system to increase the percent solids in the final latex. This procedure was initially employed to prepare a forced gradient copolymer³¹⁸ in a heterogeneous controlled copolymerization since the added pure monomer could diffuse to the latex particles containing all components required for an ATRP. An extension of the concept resulted in the development of an ab initio emulsion polymerization process, capable of directly preparing a stable latex containing block copolymers.⁹⁷ The critical requirement for this advance in dispersed media ATRP was the ability to encapsulate all agents required for an ATRP in the initially formed micelles. This allowed pure monomer to be added to the reaction medium. The added monomer was then able to diffuse to the active micelles, allowing an increase in micelle size and concomitant increase in the percent solids and decrease in percent surfactants in the system.

This two-step one-pot approach to an emulsion ATRP proved that a microemulsion ATRP could be successfully transformed into an emulsion polymerization (Scheme 13). Addition of a second monomer, after a major proportion of the first monomer polymerized, leads to preparation of a block copolymer with a 'gradient' second block.

As noted above, the use of reactive surfactants and dual functional reactive surfactants essentially reduces the amount of 'passive' agents in the final aqueous dispersion.

3.12.6.6.5 Dispersion

Dispersion polymerization is a convenient procedure to form larger solid particles. Uniform-sized polymer beads with diameters between 0.1 and 10 µm are finding an ever increasing role in a number of coatings, electronics, microelectronics, biomedical, and information technology applications.^{319–322} Particle size control and narrow size distribution are key parameters for most of these applications. Dispersion polymerization is generally recognized as a type of precipitation polymerization, conducted in the presence of a polymeric stabilizer that is soluble in the reaction medium. Dispersion polymerization was initially developed³²³ as a process that was conducted in a hydrocarbon medium. It was its extension to polar solvents, such as ethanol or methanol, which greatly expanded the utility of this polymerization procedure.^{324,325} An atom transfer radical dispersion polymerization of styrene in ethanol was successfully carried out with the formation of uniform-sized particles.³²⁶ This was accomplished by using a 'two-stage' dual-process polymerization technique, in which the first stage involved a standard RP and the second a reverse ATRP. This required that initial nucleation stage was completed in a relatively short period in order to prepare particles with uniform size. The high fraction of retained chain end functionality was readily employed for further modification of the particles. Monodisperse cross-linked PS particles were also synthesized using the same technique; these particles were successfully chain extended with HEMA, thereby modifying the surface properties of the particles.

3.12.6.6.6 Inverse miniemulsion

Inverse miniemulsion polymerization provided a new method for the synthesis and functionalization of well-defined watersoluble/cross-linked polymeric particles.³²⁷ Stable colloidal NPs of well-controlled water-soluble poly(oligo(ethylene glycol) monomethyl ether methacrylate) (POEOMA) homoand copolymers were successfully synthesized by inverse miniemulsion AGET ATRP at ambient temperatures.³²⁸ This procedure allows preparation of well-defined microgels/nanogels with narrow size distribution, a high degree of chain end functionality, a uniform cross-linked network, and properties (i.e., swelling ratio, degradation behavior, and colloidal stability) superior to microgels from conventional FRP.³²⁹

Biphasic ATRP procedures have been the subject of a recent review paper. 98

3.12.7 Control over Polymer Composition

3.12.7.1 Well-Defined Copolymers

The spectrum of (co)polymers that can be prepared by a well-controlled ATRP presently includes polymers with virtually any desired distribution of monomer units along the



Scheme 13 The preparation of a block copolymer using an *ab initio* emulsion ATRP. Reprinted from Min, K.; Gao, H.; Matyjaszewski, K. *J. Am. Chem. Soc.* 2006, *128*, 10521–10526,⁹⁷ with permission from the ACS.



Scheme 14 Compositions of copolymers prepared by CRP.

polymer backbone or within any specific segment in a copolymer. This includes homopolymers, random copolymers, alternating copolymers, gradient copolymers, block, graft, brush, and star copolymers,⁸⁴ each of which is discussed below (Scheme 14).

3.12.7.2 Homopolymers

There are still some limitations to the range of monomers that can be homopolymerized in an ATRP, see Scheme 9. The limitation is related to the requirement for repeated reactivation of the dormant species by the transition metal complex. With the current spectrum of catalysts, there should be an α -stabilizing substituent adjacent to the transferable atom or group in order to reactivate the dormant chain end. Therefore, simple alkenes are incorporated with difficulty but they can be copolymerized, especially with acrylates. Acidic monomers can protonate ligands and destroy ATRP catalysts; therefore, they should be polymerized in a protected form, for example, acetal, t-butyl esters, or used in the anionic form, sodium salts or as protonated tertiary amines. Monomers/polymers that can complex copper species such as amides, polyamines, or some proteins could displace ligands and deactivate catalysts, unless stability constants are large enough, for example, for TPMA. Finally, monomers containing groups that easily participate in radical transfer (thiols) cannot be used directly in any CRP process but should be protected.

The major differences between the polymers prepared by ATRP and prior art polymers prepared by a RP are the additional degrees of control over architecture, MW, MWD, and telechelic functionality provided by CRP.

3.12.7.3 (Co)polymers with Controlled MW

One advantage of a CRP, such as ATRP, is the ability to control the MW and MWD of copolymers containing functional monomers. Control over MW requires efficient initiation and preservation of activity in the majority of the polymeric chains. However, termination and other side reactions are also present in ATRP, and they become more prominent as higher MW polymers are targeted. For example, in the copper-mediated ATRP of styrene, a slow termination process was observed, mainly arising from the interaction of the Cu^{II} species with both the growing radical and the macromolecular alkyl halide.⁸⁹ The catalytic species can participate in the OSET reactions by either oxidation of polystyryl radicals to carbocations or reduction of radicals to carbanions via reactions with Cu(II) and Cu(I) species. Studies with model compounds and macromolecular PS species demonstrated that the elimination reaction was accelerated in the presence of the Cu(II) complex. This process was faster for bromine-mediated ATRP than for chlorine-based systems and was more noticeable in polar solvents. These processes limited the MW of the resulting homopolymers.^{89,330} However, these prior limitations on the maximum MW of the (co)polymers that can be prepared by an ATRP have been surmounted by the development of ARGET ATRP which minimized OSET catalyst-based side reactions,³⁰⁴ allowing the production of higher MW polymers such as styrene acrylonitrile copolymers (SANs)¹⁴⁸ and polyacrylonitrile (PAN) with $M_n \sim 200\,000$ and $M_w/M_n \sim 1.2$.¹⁴⁹

MWD in ARGET ATRP depends on the amount of Cu(II) species, according to eqn [2]. Thus, it is possible to prepare homopolymers and block copolymers with dispersity, defined by the concentration of the deactivator. Interestingly, the block copolymers PS-*b*-poly(methyl acrylate) with narrow MWD PS but an ~30% poly(methyl acrylate) segment with broad MWD resulted in materials with hexagonally perforated lamellar morphology, whereas the copolymers with both segments of low dispersity yielded materials with conventional cylindrical morphology. Thus, ARGET process not only benefits from reduced amount of catalyst but, by providing the possibility of dialing desired dispersity, may also lead to new materials with novel properties.³³¹

A recent extension of ARGET ATRP, using an alkyl dithioester initiator, was also demonstrated for preparation of methacrylate) poly(methyl (PMMA) with MW $M_{\rm n} \sim > 1\,000\,000.^{47,157}$ Another procedure resulting in the formation of high MW polymers was a simple and versatile ARGET ATRP of MA with inexpensive commercially available ligands, including diethylenetriamine (DETA), PMDETA, and tris(2-aminoethyl)amine (TREN). Catalytic amounts of catalyst were utilized achieving ppm levels of Cu^{II}Br₂/L in the presence of a zerovalent copper metal (i.e., copper powder or wire) at 25 °C. High MW poly(methyl acrylate) was obtained with $M_{\rm n} > 1.5$ million and $M_{\rm w}/M_{\rm n} \sim 1.25$.¹⁴⁴

Conducting the reaction under high pressure provides another approach to high MW polymers (Figure 15). The propagation rate constant is enhanced at high pressure while that of termination is suppressed – therefore the ratio of k_p/k_t is higher. For example, at 6 kbar pressure PMMA with $M_n = 1\,200\,000$ and $M_w/M_n = 1.17$ were synthesized at room temperature within a few hours with targeted MW.^{91,92} It was also possible to synthesize PS with $M_n > 1\,000\,000$ and $M_w/M_n < 1.25$ using AGET ATRP under a pressure of 6 kbar at room temperature. This is the highest MW linear PS prepared by a CRP.³³²

3.12.7.3.1 Linear copolymers: statistical and gradient

A wide spectrum of copolymers can be prepared via spontaneous or sequential ATRP of two or more monomers with precise control of molar mass, composition, and functionality.^{291,333} The reactivity ratio of comonomers in a CRP is very similar to the values found in conventional radical copolymerization, although there are some factors that may affect CRP processes with intermittent activation, where differences in



Figure 15 Conducting ATRP under high pressure. Reprinted from Kwiatkowski, P.; Jurczak, J.; Pietrasik, J.; *et al. Macromolecules* **2008**, *41*, 1067–1069,⁹¹ with permission from the ACS.

repetitive activation or deactivation and time for complete reequilibration of the system lead to slightly different rates of consumption of comonomers.²⁰⁷

Random or statistical copolymers can be prepared by one-pot ATRP of two monomers when there is essentially random incorporation of monomers into the copolymer. This type of copolymer is formed in radical copolymerization when the reactivity ratio of each comonomer is close to unity.^{72,291} In ARGET ATRP, the lower concentration of catalyst results in less frequent activation/deactivation cycles and incorporation of more monomer units in each cycle, resulting in higher values of $M_w/M_{n'}^{34}$ but this slightly longer period of intermittent chain growth improved incorporation of α -olefins into an acrylate copolymerization.^{262,335,336}

When the reactivity ratios of the comonomers differ, there is preferential incorporation of one monomer into a growing copolymer chain and spontaneous gradient copolymers are formed in a one-pot reaction. Gradient copolymers are a special class of copolymers that rose to prominence with the development of ATRP,^{111,211} since copper-based ATRP was the first CRP procedure to allow copolymerization of a range of monomers of differing reactivity. Prior reports on the preparation of gradient copolymers by iniferter techniques³³⁷ discussed the preparation of polymers with broad MWD, suggesting heterogeneity, since no compositional data were provided. True gradient copolymers can only be obtained in systems providing fast initiation, uniform chain growth, and efficient cross-propagation. These conditions are difficult to fulfill in ionic systems and earlier radical copolymerization systems.

In a standard radical copolymerization, differences in comonomer reactivity ratios result in variation in instantaneous copolymer composition as the polymerization progresses. This leads to the composition of the copolymer formed at the beginning of the copolymerization differing from the composition of copolymers prepared at later stages. In contrast, in a CRP this variation in the rate of incorporation of the monomers into the copolymer is reflected as a change, or gradient, in composition of the monomer units along the main chain of each copolymer chain.²¹¹ Gradient copolymers can also be prepared in biphasic systems by spontaneous copolymerization of appropriate comonomers such as an acrylate and a methacrylate or by controlled addition of one monomer to an active miniemulsion^{318,338} or by *ab initio* ATRP emulsion polymerization where the added comonomer diffuses from the monomer droplets to the active micelle.97 In addition to cross-propagation kinetics, the rate of diffusion of each monomer from the comonomer droplet affects the shape of gradient obtained in the final copolymer (Figure 16).

A 'forced' gradient copolymer can also be prepared by controlled feeding of one or more monomers in a manner that compels the composition to be tapered through control over the ratio of available monomers. However, reactivity ratios still have to be considered.^{111,211,339–341}

The shape of the gradient in composition along a polymer backbone can also be changed by use of a difunctional initiator, which leads to a symmetrical 'skipping rope' distribution of monomers along the backbone of the copolymer.

Gradient copolymerization can be extended to the formation of graft copolymers with a gradient distribution of grafts, see Section 3.12.8.1.2.^{339,342}

Recently another approach to a gradient copolymer was reported, where the gradient was formed by a concurrent tandem reaction procedure, one that combined a CRP with an *in situ* transesterification of the monomer, MMA, by reaction with a range of alcohols in the presence of metal alkoxides.³⁴³



Figure 16 Instantaneous mole fraction of *n*-butyl methacrylate incorporated into a gradient copolymer formed during copolymerization of an equimolar ratio of *n*BA and *n*-butyl methacrylate by ATRP in bulk and miniemulsion systems. Reprinted from Min, K. E.; Li, M.; Matyjaszewski, K. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 3616–3622,³³⁸ with permission from Wiley-VHC.

3.12.7.3.2 Alternating copolymers

Alternating copolymers may also be prepared by CRP processes. They can be obtained from comonomers that have a spontaneous tendency for alternation, such as copolymerization reactions between a strong electron-accepting monomer, like maleic anhydride or N-substituted maleimides, and an electron-donating monomer such as styrene.^{111,335,344–346} Monomers without this inherent tendency toward alternation may also be copolymerized in an alternating fashion by performing CRP in the presence of Lewis acids such as diethylaluminum chloride or ethylaluminum sesquichloride.^{347–349}

Until recently, CRP had limited success at attaining control over chain microstructure in terms of sequence distribution and tacticity since, due to the radical nature of the propagation step, the chemoselectivity (reactivity ratios), regioselectivity (proportions of head to head units), and stereoselectivity (tacticity) of polymers formed in a CRP are similar to those in conventional RP. Recently, the controlled alternating copolymerization of a donor monomer (styrene) and an acceptor monomer (alkyl methacrylate or alkyl acrylate) complexed with a Lewis acid was examined using several CRP processes. Complex formation increases the electron-accepting ability of the acceptor monomer, which strongly enhances the cross-propagation rate constants and thereby increases the tendency for alternating copolymerization (Scheme 15).^{348,349}

These results were obtained in the presence of diethylaluminum chloride and ethylaluminum sesquichloride. Moreover, the alternating copolymers obtained in this reaction retain chain end functionality and were used as macroinitiators for the synthesis of well-defined diblock copolymers poly (methyl methacrylate-*alt*-styrene)-*b*-PS.³⁴⁸

3.12.7.4 Tacticity Control

Generally, free radical addition reactions or homolytic chain propagation reactions are not stereoselective. However, Okamoto determined that Lewis acids can induce stereocontrol in the RP of acrylic monomers.³⁵⁰ Conditions for CRP in the presence of Lewis acids were developed. Therefore, all three major CRP processes, ATRP, RAFT, and NMP, were investigated



Scheme 15 Free radical propagation in the presence of a Lewis acid.

for the polymerization of *N*,*N*-dimethylacrylamide in the presence of Lewis acids, known to enhance isotacticity, such as yttrium trifluoromethanesulfonate (Y(OTf)₃) and ytterbium trifluoromethanesulfonate (Yb(OTf)₃) (Scheme 16).³⁵¹

Poly(*N*,*N*-dimethylacrylamide) with controlled MW, low values for $M_w/M_{n\nu}$ and a high proportion of meso dyads (approx. 85%) was prepared using ATRP (methyl 2-chloropropionate/CuCl/Me₆TREN) and RAFT (with cumyl dithiobenzoate transfer agent) in the presence of Y(OTf)₃. These systems were used for the first one-pot synthesis of stereoblock copolymers by RP. Well-defined stereoblock copolymers, atactic-*b*-isotactic poly(*N*,*N*-dimethylacrylamides), were obtained by adding Y(OTf)₃ to either an ongoing RAFT or ATRP polymerization, started in the absence of the Lewis acid.^{351,352}

In a recent review article, Kamigaito and Satoh³⁵³ provided a summary of the requirements for stereocontrol in a CRP. The stereo-regulation should rely on an added Lewis acid, a polar solvent, or a multiple hydrogen-bonding additive. They can interact with the polar groups around the growing polymer terminal units and/or the monomer to induce the stereospecific chain growth, while the living or controlled chain growth is governed by a metal catalyst or a reversible chain transfer agent.

Stereospecific CRP is therefore achievable by the judicious combination of the stereocontrol additive or solvent and the CRP catalyst or mediator. This methodology is relatively easily applied to the precise synthesis of stereoblock or stereogradient polymers, in which the stereochemistry of the growing chain is either abruptly or gradually changed, respectively.

3.12.7.5 Linear Segmented Copolymers

Block copolymers are normally prepared by controlled polymerization of one monomer, followed by chain extension with a different monomer.⁷² In ATRP the preferred sequence, or order of block synthesis, should follow a decreasing order of activity: AN > methacrylates > styrene ~ acrylates. However, when conducting a chain extension from a less active monomer to a more reactive monomer, for example, from a polyacrylate-based macroinitiator to effectively initiate the ATRP of MMA, the end-group on the macroinitiator should be -Br and the catalyst CuCl, that is, halogen exchange should take place forming a -Cl-terminated growing polymer chain and a CuBr catalyst complex.²⁷⁹ This form of halogen exchange requires a 1:1 ratio of macroinitiator to catalyst or transferable halogen. In situations where lower concentrations of catalyst are used, a procedure using a low concentration of a lower reactivity comonomer can be employed to form a copolymer in the second segment.¹⁵⁰ Multifunctional initiators can also be used in the process to prepare ABA or AB-star multiarmed block copolymers.133,354



Scheme 16 Tacticity control in the presence of a Lewis acid.

Indeed, it is now possible to extend the range of monomers incorporated into a block copolymer by conducting sequential RAFT and ATRP polymerizations employing a dual functional bromoxanthate iniferter (initiator-transfer agent-terminator).¹⁵⁵ Poly(vinyl acetate)-*b*-PS, poly(vinyl acetate)-*b*-poly (methyl acrylate), and poly(vinyl acetate)-*b*-PMMA block copolymers with low polydispersity ($M_w/M_n < 1.25$) were prepared by successive RAFT polymerization and ATRP employing a bromoxanthate iniferter (initiator-transfer agent-terminator) and a single catalyst complex for both steps.

Macroinitiators can be prepared by any polymerization process including conventional RP³⁵⁵ and other controlled polymerization processes such as cationic,^{22,356–359} anionic,^{360–363} CROP,^{230,364} ROMP,^{365,366} AROP,³⁶⁷ condensation,^{283,368–371} and postmetallocene catalysis,^{194,372} as long as at least one terminal functionality is, or can be, converted to an ATRP-initiating moiety. Any type of ATRP catalyst/initiation system can be employed in the second chain extension step.³⁷³

Another method for preparation of multisegmented block copolymers has been developed based on 'click' chemistry.³⁷⁴ An example is the initial preparation of α , ω -diazido-terminated PS-*b*-PEO-*b*-PS followed by coupling with propargyl ether in DMF in the presence of a CuBr/PMDETA catalyst. The same catalyst could be used for both the formation of the first precursor block copolymer and the chain-extended multiblock copolymer as shown in Scheme 17.³⁷⁵

The strategy involves one or two chain extensions in a normal ATRP block copolymerization followed by end-group transformation³⁷⁶ and click coupling to obtain copolymers with up to 25 polymer segments in a single chain.³⁷⁵ Formation of a product of higher MW and broader MWD was verified by triple-detection size exclusion chromatography, which revealed that typically 5–7 ABA block copolymers were linked together during the click chain extension reaction. Differential scanning calorimetry and dynamic mechanical analysis revealed that the amphiphilic ABA block copolymer behaves as a viscoelastic fluid, while its corresponding multiblock copolymer is an elastic material. This suggests that the PS domains aggregate to form physical cross-links in the swellable gel.

Zarafshani *et al.*³⁷⁷ described the use of click ligation of an amphiphilic block copolymer (AB type) and a hydrophilic homopolymer (B type) to prepare amphiphilic block

copolymers. Well-defined ω -azido functional diblock copolymer PS-*b*-poly(oligo(ethylene glycol) acrylate) (POEGA) and α -alkyne functional homopolymer POEGA were prepared using ATRP. The two polymers could be efficiently coupled to each other via copper-catalyzed azide–alkyne click chemistry in aqueous media. Moreover, using this coupling strategy, an ester group was introduced at the junction between AB and B segments. This labile moiety may be 'cut' by hydrolysis. Copper-catalyzed azide–alkyne click chemistry was also applied to postpolymerization cross-linking of a block copolymer formed by RAFT to control copolymer structure and the ability of the modified polymeric materials for subsequent self-assembly in response to changes in temperature.³⁷⁸

3.12.8 Polymer Topology

In this section, we will discuss polymers with nonlinear topology prepared by ATRP. Contribution of transfer to polymer in RP is relatively small and therefore most polymers prepared by RP are linear. However, more reactive radicals (e.g., in acrylate polymerization) can abstract hydrogen from the tertiary carbons in the backbone and introduce branching. Most branches are very short, since they are formed by intramolecular abstraction of H atoms from the penultimate unit via a six-member transition state. However, long branching also happens via intermolecular chain transfer.²²⁴

There are several methods to deliberately introduce branching to polymers prepared by ATRP. This includes various graftand comb-shaped copolymers, branched and hyperbranched structures, stars, and networks.

3.12.8.1 Graft- and Comb-Shaped (Co)polymers

Comb and graft (co)polymers belong to the general class of nonlinear polymers with randomly distributed branches and generally consist of a linear backbone of one composition and branches of a different composition. If the density of grafts in the backbone of a copolymer is sufficient, it may cause the backbone of the copolymer to adopt a chain-extended comb-shaped conformation that has been named a 'brush' copolymer (Scheme 18).²⁸⁴



Scheme 17 Preparation of a multiblock copolymer by ATRP, chain end transformation, and then click coupling/chain extension.



Scheme 18 Change in backbone conformation with increasing density of grafted chains.

Well-defined graft copolymers are most frequently prepared by either a 'grafting from' or a 'grafting through' controlled polymerization process; however, the development of click chemistry³⁷⁴ has led to a third approach based on site-specific 'grafting to' chemistry.

3.12.8.1.1 'Grafting from'

The primary requirement for a successful 'grafting from' reaction is a preformed macromolecule with distributed initiating functionality (Scheme 19).

Grafting from reactions have been conducted from polyethylene,^{194,379,380} poly(vinyl chloride),^{23,381} and polyisobutylene.³⁸² The only requirement for a multifunctional ATRP grafting from macroinitiator is that there are multiple radically transferable atoms distributed along the polymer backbone. The initiating sites can be incorporated by copolymerization,^{23,194} be an inherent part of the first polymer,³⁸¹ or be incorporated in a postpolymerization reaction.³⁸² Indeed, a prefunctionalized isobutylene rubber, commercially available from Exxon, EXXPRO 3050, has been employed in a grafting from ATRP of MMA, forming a spectrum of materials targeting a range of applications from elastomers to impact-resistant PMMA.³⁸²

3.12.8.1.2 'Grafting through'

The 'grafting through', or macromonomer method, is one of the simplest ways to synthesize graft copolymers with a well-defined backbone and well-defined side chains (SCs; Scheme 20).

When the reactivity ratios of low MW comonomers are compared in a conventional radical copolymerization and ATRP, there is little difference between the rate of incorporation of each comonomer.^{267,383} However, at higher conversion, the relative reactivity of a macromonomer decreases in the conventional radical copolymerization due to diffusion control, while in ATRP retention of a 'normal' reactivity of the macromonomer was observed. This is explained by different timescales for monomer addition leading to the absence, or a much later onset, of diffusion control in ATRP. The frequency for monomer addition is in the range of milliseconds for conventional polymerizations, whereas it is in the range of seconds to minutes in ATRP, which allows the system to reequilibrate. Accordingly, copolymerization of macromonomers is facilitated in ATRP and more regular structures are formed with incorporation of a higher mole fraction of the macromonomer. Indeed, a product prepared by ATRP was purer than that prepared by conventional radical polymerization (Figure 17) and even an anionic copolymerization of the same ingredients; in both cases ATRP incorporated a higher fraction of macromonomers.

Typically, a low MW monomer is radically copolymerized with a (meth)acrylate functionalized macromonomer (MM). This method permits incorporation of macromonomers prepared by other controlled polymerization processes into a backbone prepared by a CRP.³⁸⁴ Macromonomers such as polyethylene,^{380,385} PEO,³⁸⁶ polysiloxanes,²⁰⁸ poly(lactic acid),²⁶⁸ or polycaprolactone³⁸⁷ have been incorporated into a PS or poly (meth)acrylate backbone. This combination of controlled polymerization processes allows control of MWD, functionality,





Figure 17 2D chromatography analysis of graft copolymers prepared by a 'grafting through' reaction of same ratio of monomers and macromonomers by conventional RP (a) and ATRP (b) copolymerization. Reprinted from Roos, S.G., Muller, A.H.E. and Matyjaszewski, K. *ACS Symp. Ser.*, **2000**, *768*, 361–371,³⁸³ with permission from ACS.

copolymer composition, backbone length, branch length, and branch spacing by consideration of mole ratio of the MM in the feed and reactivity ratio of the monomer and macromonomer. Branches can be distributed homogeneously or heterogeneously based on the reactivity ratios of the terminal functional group on the macromonomer and the low MW monomer, and, as shown in the properties section, this has a significant effect on the physical properties of the materials.^{268,387}

A spontaneous gradient graft copolymer was prepared by grafting through two different PEO macromonomers.³⁸⁸ Selection of a PEO methacrylate with a methyl end-group (PEOMeMA, DP of the PEO = 23) and a PEO acrylate end-capped by a phenyl group (PEOPhA, DP of the PEO = 4) for the copolymerization led to a spontaneous gradient of PEO grafts along the copolymer backbone. The resulting copolymer

has PEOMeMA at one end of the polymer chain, gradually changing through hetero-sequences of PEOPhA at the other chain end. An amorphous-crystalline structure consisting of an amorphous PEOPhA and crystallizable PEOMeMA segments in the copolymers was demonstrated by DSC and WAXS. The mechanical properties indicated elastomeric properties in the range of a soft rubber.

3.12.8.1.3 'Grafting to'

The 'grafting onto' approach has become a more efficient method for the preparation of graft copolymers with the rise of various click chemistries and has been used for the preparation of well-defined star molecules,³⁸⁹ loosely grafted copolymers,²⁵⁶ and, as noted in the following section, densely grafted structures (Scheme 21).³⁹⁰



(u + v = y; u < u)

Scheme 21 Procedure for converting distributed glycidyl functionality for a 'click to' formation of a graft copolymer. Reprinted from Tsarevsky, N. V.; Bencherif, S. A.; Matyjaszewski, K. *Macromolecules* **2007**, *40*, 4439–4445,²⁵⁶ with permission from the ACS.

In order to prepare a copolymer suitable for 'grafting to' click chemistry, the epoxide ring in a glycidyl unit that had been incorporated into well-defined copolymers of glycidyl methacrylate (<40 mol%) and MMA prepared by ATRP was efficiently opened with sodium azide in DMF at 50 °C. This click-type functionalization reaction led to the formation of distributed units of the corresponding 1-hydroxy-2-azido functional groups in high yields. These azide-containing copolymers were functionalized in a second 'grafting to' click reaction, the room temperature CuBr/PMDETA catalyzed 1,3-dipolar cycloaddition of poly(ethylene oxide) methyl ether pentynoate to yield loosely grafted polymeric brushes with hydrophilic PEO SCs.

Another 'high-yield' chemical reaction was exploited in a synthesis of heterograft copolymers via 'grafting onto' by atom transfer nitroxide radical coupling chemistry.³⁹¹ The main chain was prepared by anionic ring-opening copolymerization of ethylene oxide (EO) and 4-glycidyloxy-2,2,6,6tetramethylpiperidine-1-oxyl (GTEMPO); then PS and poly (t-Bu acrylate) with bromine end (PS-Br, PtBA-Br) were prepared by ATRP. When the three polymers were mixed in the presence of CuBr/PMDETA at 90 °C, the formed carbon radicals at the PS and PtBA chain ends were quickly trapped by nitroxide radicals on poly(GTEMPO-co-EO). The density of GTEMPO groups on the main chain of the poly (GTEMPO-co-EO), the MW of PS/PtBA SCs, and the structure of macroradicals significantly affect the efficiency of the grafting to reaction.

3.12.8.2 Brush Macromolecules

Macromolecular brushes belong to the general class of graft copolymers. However, in the case of brushes, the grafting density is very high, at least in some segments of the copolymer, see Scheme 18. Indeed, polymers with one graft per backbone repeat unit, that is, every two carbon atoms, have been prepared by ATRP. This leads to an extremely crowded environment along the backbone which causes the macromolecules to adopt unusual conformations due to steric repulsion caused by the densely packed SCs. They force the backbone to deviate from the normal Gaussian random coil conformation into a chain-extended conformation with increased persistence length, as SC graft density increases.³⁹² The congested structure of the brushes arises because of the confined mobility of the tethered chain end of the grafted SCs. A recent review³⁹³ summarizes the characteristic physical properties of well-defined molecular brushes and the different strategies employed for their preparation, detailed below, with particular focus on synthesis via CRP techniques. The AGET ATRP of oligo(ethylene glycol) monomethyl ether methacrylate (OEOMA) was used in homogeneous aqueous solution targeting a DP = 1000, and in inverse miniemulsion targeting a DP = 600, at 30 °C for preparation of biocompatible, brush-like, high MW, water-soluble polymers. The results indicated that AGET ATRP retains all of the benefits of normal ATRP and additionally provides a facile route for the preparation of well-controlled high MW polymers because of the use of oxidatively stable catalyst precursors.³⁹⁴ Indeed synthesis of macromolecular brush copolymers takes advantage of all of the characteristics of CRP synthesis in that the MW and the composition of the backbone and attached SCs are

independently controlled. Additionally, polymer brushes can be prepared as random graft copolymers, block graft copolymers,³⁹⁵ gradient brush copolymers,^{341,342} and molecules with double-grafted SCs.³⁹⁶

3.12.8.2.1 Linear macromolecular brushes

The first step in a typical preparation of a densely grafted bottle brush macromolecule is the synthesis of a multifunctional macroinitiator or macroinitiator segment in a block or graft copolymer, with an initiating moiety on a high fraction of backbone monomer units. A brush macroinitiator has generally been prepared by ATRP of a monomer with a protected functional group, such as 2-(trimethylsilyloxy)ethyl methacrylate (HEMA-TMS), followed by cleavage of the TMS protective groups and esterification with 2-bromopropionyl bromide to yield poly(2-(2-bromopropionyloxy)ethyl methacrylate) (PBPEM).³⁹⁷ This approach to brush copolymers is shown in Scheme 22, where a multifunctional macroinitiator is prepared and used to initiate ATRP of various monomers from each repeating unit by a grafting from mechanism.

Macroinitiators with a backbone length from 50 to over 6000 monomer units have been prepared by ATRP and multiple graft chains, also via ATRP, with 20 to over 400 monomer units by grafting from. The MW of a brush macromolecule with a backbone containing 6000 monomer units and 150 *n*BA units in each grafted SC is over 10^8 . As seen in the image associated with Scheme 22, despite the congested steric environment along the polymer backbone, a brush macromolecule with a high DP of the backbone adopts a chain-extended random coil conformation when a dilute solution of the brush molecule is deposited on an adsorbing mica surface. The persistence length strongly increases, and curvature decreases, with the length of SCs.^{395,398,399}

Recently, 390,400 an efficient 'grafting to' approach has been successfully developed for the preparation of densely grafted brushes. Linear poly(2-hydroxyethyl methacrylate) (PHEMA) polymers were synthesized first by ATRP. After esterification reactions between pentynoic acid and the hydroxyl side groups, polymeric backbones with alkynyl groups on essentially every monomer unit (PHEMA-alkyne) were obtained. Five different azido-terminated polymeric SCs with different chemical composition and MW were used in the grafting to reactions, including poly(ethylene glycol)-N3 (PEG-N3), PS-N3, poly (nBA)-N3, and poly(nBA)-b-PS-N3. The grafting density of the molecular brushes obtained was affected by several factors, including the MW and the chemical structure of the linear polymers used in the grafting to reaction, as well as the initial molar ratio of linear chains to alkynyl groups. When linear polymers with 'thinner' structure and lower MW, for example, PEO-N3 with M_n = 775, were reacted with PHEMA-alkyne (DP=210) at a high molar ratio of linear chains to alkynyl groups in the backbone, brush copolymers with the highest grafting density were obtained; efficiency of grafting = 88%. This result indicates that the average number of tethered SCs was \sim 186 per brush (Scheme 23).

3.12.8.2.2 Brush copolymers with varying architecture

The use of a multifunctional initiator for the synthesis of the first macroinitiator backbone copolymer can lead to the preparation of bottle brush polymers displaying different topologies. For example, if a tetra-functional initiator is used



Scheme 22 Procedure for preparation of bottle brush copolymers and AFM image of a brush macromolecule with a backbone DP = 4000 and branch DP = 20.



Scheme 23 Densely grafted bottle brush copolymers formed by a grafting onto click reaction. Reprinted from Gao, H.; Matyjaszewski, K. J. Am. Chem. Soc. 2007, 129, 6633–6639,³⁹⁰ with permission from the ACS.

to polymerize HEMA-TMS, the resulting polymer can be functionalized to yield a four-arm macroinitiator. This product can, in turn, be used to prepare four-arm star macromolecular brushes.⁴⁰¹ Combining gradient copolymerization with macroinitiator synthesis provides access to brushes with a controlled gradient of graft density along the backbone.³⁴¹ Gradient macroinitiators can be formed by spontaneous copolymerization of monomers with different reactivity ratios or by controlled addition of one monomer to a copolymerization of monomers with relatively similar reactivity ratios.²¹¹ The final brush molecules have the appearance of tadpoles.³⁴²

Other brush architectures include core-shell block copolymers^{57,402} and diblock copolymer brushes.^{333,399,403}

3.12.8.3 (Hyper)branched Copolymers

There are several methods to deliberately introduce branching to polymers prepared by ATRP that employ two-step processes of grafting: -onto, -from, or -through. However, branches can also be introduced concurrently with controlled copolymerization. The simplest approach employs divinyl compounds with the amount of divinyl monomer lower than the initiator, which prevents formation of macroscopic gels and results in formation of branched polymers, cf. Section 3.12.8.5.404-406 The second approach uses a molecule containing both a reactive alkyl halide group suitable to initiate a ATRP and a polymerizable double bond, an 'ini'tiator/mono'mer' or 'inimer'. If an inimer is used in a copolymerization then relatively loosely branched polymers are formed while homopolymerization of inimers leads to hyperbranched polymers. ATRP inimers contain a styrene or (meth)acrylate moiety and benzyl halides and α -bromoesters, respectively.^{277,407,408} High inimer (=initiator) concentration may lead to significant termination and loss of the active catalyst. The addition of Cu(0) to the reaction medium controls the concentration of deactivator and allows the preparation of acrylate-based (hyper)branched structures.409 The inimer can contain additional functionality such as degradable unit⁴¹⁰ and can include AB₂ macromolecular inimers. Inimers⁴¹¹ and macroinimers^{412–414} suitable for click coupling have also been employed to prepare branched structures.

In the first case a self-condensing ATRP of a clickable initiator-monomer, 3-azido-2-(2-bromo-2-methylpropanoyloxy) propyl methacrylate, resulted in a hyperbranched polymer with azido and bromo groups. Subsequently, orthogonal one-pot 'grafting onto' azide–alkyne click coupling and 'grafting from' ATRP from the core of hyperbranched polymer afforded targeted miktoarm globular binary brushes. Hybrid hyperbranched polymer-grafted mesoporous silica NPs have been prepared by self-condensing ATRP of 2-((bromobutyryl)oxy) ethyl acrylate from surface-tethered initiators.^{415,416} Indeed, (2-chloro-2-alkoxycarbonyl)ethyl acrylate inimers can be polymerized with different substituents on the ester group to provide variations in the solubility of the resulting polymer.⁴¹⁷

3.12.8.4 Star Copolymers

Star polymers consist of several linear polymer chains connected at one point.⁴¹⁸ Prior to the development of CRP, star molecules prepared by anionic polymerization had been examined. However, due to the scope of ionic polymerization, the composition and functionality of the materials were limited. The compact structure and globular shape of stars provide them with low solution viscosity and the core-shell architecture facilitates entry into several applications spanning a range from thermoplastic elastomers (TPEs)⁴¹⁹ to drug carriers.⁴¹⁸

Based on the chemical compositions of the arm species, star polymers can be classified into two categories: homoarm star polymers and miktoarm (or heteroarm) star copolymers



Scheme 24 Topology of homoarm and miktoarm star copolymers. Reprinted from Gao, H.; Matyjaszewski, K. *Prog. Polym. Sci.* **2009**, *34*, 317–350,⁴⁰⁴ with permission from Elsevier.

(Scheme 24).⁴²⁰ Homoarm star polymers consist of a symmetrical structure comprising radiating arms with identical chemical composition and similar MW. In contrast, a miktoarm star molecule contains two or more arm species with different chemical compositions and/or MWs and/or different peripheral functionality. There are several approaches that can be employed for the synthesis of star copolymers by ATRP.

As illustrated in Scheme 25, star polymers can be synthesized by variations on one of three methods.

3.12.8.4.1 Core first

There are two approaches to star copolymers by the 'core-first' approach: one, where the controlled polymerization is conducted from a well-defined initiator with a known number of initiating groups,^{20,133,273,421,422} and the other, where a less well-defined multifunctional macromolecule, such as functional microgel or the hyperbranched copolymer discussed above, is used as the core of the star.^{277,423,424} Since the tethered chains in a grafting from reaction retain their terminal functionality they can be chain extended to form star block copolymers and/or the radically transferable atoms on the chain ends could be converted to other functional groups suitable for postpolymerization functionalization reactions.⁴²¹

A simple sequential polymerization of a cross-linker followed by polymerization of a monomer⁴²⁴ provides a broadly applicable approach to star copolymers, **Scheme 26**. This method belongs to the broader category of 'core-first' methodology and presents an alternative strategy for star synthesis, when compared with the traditional 'arm-first' method, in which monomer is polymerized first followed by formation of the core by (co)polymerization of a cross-linker.

3.12.8.4.2 Coupling onto

An approach that until recently had not received as much attention is the 'coupling onto' approach where a functional linear molecule is reacted with a preformed core molecule, containing complementary functionality.^{389,404,425,426} A highly efficient organic coupling reaction is required, such as those described as click reactions,³⁷⁴ in order to improve the coupling efficiency. The preparation of stars using click chemistry could be applied to almost any of the strategies discussed in this chapter.⁴²⁵

3.12.8.4.3 Arm first

There are two approaches to the 'arm-first' synthesis of star polymers.^{225,427–429} One is where a linear 'living' copolymer chain, or added macroinitiator, is linked by continuing copolymerization of the monofunctional macroinitiator with a divinyl monomer forming a cross-linked core.²²⁵ Initially, the simple chain extension of a linear macroinitiator with a



Scheme 25 Approaches used for the synthesis of star copolymers. Reprinted from Gao, H.; Min, K.; Matyjaszewski, K. *Macromol. Chem. Phys.* 2007, 208, 1370–1378,³⁸⁹ with permission from Wiley-VHC.



Scheme 26 Preparation of a star block copolymer in a continuous fashion. Reprinted from Gao, H.; Matyjaszewski, K. *Macromolecules* **2008**, *41*, 1118–1125,⁴²⁴ with permission from the ACS.

cross-linker provided star macromolecules with high dispersity as a result of star–star coupling reactions. However, detailed studies carried out on the coupling of monofunctional PSs and polyacrylates with divinylbenzene (DVB) and di(meth)acrylates to prepare star polymers provided the following guidelines:^{430,431}

- The ratio of difunctional reagent to growing chains is optimal in the range of 10–20.
- Monomer conversion (or reaction time) has to be controlled and stopped before star-star coupling occurs. Approximately 5% of arms cannot be incorporated into the star macromolecules under typical one-step conditions.
- Higher yields of stars are observed for polyacrylates than for PSs. This may be attributed to a lower proportion of terminated chains (due to faster propagation and lower concentration of radicals) in acrylate polymerization under 'standard' ATRP conditions.
- The choice of the difunctional reagent is important and reactivity should be similar to or lower than that of the arm-building monomers.
- Halogen exchange slightly improves the efficiency of star formation.
- Solvent, temperature, and catalyst concentration should be also optimized.

Note, however, that the arm-first star synthesis using a macroinitiator synthesized by ATRP could be significantly improved by using ARGET ATRP when compared with normal ATRP for the core-forming reaction. Not only was less catalyst used, but stars were also prepared in essentially quantitative yield (98%) and with higher MW. Additional improvements can be obtained by applying slow feeding of the reducing agent to the reaction mixture.⁴³²

The second approach is the copolymerization of a macromonomer with a divinyl monomer in the presence of a low MW initiator.^{430,431} The sequential addition of initiator and cross-linker to the reaction increases the number of macromonomer units incorporated into each star.⁴³³

A combination of 'arm-first' and 'core-first' methods is particularly useful for synthesis of miktoarm star copolymers. One employs the retained initiating functionality in the formed 'arm-first' core to initiate the polymerization of a second monomer in a 'grafting out' or a 'grafting from' copolymerization.^{420,434-437} The efficiency of initiation of the second set of arms depends on the compactness of the first formed core. Less densely cross-linked cores provide more efficient initiation for the grafting from polymerization.437 Normally, one seeks to form a chemically stable core; however, it is possible to select a cross-linking agent with a degradable link between the two functional cross-linking groups and prepare a material with a degradable core. This was accomplished by linking the first formed arms with a dimethacrylate cross-linker containing a disulfide link between the methacrylate units. The miktoarm star copolymer could be degraded in a reducing environment to form a mixture of an AB block copolymer and some residual A-homopolymer. The ratio between the block copolymer and homopolymer gave a direct measurement of the initiating efficiency of the constrained core-initiating units in the range of 5-50%.436

Another strategy for synthesis of miktoarm star copolymers, with potentially any desired molar ratio and composition of the arms, uses a simple and general 'arm-first' method, that is, one-pot ATRP cross-linking a mixture of different linear macroinitiators and/or macromonomers with a divinyl cross-linker.^{433,438}

Well-defined star macromolecules with narrow MWD can be formed in high yield in dispersed media by copolymerizing macromonomers with a divinyl cross-linking agent using standard free radical initiators.⁴³⁹ Higher yields and larger stars can be prepared under heterogeneous conditions where amphiphilic reactive block copolymers (reactive surfactants) can be preassembled into micelles and then converted to stars by copolymerization with divinyl monomers.⁴⁴⁰

3.12.8.5 Networks/Gels

The concurrent copolymerization of a monomer and higher concentrations of a divinyl cross-linker using ATRP generate branched copolymers and/or networks/gels. The dependence of experimental gel points on various parameters, including the molar ratio of cross-linker to initiator, the concentrations of reagents, the structures of monomer and cross-linker, and the reactivity of the vinyl groups present in the cross-linker and monomer, was systematically studied,⁴⁴¹⁻⁴⁴³ and, as shown in **Scheme 27**, the timing of the addition of the cross-linker and monomer controlled the architecture of the final material.

The topology of copolymer networks prepared in a one-batch concurrent copolymerization of a monomer and a cross-linker can be viewed as an extension of the sequential copolymerization reactions for arm-first and core-first strategies for synthesis of star copolymers. Topologies depend on when the cross-linker is incorporated into the copolymerization and the reactivity of each vinyl group in the cross-linker. In the presence of an appropriate mole fraction of cross-linker, the MW and/or size of the branched polymers increases exponentially with the progress of intermolecular cross-linking reactions and finally reaches an 'infinite' value with the formation of a polymeric network, a gel. The transition from a viscous liquid containing hyperbranched macromolecules, a sol, to an elastic gel is defined as the 'gel point'.

The properties of gels prepared by conventional RP and ATRP differ. Highly branched polymers and/or gels with inhomogeneous structures are formed during most conventional RP reactions because of slow initiation, fast chain growth, and exclusive radical termination reactions. A consequence of the extremely low polymer concentration at the beginning of the copolymerization in a standard RP is that polymer chains seldom overlap and many pendant vinyl groups, ~50%, are consumed via intramolecular cyclization reactions, ultimately producing highly cross-linked nanogels, see Scheme 28. As the reaction proceeds, the number of these nanogels increases and consequently, the radicals generated later in the reaction connect these preformed overlapped nanogels into large molecules and form a heterogeneous gel network.

In contrast to the conventional RP technique, ATRP has several advantages when targeting more homogeneous polymer networks, due to fast initiation and slow steady growth of all chains. Fast initiation results in rapid conversion of all initiators into primary chains and a nearly constant number of growing primary chains throughout the polymerization, **Scheme 29**. Therefore, the concentration of primary chains in






Scheme 28 Differences between RP and CRP gelation process. Reprinted from Gao, H.; Matyjaszewski, K. *Prog. Polym. Sci.* 2009, *34*, 317–350, ⁴⁰⁴ with permission from Elsevier.



Scheme 29 Illustration of chain growth and gelation process by copolymerization of monomer (M) and divinyl cross-linker (X) using ATRP with fast initiation. Reprinted from Li, W.; Gao, H.; Matyjaszewski, K. *Macromolecules* **2009**, *42*, 927–932,⁴⁴¹ with permission from the ACS.

a well-controlled ATRP is similar to the concentration of added initiators throughout the polymerization.

The relatively long 'dormant' periods, when the polymer chains cannot propagate, ensure that the chains can diffuse and relax. Thus, ATRP results in a more homogeneous incorporation of branching points into the soluble branched copolymers and a more regular network structure within the insoluble gels, compared with polymers made by conventional RP methods from copolymerizations starting with similar concentrations of comonomers.^{405,444,445} The experimental results indicate that during the chain propagation and branching process, linear primary chains coexist with branched polymers in the sols. Even after gelation, linear polymer chains and branched macromolecules could still be detected in the sols by GPC.

The observed gel points depend on the ratio of incorporated cross-linker to that of the initiator, that is, reactivity of cross-linker and initiation efficiency, as well as on the dispersity of the primary chains (Figure 18).^{447–450} Decreasing the copper concentration from tens of ppm to a few ppm broadened the MWD of the initial primary chains, which resulted in an earlier

gelation at lower monomer conversion.⁴⁴¹ Functionality of cross-linker also affects gelation.⁴⁵¹

As noted above the gel materials synthesized by ATRP have a more homogeneous network structure than those prepared by RP. The inhomogeneity of the gels prepared by RP was confirmed when cross-linkers containing a degradable unit between the vinyl units were used to prepare gels by conventional RP and ATRP. The latter were degraded while the gels prepared by RP were not degraded under similar conditions (Table 1).³²⁷

Conducting gel-forming reactions in heterogeneous systems can lead to the formation of nanogels.³²⁷ Another property of

 Table 1
 Degradability of gels prepared by FRP and CRP

	Swelling Ratio in				
	THF	Toluene	Water	Mn	M _w /M _n
FRP nanogels ATRP nanogels	13.1 21.3	13.1 19.6	16.2 28.5	Not degraded 74	1.5



Figure 18 Change in GPC curves as polymer transitions from a hyperbranched structure to a gel with increasing conversion. Reprinted from Gao, H.; Min, K.; Matyjaszewski, K. *Macromolecules* **2007**, *40*, 7763–7770, ⁴⁴⁶ with permission from the ACS.

gels and nanogels prepared by ATRP is preservation of chain end functionality. Therefore, ATRP gels can be further chain extended forming block structures⁴⁵² or hairy NPs.⁴⁵³

3.12.9 Site-Specific Functionality

Functional groups increase the utility of polymers and are fundamental to the development of many aspects of structure–property relationships. The functionality present on the monomer units determines the solubility of the polymer in a given solvent as well as thermal and mechanical properties. One can control the hydrophilicity/hydrophobicity, or polarity of a copolymer, and the elasticity or modulus of a material by selecting appropriate monomers. Examples of functional polymers are shown in Scheme 30.

Four synthetic strategies can be employed for the synthesis of well-defined polymers with site-specific functional groups using ATRP:⁷⁴

- 1. direct polymerization of functional monomers,
- 2. postpolymerization modification of a polymer,
- 3. use of functional ATRP initiators,
- 4. end-group transformation chemistry.

These approaches are summarized in Scheme 31.

3.12.9.1 Polymerization of Functional Monomers

The advantage of direct copolymerization of functional monomers in an ATRP is the direct incorporation of functional groups into the polymer backbone and the resulting absence of a need for postpolymerization modification. The degree of functionality and the arrangement of the functional units depend on (co)polymer architecture. There is a plethora of monomers containing polar functional groups that have been successfully polymerized by ATRP, see **Scheme 9** for examples of a few functional methacrylates. ATRP catalysts with strongly binding ligands should be used for copolymerization of monomers containing certain functional groups to avoid, or reduce, competitive complex formation between the monomer or polymer and the copper center, mostly substituted amides, amines, or pyridines.¹⁰⁶ The ATRP of several types of polar monomers, particularly acidic ones, has proved quite challenging, although progress continues to be made.^{106,455–457}

3.12.9.2 Postpolymerization Modification of Incorporated Monomer Units

The primary advantages of postpolymerization functionalization procedures are the ability to incorporate functionality incompatible with the polymerization process and also to provide the freedom to characterize the initial copolymer prior to further functionalization. Postpolymerization modification has been used to facilitate 'grafting to' or 'grafting from' reactions. Postpolymerization modification of incorporated monomer units focuses on two types of reactions. One is the removal of protecting groups when monomers with desired functionality are incompatible with one or more components of the selected polymerization process. The monomers are polymerized with a protected functional group that is subsequently deprotected to provide the desired functionality after the reaction is complete. Examples include acidic monomers such as (meth)acrylic acid, isomeric vinylbenzoic acids, or unsaturated sulfonic or phosphonic acids that protonate and therefore 'destroy' the transition metal complexes with N-based ligands typically used as ATRP catalysts. Although some moderately successful attempts have been made to polymerize MAA by ATRP,⁴⁵⁸ in general, protected acids are the preferred approach; examples of protective groups include *t*-Bu^{459,460} for acrylic acid functionality or the TMS group frequently used as a protective group for OH groups.²⁵³ Poly(glycidyl acrylate) copolymers can be prepared by ATRP to serve as a precursor of functional polymers, since the pendant glycidyl group can react with nucleophiles and







Scheme 31 Approaches to site-specific functionalization of copolymers. Reprinted from Tsarevsky, N. V.; Matyjaszewski, K. *ACS Symp. Ser.* **2006**, *937*, 79–94, ⁴⁵⁴ with permission from the ACS.

thereby serve as a precursor of a range of functional polymers, Scheme 32.²⁵⁶

3.12.9.3 Use of Functional ATRP Initiators

One of the advantages of functional initiators is direct incorporation of functional groups into the termini of the (co) polymer without the need for postpolymerization modification. The procedure directly yields telechelic polymers with preselected α -functionality. It is applicable to multiple protected and unprotected functionalities.

A few examples of functional initiators used in ATRP are shown in Table $2.^{74}$

3.12.9.4 End-Group Transformation

Advantages of end-group transformation include the ability to incorporate functionality incompatible with the polymerization procedure, to prepare halogen-free materials for subsequent reactive processing, to allow characterization of the initial copolymer prior to further functionalization, and an ability to prepare ω - and α, ω -telechelic polymers, block copolymers, and materials that can be immobilized to surfaces, by a full range of substitution and addition chemistry. The use of a difunctional initiator allowed for the first time in a radical process preparation of functional homo-telechelic polymers with almost any desired chain end functionality (Scheme 33).²⁷⁹



Scheme 32 Some examples of conversion of incorporated glycidyl functionality into other useful functional groups.

Initiator		Conv.	M _{n,SEC}	M _w /M _n
NC-Ph-CH ₂ -Br	4-Cyanobenzyl bromide	0.48	5500	1.10
Br-Ph-CH ₂ -Br	4-Bromobenzyl bromide	0.48	4500	1.16
CH ₃ -CH(CN)-Br CN-CH ₂ -Br	2-Bromopropionitrile Bromoacetonitrile	0.48 0.48	5100 4500	1.09 1.10
o → Br	Glycidol 2-bromopropionate	0.62	6800	1.12
D Br	tert-Butyl 2-bromopropionate	0.41	4000	1.17
HO O Br	Hydroxyethyl 2-bromopropionate	0.48	7500	1.10
CI	Vinyl chloroacetate	0.94	5800	1.12
O CI	Allyl chloroacetate	0.14	2600	1.77
Br	α-Bromo butyrolactone	0.41	4000	1.17
H ₂ N CI	2-Chloroacetamide	0.12	4000	1.51

Table 2	Some functional in	nitiators used ir	ATRP of sty	rene ²⁹¹
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An early example is the reaction of halogen-capped polymers with sodium azide.^{461–463} A diazido-terminated PS prepared in this way could be further reduced with tri(*n*-butyl)phosphine in THF in the presence of water (moisture) to yield a well-defined diamino-terminated polymer that, in turn, could be used in a step-growth process with terephthaloyl chloride, leading to polyamides with controlled-length PS segments.⁴⁶² The expansion of the ability to synthesize new materials by combining click chemistry and ATRP has been reviewed.^{375,464,465}

Azido-terminated polymers can also be used in click chemistry modifications with acetylene derivatives to incorporate various functional groups. Polymers with phosphonium end-groups were prepared from bromine-terminated PS or polyacrylates and Bu₃P.⁴⁶³ Mercapto-terminated PS was prepared by the reaction of the corresponding bromo-compound with either thiodimethylformamide or thiourea followed by reaction with a nucleophile.⁴⁶⁶

3.12.10 Hybrid Materials

In this section various hybrid materials will be discussed. We start with 'mechanistic' hybrids, prepared by transformation of end-groups in polymers prepared by non-ATRP techniques to ATRP macroinitiators (or vice versa).⁴⁶⁷ Then we cover organic–inorganic hybrids in which ATRP polymers are attached to various inorganic substrates.²⁶ Finally some examples of hybrids between natural products and ATRP polymers (bioconjugates) are presented.^{77,79,81–83,468–470}

3.12.10.1 Segmented Copolymers by Mechanistic Transformation

As discussed in the section on linear segmented copolymers, macroinitiators for an ATRP can be prepared by any polymerization process and the resulting copolymer can incorporate segments of almost any desired composition. Exemplary materials containing inorganic polymers are block and graft copolymers with poly(dimethylsiloxane) (PDMS) segments which have been synthesized by sequential living anionic ring-opening of D₃ and ATRP. The living PDMS chain was quenched with dimethylchlorosilane and converted via hydrosilation to ATRP macroinitiators (a in Scheme 34) for preparation of block copolymers or macromonomers and (b) for preparation of graft copolymers.^{471–474} Graft copolymers with PDMS SCs prepared by ATRP and by conventional radical process have very different mechanical properties. Polysiloxane



Scheme 33 Postpolymerization functionalization of ω-telechelic transferable Br atoms.



Scheme 34 Procedure for preparation of polysiloxane block and graft copolymers.

block copolymers find use in topical cosmetic and personal care compositions⁴⁷⁵ in addition to elastomer applications.

3.12.10.2 Brushes Attached to Surfaces

3.12.10.2.1 Flat surfaces

Modification of surfaces with thin polymer films can be used to tailor the surface properties such as hydrophilicity/phobicity, biocompatibility, adhesion, adsorption, corrosion resistance, and friction.^{470,476–480} Nanoscale organization of the functional surface can be directed by photolithography and microand nanoscale printing.^{481,482} The chemical nature of the underlying material becomes hidden by the presence of a film a few nm thick. The interaction of the whole system with the surrounding environment is governed by these coatings. The preparation of block copolymer brushes using a 'grafting from' ATRP approach was first accomplished by tethering PS-*block*-poly(*t*-butyl acrylate) (pSt-*b*-*pt*BA) to Si wafers.²⁸⁵ Hydrolysis of the *t*-butyl groups yielded a PS-*block*-poly(acrylic acid) brush, demonstrating a versatile approach to tune film properties and hydrophilicity. The concentration of initiating groups on the surface can be adjusted by varying the molar ratio between two chlorosilanes (one containing an active initiator functionality and the other a 'dummy' initiator), each attached through silanol groups to the surface of silicon wafers. For oxidized wafer surfaces, chlorotrimethylsilane was used as a 'dummy' initiator and 1-(chlorodimethylsilyl)propyl 2-bromoisobutyrate as an active ATRP initiator.

One advantage of ATRP for the preparation of surface-modified hybrid materials is the ease with which

targeted substrates can be functionalized using commercially available or easily synthesized functional α-haloesters or benzyl halides.⁴⁸³ Functional ATRP initiators have been successfully tethered to both organic and inorganic materials with either flat,⁴⁸⁴ concave,^{485,486} or convex²⁸⁶ surfaces. Each of these systems can lead to materials with a unique set of properties that are strongly affected by grafting density.⁴⁸⁷ As a result, well-defined flat surfaces and polymer brushes tethered to spherical particles of varying composition and dimensions have been synthesized by ATRP of organic vinyl monomers from various surfaces⁴⁸⁸⁻⁴⁹⁰ and colloidal particles.^{286,491-494} Control over the DP of each tethered segment, as well as the functionality of the selected monomers enabled precise engineering of both surface properties, 476,495 colloidal composite structures, 496 and hence the properties of the resulting hybrid nanostructures.497,498

Since the concentration of attached surface initiators is low it is almost impossible to generate the PRE based on initiatorinitiator termination reactions and either a sacrificial initiator has to be added or a fraction of Cu(II)-based catalyst complex should be added to provide control over the polymerization process.²⁸⁵ A kinetic model showed, through modeling, that adding deactivator provides better control over polymer MW and a thicker graft layer than added free initiator under similar conditions.⁴⁹⁹

There are several factors determining the structure of the polymer layer tethered to a flat surface. One is anchor distance or distribution of the tethering sites on the surface⁵⁰⁰ and another is polymer MW. A higher grafting density can be attained in a 'grafting from' reaction than from a 'grafting to' reaction as a consequence of the congested nature of tethered chains as the graft density increases. In a 'grafting from' reaction the only requirement is to tether an initiator to the surface through a complementary functional group. When a silicon surface is targeted this is accomplished either by using a substituted trichlorosilane⁵⁰¹ or coupling of an ω -unsaturated alkyl ester to the Si-H surface under UV irradiation.⁵⁰² An inherent,⁵⁰³ or formed, hydroxyl group⁵⁰⁴ can be employed in a reaction with 2-bromopropionyl or 2-bromoisobutyryl bromide to attach ATRP initiator moieties to either a flat or a spherical surface. The topic of modification of surfaces with silane coupling agents, which play a vital role in the functionalization of material surfaces by providing the crucial immobilized initiators for surface-initiated controlled polymerization processes, has recently been reviewed. 300,505

Sulfur/Au bonds can be used to tether an initiator^{484,506} or a formed polymer chain⁵⁰⁷ to a gold surface. When the concentration of the initiator was varied and monomers with substituents of varying bulk, oligo(ethylene glycol) methacrylates, were grafted from the surface it was determined that there was a limiting graft chain density based on the bulk of the monomer.⁵⁰⁸ However, this formed bond is not very stable and if a permanent structure is required then a stable network can be formed to protect the surface-tethered functionality.⁵⁰⁹ Direct C–C bonds can be formed from copolymer chains containing a radical-forming functional group in a 'grafting to' reaction.

In a variation of the 'grafting to' procedure, a block copolymer can be prepared to tether a desired polymer segment to a selected surface. One segment is selected to impart the predetermined functionality to a target surface and at least one second segment including functional groups selected to interact with the targeted surface can be employed to attach the block copolymer to the surface.⁶⁰ A similar approach has been taken to attach ATRP initiators to a surface.^{510,511} Indeed many surface-responsive polymer layers have been tethered to a solid surface including block brush copolymers, miktobrush copolymers, and ionic and zwitterionic brushes that are responsive to temperature,⁵¹² pH,⁵¹³ light,⁵¹⁴ and properties of contacting solutions.^{501,515-518}

The physical properties of solid surfaces can be controlled by the graft density of the tethered chains⁴⁸⁷ and by composition of the tethered chains.⁵¹⁹ The former provides improved compressibility while the latter can provide nonfouling surfaces that exhibit high protein resistance over a wide range of ionic strengths and are more effective than zwitterionic self-assembled monolayers. Environmentally benign zwitterionic polymers and coatings provide effective resistance to marine fouling.⁵²⁰ Bioresponsive surfaces have been the topic of several articles.^{470,490,521} Topics of interest include tailoring surface properties to provide improved biocompatibility and lubrication for artificial joints; indeed improved lubricity is desirable for several applications.^{490,522,523}

3.12.10.2.2 Brushes tethered to spherical particles

The functionalization of the surfaces of many solids, including silica (SiO₂), gold, silver, germanium, PbS, carbon black, iron oxides, and other metal oxide systems, has been achieved. This allowed for subsequent attachment of initiators for the ATRP of many monomers forming organic/inorganic hybrid NPs containing an inorganic core and tethered glassy or rubbery homopolymers or copolymers. The consequences of radical-radical termination reactions are more serious during the preparation of colloidal particles than in a normal ATRP. In traditional ATRP, termination reactions lead to linear chain-linear chain coupling whereas with a particle with ~1000 initiation sites coupling quickly leads to cross-linking and gelation is predicted at 0.1% interparticle coupling (Scheme 35).

Gelation was initially avoided by running the reaction to low conversion under high-dilution conditions, that is, under conditions where there is a low concentration of active radicals and hence lower probability of coupling but consequently slow propagation.⁴⁹² Examples of successful synthesis of hybrid NPs using multifunctional silica initiators in a miniemulsion ATRP were recently disclosed. The reaction was driven to higher conversion in a shorter time⁵²⁴ as a consequence of compartmentalization and/or by the addition of sacrificial initiator.⁴⁹⁶

The miniemulsion procedure has also been extended to functionalizing cadmium sulfide (CdS) quantum dots (QDs) with poly(nBA) using AGET ATRP.⁵²⁵ The QDs were first modified by complexation with a phosphorous-containing ligand, which was then further modified to incorporate an ATRP-initiating group. Bromine-containing functionalities degraded the QDs, but a chlorine-functionalized initiating group slowed the degradation sufficiently so that 3–4 nm QDs were obtained. The polymerization of nBA further protected the QDs from degradation, and the resulting materials were well-distributed on the nanoscale and possessed the optical properties expected from QDs of their size.



Scheme 35 Gelation as a consequence of interparticle termination reactions.

A one-pot synthesis of thermally stable core/shell gold NPs (Au-NPs) was developed via surface-initiated ATRP of BA and a dimethacrylate-based cross-linker (Scheme 36).⁵⁰⁹ The higher reactivity of the methacrylate cross-linker enabled the formation of a thin cross-linked polymer shell around the surface of the Au-NP before the growth of linear polymer chains from the shell. The cross-linked polymer shell served as a robust protective layer that prevented the dissociation of linear polymer brushes from the surfaces of Au-NPs and provided excellent thermal stability to the Au-NPs at elevated temperature (e.g., 110 °C for 24 h).

Materials suitable for use in novel chromatographic packing and adsorbents with custom-tailored surface properties and improved stability were prepared by grafting from inorganic particles.^{526,527} The composition and MW of the tethered polymers can be controlled to suppress the scattering of inorganic NP inclusions within organic embedding media. Suppression takes place by means of appropriate surface modification to match the effective refractive index of the resulting core-shell particle to the refractive index of the embedding medium.⁴⁹⁷ Control over the MW of the tethered chains can result in the formation of flexible PS-based composite structures in which chain entanglement gives rise to fracture through a polymer-like crazing process that dramatically increases the toughness and flexibility of the particle assembly.⁵²⁸

3.12.10.2.3 Brushes from concave surfaces

Grafting monodisperse polymer chains from concave surfaces, such as ordered mesoporous silicas,⁴⁸⁵ provides a procedure to modify the internal environment of porous inorganic substrates by introduction of thin layers of organic groups of controlled thickness and composition.^{485,529} In a 'grafting from' polymerization of AN there is a gradual decrease in pore diameter with the increase in the PAN content and an increase in the MW with polymerization time. Pore blocking was observed only for the polymer content that approximately corresponded to the complete filling of the pores with PAN.

3.12.10.3 Carbon Nanostructures

Recently, a novel route to well-defined nanostructured carbon materials based on the pyrolysis of PAN block copolymer precursors containing a sacrificial block (e.g., poly(nBA)) was developed.^{247,530} The structure of the final carbon nanostructure is templated by the initial structure of the PAN domains in the phase-separated block copolymer. The PAN domains are stabilized by heating to 280 °C in the presence of air and subsequently pyrolyzed by heating to 600–900 °C in an inert environment. This converts the PAN domains into partially graphitic carbon, whereas the sacrificial phase is volatilized. Stabilization therefore allows the PAN domains to retain their phase-separated nanostructure throughout the subsequent thermal treatment.

The carbon nanostructures are expected to find application in photovoltaics, field emitters, and supercapacitors.⁵³⁰

The spectrum of carbon structures that can be prepared from PAN segmented copolymers can span the continuum from carbon NPs, prepared from water-soluble shell cross-linked micelles with a PAN core,⁵³¹ through lamellar structures⁵³² to porous carbon structures.^{289,485,533,534}

Block copolymers normally self-assemble into structures with short-range order, but when precursor films, shown in **Scheme 37**, were prepared by zone-casting^{535,536} they displayed long-range order. The ordered lamellae were perpendicular to the substrate and casting direction. Upon thermal stabilization and carbonization, the precursors were converted into anisotropic carbon with long-range order.⁵³²

Nanoporous carbon with high surface area was prepared by conducting a grafting from polymerization of AN or SAN from the surface of silica NPs by ATRP.⁵³⁷ The (PAN)-grafted silica NPs were cast into a film, stabilized, carbonized, and then etched to form highly nanoporous carbon films with large specific surface area. The TEM images clearly show that a well-structured material was prepared.^{289,532,533,538} When (PAN)-grafted SiO₂ NPs were used as the carbon source template preoxidation, carbonization, and silica removal



Scheme 36 Formation of stable gold/polymer NPs. Reprinted from Dong, H.; Zhu, M.; Yoon Jeong, A.; et al. J. Am. Chem. Soc. 2008, 130, 12852–12853,⁵⁰⁹ with permission from the ACS.



Scheme 37 Formation of carbon nanostructures from phase-separated block copolymers.

from the carbon/silica composite formed spherical mesopores within the carbon, while at the same time, the loss of thermally decomposable styrene units leads to the formation of numerous micropores during preoxidation and carbonization.⁵³⁷

Well-defined carbon structures were also prepared from densely grafted bottle brush molecules with PAN di-(AB) and triblock-(ABC) copolymer SCs.⁵³² Thin films of the SC brushes were prepared by drop casting aqueous solutions onto clean silicon wafer substrates. After thermal treatment, the SC brush precursors were converted into nanostructured carbon. AFM images of the resulting films revealed a surface with characteristic round protrusions and roughness of 4.0 nm.

Carbon nanostructures derived from PAN precursors contain up to 7% nitrogen, which may affect electronic properties. Poly(vinylacetylene) is a polymer that structurally resembles PAN without an inherent nitrogen group and could possess the potential to form similar nanostructured carbon materials without the presence of preformed n-type dopants. Therefore, poly(vinylacetylene) block copolymers were prepared and evaluated as carbon precursors.⁵³⁹ The active acetylenic hydrogen atom in vinylacetylene was substituted with the trimethylsilyl group in order to prevent 1,4-polymerization and Cu(I)-catalyzed coupling reactions and provided a well-controlled homopolymerization using ATRP. Block copolymers were prepared via ARGET ATRP using PMMA macroinitiators.

PS cross-linked under UV irradiation pyrolyzed at elevated temperatures results in semi-graphitic carbon materials. Both amphiphilic block copolymers that micellize in water (PEO-*b*-PS) and brushes with PMMA backbones and PS-*b*-PAA SCs were used to template these nanocarbon structures.⁵⁴⁰ Well-defined nanostructured carbon was prepared by pyrolysis of core cross-linked micelles formed from block copolymers containing PS segments.

3.12.10.4 Bioconjugates

The field of polymer bioconjugation (i.e., covalent attachment of synthetic polymers to biological entities such as nucleic acids, oligopeptides, proteins, enzymes, carbohydrates, viruses, or cells) has evolved rapidly during the last decade.⁵⁴¹ Polymer bioconjugates were initially developed by biochemists and had been exclusively studied for biomedical applications. However, within the last few years the utility of this novel class of macromolecules has expanded and they are being examined in many emerging areas of materials science.^{76,77,81} Procedures for preparing such bioconjugates include preparation of functional telechelic polymers for direct attachment to the target bioresponsive molecule⁵⁴² or transformation of terminal groups on polymers prepared by ATRP for subsequent click reactions.^{79,464,543} The reverse approach is functionalization of a targeted bioresponsive molecule with an initiator for an ATRP followed by tethering a copolymer of desired composition and MW. 80,83,544,545 Composite structures prepared by this route include synthesis of near-uniform protein-polymer conjugates by initiating ATRP of monomethoxy PEG-methacrylate from 2-bromoisobutyramide derivatives of chymotrypsin (a protein initiator).⁵⁴⁶ Polymerization initiated from the green fluorescent protein genetically modified at position 134 with incorporation of an ATRP initiator resulted in the formation of a conjugate containing a single well-defined polymer chain per protein molecule with high MW.⁸³ Increasing the number of conjugated 2-bromoisobutyramide initiators per molecule of protein increased the MW and M_w/M_p of the final protein-polymer conjugates. The generic nature of this technique was demonstrated by initiating polymerization of nonionic, cationic, and anionic monomers from the protein initiator. Protein-polymer conjugates synthesized by this novel technique retained 50-86% of the original enzyme activity. The technique described therein should be useful in synthesizing well-defined protein-polymer conjugates exhibiting a wide range of physical and chemical properties.

Functional NPs have also been conjugated with bioresponsive molecules.⁵⁴⁷ The synthetic procedure involved combining surface-initiated polymerization from magnetic NPs with subsequent conjugation of the biologically active molecule-generated materials. The products exhibited good separation capability and binding specificity for biomolecules. Polymeric shells of nonbiofouling poly(oligo(ethylene glycol) methacrylate) were initially introduced onto the surface of magnetic NPs by surface-initiated ATRP. This step was followed by successful postfunctionalization via activation of the polymeric shells and bioconjugation of biotin. The resulting hybrids showed a biospecific binding property for streptavidin and could be separated by magnet capture.

3.12.11 Applications

Innumerable segmented copolymers with novel compositions in each segment have been prepared using ATRP procedures. The following discussion focuses on a few examples that show properties significantly different from the properties of materials that could be prepared before 1995. Indeed, it is now possible to obtain commercially available libraries of up to 25 well-defined block copolymers for evaluation in a range of targeted applications.¹⁸² In this section we discuss some existing and potential applications of materials prepared by ATRP, often referring to patent literature.

3.12.11.1 Thermoplastic Elastomers

The first class of block copolymers that will be discussed are polar thermoplastic elastomers (TPEs) whose synthesis became much simpler with the development of ATRP^{84,280,548} and even more commercially viable with the development of a continuous bulk ATRP process⁵⁴⁹ or the *ab initio* emulsion system that allows sequential addition of monomers to an ongoing emulsion ATRP.⁹⁷ The major benefit of polar TPEs is that they are oil resistant and recyclable, that is, it is possible to injection mold the materials and minimize waste by immediately recycling sprues and runners in addition to providing long-term recyclability. The potential market for such materials was estimated to be \$2.7 billion yr⁻¹ market.¹²¹ Polar TPEs are materials that are resistant to hydrocarbon solvents (i.e., fuels). TPEs provide the softness, flexibility, and resilience of elastomers with the processability of thermoplastics. In ATRP one can select the monomers to provide a spectrum of properties unattainable from materials prepared with ionic-based procedures while retaining the possibility of incorporating mid-blocks prepared by other procedures.^{356,467} TPEs can be synthesized in a one-pot process using ARGET: for example, PS-PEA-PS and PMMA-PBA-PMMA TPEs were made using such a process.⁵⁴⁹

Since multifunctional initiators are easily prepared, other nonlinear architectures can be considered, for example, star blocks, grafts, and brushes with block SCs, since polymer topology affects properties.550 Recently published data on the properties of PBA-b-PAN three-arm star block copolymers^{551,552} show that these polar materials with easily adjustable properties, based on composition, retain their useful properties over a broad temperature range: -50 to +270 °C. Samples are glassy below the $T_{\rm g}$ of PBA (~-50 °C), with $G' \sim \text{GPa.}$ Above the T_g of PBA, the materials remain elastic with a G' plateau extending up to the softening temperature of PAN (~100 °C). The height of the plateau depends on the PAN content: $G' \sim 0.1$ MPa when PAN fraction < 0.1 and $G' \sim 100$ MPa when PAN fraction is 0.3. Above the softening temperature of the PAN block the material remains elastic with a lower G' plateau (0.1-1 MPa) extending up to a temperature of ~270 °C.

The sample with only 6% PAN exhibits nearly ideal elastic behavior: no residual strains after unloading. Note that similar materials are used as precursors for nanostructured carbons.⁵⁵¹

Multiarm star materials (10–20 arms) with an inner soft PBA block and outer hard PMMA were prepared and the properties of these potential elastomers evaluated.⁵⁵³ The tensile strength of the star-like copolymers was considerably higher compared with linear and three-arm stars with similar composition.⁵⁵³

TPEs have also been prepared by 'grafting from' linear macroinitiators prepared by non-ATRP procedures including polyethylene,⁵⁵⁴ polyisobutylene,³⁸² poly(epichlorohydrine-*co*-ethylene oxide) elastomer⁵⁵⁵ or natural rubber and/or a synthetic diene rubber⁵⁵⁶ backbones.

3.12.11.2 Supersoft Elastomers

Elastomers typically have a Young's modulus (at small strains) in the order of 10⁶ Pa, with reversible extensibility reaching 1000%. They are approximately 4 orders of magnitude softer and 3 orders of magnitude more deformable than typical solids. Weakly cross-linked rubbers preserve the modulus of the rubbery plateau seen for the melt of linear entangled polymers, that is, M_c remains similar to the order of M_{el} whereas for highly cross-linked systems the modulus increases. It is not easy to move in the opposite direction and prepare stable soft rubbers, that is, rubbers with a modulus lower than the bulk plateau modulus of a given polymer. However, the plateau modulus does decrease considerably in polymer solutions,⁵⁵⁷ and soft gels can be obtained by swelling weakly cross-linked systems with a good solvent for the matrix material, as water in hydrogels. One example of an application for such a material is soft contact lenses. However, these solvent swollen states are not stable in environments in which the solvent can evaporate and also appear unstable when external forces are exerted on the gel. In water-swollen networks of hydrophilic polymers (e.g., hydrogels), shear modulus on the order of 10^3 Pa can be obtained at low cross-link densities and relatively high degrees of swelling. However, higher levels of swelling result in an increase in modulus, because of strong extension of the network chains.557-559 These unusual mechanical properties that were initially observed in aqueous gels are now generated in environmentally stable bulk cross-linked polymeric bottle brush macromolecules.560 This arises because the molecular network, consisting of a network of backbone copolymers that are 'diluted' by tethered short SCs, behaves in a manner similar to a solvent swollen network. When the MW of the SCs are below the critical entanglement MW, they do not entangle but, since they are covalently attached to the network, they provide stability against evaporation or deformation, while preventing the networks from collapsing.

The first materials recognized to be precursors to a supersoft elastomer were bottle brush macromolecules with a very long backbone and densely grafted PnBA SCs. They displayed an ultra-low-modulus plateau in the soft gel range when they were transformed to a network by a low fraction of chemical cross-links, **Figure 19**. The material became a supersoft rubber³⁸⁶ that, instead of the expected global flow range, displayed a plateau in *G'* extending toward low frequency. This plateau indicates elastomeric properties for such a cross-linked polymer network. The plateau modulus is much lower than that seen for typical polymeric rubbers, which can be attributed to the large fraction of the short dangling chains in the system. Such chains provide significant mobility, making the material extremely soft. This behavior has been observed for several materials.^{560,561}

3.12.11.3 Surfactants and Dispersants

Several examples illustrate how the components of each segment in a block copolymer can be selected to give the final material a set of properties required to accomplish a specific task. Since the preparation of polymers with terminal functionality and block copolymers or segmented copolymers is 'easy' by ATRP, materials suitable as surfactants have been prepared and used in various applications including emulsion



Figure 19 (a) Dependence of storage (G') and loss (G'') modulus of a bottle brush with polymethacrylate backbone with DP = 3500 and poly(nBA) SC with DP = 30. (b) Dynamic mechanical spectra of a cross-linked sample of polymer shown in spectrum (a).

polymerization.^{562,563} One of the earliest examples of a surfactant for a specific application was molecular engineering of a surfactant for a very specific task, for example, conducting an ATRP dispersion polymerization in supercritical CO_2 .^{103,564} Another example is the synthesis and use of a poly (ε -caprolactone)-*b*-poly(octadecyl methacrylate)-*b*-poly (dimethylaminoethyl methacrylate) block/random copolymer which was designed as a surfactant in the dispersion polymerization of L,L-lactide^{367,565} to form biodegradable NPs of controlled dimensions.⁵⁶⁶ The poly(ε -caprolactone) block was prepared first by an anionic ring-opening polymerization of ε -caprolactone initiated with hydroxyethyl 2-bromoisobutyrate/tin(II) hexanoate system followed by sequential ATRP of octadecyl methacrylate and then DMAEMA.

ATRP and NMP provide an efficient route to functional copolymers with controlled architecture. They were used for the synthesis of acrylic block copolymers, which are a promising class of dispersants for difficult-to-disperse organic-based pigments.⁵⁶⁷ Structural parameters like chemical composition, block length, and MW influence the dispersant performance, in particular, the rheological properties of the dispersion. Modified block copolymers can be designed to act as disperinorganic or organic sants for pigments. Polv (nBA)-b-(2-dimethylaminoethyl acrylate) block copolymer dispersant was prepared by ATRP and then quaternized. The pigment stabilizer was useful for preparing coating compounds, prints, images, inks, or lacquers and other disperse systems.567-570

Iron NPs are a good material to use when targeting destruction of dense nonaqueous phase liquids (DNAPL), which are mainly chlorinated solvents, for example, trichloroethylene, tetrachloroethylene, or chloroform that have accumulated in aquifers. They are environmentally friendly and have a large surface area for efficient interaction with the contaminants. Their downside is that they undergo rapid flocculation in aqueous systems and have little affinity for a DNAPL/water interface. To overcome these deficiencies a series of block copolymers were designed to deliver iron NPs to DNAPL in underground reservoirs where they can destroy the DNAPL via reductive dechlorination reactions. The modified iron particles migrate to the interface between water and organic solvents.⁵⁷¹ This behavior depends on the composition of the copolymer. The resulting Pickering emulsions were stable for more than 6 months.

Environmentally benign fire retardants remain the subject of continued research efforts. Several hybrid nanocomposites consisting of a magnesium dihydroxide (MDH) core and tethered poly(meth)acrylate chains were synthesized via ATRP to exemplify a fire retardant that can be tailored to permit facile dispersion in the targeted polymer matrix, in this case for meth (acrylate) matrices.⁵⁰³

The dispersability of hybrid particles with matrix-selected graft copolymers was examined by studies on the effect of dispersing different concentrations of SiO_2 -poly(*n*BA) hybrid NPs in a poly(*n*BA) matrix. One potential drawback of reinforcing a polymer by the addition of a hybrid composite particle is a loss of transparency due to scattering from the embedded particles – a consequence of the significantly different refractive index of most inorganic materials and the organic embedding medium. A method to suppress the scattering of inorganic nanoparticle inclusions within an organic embedding media was recently presented.⁴⁹⁷ Suppression of scattering takes place by means of appropriate surface modification of the particle using ATRP such as to match the effective refractive index of the resulting core-shell particle to the refractive index of the embedding medium.

3.12.11.4 Functional Flat Surfaces

ATRP is particularly advantageous in a 'grafting from' a flat surface as the thickness of the polymer brush can be precisely controlled by systematic variation of grafting density and DP_n of the tethered polymers.^{145,572} Modification of surfaces with thin polymer films can be used to tailor the surface properties such as hydrophilicity/phobicity, biocompatibility, adhesion, adsorption, corrosion resistance, and friction. The surface properties can be tuned by the tethering of block copolymers, where the composition and DP_n of each polymer segment directly affect the morphology and behavior of the polymer brushes.⁴⁸⁷ Grafted chains in such a high-density polymer brush are highly extended in good solvent, even to their fully extended lengths. A high-density polymer brush has a different set of characteristic properties, in both swollen and dry states, quite different from those of the semidilute or moderately dense polymer brushes previously studied. A recent review highlights the developments in surface-initiated LRP and the structures, properties, and potential applications of high-density polymer brushes.⁴⁷⁶

Polymers can be designed for self-tethering to a contacting surface. Block copolymers bearing phosphate and/or phosphonate functions can function as adhesion promoters or as protecting agents in paints or mastic compositions to ensure or promote the adhesion of the copolymer to a metallic surface and protect the surface against corrosion. Solutions containing a substantially water-soluble silicone-containing surfactant are retained on the surface of an unused contact lens for extended periods of time, resulting in surface modification that persists in the eye, providing significant improvement in the wetting properties of fresh contact lenses used for the first time, and even several hours after lens insertion, preventing dryness and improving lubricity.⁵⁷³

Nanoscale organization of the functional surface can be directed by photolithography and micro- and nanoscale printing.481 The chemical nature of the underlying material becomes hidden by the presence of a film a few nm thick and the interaction with the surrounding environment is governed by these coatings. Silicon wafers are among the most commonly used flat surfaces for these grafting from reactions and initiators can be attached to oxidized (Si-OH) or hydrogenated silicon (Si-H).⁵⁰⁵ Tethering a chlorosilane (monoor trichloro)-functionalized initiator to an oxidized substrate is the most frequently documented route for the preparation of a surface for a grafting from ATRP. 125 nm thick brushes were prepared in water/methanol solutions of various monomers, including glycidyl methacrylate and HEMA at room temperature.^{254,500} Responsive coatings have been prepared and the nature of the coating is dependent on graft density, for example, the upper critical solution temperature (UCST) wetting transitions of polyzwitterionic brushes driven by selfassociation.574

Surfaces with densely grafted brushes act as solid lubricants and find application in medical fields including artificial joints.⁵⁷⁵

3.12.11.5 Conducting Polymers

Conjugated polymers conduct electricity when properly doped, through either chemical or electrochemical means. The majority of these polymers, due to their conjugated backbone, are also extremely brittle and difficult to process.^{576,577} The addition of more soluble SCs has frequently improved the solubility and processability of these materials, but the addition of SCs tends to result in a significant decrease in conductivity, particularly for systems other than polythiophene.⁵⁷⁸ Block copolymers with polythiophene segments, preferably regioregular polythiophenes prepared by CRP procedures, are targeting applications that include LEDs, sensors, and optoelectronics.⁵⁷⁹

Well-defined poly(diethylhexyl-*p*-phenylenevinylene-*b*styrene) (PPV-*b*-PS) semiconducting block copolymers were prepared as potentially efficient organic photovoltaic devices.⁵⁸⁰ The original conjugated macroinitiators were synthesized from PPV and then used for chain extension with styrene by ATRP, producing microphase-separated semiconducting PPV-b-PS block copolymer morphologies.

Another templating approach for polyaniline (PANI) was demonstrated by the preparation of block copolymers where one segment contained suitable dopant functionality. AGET ATRP of 2-acrylamido-2-methyl-N-propanesulfonic acid (AMPSA) was successful using CuCl/2,2'-bipyridine (bpy) catalyst after in situ neutralization of the acidic proton in AMPSA with tri(n-butyl)amine (TBA). A 5 mol% excess of TBA was required to completely neutralize the acid and prevent protonation of the bpy ligand.^{457,539,581} The other block was a soft and hydrophobic polyacrylate. The phase separation in this system drives the formation of continuous structures in the acidic phase.⁵⁸¹ The addition of PANI resulted in the doping of the conducting polymer by the acidic block, leaving PANI 'complexed' to the hard-phase polymer and thus adopting the morphology of that block. The stretchable material was conducting (30 S cm⁻¹).⁵⁸¹

A stable aqueous dispersion of star-shaped PBA-*b*-PSS/ PEDOT complex, formed as core–shell NPs, was characterized by FT-IR and UV-Vis spectroscopy. All thin films prepared by casting from 4-, 6-, and 12-armed complexes exhibited excellent flexibility and strong adhesion to glass substrate; their conductivities were ~6 mS cm⁻¹.⁵⁸²

3.12.11.6 Biorelated Applications

3.12.11.6.1 Antibacterial surfaces

Polymers with quaternary ammonium ions (PQAs) effectively kill cells and spores by disrupting cell membranes. Monomers, such as DMAEMA, 4-vinylpyridine (4-VP), and N-substituted acrylamides, that can be quaternized thereby providing biocidal activity, can be polymerized by ATRP. The corresponding antimicrobial surfaces were prepared by grafting from^{287,521,583,584} or grafting onto surfaces^{287,585} and blended with⁵⁸⁶ or deposited on other polymers.⁵⁸⁷ Many surfaces have inherent functional groups that can be employed to conduct a 'grafting from' reaction; the only requirement is the ability to tether initiators to the target substrate. In the case of paper and glass, this is readily accomplished by reacting surface hydroxyl groups with 2-bromoisobutyryl bromide.588,589 ATRP of DMAEMA followed by quaternization with ethyl bromide provided effective tethered biocidal functionality.85 When paper was treated, the modified surfaces were very effective in killing Escherichia coli (E. coli), reducing the number of cells by 4 orders of magnitude, from 1.6×10^9 to 4.9×10^5 , in 1 h. The surface also showed activity against B. subtilis spores. The activity of a biocidal film on a glass surface survived repeated washing with aqueous detergent solution.

A nonleachable biocidal polypropylene (PP) surface was created by chemically attaching PQA chains to the surface of PP. A well-defined poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA), a precursor of a PQA, was grown from the surface of PP via ATRP.²⁸⁷ The tertiary amine groups in PDMAEMA were subsequently converted to quaternary ammonium groups in the presence of ethyl bromide. Antibacterial activity test against *E. coli* indicated that biocidal activity of the resultant surfaces depends on the amount of polymers grafted to the surface and the number of available quaternary ammonium units. Surfaces grafted with relatively high MW polymers ($M_n > 10\,000$) showed almost 100% killing efficiency, that is, killing all of the added *E. coli* (2.9×10^5) in a shaking test, whereas a lower biocidal activity (85%) was observed for the surface grafted with shorter PQA chains ($M_n = 1500$).²⁸⁷ Introduction of hydrophobic units into a poly(quaternary ammonium) segment led to 100 times enhancement of biocidal activity with a log(kill) of 7.0.⁵⁹⁰ It is envisioned that such a permanent, nonleaching biocidal surface treatment would find utility in hospitals, cruise ships, food packaging facilities, household items, and military applications.

While grafting from is an efficient method of tethering quaternizable polymers to a substrate, a more convenient approach for existing household equipment, and even hospital use, would be a 'consumer-friendly' 'grafting onto' approach such as spraying a solution of a reactive copolymer onto a surface.

Surface plasmon resonance was used to measure binding of proteins from solution to PDMAEMA brushes end-grafted from gold surfaces.⁵⁹¹ These brushes displayed a high capacity for electrostatically selective protein uptake. The net negatively charged protein BSA was taken up in amounts that approach its aqueous solubility limit in the case of PDMAEMA brushes at high grafting densities. These are among the highest reported protein binding capacities for ion exchange media. BSA binding scaled linearly with the mass of PDMAEMA grafted per unit area, with a constant ratio of approximately 120 DMAEMA monomer units per bound BSA molecule. The kinetics of BSA uptake in the brush is considerably more rapid than the slow asymptotic approach to adsorption saturation that is often seen for BSA adsorption to a solid surface.⁵⁹²

3.12.11.6.2 Drug delivery

There are many papers describing the preparation of functional copolymers for drug delivery. 49,329,464,541,592-598 An early paper described the ATRP of 2-methacryloyloxyethylphosphorylcholine (MPC) in aqueous solution or methanol at 20 °C and then chain extension with 2-(diethylamino)ethyl methacrylate (DEA) to form a diblock copolymer. This diblock copolymer dissolved in acidic solution due to protonation of the DEA residues but formed micelles at pH 8, with hydrophobic DEA as core and MPC as solvated corona. The MPC-DEA diblock copolymer micelles are biocompatible and show considerable promise for drug delivery applications.⁴⁹ Triblock acrylate-based block copolymers were prepared by ATRP as matrices for paclitaxel delivery from coronary stents.^{599,600} Stable biodegradable poly(oligo (ethylene oxide) monomethyl ether methacrylate) (POEOMA) nanogels, cross-linked with disulfide linkages, were prepared by conducting ATRP in a cyclohexane inverse miniemulsion copolymerization conducted in the presence of a disulfide-functionalized dimethacrylate cross-linker.327,328 These nanogels could be used for targeted drug delivery scaffolds for biomedical applications since they can be degraded into lower MW polymers to release the encapsulated (bio)molecules. These nanogels can be degraded to individual polymeric chains using a reducing agent. Suitable reducing agents include glutathione tripeptide, which is commonly found in cells at millimolar concentrations, to release the encapsulated biomolecules. The encapsulation and controlled release of florescent dyes and doxorubicin (Dox), an anticancer drug, has been reported.⁵⁹³ The procedure was also used to entrap rhodamine isothiocyanate-dextran (RITC-Dx) as a model for water-soluble biomacromolecular drugs.⁶⁰¹ UV-Vis spectroscopy was used to characterize the extent of incorporation of RITC-Dx into the

nanogels. The loading efficiency of RITC-Dx into the nanogels exceeded 80%. These nanogels were degraded into polymeric solutions in a reducing environment to release the encapsulated carbohydrate drugs.^{329,594} Another method to prepare nanostructured hybrid hydrogels was developed by incorporating well-defined poly(oligo (ethylene oxide) monomethyl ether methacrylate) (POEO300MA) nanogels of sizes 110–120 nm into larger three-dimensional (3D) matrix. The hydrogels are suitable for drug delivery scaffolds for tissue engineering applications.⁵⁹⁵ These results confirmed that uniform nanogels prepared by ATRP in inverse miniemulsion are endocytosed and are applicable as drug delivery devices.

PEG star polymers containing GRGDS (Gly-Arg-Gly-Asp-Ser) peptide sequences on the star periphery were synthesized by ATRP of poly(ethylene glycol) methyl ether methacrylate (PEGMA), GRGDS-modified poly(ethylene glycol) acrylate (GRGDS-PEG-Acryl), fluorescein o-methacrylate (FMA), and ethylene glycol dimethacrylate (EGDMA) via an 'arm-first' method. Conjugation of FMA to the stars was confirmed by fluorescence microscopy, and successful attachment of GRGDS segments to the star periphery was confirmed by 1H NMR spectroscopy. Both fluorescent PEG star polymers with and without peripheral GRGDS peptide segments were cultured with MC3T3-E1.4 cells. These star polymers were biocompatible with greater than 90% cell viability after 24 h of incubation. Cellular uptake of PEG star polymers in MC3T3-E1.4 cells was observed by confocal microscopy. Rapid uptake of PEG star polymers with GRGDS peptides (approximately 100% within 15 min as measured by flow cytometry) suggested enhanced delivery potential of these functional star polymers.⁸²

3.12.11.7 Other Industrial Applications

Many corporations are examining ATRP procedures to expand and improve the properties of materials for their markets; currently over 700 US patents have been issued using the term 'ATRP' in the text and over 1500 published US applications in the past decade. Applications include sealants^{602,603} and lubricants,⁶⁰⁴ including use of poly(alkyl methacrylates) as oil additives to improve performance⁶⁰⁵ and star-shaped polymers that exhibit improved long-lasting relationship between thickening behavior, shear stability, and temperature-dependent viscosity control in lubricating oils.⁶⁰⁶ Telechelic copolymers,⁶⁰⁷ gradient copolymers,⁶⁰⁸ and block copolymers⁵⁶⁸ are being produced according to differently controlled polymerization technologies and the site-specific functionality and MWD of these copolymers relate to the production of mixtures incorporating these materials and their use as sealants, 609,610 wetting agents, pigment dispersants, ^{568,611} and reactive surfactants.^{64,271,568,611–613} Surface-modifying block copolymers include a first segment to be attached to a target surface and a second segment that can include additional functionality.

Comb polymers and macromonomers based on acrylates prepared by ATRP display improved capability of dispersing pigments⁶¹⁴ in a given solvent and can be used to prepare dispersible inorganic or organic pigment particles for applications such as inks and coating materials that can be applied to any suitable substrate, such as metal, wood, plastic, or ceramic materials.²⁷¹ End-functionalized polymers are used for blend compatibilization⁶¹⁵ during reactive processing and in many thermosetting compositions, for example, epoxy-functional polymers and functional materials, form the basis of the majority of products prepared for dispersant, coating, adhesive, and sealant applications.

Core-shell-type hyperbranched polymers, with a core formed from poly(*p*-chloromethylstyrene) and triphenylsulfonium 4-(acryloxy)2,3,5,6-tetrafluorobenzenesulfonate, and *t*BA arms form a resist with improved adhesion properties and surface smoothness suitable in photolithography and nanofabrication when spin-coated on a Si wafer and baked to form a 100-nm film showing 254-nm UV sensitivity of 2 mJ cm⁻² and allowing the manufacture of semiconductor devices.⁶⁵

Several polyolefin segmented copolymers containing polar blocks/grafts providing surface hydrophilicity, conductivity, and antibacterial properties to materials were developed.^{584,616,617} The hybrid materials also act as surfactants to stabilize PP/polylactide blends.

A higher value application, based on functionalization of a solid particle, is the development of the stationary phase of nanoengineered analytical immobilized metal affinity chromatography columns by ATRP for separation of proteins and synthetic prion peptides.^{527,618}

3.12.12 Conclusions

Copper-based ATRP is a robust broadly applicable method of CRP that provides control over the MW, MWD, composition, molecular architecture, and chain end functionalities of a spectrum of polymeric materials prepared by copolymerization of a broad range of radically copolymerizable monomers. ATRP provides unique access to various organic/inorganic hybrids and also biorelated materials. ATRP has been commercialized in the United States, Europe, and Japan in 2004. Some current and forthcoming applications include specialty materials for coatings, dispersants, sealants, health and beauty products, as well as materials for optoelectronic and biomedical areas.

Acknowledgments

The support from the National Science Foundation (DMR 09-69301 and CHE 10-26060) and CRP Consortium at CMU is gratefully acknowledged.

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3.13 Transition Metal Complexes for Metal-Catalyzed Atom Transfer Controlled/Living Radical Polymerization

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3.13.1	Introduction	429
3.13.2	Scope of Transition Metal-Catalyzed Living Radical Polymerization	429
3.13.3	Late Transition Metal Complexes for Living Radical Polymerization	432
3.13.3.1	Group 8 Metals	432
3.13.3.1.1	Ruthenium	432
3.13.3.1.2	Iron	440
3.13.3.1.3	Osmium	446
3.13.3.2	Group 9 Metals	446
3.13.3.2.1	Cobalt	446
3.13.3.2.2	Rhodium	448
3.13.3.3	Group 10 Metals	448
3.13.3.3.1	Nickel	448
3.13.3.3.2	Palladium	450
3.13.3.4	Group 11 Metal (Copper)	450
3.13.4	Early Transition Metal Complexes for Living Radical Polymerization	452
3.13.4.1	Group 7 Metal	452
3.13.4.1.1	Manganese	452
3.13.4.1.2	Rhenium	452
3.13.4.2	Other Early Transition Metals	453
3.13.4.2.1	Group 6 metals: molybdenum and tungsten	453
3.13.4.2.2	Group 5 metals: niobium and vanadium	454
3.13.4.2.3	Group 4 metals: titanium	455
3.13.4.2.4	Group 3 metals: lanthanide	455
3.13.5	Prospective View of Catalysts for Living Radical Polymerization	455
References		456

3.13.1 Introduction

Radical polymerization is one of the most favorable procedures employed on both industrial and laboratory scales, because it can convert a wide variety of vinyl monomers, sometimes possessing functional groups, into high-molecular-weight polymers without the rigorous purification of monomers and solvents even in the presence of large amounts of water and polar compounds. During the past 15 years, noteworthy developments in living or controlled radical polymerizations have been achieved to attain well-defined polymers with controlled molecular weights, end functionalities, and narrow molecular weight distributions (MWDs). Most of the widely used controlled/living radical polymerizations can be categorized into three processes, including the nitroxide-mediated polymerization (NMP),1-6 the metal-catalyzed living radical polymerization or atom transfer radical polymerization (ATRP),⁷⁻²⁰ and the reversible addition-fragmentation chain transfer (RAFT)²¹⁻³³ polymerization, as reviewed in this volume. All of the processes are based on reversible and intermittent formation of the growing radical species from a stable covalent bond (dormant species) at the polymer terminal, in which most of the polymer chain ends are in the dormant state. The reversible interconversion of the growing chain end not only gives almost the same chance for propagation to all of the dormant species, but also reduces the

probability of a termination reaction between two growing neutral radical species, affording polymers in a living fashion.

Now that many facile controlled/living radical polymerization systems have been developed for a wide range of monomers, many researchers have adopted them as a tool for preparing well-defined structure polymers not only in polymer chemistry³⁴⁻⁴⁰ but also in the biochemical, medical, and optoelectronic fields.⁴¹⁻⁴⁹ Among the various radical polymerization systems, the transition metal-catalyzed atom transfer process is one of the most promising processes in terms of controllability, facility, and versatility. In this reaction, one polymer chain forms per molecule of organic halide as an initiator, while a catalytic amount of the metal complex serves as an activator, which would homolytically cleave the carbon– halogen terminus (Scheme 1).

3.13.2 Scope of Transition Metal-Catalyzed Living Radical Polymerization

The addition of a halogenated compound to an olefin via a free radical process is an effective method for the formation of carbon–carbon bonds, which is commonly referred to as Kharasch reaction or atom transfer radical addition (ATRA).^{50–57} The reaction was first found as a free radical



Scheme 1 Metal-catalyzed atom transfer controlled/living radical polymerization.

chain reaction, and subsequently a large number of transition metal complexes have been reported to catalyze the reaction via the one-electron activation of the carbon-halogen bond generating the carbon radical intermediate.

The transition metal-catalyzed ATRP relies on iterative processes of the one-electron redox reaction during the entire polymerization reaction in the following order: the halogen abstraction, radical formation, addition to double bond of the monomers, and regeneration of the carbon-halogen terminal. During the process, the concept or the strategy for controlling radical polymerization is implemented, that is, the instantaneous concentration of a growing active radical species should be kept low to avoid radical bimolecular termination by introducing a covalent dormant species with a low equilibrium constant. The dynamic and rapid equilibrium between the dormant and active species can not only minimize the probability of the termination (disproportionation and recombination) but also give an equal opportunity of propagation to all dormant terminals via frequent interconversion. Therefore, the number-average molecular weight (M_n) of the resulting polymer increases in direct proportion to the monomer conversion and agrees with the calculated value on the assumption that one halide molecule (initiator) generates one polymer chain, indicating that all of the polymer chains bear the halide-derived initiating moiety at the α-end terminal as well as the active carbon-halogen bond at the ω -end. When the reversible interconversion between the dormant and active species is sufficiently fast compared with the chain propagation, the reaction provides the polymers with a very narrow MWD as the index of polydispersity $(M_w/M_{n'})$ $M_{\rm w}$: weight-average molecular weight).

Thus, the initiating systems for the living polymerization consist of a halogenated initiator and a transition metal complex. The effective metal complexes for the catalysis now include various early and late transition metals as reviewed in this chapter, while the initiators are typically polyhaloalkanes, α -haloesters, (α -haloalkyl)benzenes, and sulfonyl halides. The metal-catalyzed polymerization can control the reactions of a

wide range of monomers including methacrylates, acrylates, styrenes, dienes, acrylamides, and acrylonitrile (AN), most of which are radically polymerizable conjugated monomers, to produce well-defined polymers in terms of the molecular weight, MWD, and end-functionality. The metal-based system has been further used for the synthesis of a wide variety of functional materials based on the controlled polymer structures, such as block, graft, star, and more complicated copolymers. Because the terminal carbon-halogen bonds in the initiator are both ubiquitous in the chemical reaction and fairly stable in the ambient atmosphere, they are attachable prior to the polymerization onto the surface of inorganic or organic materials to create new and unique materials via the metal-catalyzed polymerization as a method for surface modification. The products with the active carbon-halogen bonds are also mutable as macroprecursors of various other functionalities.

Meanwhile, the transition metal-initiated radical polymerization in conjunction with halides had its origins in the 1960s. The combination of transition metal salts and halogen atoms had been employed in the conventional radical polymerization, the so-called redox initiating systems, before the discovery of the metal-catalyzed atom transfer living radical polymerization. In the 1960s, Bamford's and Otsu's groups reported that metal complexes, typically carbonyl complexes of zero-valent metals, could initiate radical polymerizations when combined with alkyl halides, in which the metal catalyst activated the carbon-halogen bond to generate the initiating radical via a one-electron transfer.⁵⁸⁻⁷³ In these earlier and premature attempts, the organic halides/transition metal complexes were involved only in the initiation step for radical polymerization with irreversible formation of the carbon radicals, and this resulted in uncontrolled propagations to generate ill-defined polymers in terms of the controlled molecular weights and distribution. These initiating reactions, however, allowed block or graft radical copolymerizations of various monomers by introducing carbon-halogen bonds, such as trichloroacetyl moiety, to the prepolymers, though the products also showed

broad MWDs contaminated by ill-defined architecture (co)polymers. In a contrasting situation, a higher valent metal salt, such as ferric chloride (FeCl₃) and cupric chloride (CuCl₂), had also been employed in conventional free radical polymerizations acting as an inhibitor or retarder.74-79 The radical polymerization usually ceases upon the addition of FeCl₃, in which the growing radical species is terminated by the salt to form a carbon-halogen bond via a one-electron reduction of the metal center. Again, for achieving living polymerizations via the atom transfer process, it is important for the metal complex to contribute to the two antithetical processes, that is, activation (initiation or reinitiation) and deactivation (termination) via the one-electron redox reaction of the metal center with a low equilibrium constant. For this, the central metal needs to take at least two states of valence with a one-electron difference, even though either species is neither detectable nor unstable, to be isolated. The higher equilibrium constant induces not only bimolecular radical termination but also the consequent increase in the concentration of higher valent metal complex resulting in the retardation or inhibition of the polymerization. In an ideal situation, the metal complex should have a higher reducing power with a lower redox potential as well as a redox reversibility with a small energy barrier between the two oxidation states. In addition, the catalyst also has to carry a moderate halogenophilicity to accept and release a halogen atom without any unfavorable reactions such as the carbon-metal bond formation between the growing radical and catalyst.

The nature of the complex depending on the combination of the central metal and ligands plays a pivotal role in such a catalytic cycle of the metal-catalyzed radical polymerization. Scheme 2 illustrates a mechanistic scheme based on the equilibrium between the dormant carbon-halogen bond and active radical species (Scheme 2-(1)) along with the related metal-induced and other radical reactions, all of which can potentially occur during the polymerization as side reactions. First, the catalyst must be involved in single-electron transfer process throughout the reaction from the first activation of the carbon-halogen bond, despite the fact that most of the metal-catalyzed reactions found in the organic synthesis proceed via a two-electron transfer. For example, a metal-catalyzed cross-coupling reaction involves an oxidative addition and subsequent reductive elimination (Scheme 2-(2)). In general, the metal complexes that can induce such reactions include elements from Group 9, such as nickel and palladium. Meanwhile, Lewis acid-catalyzed cationic polymerization and electrophilic addition such as Friedel-Crafts reaction can be triggered by the activation of carbon-halogen bonds with Lewis acids (Scheme 2-(3)). The transition metal in the higher valent state with an electron-withdrawing ligand or early transition metals tend to have a stronger Lewis acidity.

Second, even though the metal center can take two consecutive valence states, some metal centers in a lower valent state may prefer to form a carbon-metal bond upon meeting with the growing radical species rather than activate the more abundant carbon-halogen bond in the dormant termini (Scheme 2-(4)). In this case, if the carbon-metal bonds may be homolytically cleaved with a fast and reversible equilibrium, the polymerization would result in another controlled/living radical polymerization, the so-called organometallic-mediated



Scheme 2 Metal-catalyzed and related reactions in controlled/living radical polymerization.

radical polymerization (OMRP).^{80,81} When the newly formed carbon–metal bond is followed by β -H transfer elimination during the OMRP process or when the lower valent state metal favors the β -H abstraction from the growing radical rather than the activation of the carbon–halogen bond or the formation of a carbon–metal bond, the process would follow another path called the catalytic chain transfer (CCT) (Scheme 2-(5)-1). These tendencies can be typically found in the polymerizations with cobalt, molybdenum, and titanium complexes, which belong to the Groups 9, 6, and 4 metals, respectively.

Finally, free radical reactions should be considered in addition to the metal-induced reactions. The degenerative transfer (DT) process (Scheme 2-(6)) possibly occurs via reversible transformation between the growing radical and carbonhalogen (or carbon-metal) bond.⁸²⁻⁸⁴ As in free radical polymerizations, the distinctive radical reactions, such as the bimolecular termination reaction, may take place when the concentration of the growing radical would unexpectedly increase (Scheme 2-(7)). In some cases, other reactions are also competitive when the metal catalysts react with monomers via undesirable paths rather than polymerization; the anion ligand-exchange reaction with functional groups in the monomer to debilitate the catalysis as in the case of the copper-catalyzed polymerization of methacrylic acid and olefin metathesis of the vinyl monomers typically found for the ruthenium carbene-catalyzed polymerization are a few examples.

From these requirements, the late transition metals of Groups 8–11, especially iron (Fe), ruthenium (Ru), and copper (Cu), have been typically employed as the central metal for the metal-catalyzed polymerization as well as some exceptions with the early transition metals, as described in the following sections. Depending on the monomer structure, the design of the polymerization system, such as the initiator (structure and halide), solvents, concentration, and temperature, and the combination of the metal center and organic ligands are required. However, a wide variety of metal catalysts are now available for the precisely controlled propagation of the polymerization. This comprehensive review focuses on the scope and requirements of the metal catalysts for metal-catalyzed atom transfer living radical polymerization.

3.13.3 Late Transition Metal Complexes for Living Radical Polymerization

3.13.3.1 Group 8 Metals

3.13.3.1.1 Ruthenium

3.13.3.1.1(i) RuCl₂(PPh₃)₃ and related complex

The transition metal-catalyzed living radical polymerization was first demonstrated in 1994 by Sawamoto *et al.*^{7,85} using RuCl₂(PPh₃)₃ (Ru-1) complex as the catalyst. Among the various oxidation states of the central ruthenium atom (-2 to +6), the divalent forms (+2) with phosphine ligands have effectively been employed for the metal-catalyzed living radical polymerization as well as Kharasch addition reactions. The first example for the controlled/living polymerization of methyl methacrylate (MMA) was conducted with Ru-1 in conjunction with CCl₄ as the initiator in the presence of a metal alkoxide such as MeAl (ODBP)₂ (ODBP = 2,6-di-*tert*-butylphenoxy) as the additive.⁷

In the presence of the additive, the polymerization homogeneously and smoothly proceeded in toluene at 60 °C to provide polymers with well-controlled molecular weights, which were predetermined by the feed ratio of the monomer to initiator, and retained relatively narrow MWDs (M_w / $M_{\rm n} \sim 1.3$). Later, the radical nature of the polymerization was suggested by being inhibited upon the addition of a radical scavenger or inhibitor such as galvinoxyl and 2,2,6,6tetramethyl-1-piperidinyloxy (TEMPO) and by the tacticity of the resulting polymers as the same as those in conventional radical systems.⁸⁶ Soon after the report with 1, the radical polymerization of styrene with CuCl/2,2'-bipyridine was reported by Wang and Matyjaszewski^{8,87} who denominated the reaction as ATRP after the one-electron redox mechanism passing a halogen atom at the growing terminal. By judiciously combining the halogenated initiator and the additives, like aluminum alkoxides or amine compounds, Ru-1 was promising for controlling the polymerizations of methacrylates, acrylates, styrenes, and acrylamides, which result in polymers with very narrow MWDs $(M_w/M_n \sim 1.1)$.^{88–94} One of the advantages of ruthenium catalysts, in general, would be the high tolerance toward functional groups such as an alcoholic moiety in both the monomer and solvent due to the low oxophilicity of the ruthenium metal. With Ru-1, water and alcohols could be employed as the solvents for the living radical polymerization of MMA either in the presence or in the absence of Al(Oi-Pr)3 at 80 °C.95 The system indeed led to a living suspension polymerization in such protic solvents to give polymers with controlled molecular weights and narrow MWDs ($M_w/M_n = 1.1-1.3$). The characteristics also allowed the ruthenium complex to catalyze living polymerization of functional monomers. 2-Hydroxyethyl methacrylate (HEMA) could be polymerized in alcoholic solvents with Ru-1 in conjunction with halide initiators, though the MWDs were slightly broad $(M_{\rm w}/M_{\rm n} \sim 1.6)$ ⁹⁶ The catalyst also worked for the living polymerization of poly(ethylene glycol) methacrylate (PEGMA), which was followed by the addition of a divinyl compound to generate water-soluble star-shaped polymers.⁹⁷

From the first discovery of the polymerization with Ru-1, a wide variety of ruthenium complexes have been created for controlling radical polymerizations. Figure 1 shows examples of ruthenium complexes based on phosphine ligands, all of which are effective for living radical polymerization. The activity of the ruthenium complexes depends on the structure of their anion ligands, typically halogen anions, and thus even with the same phosphorus ligands, apparent differences could be observed in the polymerization rate and controllability of the products. A similar PPh₃-based ruthenium(II) hydride complex (Ru-2) showed a higher reactivity than the chloride analog (Ru-1), which allowed the polymerization of MMA to proceed in a living fashion even at 20 °C.98 A ruthenium complex with a water-soluble ionic phosphine ligand (Ru-3) catalyzed a homogeneous controlled radical polymerization of HEMA in methanol $(M_w/M_n \sim 1.4)$.⁹⁶ It is noteworthy that the ionic complex could be easily separated from the product polymer by precipitation after polymerization of the hydrophobic monomers.

3.13.3.1.1(ii) Cyclopentadienyl (Cp) and related complex

Among the various ruthenium complexes, half-metallocene ruthenium(II) complexes were found to induce the efficient



Figure 1 Ruthenium catalysts with phosphine- and cyclopentadiene-based ligands.

polymerizations of various vinyl monomers by Takahashi et al.,⁹⁹ most probably because the single-electron transfer from the central metal to the dormant carbon-halogen bond would readily take place with the aid of highly electron-donating cyclopentadienyl ligands. The triphenylphosphine ruthenium complexes with cyclopentadienyl (Cp) (Ru-4), indenyl ligands (Ind) (Ru-5), and pentamethylcyclopentadienyl (Cp*) (Ru-6) induced a faster and better controlled polymerization of MMA than Ru-1 even in the absence of the additives to give fairly narrow MWDs $(M_w/M_n \sim 1.1)$.¹⁰⁰ The catalytic activity of these half-sandwich Ru complexes increased in the order Ru-4 < Ru-5 < Ru-6, namely, the lower the redox potential of the complex, the faster the polymerization. Note that Ru-6 enabled living radical polymerizations of styrene and methyl acrylate (MA) as well as MMA under the same condition in combination with a chloride initiator and Al(Oi-Pr)3.¹⁰¹ The polymerizations of *n*-butyl acrylate (BA) and styrene were also tested to produce narrow MWD polymers in the absence of the additive $(M_w/M_n = 1.1-1.2)$.¹⁰² The complex with an η^5 -benz[f] indenyl ligand (Ru-7) was also reported to catalyze the living polymerizations of MMA and styrene in the presence of α-bromoester as the initiator and Al(Oi-Pr)₃ as the additive

to give narrow MWDs $(M_w/M_n \sim 1.1)$.¹⁰³ The Ru complexes with other electron-donating dimethylamino-, azacrown-, or phenyl-groups at the 2-position of η^5 -indenyl ligands (Ru-8–Ru-10) also effectively produced the living polymers of MMA, MA, and styrene with narrow MWDs, although the judicious choice of halogen atom in the initiator is necessary.^{104,105} Meanwhile, the presence of such a substituent at the 1-position (Ru-11) resulted in a poorer control during MMA polymerization.¹⁰⁵ Different from the after-mentioned iron(II), the Cp*Ru (II) (Ru-12) complex with a carbonyl ligand and its derivatives resulted in uncontrolled polymerizations of either MMA or styrene.¹⁰⁶

The Cp and its related complexes have also inherited tolerance toward functional protic groups. Ru-6 was also effective in producing very narrow MWDs ($M_w/M_n = 1.07-1.20$) of poly (MMA) and poly(HEMA) even at 0 °C in fluorinated alcohols of (CF₃)₃COH and (CF₃)₂C(Ph)OH or in dimethylformamide (DMF), which were solvents for changing the syndiotacticity of the resultant polymers to rr = 50-80%.^{107,108} The controllability of the molecular weights along with the specific stereocontrol enabled the synthesis of stereoblock and unprecedented stereogradient polymers via ruthenium-catalyzed living polymerization of HEMA along with its silyl-protected monomer. A Cp*-ruthenium complex with a thermosensitive PEO-carrying phosphine ligand (Ru-13) was accessible to dispersion living polymerization of MMA, in which the catalyst worked in the organic phase, that is, the polymerization media, at 80 °C and became highly soluble in the aqueous phase below 80 °C to allow the efficient catalyst removal from the polymer solution.¹⁰⁹ More recently, an *in situ* formed complex with Cp* and hydrophilic phosphine ligands (Ru-14) was examined for controlling the radical polymerizations of HEMA in ethanol $(M_w/M_n \sim 1.2)$.¹¹⁰

Further improvement in the catalytic activity of the ruthenium complex has been achieved by creating a vacant active site on the ruthenium metal, which leads to enhancing the capability for receiving a halogen anion from the dormant C-Cl species, thus generating the active radical species. A halfmetallocene-type ruthenium complex with 16 electrons (Ru-15) was more active than Ru-6 with coordinatively saturated 18 electrons, because the former had a vacant site that could interact with a halogen at the polymer terminal without release of the phosphine ligand.¹⁰¹ A cationic ruthenium complex stabilized with an η^2 -ethylene ligand (Ru-16) induced a faster polymerization probably due to the displacement of the labile ethylene ligand into a vacant site for the incoming halogen.¹¹¹ A similar tendency was reported by Quebatte et al.¹¹² for the Kharasch addition of CHCl₃ to styrene using another cationic complex [Cp*Ru(PPh₃)₂(CH₃CN)][OTf], though the complex has not yet been employed for the polymerization. By using the acetonitrile η^2 -coordinated neutral complex (Ru-17) coupled with Et₂NH, the fast and controlled polymerization of styrene also proceeded at 90 °C and the $M_{\rm p}$ of the products was very close to the theoretical values with relatively narrow MWDs $(M_w/M_n = 1.09 - 1.17)$.¹¹³ Further improvements of the Cp*Ru catalysts were achieved by a thorough screening of the phosphine coligands using $[RuCp^*(\mu-Cl)_3]_4$ as the precursor.¹¹⁴ Among the various phosphines, tri(m-tolyl) phosphine $[P(m-tol)_3]$ as the coligand (Ru-18) in conjunction with a primary diamine as the additive gave the best results in terms of narrow MWDs ($M_w/M_n < 1.1$) and required low catalyst loadings ($[Ru]_0/[initiator]_0 = 1/40$). Furthermore, the in situ formed complex proved universally accessible to a variety of functional methacrylates in ethanol.¹¹⁰ A complex with a heterochelating P-N ligand (Ru-19) also exhibited higher activity for MMA polymerization, whereas similar homochelating P-P and N-N ligands were less effective.¹¹¹ This is probably because the weakly coordinating ligand or weaker coordinating N-site between the heterochelation in the 18-electron Cp*-based complexes must be released to open a vacant site for the incoming halogen to contribute the fast equilibrium between the growing radical and dormant C-Cl species. This concept was further applied to another heterochelating ligand of bisphosphine monoxide.¹¹⁵ The in situ formed Cp*Ru complex with Ph₂P(O)(CH₂)_nPPh₂ (Ru-20) catalyzed living radical polymerizations of a variety of monomers including MA, MMA, styrene, HEMA, and PEGMA, of which the controllability and activity were extraordinarily high enough using a small amount of catalyst $([Ru]_0/[initiator]_0 = 1/200)$ to produce a relatively highmolecular-weight PMMA with a narrow MWD ($M_{\rm n}$ > 100 K, $M_{\rm w}/M_{\rm n}$ < 1.2) even in the absence of additives.

The ruthenium complexes are particularly efficient for inducing the 1:1 Kharasch addition reactions in organic synthesis. The Cp and the related ruthenium complexes, especially the highly active and versatile Ru-6, were also proved to induce the fast and efficient 1:1 Kharasch addition (ATRA) reactions in good vields by Simal et al.^{116,117} Similar to the polymerization, the Ru complexes with P-N ligands based on indene or indenide were actually employed in 1:1 Kharasch addition reactions to induce effective reactions even at low catalyst loadings under mild conditions using the appropriate substituents, coligands, and counteranions.¹¹⁸ For the creation of a new chiral center through the reaction, the asymmetric induction catalyzed by chiral metal complexes has also received considerable interest. Indenyl and Cp* ruthenium complexes (Ru-21 and Ru-22, respectively) with a chiral phosphine chelating ligand (DIOP: 2,3-(isopropylidenedioxy)-2,3-dihydroxy-l,4-bis(diphenylphosphanyl)butane) were examined for the asymmetric halogen transfer radical addition of olefins, such as styrene, MA, and MMA, as well as their polymerizations.¹¹⁹ Although the enantiomeric selectivity in the 1:1 addition occurred, the polymerizations were uncontrolled. As mentioned later, the molecular weight control was achieved using a DIOP binuclear complex.

3.13.3.1.1(iii) Borate, N-heterocyclic carbene, and carborane

A trispyrazolyl borate-based complex (Figure 2, Ru-23), which is isoelectronic to the 18-electron half-metallocene-type complexes, also induced living radical polymerization of MMA either with or without additives, in which the rates and molecular weights were not changed upon the addition of $Al(Oi-Pr)_3$.¹⁰⁰

Triazol-5-ylidene, a kind of *N*-heterocyclic carbene (NHC) ligand, was also reported by Melis and Verpoort¹²⁰ as an efficient ligand for the ruthenium catalyst (Ru-24), with which the MMA polymerization proceeded in a controlled fashion coupled with a bromide initiator in the presence of *n*-Bu₂NH.

Fourteen-electron complexes with *ortho-nido*-carborane ligands have also been investigated as catalysts for the radical reactions and used for the metal-catalyzed polymerization.^{102,121-123} For example, an *exo-nido*-hydride complex (Ru-25) proved effective in producing narrow MWDs ($M_w/M_n \sim 1.2$) and controlled molecular weights without additives for the MMA polymerizations.¹²¹ More recently, the carborane complexes with *closo*-structures, such as Ru-26 and Ru-27, also exhibited an activity for the polymerization of MMA and styrene in the presence of a chloride initiator to give narrow MWDs for MMA ($M_w/M_n \sim 1.25$).^{122,123} With these complexes, there was no distinguishable difference between the 18e-diamagnetic Ru-26 and 17e-paramagnetic Ru-27.

3.13.3.1.1(iv) Arene and related complex

Ruthenium complexes with neutral arene ligands have also been reported as effective catalysts for the controlled/living radical polymerization (**Figure 2**, **Ru-28**–**Ru-33**). A series of η^6 -*p*-cymene-based ruthenium dichloride complexes (**Ru-28**) with various phosphines and related two-electron-donor ligands were first synthesized and used for the radical polymerizations of several monomers as well as Kharasch addition reactions by Simal *et al.*^{124,125} The controlled polymerizations of methacrylates and styrene were achieved with bulky phosphine or arsenic ligands (L=PCy₃, P(*i*-Pr)₃, P(*c*-C₅H₉)₃, PPhCy₂, AsCy₃, and PCy₂CH₂CH₂CH₂CG₄C₅), among which



Figure 2 Ruthenium catalysts with borate-, carbene-, carborane-, arene-, and vinylidene-based ligands.

 PCy_3 , $P(i-Pr_3)$, and $P(c-C_5H_9)_3$ are the most active and efficient in producing well-controlled molecular weights and narrow MWDs ($M_w/M_n \sim 1.1$ for methacrylates and ~ 1.2 for styrene). In contrast, less basic or less bulky phosphine-, pyridine-, piperidine-, isocyanide-, and antimony-based ligands led to less efficient and/or less controlled polymerizations. In a complement study, various phosphines with a strong basicity and moderate steric bulkiness, such as the above-mentioned ligands and $P(t-Bu)Cy_2$, were effective not only for MMA but also for the *p*-substituted styrene derivatives except for *p*-methoxystyrene.¹²⁶

Similar complexes carrying benzene (Ru-29) or tetralin (Ru-30) can also be employed, in which the activity decreased in the order *p*-cymene > benzene > tetralin.¹²⁷ A complex with a bridged ligand with arene and phosphine can be obtained via release of the *p*-cymene ligand from Ru-28 (L=PCy₂CH₂CH₂CH₂CG₄H₅), but it was significantly less active. This indicates that the activation process by the

arene-based complexes is triggered by releasing arene ligands.¹²⁷ It was also shown that microwave irradiation accelerated the MMA polymerization as well as ATRA with Ru-28 using PCy₃ as the ligand under limited conditions.^{128,129} A similar complex with 2,4,6-triisopropylbenzene in place of cymene (Ru-31), which was formed *in situ* from the corresponding (μ -Cl)₂ dimer, was reported by Quebatte *et al.*¹³⁰ to induce a better controlled polymerization of MMA and ethyl methacrylate (EMA) at 50 °C than the cymene analog (Ru-28).

In contrast to Ru-24, the reaction between [RuCl₂ (*p*-cymene)]₂ as a precursor and an NHC carbene of 1,3,4-triphenyl-triazol-5-ylidene resulted in *ortho*-metallation of the phenyl ring in position 1 to form Ru-32.¹²⁶ Although the controllability was lower than Ru-24, Ru-32 could polymerize MMA and styrene derivatives ($M_w/M_n \sim 1.5$). By using other ligands, the *p*-cymene complexes with a series of NHC ligands were successfully synthesized and used for the metal-catalyzed

polymerization by Delaude *et al.*¹³¹ Among them, the complex bearing mesityl substituents (Ru-**33**, R₁ = Mes) with R₂ = H or Cl efficiently catalyzed the polymerization of MMA with controlled molecular weights and relatively narrow MWDs ($M_w/M_n \sim 1.3$).

Note that the ruthenium *p*-cymene complex with NHC ligands, as well as the following alkylidene complexes, can also induce metathesis reactions, which indicates that the olefin metathesis reaction of the vinyl monomers should be considered as a competitive process, for example, stilbene formation during styrene polymerization.¹³²

3.13.3.1.1(v) Alkylidene and related complex

Ruthenium alkylidene complexes are well known to catalyze metathesis reactions. It was also reported that Grubbs' ruthenium carbene and related complexes (Figure 2, Ru-34–Ru-44) were applicable for the polymerization of a vinyl monomer via the atom transfer mechanism when combined with a halogenated initiator.

Simal *et al.*¹³³ first reported that a series of Grubbs' benzylidene complexes (Ru-34) can also mediate living radical polymerizations of MMA and styrene to afford controlled polymers with narrow MWDs ($M_w/M_n \sim 1.2$). Ruthenium alkylidene complexes with the NHC ligand are so-called second-generation catalysts in the metathesis chemistry. The benzylidene complexes (Ru-35 and Ru-36) with phosphine or NHC ligands were also employed for the radical polymerization of MMA and styrene to give controlled molecular weights but broader MWDs than Ru-35.¹³⁴

Bielawski *et al.*¹³⁵ reported a ruthenium alkylidene complex (**Ru-37**) carrying a bromoisobutyrate group that can not only initiate but also catalyze living radical polymerization of MMA without an initiator. The complex was also active for the ring-opening metathesis polymerization of 1,5-cyclooctadiene (COD), in which the ruthenium–carbene bond was then the initiating point. Therefore, a mixture of MMA and COD underwent a dual or tandem living polymerization of both monomers to generate block copolymers of COD and MMA. The produced copolymer could also subsequently be converted into ethylene-*block*-MMA copolymers by hydrogenation using the same complex.

The indenylidene complexes were prepared by Opstal and Verpoort,¹³⁶ among which the complexes with phosphine or NHC ligands (Ru-38 and Ru-39) were also effective for the MMA and styrene polymerization resulting in the linear evolution of $M_{\rm n}$, but with a nonquantitative initiator efficiency and broad MWDs ($M_w/M_n > 1.6$ for MMA and ~ 1.4 for styrene). The cationization of Ru-38 and Ru-39 into 14-electron homologs, in which one of the chloride anion ligands was replaced by a BF₄ anion, resulted in a better activity and control for the MMA polymerization ($M_w/M_n \sim 1.2$), and the ionized complex also worked in suspension media. In addition, the neutral indenylidene complexes were also subsequently converted into the corresponding Fischer-type ethoxymethylidene (Ru-40 and Ru-41) and also followed by cationization with AgBF₄. Both the neutral ethoxymethylidene and their cationized complexes exhibited a higher activity and controllability for MMA than the original indenylidene complexes $(M_w/M_n = 1.1 - 1.4)$.

Vinylidene analogs (Ru-42) and their cationic derivatives were prepared and examined for the Kharasch addition of CCl₄

and CHCl₃ to MMA, styrene, and 1-octene.¹³⁷ The cationic allenylidene ruthenium complexes (Ru-43 and Ru-44) were also implemented as versatile catalysts for the controlled ATRP of MMA, isobutyl methacrylate, MA, BA, and styrene.¹³⁸ Although the initiator efficiency was low, all of the polymerizations gave linearly increasing $M_{\rm n}$ s and moderate MWDs ($M_{\rm w}/M_{\rm n}$ = 1.2–1.5), in which the complex with the NHC ligand (Ru-44) exhibited higher activity than the PCy₃ homologue (Ru-43).

3.13.3.1.1(vi) Phenoxyimine (Schiff base) and related complex

Drozdzak *et al.*^{139,140} introduced a Schiff base (phenoxyimine) as a ligand of the ruthenium complexes to create a new class of ruthenium catalysts (**Figure 3**, **Ru-45**–**Ru-55**). Arene complexes with the phenoxyimine ligand (Ru-45) exhibited an activity for both metathesis and metal-catalyzed polymerization.¹⁴¹ The linear increases in M_n were observed for the MMA and styrene polymerizations with **Ru-45**, though the MWDs were broad ($M_w/M_n > 1.7$). A similar analog (Ru-46) was also tested for MMA polymerization, in which the pentafluorophenyl ligand (X = C₆F₅) showed a higher activity for producing narrower MWDs ($M_w/M_n \sim 1.5$).¹⁴²

The introduction of phenoxyimine to the ruthenium alkylidene complexes was also examined for Kharasch addition and metal-catalyzed polymerization.^{143,144} For the combination with Ru-benzylidene complexes (Ru-47 and Ru-48), the N-substituents on the phenoxyimine ligand were crucial for both the activity and controllability of the polymerization. For example, the polymerizations of MMA, MA, and styrene by Ru-47 with the N-aryl complex bearing electron-withdrawing moieties $(R = NO_2, R' = 2,6-Me-4-BrC_6H_2)$ proceeded to give relatively narrow MWDs ($M_w/M_n = 1.28$, 1.44, and 1.22 for MA, styrene, and MMA, respectively), whereas the N-alkyl ligand $(R = CH_3)$ did not produce polymers and N-aryl ligand without electron-withdrawing moieties (R = H, R' = 2,6-i-PrC₆H₃) resulting in broader MWDs $(M_w/M_n = 1.52, 1.75, and 1.56,$ respectively).¹⁴³ The cationic complexes of Ru-47 were also investigated to enhance the activity. In the case of the NHC version of the complexes (Ru-48), the same tendencies were observed as for Ru-47, but the MWDs became slightly narrower for $R' = 2_6 - i - PrC_6 H_3$.¹⁴⁵

A higher activity was obtained in the study of the phenoxvimine complexes with indenvlidene (Ru-49 and Ru-50) and subsequent ethoxymethylidene ligands (Ru-51 and Ru-52).^{136,146} The catalytic activity of these phenoxyimine Ru complexes increased in the order Ru-49 < Ru-50 < Ru-51 < Ru-52, namely, the coligands enhanced the activity, in which the replacement of the alkylidene ligand was more dominant than that of NHC. Furthermore, the cationization of these complexes also enhanced the activity compared with the original neutral versions. Actually, with Ru-51 or Ru-52, a quantitative conversion was achieved for the MMA polymerization at 85 °C for 16 h producing relatively narrow MWDs ($M_w/M_n = 1.2-1.3$). The indenylidene complexes Ru-49 and Ru-50 not only induce the polymerization of MMA and styrene but also catalyze the ring-opening metathesis polymerization of low-strain cyclic olefins, such as cyclooctene and cyclopentene, as well. A vacant site for the C-X bond activation was most probably derived from the carbene fragment, which was supported by the inactivity of the complex with PPh₃ in place of the alkylidene ligand in Ru-50 or Ru-52.



Figure 3 Ruthenium catalysts with phenoxyimine- and phenylpyridine-based ligands.

3.13.3.1.1(vii) Cyclometallated complex

Camacho *et al.*^{147,148} reported that ionic 2-phenylpyridine-based cyclometallated ruthenium complexes, which have a σ -Ru–C bond as in Ru-32, with labile acetonitrile ligands (Ru-53) could catalyze the polymerizations of MMA, BA, and St. Although a high loading concentration of the complex under a saturated heterogeneous condition was required (twofold excess to the bromide initiator), the polymerizations proceeded in a controlled manner in the presence of both Al(O*i*-Pr)₃ as the additive agent and SnCl₂ as the reducing agent to give relatively narrow MWDs for all of the monomers ($M_w/M_n = 1.2-1.3$).

The 2-phenylpyridine-based cyclometallated complexes with bidentate pyridine ligands, such as bipyridine derivatives and *o*-phenanthroline (Ru-54 and Ru-55), were also accessible for the polymerization of styrene.¹⁴⁹ Although an osmium homolog was inactive, Ru-54 and Ru-55 successfully induced the controlled polymerization of styrene even in the absence of the additives ($M_w/M_n = 1.2-1.3$). The addition of Al(O*i*-Pr)₃ accelerated the polymerization, but the controllability decreased with an excess amount ([Al]₀/[Ru]₀>4). It was suggested that the key to a higher activity with these catalysts is the cleavage of the Ru–N coordination bond presumably at the *trans*-position of Ru–C σ -bond due to the *trans*-influence.

3.13.3.1.1(viii) Bimetallic complex

Bimetallic complex is one of the promising catalysts to produce a remarkably high activity via the cooperative effect. Although the intermediacy of additional or true active species cannot be excluded during the polymerization process, binuclear ruthenium complexes have been employed in living radical polymerizations (Figure 4, Ru-56–Ru-69).¹⁵⁰

A binuclear complex was first reported by del Rio *et al.*,¹⁵¹ in which an azo-bridged complex with nitrogen ligands (Ru-56) was used for MMA polymerization coupled with CCl₄ as an initiator to give polymers with relatively narrow MWDs ($M_w/M_n = 1.4-1.6$). Verpoort *et al.*^{139,140,142,152} evolved their Schiff base (phenoxyimine) complexes into bimetallic complexes. Especially, when coupled with a *p*-cymene as a coligand, the (μ -Cl)₂ bimetallic complex (Ru-57) gave good results with controlled M_n and MWDs ($M_w/M_n = 1.35$) for the styrene polymerization.¹⁵² Although the MWDs were broad ($M_w/M_n > 1.7$), the polymerization of styrene by the bimetallic phenoxyimine complexes with COD or norbornadiene as a coligand (Ru-58) also resulted in controlled molecular weights.¹⁴²

The dinuclear arene complexes as precursors (Ru-59 and Ru-60) can *in situ* form the corresponding mononuclear complexes (Ru-28 and Ru-31) upon the addition of the phosphine



Figure 4 Bimetallic ruthenium catalysts.

ligand to induce controlled polymerizations.^{124,130} During the course of the investigation with Ru-60, in 2005, Quebatte et al.130 developed a µ-N2-bridged tetranuclear complex (Ru-61) as a result of the N₂ atmosphere, which itself was highly efficient for the Kharasch reactions, but was less soluble in solvents. As an alternative to N₂, ethylene was used as a labile two-electron donor ligand. Similar to Ru-16, ethylene afforded η^2 -coordination to the ruthenium metal forming $(\mu$ -Cl)₃ binuclear complexes (Ru-62 and Ru-63).¹⁵³ The bimetallic Ru-63 induced very efficient polymerizations of methacrylates even at ambient temperature (35 °C) without additives $(M_w/M_n \sim 1.1)$.¹⁵⁴ A similar (µ-Cl)₃ homobimetallic ruthenium complex with an NHC (Ru-64) was prepared by Sauvage et al.¹⁵⁵ The NHC bimetallic catalyst induced a faster polymerization of MMA than the corresponding phosphine catalyst (Ru-62), as well as the ring-opening polymerization of cyclooctene. Unfortunately, Ru-64 favored the metathetical coupling during the polymerization of BA or styrene, whereas Ru-62 was also effective for the polymerization.

Motoyama *et al.*¹⁵⁶ reported a cationic bimetallic Cp*-based complex (Ru-65) for the polymerization of MMA. Both the *in situ*-generated and isolated Ru-65 catalysts were active for MMA polymerization, in which the isolated complex gave narrower MWDs ($M_w/M_n = 1.2$). All of the neutral halide and mononuclear homologues of Ru-65 were also effective for Kharasch addition. A similar bimetallic and neutral complex (Ru-66) was also employed for the polymerization of MMA with a series of initiators such as CCl₄, Cl₃CCO₂Me, Cl₂HCCO₂Et and a macroinitiator with a Br terminal.¹⁵⁷ While the polymerization with Ru-66 was well controlled during the initial stage, the catalyst was less stable for achieving complete conversion.

Bimetallic ruthenium complexes with a chiral ligand (Ru-67) have been known to induce asymmetric radical addition reactions by enantiomeric selectivity during retrieving process of the halogen from the oxidized metal catalyst.^{158,159} The complex structure of Ru-67 and its catalysis for the addition of CCl_4 to vinyl monomers, such as styrene, MA, and

MMA, were investigated by Iizuka *et al.*¹¹⁹ Ru-67 can control the molecular weights and the terminal groups during the polymerization of styrene in conjunction with a chloride initiator and Al(Oi-Pr)₃. In contrast to the enantiomeric selectivity during the 1:1 addition (enantiomeric excess ~40%), however, no tacticity control during the radical polymerizations was achieved even with all these DIOP-based ruthenium complexes.¹¹⁹

The heterobimetallic complex might be more promising in terms of the cooperative effect by the two different natures of the central metals. For example, the (μ -Cl)₃ heterobimetallic complex with Ru(II)–Rh(III) (Ru-68) was found by Severin *et al.*^{160,161} using combinatorial search methods. It is of interest that Ru-68 induced an extremely high efficiency during Kharasch addition of CCl₄ to styrene, though the catalyst has not yet been used for the metal-catalyzed polymerization. More recently, heterobimetallic ruthenium–titanium complexes (Ru-69) were employed for radical polymerization.¹⁵⁰ The heterobimetallic Ru(II)–Ti(IV) complexes bearing dihalotitanocene moieties were highly efficient for the polymerization of MMA to produce controlled molecular weights and relatively narrow MWDs ($M_w/M_n \sim 1.2$), although the cooperative effect during the polymerization is still unclear.

3.13.3.1.1(ix) Immobilized catalyst

Immobilized catalysts have been studied for, in part, easy separation and removal of the catalysts from the products and subsequent reusability of the catalyst. In most examples, the catalytic metal centers are attached to solid supports, such as silica gel and polystyrene beads, via spacers and/or coordinating ligands (Figure 5, Ru-70–Ru-74).

The first example of the immobilized ruthenium complex was reported by Haddleton *et al.*,¹⁶² in which Ru-1 was supported on a 3-aminopropyl-modified silica gel by coordination bonding as a consequence of ligand exchange (Ru-70). The MMA polymerization gave controlled molecular weights, closer to the calculated values, and moderate MWDs ($M_w/M_n = 1.5-1.7$). Block copolymerization and the reuse of

the catalysts were possible. The residual ruthenium in the reaction mixture was estimated to be about 10% of the initial feed. [RuCl₂(*p*-cymene)]₂ in the form of its mononuclear complex (Ru-71) was immobilized on the surface of the silica gel and mesoporous silica (MCM-41), which were first modified by diphenylphosphino- or dicyclohexylphosphinoethyltrimethoxysilane, and used as a catalyst for the polymerization of styrene, MMA, and AN.¹⁶³ The heterogeneous catalyst has a comparable activity as the homogeneous analog, but gave much broader MWDs than in a homogeneous solution. The catalyst also showed no significant loss of catalytic activity during the recycling process.

The bidentate phenoxyimine is one of the most promising ligands to immobilize the complex, because it links to the ruthenium metal via both coordination and covalent bonds. The immobilized phenoxyimine ruthenium complexes (Ru-72-Ru-74) were prepared by introducing propyltrimethoxvsilane group in phenoxyimine ligands to produce the analogs of Ru-45 and Ru-47 attached onto MAM-41.164,165 Both of the complexes also effectively catalyzed the polymerizations, and the products had broader MWDs. The latter catalyst was also effective for the ring-opening metathesis polymerizations. The broadening MWDs for all of the immobilized catalysts are consistent with that with other metals, which is convincingly explained by the metal-catalyzed polymerization mechanism, that is, the immobilization may affect the regeneration of the carbon-halogen terminal from the growing radical and nondiffusible metal complex.

3.13.3.1.1(x) Additives in Ru-catalyzed polymerization

As earlier described, the additives have often been employed for acceleration and/or better control of the polymerizations, which most probably can effectively reduce the metal species in higher oxidation states as a reducing agent or form more efficient catalysts via coordination as a ligand.

The MMA polymerization with Ru-1 was further improved by using $Al(Oi-Pr)_3$ in place of MeAl(ODBP)₂ as the additive in conjunction with an α -haloester or α -haloketone as



Figure 5 Immobilized ruthenium catalysts.

initiator, resulting in very narrow the MWDs $(M_w/M_p = 1.1)$.^{90,91,166} The same system can also be applicable for styrene polymerization combined with an iodide initiator to give relatively narrow MWDs $(M_w/M_p \sim 1.2)$.⁹² More recently, Kamigaito et al. reported that the bulky aluminum-Lewis acid [EtAl(ODBP)2] induced the chemoselective radical polymerization of vinyl methacrylate (VMA) to give linear and soluble polymers with a quantitative yield of intact vinyl ester pendant groups and relatively high molecular weights. When coupled with Ru-1 and an iodine initiator, the VMA polymerization in the presence of EtAl(ODBP)₂ also proceeded even at 20 °C in a controlled manner.167

With other metal alkoxides, such as Ti(Oi-Pr)4 and Sn (Oi-Pr)4, Ru-1 induced faster polymerizations of MMA than Al(Oi-Pr)₃, though the MWDs became slightly broader.¹⁶⁸ Aluminum acetylacetonate [Al(acac)₃] was a mild alternative additive that did not induce an ester-exchange reaction between the ester group and the monomer or monomer units in the polymer chain, which might occur using aluminum alkoxides.¹⁶⁹ These metal alkoxides were also effective for other metal complexes, such as iron,¹⁷⁰ nickel,¹⁷¹ rhenium,¹⁷² and copper.^{173,174} It is noteworthy that Al(Oi-Pr)₃ could even make the Cu(II) species active, in which the controlled polymerizations of styrene, MMA, and ethyl acrylate were possible.^{175,176} Ti(Oi-Pr)₄ was also efficient for the half-metallocene Fe(II)-catalyzed polymerizations, as will be mentioned in Section 3.13.3.1.2.177 Based on calculation studies by Poli et al.,178 the nature of Al(Oi-Pr)3 in the metal-catalyzed polymerization was suggested as the result of a more favorable Lewis acid-base interaction with the halogen atom in the oxidized metal complex, which slightly shifts the atom transfer equilibrium toward the formation of the active radical.179

The metal alkoxides were used for concurrent and/or tandem reaction of ester groups, such as ring-opening polymerization or *trans*-esterification reaction, along with the living radical polymerization. With the Ni-catalyzed polymerization, the block or graft copolymers of ε -caprolactone and MMA were successfully prepared using the cocatalysis of Al(Oi-Pr)₃.^{180,181} Unusual gradient copolymers of the methacrylates were synthesized from MMA and various alcohols with the Ru-catalyzed polymerization in the presence of Al(Oi-Pr)₃ or Ti(Oi-Pr)₄, in which concurrent living polymerization and *trans*-esterification of MMA took place in one pot to produce the gradient copolymerization of the corresponding monomers.¹⁸²

The addition of alkylamines also significantly accelerated the metal-catalyzed radical polymerizations.^{93,183} For example, upon the addition of *n*-butylamines to the polymerization of MMA with Ru-1 in toluene at 80 °C, the rate was dramatically increased as follows: 269 h (no additive) > 29 h [Al(Oi-Pr)_3] > 17 h (*n*-Bu_3N) > 9 h (*n*-Bu_2NH) > 4 h (*n*-BuNH₂) for *c*. 75% conversion. Similar to Al(Oi-Pr)_3, *n*-Bu_3N and *n*-Bu_2NH produced controlled molecular weights and narrow MWDs with Ru(Ind)Cl(PPh_3)₂ ($M_w/M_n = 1.2$), whereas broader MWDs were obtained with *n*-BuNH₂ ($M_w/M_n = 1.8$). These added amines most probably coordinate with the ruthenium metal via ligand exchange to produce more active complexes, which was suggested by NMR analysis of the amine/Ru(II) catalyst mixtures. Increased catalytic activity was also observed upon the addition of silica gel-supported amine ligands (Ru-70).¹⁶²

Aminoalcohols such as 2-(diethylamino)ethanol dramatically accelerated the polymerization of MMA with Ru-1 at 60 °C (>90% for 23 h) and gave polymers with narrower MWDs ($M_w/M_n \sim 1.1$).¹⁸⁴ Hydrophilic aminoalcohols as additives are helpful not only for enhancing the catalytic activity but also for the catalyst removal of the Cp*Ru (Ru-6 or Ru-16) catalyst, in which the catalyst was almost quantitatively removed (>97%) after polymerization just by washing with water due to the *in situ* transformation into a hydrophilic catalyst carrying the hydroxyl group via ligand exchange.¹¹⁴ When (S)-binaphthol was employed as a chiral additive, the cyclopolymerization of 2,4-pentanediyl dimethacrylate proceeded in an enantiomer-selective and living fashion with Ru-1 in the presence of a bromide initiator.¹⁸⁵

3.13.3.1.2 Iron

3.13.3.1.2(i) FeCl₂(PPh₃)₂ and related complex

Iron also belongs to the Group 8 series of elements and can similarly take various oxidation states (-2 to +4), among which the Fe(II), Fe(I), and Fe(0) species have been reported to be active for Kharasch addition reactions. In addition, iron catalysts are now highly promising in all chemical and industrial areas from the viewpoint of nontoxicity, being environmentally benign, abundance on the earth, availability, and low cost. Therefore, further developments have still been required for effective iron-based catalytic systems in order to facilitate polymerization. The iron-based catalytic systems for the controlled/ living radical polymerization are shown in this section.

The first example of the iron-mediated living radical polymerization was reported for the isolated complex (Figure 6, Fe-1) by combining a ferrous salt (FeCl₂) and triphenylphosphine ligand by Ando *et al.* in 1997.¹⁸⁶ Fe-1 was employed for the polymerization of MMA in conjunction with a chloride or a bromide initiator, and the polymerization proceeded faster than with RuCl₂(PPh₃)₃. The polymerization with Fe-1 was best controlled when coupled with CH₃C(CO₂C₂H₅)₂Br as the initiator without additives in toluene at 80 °C (M_w/M_n = 1.1–1.3).

The *in situ* formed complexes by mixing iron(II) halides (FeX₂, X = Cl or Br) and ligands have also been widely employed for the iron-catalyzed radical polymerization. Matyjaszewski *et al.*¹⁸⁷ reported that controlled radical polymerizations of MMA and styrene were achieved with the catalysts (Fe-2) *in situ* prepared from FeBr₂ and phosphine ligands, such as PPh₃ or *n*-Bu₃P, as well as nitrogen ligands. Similar controlled polymerizations were also obtained with the *in situ* formed complex from a commercially available hydrate (FeCl₂·4H₂O) with PPh₃.^{188,189} It is of interest that better control of the MMA polymerization was attained in the presence of a free radical inhibitor of 2,4,6-trinitrophenol.¹⁹⁰

Further improvements of the FeX₂(PR₃)₂ catalyst were achieved by screening of the phosphine coligand as well as the halogen ligand.¹⁹¹ The introduction of more basic ligands, such as PMe(Ph)₂ and *n*-Bu₃P, in place of PPh₃ (Fe-3) improved both the activity and controllability of the MMA polymerization. In particular, Fe-3 in conjunction with a bromide initiator allowed a faster and more controlled polymerization of MMA ($M_w/M_n \sim 1.2$) and block copolymerization with butyl methacrylate (BMA).



Figure 6 Iron catalysts with phosphine- and cyclopentadiene-based ligands.

3.13.3.1.2(ii) Polymerization with Fe(II) and Fe(III) complexes

Almost all of the iron-catalyzed polymerizations proceed under an equilibrium between the ferrous [Fe(II)] and ferric [Fe(III)] states, in which the complexes of the former are usually used for the iron-catalyzed polymerization in combination with the halide initiator in spite of the air sensitivity. From the viewpoint of practical use including pot-life, stability during transportation, and handling, one can take advantage of the use of ferric complexes. Despite the fact that ferric halide has a relatively strong Lewis acidity, the higher oxidation state species can also be employed in the so-called reverse or alternative ATRP, in which a free radical initiator is used to generate the growing radical species that can be readily capped by the halogen atom from the ferric salt to form the dormant C-X bond.¹⁹² Moineau and coworkers¹⁹³ first reported the iron-based reverse system in 1998, in which a mixture of FeCl₃ and PPh₃ can mediate the controlled polymerization of MMA in the presence of AIBN to give similar narrow MWDs ($M_w/M_p = 1.1-1.3$). The reverse systems with FeCl₃/PPh₃ have been further developed by using 1,1,2,2tetraphenyl-1,2-ethanediol,194 tetraethylthiuram disulfide,195 benzophenone-modified polyethylene,196 diethyl 2,3-dicyano-2,3-diphenylsuccinate,¹⁹⁷ and so forth as thermal initiators in place of AIBN. It is noteworthy that AN could be polymerized in a controlled fashion with the reverse system by the simple FeCl₃/PPh₃.¹⁹⁷ For the reverse process, microwave irradiation improved the polymerization rate and initiator efficiency.¹⁹⁸

Recently, another system was proposed using the higher oxidation state complex and halide initiator in combination with a reducing agent, such as Sn(EH)₂ (EH: ethyl-2-hexanoate), and ascorbic acid by Matyjaszewski et al.^{199,200} in 2005, which is referred to as an activator generated by electron transfer (AGET) process. The AGET polymerization has also been proven available for the various iron(III)-based systems, while the first use of the reducing agent in the iron(III) system dates back to 2004. In the presence of $SnCl_2 \cdot 2H_2O_1$, a bromide initiator, and an amine ligand, FeCl3 · 6H2O produced the controlled polymerization of MMA, in which SnCl₂ could work as the reducing agent to form Fe(II) species under the polymerization conditions.²⁰¹ With the FeCl₃/PPh₃ system, the styrene polymerization proceeded in a controlled fashion affording a well-defined polystyrene in conjunction with ascorbic acid as a reducing agent even in the presence of a limited amount of air.202,203 As described later in Sections 3.13.3.1.2(iii) and 3.13.3.1.2(viii), the AGET process also worked well with the several iron(III) complex and/or ligand systems for the iron-catalyzed living radical polymerizations.

Contrary to the long time belief that a higher oxidation state iron(III) complex is inactive for the homolytic activation of the dormant C–X bond, the Fe(III) complexes alone were quite recently employed as the catalyst without any intentionally added reducing agents.^{204–209} The detailed mechanism of the polymerization only by Fe(III) is still unclear, although the processes through the reduction of Fe(III) into Fe(II) by either the monomer or ligand have been advocated so far. Actually, the well-controlled polymers of MMA and styrene were obtained using the simple FeX₃ systems (Fe-4), of which the ligands include phosphines,^{205,209} amines,²⁰⁷ and bidentate ligands.^{204,206,208} For example, the styrene polymerization took place using FeCl₃ in the presence of *n*-Bu₃P as the ligand and H-(MMA)₂-Cl as the initiator without any reducing agents to afford polymers with narrow MWDs ($M_w/M_n = 1.1-1.2$).²⁰⁵

3.13.3.1.2(iii) Monodentate ligand

The iron(II) complexes other than the phosphine-based ligand have also been intensively studied for controlling the polymerization. In 1997, Matyjaszewski et al.187 reported the polymerizations of MMA and styrene with nitrogen-based ligands such as *n*-Bu₃N and 4,4'-bis(5-nonyl)-2,2'-bipyridine (Figure 6, Fe-2). With these nitrogen-based ligands, FeBr₂ along with judicious choice of the initiator afforded a well-controlled polymer for both monomers $(M_w/M_n = 1.2-1.3)$. More recently, the AGET system with the FeBr₃/n-Bu₃N/Sn(EH)₂ system was found to be accessible for various styrene derivatives.²¹⁰ Based on Louie and Grubbs,²¹¹ the fast living polymerization of styrene and MMA could be achieved using an iron complex bearing a high-electron-donating NHC ligand of imidazolidene (Fe-5) in conjunction with a bromide initiator, resulting in narrow MWDs $(M_w/M_p = 1.1-1.3)$. The addition of FeCl₃ retarded the polymerization but further narrowed the MWDs ($M_w/M_n = 1.1$). A water-soluble amine, tris(3,6-dioxaheptyl)amine, was applicable as the ligand of FeX₂ (Fe-6) for the living polymerization of styrene, which resulted in the easy removal of the catalyst residue by washing with water after polymerization.²¹² The system was also applicable for the AGET and related processes.²¹³⁻²¹⁵ Hexamethylphosphoric triamide (HMPA), which is a common aprotic polar solvent, could be a ligand with FeCl₂·4H₂O to form the FeCl₂(HMPA)₂ complex (Fe-7) and induce a well-controlled MMA polymerization at 90 °C.²¹⁶ More recently, it was reported that FeBr2 successfully catalyzed the MMA polymerization in the absence of ligands in polar solvents, such as N-methylpyrrolidone, DMF, acetonitrile, and anisole, which would probably act as the ligand, though the monomer consumption did not achieve a quantitative conversion.²¹⁷

3.13.3.1.2(iv) Cyclopentadienyl (Cp) and related complex

As with the ruthenium complexes, the use of Cp- or Cp*-based ligands are also beneficial for the iron-based systems for better control of the radical polymerization. FeCpI(CO)2 (Fe-8, X = I) induced the living radical polymerization of styrene in conjunction with an iodide initiator [(CH₃)₂C(CO₂C₂H₅)I] in the presence of Ti(Oi-Pr)₄ to give very narrow MWDs $(M_w/M_n = 1.1)$ and controlled molecular weights.^{170,218} The styrene polymerization was accelerated with the corresponding bromide complex (Fe-8, X = Br) and initiator [(CH₃)₂C $(CO_2C_2H_5)Br$ without loss of the controlled M_n and narrow MWDs ($M_w/M_n = 1.14$), which excluded the contribution of iodine DT process.¹⁷⁷ By replacement of Cp with Cp* (Fe-9), the MWD became narrowed as in the case with ruthenium.¹⁷⁷ The half-sandwich complexes were also effective for the controlled polymerization of MA, BA, and t-butyl acrylate (t-BA) and their block copolymerization.¹⁷⁸ Fe-8 and Fe-9 were also applicable for suspension polymerization of acrylate and

giving relatively narrow MWD styrene polymers $(M_w/M_p = 1.2-1.3)$, of which the reaction took place in the oil phase of water suspension.²¹⁹ More recently, the half-metallocene iron complexes coordinated by one carbonyl (CO) and one phosphine (Fe-10) were employed as the catalyst for the iron-catalyzed polymerization with varying phosphine ligands, of which the mechanism was proposed to be triggered by a carbonyl release from the original coordinatively saturated 18e complex into the unsaturated 16e form.^{220,221} Among them, the complex with $P(m-tol)_3$ was proven to be fairly active for the polymerization of MMA and MA ($M_{\rm n}$ up to 90000 and $M_{\rm w}/M_{\rm n} \sim 1.2$), whereas that with PMePh₂ showed a unique feature as it worked well for the functional PEGMA polymerization.

The faster and better controlled polymerization was attained with dinuclear Fe(I) complexes (Fe-11) even in the absence of additives such as metal alkoxides.¹⁷⁷ Due to its low redox potential, the dinuclear Fe(I) complex proved very versatile in terms of the high activity for various monomers including unconjugated monomers and induced the rapid living/controlled radical polymerization of various monomers. Although the polymerization ceased at around 70% and the MWDs broadened, the metal-catalyzed controlled polymerization of vinyl acetate (VAc) was first achieved with Fe-11 in the presence of an iodide initiator to produce polymers with a linearly increasing M_n .²²² Acrylamides, such as N, N-dimethylacrylamide, and acrylates were polymerized with the Fe-11/iodide initiator in the presence of I₂ as a modifier to afford polymers with controlled molecular weights and narrow MWDs.²²³ In combination with Y(OTf)₃-induced stereospecific radical polymerization, the simultaneous control of the molecular weight and tacticity was accomplished for the polymerization of acrylamides.²²⁴ Using the highly active Fe-11 system, nonhomopolymerizable unconjugated olefins could be copolymerized with various functional acrylates in a controlled fashion.14,105

3.13.3.1.2(v) Bidentate ligand

Gibson and his co-workers^{225–229} have intensively studied the bidentate diimine ligands, which form four-coordinate iron complexes (Figure 7). An interesting feature of the diimine complexes was to mediate the polymerization of styrene possibly via either the ATRP or CCT process, depending on the ligand structure.

The diimine complex with alkyl groups (Fe-12, R = alkyl) significantly catalyzed the radical polymerization in a controlled fashion. Meanwhile, those with the aryl substituents preferentially underwent CCT, in which the Fe(II) complex reacted with the growing radical to abstract the β-H forming oligomers with unsaturated terminus and the H-Fe(III) species. For example, using cyclohexyl diimine complexes combined with the halide initiator, the controlled polymerization of styrene, MMA, and p-methoxystyrene proceeded to afford the increasing M_n and relatively narrow MWDs $(M_w/M_n \sim 1.2)$.²²⁷ In addition, its tolerance to protic media allowed the polymerization in methanol at ambient temperatures of functional monomers like 2-hydroxypropyl methacrylate to be possible in a well-controlled manner. With the cyclododecyl analog, the MA polymerization was also moderately controlled $(M_w/M_p \sim 1.2)$. Meanwhile, when the diffine bearing an aryl group like mesityl was employed under the same conditions,



Figure 7 Iron catalysts with bidentate ligands.

all of the polymerizations resulted in low M_n oligomers. The substituents on the alkyl diimine complex (Fe-13) are also crucial for determining the process; electron-donating substituents, such as OMe and NMe₂, on the phenyl rings were required to achieve successful polymerization of styrene. The (μ -Cl)₂ dinuclear complex of the cyclohexyl diimine Fe-14 exhibited a lower activity as well as broader MWDs ($M_w/M_n > 1.5$) than the original monomeric complex for styrene polymerization.²³⁰ Although its redox potential was expected to be lower than the corresponding diimine due to the increasing σ -donor ability, the N,N,N',N'-tetraethylethylenediamine complex (Fe-15) exhibited a lower activity, but actually worked well for both the MMA and styrene polymerizations to afford controlled polymers with moderate MWDs ($M_w/M_n \sim 1.3$).²²⁷

A series of iron complexes with bidentate pyridylimine and pyridylamine ligands (Fe-16 and Fe-17) were also synthesized and tested for the polymerization of styrene by Gibson *et al.*,²³¹ in which the substituents and monomeric structure also proved important as with the diimine version. With the *N*-alkyl pyridylimine and pyridylamine ligand, styrene polymerization proceeded in a controlled manner with moderate MWDs ($M_w/M_n = 1.4-1.5$), among which only the bulkiest ligand (Fe-16; $R = c-C_{12}H_{23}$, $R' = CH_3$) gave a monomeric X-ray crystal structure and higher activity in the polymerization to enable controlled MMA polymerization. On the other hand, the CCT process dominated the reaction with an *N*-aryl version ($R = 2, 6-i-Pr_2Ph$, R' = H). The reverse ATRP process of styrene was also tested using the FeCl₃ analog of Fe-16 and AIBN to afford the controlled polymer of styrene ($M_w/M_n \sim 1.4$). The

in situ formed complexes of N-alkyl pyridylimine were also tested by Zhang and Schubert^{232,233} for the polymerization of MMA in conjunction with FeX_2 (X = Cl, Br) as well as the intentional addition of FeCl₃. A bis(oxazoline) FeCl₂ complex (Fe-18) was also found to catalyze the styrene polymerization with moderate control using 1-phenylethyl chloride $(M_w/M_p \sim 1.4)$.²³⁴ While the reverse version with FeCl3 afforded better control of the polymerization in the presence of AIBN ($M_w/M_n \sim 1.2$) than the normal process, a bispyrazolyl analog resulted in uncontrolled polymerization.²³⁵ The in situ formed FeBr₂ complex with diphenylphosphino propane (PhPCH₂CH₂CH₂PPh) as a P-P chelating ligand (Fe-19) induced the relatively fast polymerization of MMA (>90%, 16h) with moderate MWDs $(M_w/M_n = 1.34)$ in the presence of a bromide initiator at $80 \,{}^{\circ}\text{C}_{1}^{236}$ while the isolated ethylene-linked complexes of FeCl₂ $(R_2PCH_2CH_2PR_2)$ $(R=i-Pr, Ph, C_6F_5, C_6H_{11}, Et)$ resulted in the uncontrolled polymerization of styrene with 1-phenylethyl chloride at 120 °C ($M_w/M_n > 2.5$).²²⁷

As for the hetero bidentate chelating ligands, Xue *et al.*^{237–239} reported that the *in situ* formed complexes with pyridylphosphine ligands [PPh₂(Py) and PPh₂(CH₂Py)] (Fe-20) worked well for the polymerizations of MMA and styrene. Under appropriate conditions, the controlled polymerizations of both monomers proceeded to afford relatively narrow MWDs ($M_w/M_n \sim 1.2$), though the structure of the actual catalyst was unknown. The polymerizations with these ligands as well as the related phosphorus-containing ligands (Fe-20) were also employed with FeX₃ without any intentionally added reducing agents.^{204,206,208,209} Other heterochelating ligands were also

examined by Uchiike *et al.*²³⁶ as well as the homochelating P–P and N–N ligands. Especially, as in the case of the ruthenium complex, the complex with a P–N chelating ligand (Fe-22, R=CH₃) could be isolated and efficiently worked for the polymerization of MMA and styrene to afford polymers with fairly controlled molecular weights and MWDs ($M_w/M_n = 1.1-1.3$).

3.13.3.1.2(vi) Multidentate ligand

Tridentate ligands were first reported in 2000 with pyridyldiimine employed as the *in situ* formed FeBr₂ complexes (Fe-23, X = Br) for the polymerization of MMA, which was less controlled than that in combination with CuBr (Figure 8).²⁴⁰ In 2003, O'Reilly *et al.*²⁴¹ reported that tridentate salicylaldiminato ligands produced a highly active iron catalyst (Fe-24) for the polymerization of styrene with near-ideal Nernstian behavior of the redox reversibility. Most probably due to the small energy barrier between Fe(II) and Fe(III), the FeCl₂ complexes with the phenoxyimine ligands bearing an amine, pyridine, or quinoline moiety exhibited a high activity and gave very narrow polystyrene MWDs ($M_w/M_n < 1.1$) with 1-phenylethyl bromide, whereas that with the bidentate analog of phenoxyimine resulted in poor control of the polymerization.

A series of five-coordinate Fe(II) complexes were thoroughly studied with tridentate ligands, including triamines, like N, N, N', N'', N''-pentamethyldiethylenetriamine (PMDETA) (Fe-25, R=CH₃), pyridylamine (Fe-26), N-aminoethyl-pyridylimine

(Fe-27), and pyridyldiimine (Fe-23, $R = c-C_{12}H_{23}$), for the polymerization of styrene.²⁴² The styrene polymerization proceeded well to give a linearly increasing M_n with slightly broad MWDs ($M_w/M_n \sim 1.5$), although the judicious choice of the substituent was required to avoid CCT as in the case with pyridylimine ligands. An aliphatic triamine derived from diethylenetriamine and MA (Fe-25, $R = CH_2CH_2CO_2CH_3$) was used with FeCl₂·4H₂O for the polymerization of MMA, in which the addition of FeCl₃·6H₂O retarded the polymerization, but a controlled manner was obtained with narrowed MWDs ($M_w/M_n < 1.3$).²⁰¹ The reverse process was also accessible for the system.²⁴³

Niibayashi *et al.*²⁴⁴ reported that 1,4,7-trimethyltriazacyclononane formed an ionic trinuclear complex (Fe-28) with FeCl₂ that was a recyclable catalyst for the controlled polymerization of styrene. It was suggested that the ionic complex would be in equilibrium with the actual catalyst of coordinatively unsaturated mononuclear species in the reaction medium. The mononuclear complexes (Fe-29) using a triisopropyl version as the ligand with FeX₂ (X = Cl, Br) showed a high performance for inducing the well-controlled polymerizations of styrene, MMA, and BA ($M_w/M_n \sim 1.2$), of which the high reactivity led to block copolymerization even for lower catalyst concentrations ([Fe]₀/[initiator]₀ = 1/20).²⁴⁵

A series of tetradentate ligands were tested by Ibrahim *et al.*²⁴⁶ Among them, the *N*,*N*-diphenyl-di(quinolylmethyl)



Figure 8 Iron catalysts with multidentate ligands.
diamine ligand produced an isolated complex (Fe-30) that could produce moderate controlled polymers ($M_w/M_n \sim 1.4$) of MMA and BMA at 90 °C in 90 min, while the other ligands, such as the *N*,*N*-dialkyl analog and di(quinolylmethyl)diimine, resulted in uncontrolled polymerizations.

3.13.3.1.2(vii) Other complexes

The complexes without halogen anion ligands have also been used for the metal-catalyzed polymerization combined with the initiator as typified by the aforementioned dinuclear iron complex (Fe-10). A combined system of the metal-catalyzed polymerization with transition metals and dithiocarbonyl groups was first reported for the styrene polymerization with Fe[SC(S)NEt₂]₃ (Figure 8, Fe-31). In the presence of AIBN or diethyl 2,3-dicyano-2,3-diphenylsuccinate as the thermal initiator or 2,2-dimethoxy-2-phenylacetophenone as the photo-initiator, the pseudohalogen C-SC(S)NEt₂ dormant bond was generated from the radical species and Fe-31 via the reverse process, which resulted in well-defined polymers $(M_w/M_n = 1.1-1.2)$.²⁴⁷⁻²⁵⁰ Importantly, such a dithiocarbamate cannot efficiently induce RAFT process for the styrene polymerization unlike dithiobenzoate and trithiocarbonate. A mixed system of Fe-31 and FeCl₃/PPh₃ was found effective for the polymerization of MMA.^{195,251} When coupled with a RAFT agent, like dithionaphthalate, as the initiator, a simple ferrocene (Fe-32) induced a faster living polymerization of MMA than that by thermal initiation at 115 °C, though the contribution of the iron complex for the propagation was unclear.252

Ferrous acetate, Fe[OC(O)CH₃]₂, was employed for the polymerization of VAc in combination with PMDETA as the ligand and CCl₄ as the initiator (Fe-33). The VAc polymerization proceeded to result in a linear relationship between the M_n of the polymer and initial feed ratio of [VAc]₀/[CCl₄]₀ with moderately narrow MWDs ($M_w/M_n \sim 1.5$).²⁵³ However, the polymerization mechanism was attributed not to the reversible activation of the C–Cl bond at the chain end, but to the combination of iron-triggered radical generation and chain transfer telomerization by CCl₄.

Assandei and Percec²⁵⁴ reported that the *in situ* formed complex (Fe-34) from Fe(0) and *o*-phenanthroline induced the polymerization of vinyl chloride when employed with appropriate bromide initiators. Though the polymerization ceased around 40%, moderate M_n and MWDs ($M_w/M_n \sim 1.5$) were obtained for the vinyl chloride polymerization by metal catalysts for the first time. For the polymerization of stearyl methacrylate, a trivalent [Fe(DMF)₆](ClO₄)₃ with bipyridine (Fe-35) was employed in conjunction with either AIBN or AIBN/CBr₄.^{255,256} Though the details were unclear, a linearly increasing M_n with moderate MWDs was observed.

3.13.3.1.2(viii) Organic acid as ligand

In sharp contrast to the fact that most of the metal catalysts could be poisoned by the presence of organic acids leading to inhibition or uncontrollability of the polymerizations, some iron complexes with simple organic acids were shown to mediate the metal-catalyzed living polymerization. In search of less toxic ligands, Zhu and Yan reported that carboxylic acids, such as iminodiacetic acid $[NH(CO_2H)_2]$ (Fe-36 in Figure 9),²⁵⁷





isophthalic acid [1,3-Ph(CO₂H)₂] (Fe-37),²⁵⁸ succinic acid [HO₂CCH₂CH₂CO₂H] (Fe-38),²⁵⁹ and acetic acid (Fe-39),²⁶⁰ were used in combination with FeCl₂, and the resulting complexes induced the controlled polymerizations of MMA and styrene to give relatively broad MWDs $(M_w/M_p = 1.3 - 1.8)$.²⁶¹ The reverse ATRP process was also applicable to the radical initiator/FeCl₃/acid system. Pyromellitic acid [1,2,4,5-Ph (CO₂H)₄] (Fe-40) showed a better controllability $(M_w/M_p = 1.25)$ than isophthalic acid in the reverse system with AIBN.²⁶² The series of picolinic acid [Py(CO₂H)], diacid [Py(CO₂H)₂], and its derivatives were also examined for the reverse polymerization of MMA with AIBN, among which 3,5-pyridine (Fe-41) or 2,5-thiophene diacid (Fe-42) and isoquinoline-1-acid (Fe-43) gave better results with moderate MWDs $(M_w/M_n \sim 1.4)$.²⁶³ Importantly, the controlled polymerization of AN was achieved with succinic acid/FeCl₂ (Fe-38), reverse iminodiacetic acid/FeCl₃ (reverse Fe-36), and isophthalic acid/FeCl₃ (reverse Fe-37) systems in DMF to afford relatively narrow MWD polymers $(M_w/M_n \sim 1.2)$.^{264–266} The AGET process was also employed for the MMA polymerization with the iminodiacetic acid/FeCl₃/ascorbic acid (AGET Fe-36) system in a well-controlled fashion even in the presence of air.²⁶⁷ With ethylenediaminetetraacetic acid (EDTA) as the ligand for FeCl₂ (Fe-44), the heterogeneous polymerization of styrene took place in a controlled manner.²⁶⁸

3.13.3.1.2(ix) Anion in organic salt as ligand

As another characteristic feature of the iron-catalyzed system, there have been reports that ionic compounds such as onium salts offered controlled polymerizations coupled with FeX₂, in which the halide anions acted as ligands (Figure 9). Ammonium or phosphonium salts [n-Bu₄NX (X = Cl, Br, I) (Fe-45) and n-Bu₄PBr (Fe-46)] were accessible for FeBr₂ to mediate the controlled polymerizations of styrene, MMA, and MA, although the systems were heterogeneous.²⁶⁹ Ionic liquids, such as 1-methyl-3-butylimidazolium salts (Fe-47), were also tested for the polymerization of MMA with a bromide initiator and FeX₂ in the absence of the added organic ligand.²⁷⁰ It is noteworthy that the ionic liquids containing transition metal salts can readily be separated and reused to achieve controlled polymerization.

More recently, an improved system using phosphazenium halides with FeBr₂ (Fe-48) was reported for the living radical polymerization of methacrylates using an α -bromoester as the initiator, which had a higher activity to provide better control for the MMA polymerization ($M_w/M_n = 1.14$ and $M_n > 90\,000$) and to enable the first controlled polymerization of PEGMA with an iron-based catalyst.²⁷¹

3.13.3.1.3 Osmium

Osmium, another homologous element to ruthenium and iron, was also employed as a metal center for the complex utilized in the metal-catalyzed atom transfer polymerization (Figure 10).

In 2005, OsCl₂(PPh₃)₃ (Os-1), an analog of Ru-1, was first employed as the catalyst for the polymerizations of styrene, MMA, and BA by Braunecker et al.²⁷² The polymerization of styrene with Os-1 in conjunction with a bromide initiator achieved a 90% conversion in 20 h to give controlled molecular weights with narrow MWDs $(M_w/M_p = 1.11)$, whereas the MWDs were broader for the MMA and BA polymerizations $(M_w/M_p > 1.6)$. In sharp contrast to the polymerizations with Ru-1, interestingly, the addition of Al(Oi-Pr)₃ to that with Os-1 resulted in faster polymerizations, but less controlled MWDs. The coordinatively unsaturated Os-1 could also mediate the controlled polymerization of styrene under OMRP conditions with reversible forming carbon-osmium bonds by trapping the propagating radicals.²⁷³ Although the monomer consumption ceased at a low conversion (\sim 30%) even in the presence of a 1/10 amount of the trivalent complex, the OsCp*BrP(*i*-Pr)₃ (Os-2) gave narrower MWDs ($M_w/M_n = 1.05$) for the styrene polymerization with a bromide initiator than its ruthenium analogue ($M_w/M_n > 1.5$). In addition, Os-2 also exhibited a possible OMRP feature with the linear increase in molecular weight with conversion during the AIBN-initiated styrene polymerization.²⁷³

In contrast to Ru-54, an osmium complex with 2-phenylpyridine-based cyclometallated ligand (Os-3) was not effective for the metal-catalyzed polymerization, though it had a lower redox potential than the ruthenium homologues.¹⁴⁹

3.13.3.2 Group 9 Metals

3.13.3.2.1 Cobalt

The coordinatively unsaturated cobalt(II) complex has a significant tendency to react with the growing carbon radical and form the carbon–cobalt(III) bond, which enables several radical reactions with cobalt complexes, but inhibits the atom transfer radical reactions. Thus, cobalt is the representative transition metal, of which complexes can mediate the controlled OMRP via a reversible formation of the growing radical from the C–Co(III) bond.

Since Wayland *et al.* first used organocobalt porphyrins to mediate the OMRP of MA in 1994,²⁷⁴ Co porphyrin complexes (Co-1) have been used for the polymerization of acrylates, acrylic acid, and VAc, in which the DT process dominated the controlled propagation for VAc (Figure 11).^{275–279} Cobalt(II)



Figure 10 Osmium catalysts.



Figure 11 Cobalt catalysts.

acetylacetonate (Co-2) was also reported by Debuigne *et al.*^{280,281} to mediate OMRP of VAc and BA with an excess amount of V-70 at 30 °C in a bulk monomer or water suspension. It is noteworthy that poly(VAc) with very high molecular weights (up to 99 000) could be prepared by Co-2 forming narrow MWDs ($M_w/M_n < 1.20$). Similar Co(II) catalysts with trifluoromethylated acetylacetone (Co-3) were also efficiently employed for the vinyl esters, BA, and *N*-vinylpyrrolidone.^{282,283} Furthermore, depending on the monomer structure, such as MMA and styrene, the cobalt complexes preferentially underwent CCT associated with fast β-H abstraction from the C–Co(III) terminus to form a metal hydride along with oligomers bearing unsaturated termini.²⁸⁴

Contrary to the aforementioned inherent nature of the cobalt complex, zero-valent cobalt carbonyl complexes had also been known to initiate radical polymerization in the presence of organic halides since the 1960s.^{72,73} More recently, some cobalt complexes were employed in the transition metal-catalyzed ATRP in conjunction with alkyl halides as initiators. Cobaltocene (Co-4) induced the controlled polymerization of MMA in conjunction with a bromide initiator at 70 °C, in which a linear increase of the molecular weights with conversion and narrow MWDs $(M_w/M_n < 1.15)$ was obtained with a low initiator efficiency.²⁸⁵ The controlled polymerization of styrene was also achieved by Co-4 with bromide initiators at 80 °C ($M_w/M_n \sim 1.3$), and the block copolymer of PMMA-b-PSt was prepared with a slightly improved initiator efficiency $(I_{\rm eff} \sim 0.5)$.²⁸⁶ As the cobaltocene is a coordinatively supersaturated 19-electron complex, it was suggested that the complex can hardly contribute to the activation-deactivation equilibrium requiring an outer single-electron transfer reaction.⁸⁰ Subsequently, the exo-substituted η^4 -cyclopentadiene CpCo(I) (Co-5) complex was found to be the actual catalyst for the cobaltocene-catalyzed polymerization. The isolated or in situ prepared η^4 -cyclopentadiene CpCo(I) complex was used for the MMA and styrene polymerizations to afford very narrow MWD polymers $(M_w/M_p < 1.1)$ as well as the PMMA-*b*-PSt block copolymer.287,288

CoCl₂·6H₂O/tris(2-(dimethylamino)ethyl)amine (Me₆TREN) (Co-6) was used to catalyze the polymerization of MMA coupled with a bromoester and tosyl chloride as the initiators, although the produced polymers had relatively broad MWDs $(M_w/M_p > 1.5)$ ²⁸⁹ Upon the addition of a small amount of a deactivator of FeBr3 or CuBr2, however, the controllability was significantly improved $(M_w/M_n = 1.15 - 1.46)$ and the block copolymerization of MA was also achieved. Matsubara and Matsumoto²⁹⁰ reported that a cobalt(I) iodide complex (Co-7) catalyzed the controlled polymerization of MMA in the presence of CCl₄ or CCl₃Br as the initiator. The MMA polymerization with Co-7 proceeded in a controlled manner without additives to give relatively narrow MWDs $(M_w/M_p = 1.2-1.3)$. To control the polymerization with the Co(I) catalyst, the iodine in the metal center proved pivotal to enable the equilibrium between the dormant and radical species.

Weiser and Mulhaupt²⁹¹ reported that cobalt(II) octanoate (Co-8) and perfluorooctanoate (Co-9) catalyzed the normal atom transfer polymerization in the presence of the bromide initiator under homogeneous and fluorous biphasic conditions. The cobalt(II) perfluorooctanoate, which was prepared in situ from CoCl₂ and sodium salts, and 1-phenylethylbromide produced polystyrene ($M_{\rm p}$ < 2500) with relatively narrow MWDs $(M_w/M_n < 1.5)$ at 90 °C. Temperature-induced lower critical solution temperature (LCST) phase separation occurred at room temperature for the effective separation of the perfluorinated catalyst from the products. Furthermore, both the cobalt catalysts and fluorous media were recyclable without any loss in the catalytic activity. A simple cobalt(II) acetate (Co-10) could also induce the controlled polymerization of MMA and styrene.²⁹² Using cobalt acetate as a catalyst and tosyl chloride as an initiator, the polymerization of MMA took place without additives in DMF at 60 °C, in which the M_n of the obtained polymer linearly increased with the conversion along with narrow MWDs $(M_w/M_n = 1.26)$. The bulk polymerization of styrene was also successfully catalyzed by cobalt acetate and the obtained

polystyrene could be used as a macroinitiator to yield the well-defined PS-b-PMMA.

Jérôme et al.^{293–296} reported that cobalt(II) acetylacetonate (Co-2), which is effective for OMRP of VAc and acrylate, could also be used for quinone transfer radical polymerization (QTRP) of styrene, in which the quinone derivatives were employed in place of the halide initiator to produce the pseudohalogen transferring group. The polymerization mechanism became clear when coupled with the monomer adduct of ortho-quinone derivatives, in which the polymerization of styrene smoothly took place in the presence of Co-2 to produce a well-defined polystyrene with narrow MWDs $(M_w/M_p \sim 1.2)$ ²⁹⁶ When coupled with a RAFT agent of dithionaphthalate as the initiator, cobalt(II) 2-ethylhexanoate (Co-11) induced a faster living polymerization of MMA than that with thermal initiation at 115 °C.²⁹⁷ Similar results were obtained when cobaltocene (Co-4) was used in place of Co-11. The authors proposed a switch from RAFT to ATRP mechanism in the presence of the cobalt complexes with the RAFT agent acting as a pseudohalogen initiator.

Immobilized cobalt(II)/copper(II) bimetallic catalysts were also employed for the polymerization of MMA.^{298–300} Although the structure of the true active catalyst was unclear, well-defined polymers of MMA, BA, and styrene were obtained with CoCl₂ or a binary CoCl₂/CuCl₂ combined with Me₆TREN (Co-6) system immobilized on poly(acrylic acid) or a commercial ion-exchange resin in the presence of the appropriate halide initiators, in which the catalyst was almost quantitatively removed after polymerization by simple centrifugation (Co residue < 0.1 ppm).³⁰⁰

3.13.3.2.2 Rhodium

Among the possible oxidation states of rhodium ranging from +4 to -3, the most common are +1 and +3. One of the most famous Rh(I) complexes is the Wilkinson catalyst (Rh-1), which is now widely used for organic syntheses such as hydrogenation. Rh-1 and its related complexes have also been investigated for radical polymerizations by several researchers in conjunction with a halide initiator (Figure 12). Kameda and Itagaki³⁰¹ first applied Rh-2 for the initiation of the radical polymerization of MMA in benzene at 50 °C in the presence of CCl₄, though the controlled nature of the polymerization was unclear at that time.

The Wilkinson complex Rh-1 was examined for styrene in the bulk at 130 °C coupled with sulfonyl chloride as the initiator by Percec et al. in 1996.88 The obtained polystyrene had broader MWDs ($M_w/M_p = 1.7$) than those with the ruthenium or copper catalysts. Meanwhile, it induced faster polymerizations of MMA in the presence of CCl₄ or CHCl₂COPh in a mixture of THF and water at 60 °C, in which the conversion reached 90% in 4 h to give PMMA with relatively narrow MWDs $(M_w/M_n = 1.3-1.7)$.³⁰² The effects of galvinoxyl and the tacticity of PMMA agreed again with that for the free radical polymerization. A bromide complex (Rh-3) in conjunction with a bromide initiator afforded PMMA with narrower MWDs $(M_w/M_n = 1.3)$.¹⁸⁰ RhCl(CO)(PPh₃)(NHEt₂) (Rh-4) was prepared from a (µ-Cl)₂ bimetallic [RhCl(CO)(PPh₃)]₂ and employed for MMA and styrene bulk polymerizations in the presence of CCl₄ at 60 °C.³⁰³ The MMA polymerization with Rh-4 afforded polymers with controlled molecular weights with relatively narrow MWDs $(M_w/M_p = 1.43)$, of which the living nature was confirmed by the monomer addition experiment.

Vohlidal and Opstal *et al.*³⁰⁴ introduced dinuclear Rh(I) (diene) complexes (Rh-5 and Rh-6) as a new class of catalysts for the radical polymerization. Although the initiator efficiency was rather low, Rh-5 promoted the controlled radical polymerization of MMA and styrene in the presence of bromide initiators with MWDs ranging from 1.45 to 1.65. The addition of *n*-Bu₂NH remarkably improved the catalyst activity and MWDs ($M_w/M_n = 1.27$), which was claimed probably due to the dissociation of the dinuclear into mononuclear species. A trivalent rhodium (III) complex [RhH₂(Ph₂N₃)(PPh₃)₂] (Rh-7) was employed as a catalyst for the polymerization of MMA with an organic halide (CCl₄, BrCCl₃, or CBr₄) as the initiator in DMSO at 50 °C. Although the M_n of the produced polymers increased in direct proportion to the conversion, the MWDs were very broad ($M_w/M_n \sim 3$).³⁰⁵

3.13.3.3 Group 10 Metals

3.13.3.3.1 Nickel

Among the various oxidation states of nickel (0–IV), Ni(II) and Ni(0) are the most stable, which enables the C–C bond forming cross-coupling reactions via the oxidative addition and reductive elimination process in organic chemistry such as cross-coupling reactions. Since the nickel chemistry often







Figure 13 Nickel and palladium catalysts.

accompanies a two-valence change in its oxidation state rather than the one-electron redox cycle as required for the radical addition processes, there have been only a limited number of examples of the nickel-catalyzed Kharasch addition reactions in contrast to those of ruthenium, iron, and copper.^{306,307} However, various zero-valent Ni catalysts have initiated radical polymerizations in the presence of organic halides most probably via the one-electron transfer from the metal in the earlier studies.^{66,73} Now, several Ni(II) and Ni(0) complexes with selected ligands have been found as efficient catalysts for metal-catalyzed living radical polymerizations via a one-electron redox cycle, when coupled with halide initiators (Figure 13).

An Ni(II) complex with a bis-ortho-chelating nitrogen (NCN) ligand (Ni-1) was successfully employed for the living radical polymerization of methacrylates with CCl_4 or $(CH_3)_2C$ $(CO_2C_2H_5)Br$ as the initiator as well as the Kharasch 1:1 addition.^{10,308} The polymerization proceeded both in homogeneous toluene and a water suspension to give polymers with controlled MWDs $(M_w/M_n = 1.1-1.2$ in toluene and 1.7 in water), although the initiation efficiency was lower than unity $(I_{eff} < 0.8)$. In contrast, a similar Phebox Ni(II) complex (Ni-2) was inactive in the atom transfer polymerization and addition probably

ascribed to the relatively high oxidation potential of the complex, which excludes the reversible formation of a d^7 -Ni(III) species.³⁰⁹ Another chelating nickel complex (Ni-3) induced a possible MMA polymerization with a bromoester initiator but resulted in broad MWDs ($M_w/M_n > 2$).³¹⁰

A phosphine-based nickel(II) bromide complex (Ni-4) also induces the living radical polymerization of MMA when specifically coupled with a bromide initiator in the presence of Al(Oi-Pr)₃ as an additive in toluene at 60 and 80 °C, whereas the chloride complex (X = Cl) produced less controlled MWDs with bimodal distributions.¹⁷¹ The additives were not necessary for Ni-4 when the polymerization was carried out in the bulk or at a high monomer concentration for both methacrylates and BA, which allowed the synthesis of block copolymers consisting of hard and soft segments as a promising novel thermoplastic elastomer.³¹¹⁻³¹³ The copolymerizations of MMA with functional methacrylates, such as HEMA and PEGMA, were performed with Ni-4 in conjunction with a bromoester at 80 °C to give polymers with controlled molecular weights and MWDs.314 When coupled with Zn and PhI, Ni-4 induced efficient polymerizations of styrene and MMA, though the mechanism is unclear.^{315,316} Styrene polymerization was performed with an in situ formed complex from nickel(II)

chloride and PPh₃ in the presence of tetraethylthiuram disulfide as the initiator, which resulted in the polymers with the α -diethyldithiocarbamoyl and ω -chlorine atom at the chain end.³¹⁷ More recently, Ouchi *et al.*¹⁰⁵ reported that NiBr₂ complexes with more basic phosphine ligands, such as tri-*p*-tolyland tri-*p*-methoxyphenylphosphines (Ni-5), induced faster polymerizations as well as a better control of the molecular weights and MWDs ($M_w/M_n = 1.2-1.4$) than that with triphenylphosphine (Ni-4). Further improvement was achieved with methyldiphenylphosphine (PMePh₂), of which the complex (Ni-6) would be in an equilibrium between the 'square planar' and 'pseudotetrahedral' forms. Ni-6 could catalyze the well-controlled polymerizations of a wide variety of monomers including MA, styrene, MMA, PEGMA, and (dimethylamino) ethyl methacrylate (DMAEMA).¹⁰⁵

The *n*-butylphosphine complex (Ni-7) has a higher thermal stability and solubility in organic solvents than the triphenylphosphine analog (Ni-4). Ni-7 could be employed for MMA, MA, and BA over a wide range of temperatures (60-120 °C) without additives, and a fast polymerization of MMA proceeded at 120 °C to reach a 90% conversion within a couple of hours.³¹⁸ Furthermore, the polymerization of phenethyl methacrylate was induced by air with Ni-7 even in the absence of the added halide initiator to achieve a high M_n with relatively narrow MWDs, though further extensive research is required to clarify the initiation mechanism.³¹⁹ A zero-valent nickel complex (Ni-8), the analogs of which have also been used in the redox initiating systems by Uegaki et al., 320 is another class of catalysts for the living radical polymerization of MMA in conjunction with a bromide initiator and Al(Oi-Pr)3 to afford polymers with controlled molecular weights and narrow MWDs $(M_w/M_p = 1.2 - 1.4)$.

As with iron(II), O'Reilly et al.³²¹ reported that nickel complexes with an α -diimine ligand (Ni-9), which is an analog of the precursor for a coordination polymerization catalyst, efficiently worked for controlling the radical polymerization of styrene. When coupled with 1-phenylethyl bromide as the initiator, the styrene polymerization with Ni-9 provided well-controlled molecular weights and **MWDs** $(M_w/M_n = 1.15)$. Neutral Ni(II) acetylides (Ni-10 and Ni-11) were used for the polymerization of DMAEMA and MMA in conjunction with an organic halide as the initiator by Sun et al.³²²⁻³²⁴ Although judicious conditions, such as concentration ratio of [I]₀/[Ni]₀, were required, the controlled fashion was observed in the MMA polymerization with relatively narrow MWDs $(M_w/M_n = 1.33)$.

The immobilized NiCl₂ and NiBr₂ catalysts were employed for the controlled polymerization of MMA, which was supported on a cross-linked polyacrylate ion-exchange resin or polystyrene resin carrying triphenylphosphine moieties, respectively.^{325,326}

3.13.3.3.2 Palladium

Palladium belongs to the Group 10 elements and, as with nickel, it forms stable Pd(0) and Pd(II) complexes. In the earlier studies, Otsu and Yamaguch⁶³ reported that Pd(0) metal can initiate MMA polymerization in the presence of CCl₄. The Kharasch addition of alkyl halides to olefins was possibly catalyzed by some palladium catalysts, such as Pd(OAc)₂/PPh₃/K₂CO₃ and PdCl₂(PhCN)₂, in which it was plausibly assumed that the actual active species is Pd(0).^{327–330}

In contrast to the other metal-catalyzed systems, the reaction was proposed to proceed not via the other metal-catalyzed ATRAs, but via the oxidative addition/reductive elimination process in some cases.³³⁰

The *in situ* formed Pd(PPh₃)₄ and Pd(OAc)₂/PPh₃ (Pd-1 and Pd-2 in **Figure 13**, respectively) were reported for the polymerization of MMA with a CCl₄ initiator in toluene at 70 °C by Lecomte *et al.*³³¹ The authors proposed that Pd (PPh₃)₄ should be the active species in both cases, which was also formed *in situ* from the reaction of Pd(OAc)₂ and PPh₃. Similar to the nickel complexes, the activity for the MMA polymerization was moderate (conversion 70–80% in 24 h), in which the M_n increased in direct proportion to the monomer conversion, but the MWD was broader ($M_w/M_n \sim 1.8$). In addition, the polymerizations of styrene and acrylates were not controlled by the Pd(0) catalysts.

As with the nickel metal center, the neutral Pd(II) acetylide (Pd-3) was also prepared and employed for the MMA and DMAEMA polymerizations in the presence of alkyl halides, although they were less well controlled $(M_w/M_n > 1.6)$.^{322,323} During the course of the study, PdCl₂(PPh₃)₂ (Pd-4) also worked for the polymerization of DMAEMA. The acetylide Pd-3 complex was also used for the copolymerization of DMAEMA with MMA, BMA, MA, and BA.³³²

3.13.3.4 Group 11 Metal (Copper)

As the details of the copper-catalyzed ATRP can be found in another chapter of this book, the outline of the copper catalyst is described here. Since the first discovery of the Cu(I)-based initiating system for styrene polymerization by Wang and Matyjaszewski,^{8,87} copper catalysts have been most extensively employed for the atom transfer metal-catalyzed living radical polymerizations in terms of commercial availability including cost, high activity with the judicious choice of ligands, versatility for various monomers, and simple manipulation for the experiments. Most of the polymerizations can be conducted by mixing copper(I) bromide or chloride and a nitrogen-based ligand except for some examples of the isolated complexes. A wide variety of nitrogen ligands have been searched and employed for the copper-catalyzed system. Some specific examples are listed in Figure 14, and they can be classified into bidentate (Cu-1-Cu-4, e.g., bipyridines, pyridinimines, and diamines), tridentate (Cu-5 and Cu-11), quadridentate (Cu-8-Cu-10), and formally hexadentate (Cu-12). A detailed overview of these ligands has been described in review papers. 13, 15, 16, 333-335

The copper-catalyzed polymerization was first discovered using the bipyridine ligand (Cu-1) for the polymerization of styrene. After that, the activity of the copper catalyst has been examined and proved to be highly dependent on the structure of the ligands as with the other metals. For example, simple trialk-ylamines as the ligand are accessible for the Kharasch addition, but results in uncontrolled polymerizations. Meanwhile, multi-dentate aliphatic amines offer quite efficient catalytic systems for the copper-catalyzed ATRP when coupled with CuX. In general, there is a tendency that the polymerization activity rises as the coordination number increases from 1 to 3. The activities often become higher in the following structural and topological order: arylamine < arylimine < arylimine < pyridine \sim amine with a linear < branched < cyclic structure.^{334,336} However, there are



Figure 14 Copper catalysts.

considerable exceptions caused by the three-dimensional conformation, the electronic influence, solubility, and side reactions as well as the equilibrium constant between the dormant and active species along with the Cu(I) and Cu(II) species. The difference in the reactivities for the polymerization attributed to the nitrogen-based ligand can be found in the model reaction rate, in which the radical species is generated from ethyl α -bromoisobutyrate in combination with CuBr accompanied by the homolytic cleavage of the C–Br bond. The relative rate of the activation reaction is in the following order: Cu-2 < Cu-1, Cu-6 < Cu-8 < Cu-11 < Cu-5 < Cu-10 < Cu-7 < Cu-9.

Among the various nitrogen-based ligands, PMDETA is one of the most promising ligands in terms of commercial availability, activity, and versatility for the polymerizations of various monomers, such as methacrylate, styrene, and acrylate, and has actually been most widely used. The branched tetradentate Me₆TREN (Cu-7) afforded an active catalyst to produce a sufficiently fast polymerization of MA even at ambient temperature with a low loading concentration of the catalyst ([Cu]₀/[initiator]₀ = 1/10). The complex with Cu-7 can also exclusively mediate the well-controlled polymerization of *N*-isopropylacrylamide (NIPAM) even at room temperature.³³⁷ The cross-bridged ligand combined with CuX (Cu-9) is the most active catalyst in terms of the activation of the C-X bond with the rate 1.5 times greater than that of Me₆TREN.³³⁸ The high activity along with the addition of deactivator [Cu(II)], which is necessary for controlling the polymerization, afforded the well-controlled polymerization of acrylates at ambient temperature. A catalyst with the branched tetrapyridyldiamine Cu-12 produced the well-controlled polymerizations of MA, MMA, and styrene under certain conditions. The high activity is presumably due to the fact that the complex exists in solution as an equilibrated binuclear and mononuclear state, whereas the higher valent Cu(II) complex is mononuclear. The Cu-12 catalyst can mediate the polymerization even with an extraordinarily low loading concentration of catalyst ([Cu]₀/[initiator]₀ = 1/200) to give well-controlled molecular weights and narrow MWDs.³³⁹

In sharp contrast to the other metals, such as ruthenium, phosphine ligands have been inefficient in the coppercatalyzed systems probably due to the inappropriate electronic effects or unfavorable binding constants. Another mechanistic difference in the copper catalysis from other metals is the so-called halogenophilicity as well as oxophilicity, which determines the dissociation constant between the metal cation and halogen anion in concert with the redox reaction triggered by a one-electron transfer. This aspect is a disadvantage for the copper system regarding the stability to functional groups in monomers, in which the copper catalysts are easily poisoned by acidic compounds like carboxylic acids The copper-catalyzed ATRP in protic solvents is characterized by an inefficient deactivation due to the reversible dissociation of a halide ligand from the higher oxidation state of Cu(II).³⁴⁰ In a specific case of the heterogeneous aqueous suspension polymerization, the judicious choice of the ligands with a sufficient hydrophobicity was necessary for controlling the polymerization because most of the copper catalysts tend to be readily ionized or disproportionated at the Cu(II) state to diffuse in water, whereas most of the ruthenium complexes can work in either homogeneous or heterogeneous aqueous media without any special care.³⁴¹ The selected ligand, such as the pyridyl methanimine-based ligands, enabled the well-controlled polymerization of PEGMA even in homogeneous water at ambient temperature.^{342,343}

3.13.4 Early Transition Metal Complexes for Living Radical Polymerization

3.13.4.1 Group 7 Metal

3.13.4.1.1 Manganese

In general, the Group 7 metals display the characteristics of both the early and late transition metals. They can also take a wide range of oxidation states and produce stable high-valent complexes as the Group 8–10 metals.

The control of the molecular weight during the polymerization of styrene and MMA was reported using manganese(III) acetylacetonate (Mn(acac)₃: Mn-1 in Figure 15) in the presence of bromide initiators in toluene at 80 °C.^{344,345} The $M_{\rm n}$ s of the products increased with the monomer conversions, although the initiator efficiency was low and the MWDs were broad ($M_{\rm w}/M_{\rm n}$ > 2). It was suggested that the polymerization initiated with the *in situ* formation of a divalent Mn(II) from Mn-1 by releasing the acetylacetonate radical. Mn-1 was also employed in QTRP in conjunction with the quinone derivatives as initiators, in which the addition of bipyridine as a ligand improved the controllability of the polymerization of styrene.²⁹³

A dinuclear manganese carbonyl complex $(Mn_2(CO)_{10}: Mn-2)$ readily undergoes both photochemical and thermal homolyses of the metal-metal bond to form the highly reactive metal-centered radical $[\bullet Mn(CO)_5]$. Its first use for radical polymerizations dates back to the reports of Bamford *et al.*, ^{67,70,71} in which the thermal and photochemical homolyses of $Mn_2(CO)_{10}$ in the presence of CCl_4 led to the free

radical polymerization of MMA. The dinuclear Mn complex had been further combined with the trichlorinated and tribrominated methyl compounds and then utilized for preparing graft and block copolymers of various monomers, though the obtained polymers showed uncontrolled molecular weights and broad MWDs.^{346,347}

More recently, the photoresponsive controlled/living radical polymerizations of VAc, MA, and styrene were developed using Mn-2 coupled with an alkyl iodide initiator (R-I) under weak visible light by Koumura et al.³⁴⁸ Especially, the polymerization of VAc proceeded very fast even at 40 °C with a catalytic amount of Mn2(CO)10 (0.025 mol.% of VAc or 5.0 mol.% of R-I) and completed within a few hours to give the polymers with controlled molecular weights up to 10⁵. The contributions of the metal-catalyzed and the degenerative iodine transfer processes were suggested by analyzing the model reactions. Owing to the high activity and tolerance of the Mn-2-based system, the controlled copolymerizations of VAc/MA and MA/1-hexene were also successfully attained with Mn-2 in fluoroalcohols as solvents in conjunction with an alkyl iodide (R-I) as the initiator under weak visible light.^{349,350} Not only was the copolymerization of MA/1-hexene with Mn-2 in a fluoroalcohol well controlled, but also the content of 1-Hex increased up to 50 mol.% with predominant alternating sequences.³⁵⁰ The Mn-2 complex could also be combined with various RAFT agents as the initiators to produce the controlled polymers of VAc, MA, and styrene with narrow MWDs $(M_w/M_p = 1.09 - 1.5)$, which would concurrently proceed via the reversible pseudohalogen transfer and RAFT processes.³⁵¹

3.13.4.1.2 Rhenium

Rhenium belongs to the Group 7 elements and, as with manganese, its carbonyl dinuclear complex $[\text{Re}_2(\text{CO})_{10}]$ is also known to induce free radical polymerizations combined with alkyl halides similar to manganese.⁶⁶ A rhenium(V) iodide complex (Re-1 in Figure 15) induced the efficient living radical polymerizations of styrenes coupled with an iodide initiator and Al (O*i*-Pr)₃ over a wide range of temperatures between 30 and 100 °C, in which the MWDs became narrower with decreasing temperature ($M_w/M_n = 1.2-1.5$).^{172,352} Presumably, the system also includes some contributions of the degenerative iodine transfer processes.³⁵³ The system could be employed for acrylate polymerizations, such as MA and BA. Although the MWDs are



Figure 15 Manganese and rhenium catalysts.

broader throughout the polymerization ($M_w/M_n = 1.6-1.8$), the reaction was faster than with NiBr₂(P*n*-Bu₃)₂.

There was a report on the use of a Re(I) complex (Re-2) in 1,2-dichloroethane at 50 °C, in which an increase in the molecular weights with conversion was observed for the MMA polymerization.³⁵⁴ Due to the absence of an initiator, the solvent presumably served as a supplier of the initiating radical species. The radical nature of the polymerization was suggested from the copolymerization behavior of MMA and styrene.

3.13.4.2 Other Early Transition Metals

3.13.4.2.1 Group 6 metals: molybdenum and tungsten

A lithium molybdate(V) complex (Mo-1 in Figure 16) was first employed by Brandts and co-workers³⁵⁵ for the controlled polymerization of styrene in conjunction with benzyl chloride in toluene at 80 °C to yield relatively broad MWDs ($M_w/M_n = 1.5-1.7$). As decomposition of the complex was observed, the initiation efficiency was low ($I_{eff} \sim 10\%$).

As with ruthenium and iron, there appeared effective systems for the living polymerizations by Mo(III) complexes with half-sandwich Cp ligands. In 2001, Le Grognec et al.356 first reported a series of half-sandwich Mo complexes (Mo-2-Mo-4) for the styrene polymerization via either the ATRP or OMRP mechanism, in which the former proceeds via the reversible activation of a C-X bond by Mo(III) species and the latter reversibly generates radical species from the in situ formed covalent C-Mo(IV) bond. Whereas the Mo-2 (X = Cl) induced a CCT with the halide, but mediated OMRP, the Mo-3 and Mo-4 were active for both the Mo-catalyzed ATRP of styrene with AIBN and 1-phenylethyl bromide as the initiator and OMRP of styrene in the presence of AIBN to produce polymers with an increasing $M_{\rm p}$ in direct proportion to the monomer conversion with moderate MWDs ($M_w/M_n \sim 1.4$ for ATRP and 1.7 for OMRP).

The complexes with diazadiene ligands (Mo-5) were also examined for OMRP and ATRP.³⁵⁷ The structure of the ligands and the polymerization conditions were crucial for the dual activity; for example, the diaryl diazadiene complex



Figure 16 Molybdenum and tungsten catalysts.

(Mo-6, R = 2,6-*i*-Pr₂Ph) induced both OMRP and ATRP, while the dialkyl version (Mo-5, R = *i*-Pr, X = Cl) worked only for ATRP due to the irreversible formation of the C–Mo(IV) bond.³⁵⁸ Furthermore, when coupled with an α -iodoester initiator in the presence of Al(O*i*-Pr)₃, Mo-5 (R=*i*-Pr, X = Cl or I) could be conducted to MA, BA, and styrene polymerizations, which resulted in the accelerated polymerization to give polymers with narrower MWDs ($M_w/M_n \sim 1.2$) and their block copolymerization.^{358–360} A chiral bisoxazoline ligand produced a (μ -Cl)₂ binuclear Mo(III) complex (Mo-7), with which the faster and controlled polymerization of styrene proceeded with 1-phenylethyl bromide/Al(O*i*-Pr)₃ than with another chiral dialkyl diazadiene complex (Mo-5, R = (S)-CH(CH₃)Ph, X = Cl), although the effects of the chirality were unknown.³⁶¹

A simple trivalent Mo complex with the trialkylphosphine ligand, $Mo(III)X_3(PMe_3)_3$ (Mo-8, X = Cl, Br, or I), was also employed for the styrene polymerization with 1-phenylethyl bromide as the initiator to afford well-controlled polymers with moderate MWDs $(M_w/M_n = 1.2-1.4)$.^{362,363} The addition of Al(Oi-Pr)3 improved the reaction rate, giving narrower MWDs, and the reverse ATRP process was also attained using $Mo(IV)Cl_4(PMe_3)_3$ with AIBN. The chloride complex (Mo-8, X = Cl) was also applicable for the MA polymerization in the presence of a bromine-containing initiator and Mo(IV)Cl₄ $(PMe_3)_3$ in an ionic liquid, whereas the bromide complex formed insoluble products by an unknown side reaction.³⁶⁴ MoOX₂(PMe₃)₃ (Mo-9), a tetravalent oxo-Mo(IV) complex, was employed for the polymerization of styrene and MA with a bromide or iodide initiator, respectively, in the presence of Al (Oi-Pr)₃ to give linearly increasing molecular weights, though the initiation efficiency was low with broad MWDs for the MA

polymerization.³⁶⁵ Hua *et al.*^{366,367} reported that the pentavalent analog, MoO₂Cl/PPh₃ (Mo-10), or the *in situ* formed MoCl₃(OC₈H₁₇)₂/PPh₃ (Mo-11) successfully induced the butadiene polymerization in the presence of the chloride initiators at 120 °C, which resulted in the controlled molecular weights with moderate MWDs ($M_w/M_n \sim 1.5$). The ATRP mechanism was supported by the reverse process with AIBN/MoO₂Cl₂/PPh₃.

In earlier studies, carbonyl complexes of all the zero-valent Group 6 metals, including $Cr(CO)_6$, $Mo(CO)_6$, $Mo(CO)_5$ Py, W (CO)₆, and so on, had been reported to initiate the radical polymerizations in the presence of alkyl halides probably with an uncontrolled chain growth.^{66,368} Recently, some new zero-valent Mo complexes with chelating ligands (Mo-12 and Mo-13) were also examined for the polymerization of MMA in conjunction with the halide initiators by Mentes *et al.*,^{369–371} although the controllability with the complexes was still unclear.

As for the other Group 6 metals, there was only one example of the MMA polymerization with a tetravalent metallocene complex of tungsten (W-1) in the presence of AIBN to produce the linearly increasing M_n but broad MWDs ($M_w/M_n \sim 2$), though it was unclear via which reaction it proceeded, the reverse ATRP or OMRP process.³⁷² Meanwhile, a certain chromium complex with the Cp ligand (Cr-1) was somehow efficient for the controlled OMRP of VAc.³⁷³

3.13.4.2.2 Group 5 metals: niobium and vanadium

Little progress has been reported about the metal-catalyzed radical polymerization with Group 5 metals. One notable exception is the MMA polymerization with a niobocene $(EtC_5H_4)_2NbCl_2$ (Nb-1 in Figure 17).³⁷² In the presence of



Figure 17 Niobium, vanadium, titanium, and lanthanide catalysts.

AIBN at 70 °C, Nb-1 produced controlled PMMA, of which M_n increased in direct proportion to the conversion or with reduced AIBN loading. However, it is again not clear whether the controlled propagation took place through the reverse ATRP, OMRP, or addition to the cyclopentadienyl ring.³⁷⁴

More recently, there was a report about the vanadium-mediated OMRP of styrene and VAc using the bisiminopyridine complex (V-1) combined with AIBN, of which the dormant species was presumably the C–V bond.³⁷⁵

3.13.4.2.3 Group 4 metals: titanium

In general, the compounds of the Group 4 metals, such as halides and alkoxides, are well known as Lewis acids to catalyze two-electron electrophilic reactions, and their metallocenes coupled with alkylation and/or reduction agents were effective catalysts for the coordination polymerization of olefins. For the transition metal-catalyzed radical polymerization, their alkoxides, such as $Ti(Oi-Pr)_4$, have also been employed as an additive for a better control of the products.^{168,177,178} Contrary to the common belief that the Group 4 metals rarely undergo a one-electron redox reaction under mild conditions, there have been some reports on the controlled radical polymerization catalyzed or mediated by titanium complexes, although the conflict in the mechanism between the (reverse) ATRP and OMRP is also the case with the Group 4 metal complexes.

In 2003, a series of titanium(III) halides and n-butoxide (Ti-1-Ti-3 in Figure 17) were conducted for the radical polymerization of styrene in conjunction with several mono-, bi-, and tridentate ligands coupled with 1-phenylethylbromide or chloride as the initiator.^{376,377} For example, the 1-phenylethylbromide/TiBr₃/PMDETA system produced polystyrene having a controlled $M_{\rm p}$ in good agreement with the calculated values, whereas TiCl₃ combined with 1,2-bis(hexylthio)ethane added to 15 mol.% of 1,8-bis(dimethylamino)naphthalene as the ligands afforded not only a well-controlled Mn but also relatively narrow MWDs with the chloride initiator $(M_w/M_n = 1.26)$. A similar Ti(III)/Ti(IV) redox system was reported for the polymerization of styrene and MMA with 1-phenylethylchloride and Cp₂Ti(IV)Cl₂ or related compounds (Ti-3-Ti-5), in which the actual catalyst was presumed to be the in situ formed Cp2Ti(III) Cl. 372,378,379 Based on the model reactions and the success for the postpolymerization of styrene, the controlled or living nature of the system was suggested to be via the ATRP mechanism.

In contrast, Asandei and Moran³⁸⁰ reported in 2004 that titanocenes (Ti-3) could also efficiently induce another controlled radical polymerization of styrene most probably via the OMRP process. The Cp2Ti(III)Cl system, which was in situ generated from Cp₂Ti(IV)Cl₂ and reducing agents such as Zn, in combination with an epoxide or aldehyde as the initiator accomplished the controlled radical polymerization of styrene affording polymers with an increasing M_n and relatively narrow MWDs $(M_w/M_n \sim 1.2)$.^{381–384} It was suggested that the polymerization was initiated by the radical ring-opening of epoxides by Ti(III) species and recombination with another Ti(III) to form a C-Ti(IV) bond and presumably proceeded via the reversible and homolytic dissociation of the C-Ti(IV) bond (OMRP) with some contribution of the reversible transfer (DT), as in the VAc polymerizations with Co complexes. Recently, the polymerization of isoprene was also reported for the same system to produce polymers with M_n values up to 60 000 and moderate range of MWDs $(M_w/M_n = 1.3-1.8)$.³⁸⁵

Other Ti(IV) compounds with dithio anion ligands (Ti-6 and Ti-7) were employed for the polymerizations of MMA and styrene via the reverse ATRP using a pseudohalogen transfer group.³⁸⁶

3.13.4.2.4 Group 3 metals: lanthanide

The halide complexes of the Group 3 metals usually act as electrophilic Lewis acids and are rarely active during the one-electron redox reactions with some exceptions: the lanthanides, such as Nd, Sm, and Yb, were capable of forming divalent and trivalent compounds. A series of rare-earth metal triflates (Y(OTf)₃, Yb(OTf)₃, Lu(OTf)₃, Sc(OTf)₃) (Ln-1, Figure 17), which were already known as effective additives for the stereocontrol during radical polymerizations,³⁸⁷ were first used as the catalysts for the radical polymerization of NIPAM in the presence of alkyl halides as initiators.³⁸⁸ Although the control of the molecular weights was not attained $(M_w/M_p > 2)$ and the reaction might not occur via redox mechanism, the radical polymerization occurred smoothly in the presence of the Lewis acids when coupled with the halides to produce isotactic poly(NIPAM), which served a dual role as the promoter of the radical initiation from the carbon-halogen bond and the controller of the stereospecific polymerization.

An interesting result of the dual control of molecular weights and tacticity was reported using YbI₂, which might also serve as a metal catalyst for the living radical polymerization as well as the mediator for the stereospecific radical polymerization.³⁸⁹ The MMA polymerizations were carried out with 1-phenylethyl bromide/YbI₂ at 90 °C to produce polymers with controlled molecular weights ($M_w/M_n = 1.24$) and a slightly higher syndiotacticity (mm/mr/rr = 3/29/68) than that obtained by AIBN (mm/mr/rr = 7/40/52). The effect of the rare-earth metal iodide on the tacticity was opposite that of the triflate [Yb(OTf)₃],³⁸⁷ which increased the isotacticity similar to Sc(OTf)₃. Neodymium(II) iodide was also employed with a bipyridine ligand (Ln-3) in conjunction with a bromide initiator to induce the controlled polymerization of MMA and styrene ($M_w/M_n = 1.4-1.5$).³⁹⁰

A reverse ATRP system was investigated with the free radical initiator/SmCl₃/lactic acid system (Ln-4) to mediate the controlled polymerizations of MMA and methacrylonitrile (MAN).^{391,392} The MMA polymerization with AIBN/SmCl₃/lactic acid at 80 °C produced well-controlled polymers bearing narrow MWDs ($M_w/M_n \sim 1.3$) with the M_n increasing in direct proportion to the conversion up to 20 000, in which the catalysis was proposed to take place with an equilibrium between the Sm(II) and Sm(III) species.³⁹¹ The MAN polymerization was conducted by SmCl₃ and lactic acid in DMF with diethyl 2,3-dicyano-2,3-diphenyl succinate as the thermal initiator to produce a fairly narrow MWD poly (MAN) ($M_w/M_n = 1.1-1.2$).³⁹²

3.13.5 Prospective View of Catalysts for Living Radical Polymerization

Since the first discovery of the transition metal-catalyzed polymerization using $RuCl_2(PPh_3)_3$ and CuCl/2,2'-bipyridine in the mid-1990s, transition metal-catalyzed atom transfer living radical polymerization has been further developed in this decade by establishing its principle, that is, the scope of applicable monomers, metal catalysts, and initiators.

As described in this comprehensive review, numerous metal complexes have been found to efficiently accomplish the controlled radical polymerization one after another. Most importantly, the metal-catalyzed system requires catalytic amounts of a transition metal complex, while all of the polymer chains emerge from the stable and easy-to-introduce carbon-halogen bond in an initiator molecule or on the surface of specific materials. The judicious combination of the central metal and ligand leads to an extraordinarily high activity, such as ruthenium with bisphosphine monoxide (Ru-20) and copper with branched tetrapyridyldiamine (Cu-12), which can make the catalyst loading down to 1/200 without any significant loss in the controllability.^{115,339} As for reducing the catalyst amount, two methodologies were also recently reported for the copper-based system to effectively and significantly improve the catalytic cycle. They are ARGET (activators regenerated by electron transfer) or ICAR (initiators for continuous activator regeneration) and SET (single-electron transfer), which are implemented in combination with reducing agents and the disproportionation in the copper valence, respectively.^{19,335,393} ICAR was applicable not only to the copper-based system but also to the polymerization with highly versatile Ru(Cp*)Cl(PPh₃)₂ (Ru-6) with reduced catalyst loading.³⁹⁴ A mechanism for SET has been reported,^{19,395} and discussion is still continuing about possible pathways of this interesting catalysis.396-398

The highly active, versatile, reproducible, and robust catalysts meet not only requirements for industrial applications, in which less expensive, metal residue-free, and nontoxic systems are favorable, but also those concerning environmental issues and applications for the conjugation with other disciplines, like biological and inorganic materials. Owing to its simplicity and versatility, metal-catalyzed polymerization is now recognized as a common tool for the polymer preparation, rather than as a special technique of polymer chemists, and will further develop to reach a variety of research fields of various academic disciplines including material engineering, biochemistry, and medicinal sciences as well as practical use in industry.

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3.14 Vinyl Polymerization in Heterogeneous Systems

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3.14.1	Introduction	463
3.14.2	Vinyl Polymerization in Aqueous Dispersed Systems	463
3.14.2.1	Conventional Radical Polymerization	463
3.14.2.1.1	Suspension polymerization	463
3.14.2.1.2	Emulsion polymerization	465
3.14.2.1.3	Miniemulsion polymerization	474
3.14.2.1.4	Microemulsion polymerization	478
3.14.2.1.5	Aqueous dispersion and precipitation polymerizations	479
3.14.2.2	Controlled Radical Polymerization	480
3.14.2.2.1	Overview of CRP in aqueous dispersed systems	480
3.14.2.2.2	Nitroxide-mediated radical polymerization	480
3.14.2.2.3	Atom transfer radical polymerization	483
3.14.2.2.4	Reversible addition-fragmentation chain transfer	485
3.14.2.2.5	Other CRP methods	488
3.14.2.3	Other Vinyl Polymerization Methods	488
3.14.2.3.1	ROMP in aqueous dispersed systems	488
3.14.2.3.2	Ionic polymerizations	490
3.14.2.3.3	Catalytic polymerization	490
3.14.3	Vinyl Polymerization in Nonaqueous Dispersed Systems	491
3.14.3.1	Conventional Radical Polymerization	491
3.14.3.1.1	Inverse emulsion, miniemulsion, and microemulsion polymerizations	491
3.14.3.1.2	Dispersion polymerization	492
3.14.3.2	Controlled Radical Polymerization	493
3.14.3.2.1	Dispersion polymerization in organic solvent	493
3.14.3.2.2	Dispersion polymerization in scCO ₂	494
3.14.3.3	Ionic Polymerization of Vinyl Monomers	494
3.14.4	Conclusion	494
References		494

3.14.1 Introduction

This chapter is devoted to the chain-growth polymerization of vinyl monomers in dispersed systems, including aqueous and nonaqueous systems. It covers the various polymerization methods such as conventional and controlled/living free radical polymerizations, anionic polymerization, cationic polymerization, ring-opening metathesis polymerization (ROMP), and catalytic polymerization of olefins. The aqueous dispersed systems are mainly suspension, emulsion, miniemulsion, microemulsion, and dispersion/precipitation. In nonaqueous systems, the systems are inverse emulsion, miniemulsion, and microemulsion for the polymerization of hydrophilic monomers and mainly dispersion polymerization for a broader variety of monomers polymerized in various dispersing solvents such as organic solvents, supercritical carbon dioxide ($scCO_2$), and ionic liquids.

3.14.2 Vinyl Polymerization in Aqueous Dispersed Systems

3.14.2.1 Conventional Radical Polymerization

3.14.2.1.1 Suspension polymerization 3.14.2.1.1(i) General principles

Free radical polymerization, when conducted in bulk and converted to high conversions, yields a highly viscous mixture that poses various reaction engineering problems. Stirring the mixture during polymerization (which is essential for adequate removal of the enthalpy of polymerization), pumping the mixture from the reactor through process lines and into storage vessels, and monomer devolatilization are significant challenges when viscosity is high. If the process requires semibatch addition of other components during polymerization (e.g., initiator, monomer, chain transfer agent), high viscosity and the consequent poor stirring may preclude effective mixing of those components throughout the reaction mixture, particularly in large reactors. While solvent can be used to reduce viscosity, solvent removal becomes an additional (and expensive) process step. If it is desired to crosslink the polymer, even lightly, bulk or solution polymerization often becomes unfeasible.

The challenges described above can be readily overcome by suspending monomer droplets in an aqueous medium and then polymerizing the droplets. The final product in a suspension polymerization is a low viscosity, two-phase mixture of solid polymer particles suspended in water. The formulation of the monomer phase is similar to a bulk polymerization, including the use of monomer-soluble initiators and chain transfer agents. Typical particle sizes are \sim 50–1000 µm, large enough so that the particles settle quickly in the absence of stirring. Solids contents for industrial processes are ~50 wt.%. Recovery of the particles can usually be done by filtration. Removal and recovery of residual monomer by techniques such as steam stripping are facile, although it is desirable to attain the maximum possible monomer conversion in the polymerization stage. For these reasons, suspension polymerization is generally preferred over bulk or solution for most applications, and is widely used industrially. Specific examples of important industrial polymers made by suspension polymerization are given in Section 3.14.2.1.1(i). Several extensive reviews of suspension polymerizations are available.^{1–4}

3.14.2.1.1(i)(a) Kinetics of suspension polymerization versus bulk polymerization It has often been stated that suspension polymerization is analogous to conducting a polymerization in miniature bulk reactors. While this is a reasonable approximation for some cases, the causes of possible differences in the kinetics between bulk and suspension should be understood. If all components in the formulation (e.g., monomer, initiator, chain transfer agent) have low or negligible water solubility, and if the monomer droplet (or polymer particle) size is large ($\gtrsim 50 \,\mu$ m), the kinetics of a suspension polymerization will likely resemble bulk polymerization. Primary factors contributing to deviation from bulk-like kinetics are the following: (1) components of the formulation, especially one or more of the monomers, having moderate to high water solubility; and (2) small droplet/particle size. Significant monomer partitioning into the aqueous phase can result in lower overall monomer conversions, lower rates of polymerization, and changes in the copolymer composition distribution compared to bulk. When the droplet/ particle size becomes quite small, the likelihood of having concurrent emulsion polymerization also becomes a concern. A population of very small droplets, especially if coupled with moderately water-soluble monomer and initiator, create conditions suitable for homogeneous/coagulative nucleation of emulsion polymer particles. (Suspension polymerization where the mean particle size is under $\sim 10 \,\mu\text{m}$ is often referred to as 'microsuspension polymerization'.) Concurrent emulsion polymerization is highly undesirable, since the emulsion particles will have a different molar mass distribution (MMD), copolymer composition distribution, and particle size distribution (PSD) than the desired suspension particles. Of greater concern is that emulsion polymer particles compete for stabilizer with suspension particles, often causing severe coagulation. Water-soluble inhibitors can be added to minimize emulsion particle nucleation.

3.14.2.1.1(i)(b) Suspension stabilization Polymerizing droplets are stabilized by either water-soluble polymers (including, e.g., poly(vinyl alcohol), hydroxyalkyl celluloses, carboxymethyl cellulose, poly(acrylic acid) (PAA) and its salts, and water-soluble acrylic copolymers) or insoluble inorganic powders (usually salts of calcium, aluminum, or magnesium). Polymeric stabilizers reduce the interfacial tension between the organic and aqueous phases, and provide a protective layer on the droplet/particle surface that inhibits coalescence. Surfactants such as sodium dodecyl sulfate (SDS) may be added to further reduce the interfacial tension, thereby facilitating smaller particle sizes. Inorganic powders such as calcium phosphate preferentially locate at the droplet/particle interface with the aqueous phase to provide a physical barrier against coalescence. Advantages include reduced reactor fouling and ease of removal from the particle surface after polymerization, for example, with a dilute acid wash. Polymeric stabilizers, having numerous adsorption sites per molecule, are difficult to effectively remove from the particles after polymerization.

3.14.2.1.1(i)(c) Particle size distribution Several factors contribute to the final PSD in a suspension polymerization, including the monomer type, stabilizer type and concentration, solids content in the reactor, and very importantly, mixing in the reactor. In the early stages of polymerization, the droplets/ particles are of low enough viscosity that both breakage and coalescence occur - breakage in the vicinity of the impeller and coalescence in the quiescent regions of the reactor. The overall droplet/PSD is determined by a dynamic equilibrium between breakage and coalescence. As the viscosity in the particles increases, they will become too viscous to easily undergo breakage but can still undergo coalescence. This phase, sometimes referred to as the 'sticky region', is where serious coagulation problems are most likely to occur. At even higher viscosities, the particles become less prone to coalescence and suspension stability improves considerably.

The formulation largely determines the interfacial tension and is readily reproduced during scale-up but the same cannot be said of mixing. One of the major challenges in scaling up suspension polymerizations lies in scaling up the mixing pattern. Larger reactors have inherently different mixing behavior than laboratory reactors,⁵ including lower average shear rates, higher maximum shear rates, and longer circulation times. A further challenge is that the mixing requirements change during the course of polymerization. At low conversion, the droplets/ particles are usually less dense than the aqueous phase and are prone to pooling on the surface, while higher conversion particles are usually denser than water, requiring the agitator to effectively suspend solids that are prone to settling on the reactor bottom.

3.14.2.1.1(ii) Industrial applications

Several commercially important vinyl copolymers are manufactured using suspension polymerization, including polystyrene (general purpose, expandable and high impact), poly (methyl methacrylate), poly(vinyl acetate), styrene–acrylonitrile

(SAN) copolymers, acrylonitrile-butadiene-styrene (ABS) copolymers, and poly(vinyl chloride) (PVC). Crosslinked particles (e.g., based on styrene and divinylbenzene) used as ion exchange resins, as beads for chromatographic separation, or as solid support for chemical reactions are also prepared by suspension polymerization. While for most monomer-polymer systems the polymer is fully soluble in the monomer, for some systems (vinyl chloride, acrylonitrile) the polymer is only slightly soluble in the monomer. During polymerization, the polymer begins precipitating at very low conversions. In suspension polymerization, these systems are commonly referred to as 'powder suspension polymerizations', while the more common systems where the monomer and polymer are mutually soluble are called 'bead suspension polymerization'. Examples of industrial formulations and process diagrams are available in the literature.⁴

3.14.2.1.2 *Emulsion polymerization* 3.14.2.1.2(*i*) *General principles*

3.14.2.1.2(i)(a) Overall description Free radical polymerization of vinyl monomers in emulsion has been widely studied in the past 60 years, and has still been the topic of a multitude of books^{6–15} and review articles^{16–21} in the past 10 years. This is mainly because of its huge industrial interest as well as its intrinsic complexity. This polymerization process is indeed used in the large-scale production of a broad variety of polymers as it offers many technical and environmental advantages. Although mature, it remains very attractive and has undergone continuous improvement over the years, the most recent advances being, for instance, in the domain of controlled free radical polymerization.

Emulsion polymerization is a way of polymerizing hydrophobic, liquid monomers in water, in which they form an emulsion at the initial stage, most generally in the presence of a surfactant. The monomer is then initially partitioned between different phases: the large monomer droplets (diameter >1 μ m) formed by stirring and stabilized by the surfactant adsorbed at the interface, the continuous water phase (saturation concentration), and the micelles (when the surfactant concentration). Upon polymerization in the presence of a water-soluble radical initiator, the process leads to a latex, that is, an aqueous suspension of submicrometer polymer particles, which are stabilized against flocculation and coalescence by the surfactant, adsorbed at their surface.

The number of particles per unit volume of latex (N_p) cannot be determined directly but is calculated from the experimental measurement of the particle diameter (D, by transmission electron microscopy, dynamic light scattering, capillary hydrodynamic fractionation, to cite the most popular techniques) and the amount of polymer in the latex (τ), according to the eqn [1], in which d_p is the polymer density.

$$N_{\rm p} = \frac{6\,\tau}{\pi\,D^3\,d_{\rm p}}\tag{1}$$

An *ab initio* emulsion polymerization can be divided into three successive steps, each of them corresponding to a particular state of the system (Figure 1). The interval I is related to the nucleation, that is, the formation of particles. Its duration corresponds approximately to 2-10% monomer conversion,



Figure 1 Typical conversion vs. time plot in emulsion polymerization, showing the three intervals.

and it exhibits an increasing conversion rate. Once the number of particles has reached a constant value, the system enters the interval II, which corresponds to the particle growth by propagation (it may extend from 5-10% to 30-70% conversion, depending on the monomer system). The monomer concentration within the particles remains constant, as far as monomer droplets are present, because the latter supply the consumed monomer by molecular diffusion through the aqueous phase. In consequence the conversion rate is also constant. When the emulsion polymerization is started with preformed polymer particles, it is called 'seeded emulsion polymerization' and begins directly with interval II. The interval III is the final stage, during which the polymerization takes place within the particles in the absence of monomer droplets, that is, at a decreasing local monomer concentration. It is thus characterized by a reduction of the polymerization rate until a possible gel effect takes over, and the polymerization rate can start to increase again.

3.14.2.1.2(i)(b) Nucleation (interval I) Formation of the particles follows complex nucleation mechanisms that strongly depend on the surfactant concentration and the water solubility of the monomer(s). Droplet nucleation remains a negligible event. In all cases, the polymerization starts in the aqueous phase with the introduction of a water-soluble radical initiator, which forms oligoradicals upon initiation and subsequent polymerization with the dissolved monomer molecules. These oligoradicals may behave in different ways: either they self-terminate in the aqueous phase to form water-soluble or amphiphilic oligomers or they exclude themselves from the aqueous phase upon decrease of their water solubility by chain extension. It is now well established that the particles originate from these oligoradicals when they reach a given degree of polymerization, at which their physicochemical properties and water solubility are strongly altered. Their fate is then dictated by the presence or absence of surfactant micelles. When the surfactant concentration is above the CMC and the monomer is rather hydrophobic, the oligoradicals are captured by the monomer-swollen micelles as soon as they become surface active (i.e., degree of polymerization = z) and generate particles by the so-called micellar nucleation mechanism (Figure 2(a)). The local monomer concentration is high enough to allow for a fast chain growth and hence an irreversible entry process. Only part of the micelles is actually nucleated, while the others serve as surfactant reservoirs to stabilize the created interfaces. Nucleation then ceases when



Figure 2 Schematic representation of (a) micellar nucleation and (b) homogeneous-coagulative nucleation, for an emulsion polymerization initiated by sulfate radicals (i.e., persulfate initiator).

all micelles have been consumed. At this stage, and according to the Smith and Ewart law,²² N_p is theoretically proportional to $[initiator]^{2/5}[surfactant]^{3/5}$. More generally, $N_{\rm p}$ is proportional to $[surfactant]^{\alpha}$ with α being usually below 1. At surfactant concentration below the CMC or in the absence of surfactant and for hydrophilic monomers such as methyl methacrylate and vinyl acetate (VAc), formation of the particles follows a so-called homogeneous nucleation mechanism (Figure 2(b)). In that situation, the oligoradicals grow in the water phase by addition of monomer units until they become insoluble (critical degree of polymerization = i_{crit}) and precipitate to form primary nuclei. Their colloidal stability is ensured by the surfactant, when present, and the charged fragment of the initiator at the chain end. It might be enhanced by the limited coagulation of several nuclei in order to increase the charge surface density (homogeneous-coagulative nucleation). Nucleation ceases when capture of the oligoradicals by the already existing particles prevails.

3.14.2.1.2(i)(c) Particle (interval II), growth polymerization kinetics, and average molar masses During interval II, the monomer-swollen polymer particles become the main polymerization loci and this corresponds to their growth by propagation, which is permitted by the presence of both radicals and monomer. The radicals come from the capture of oligoradicals generated in the aqueous phase, while monomer is continuously supplied from the droplets (which act only as monomer reservoirs), by diffusion through the water phase. For traditional monomers with sufficient water solubility (i.e., solubility equal or higher than that of styrene), the diffusion process is generally much faster than propagation, and hence the monomer concentration within the particles is governed by thermodynamic equilibrium. The local monomer concentration [M]_p remains, thus, constant as the result of the balance between opposing effects: reduction of the surface free energy by a decrease of the surface area (i.e., leading to a decrease of the particle volume and consequently of [M]_p) and reduction

of the free energy of mixing of polymer and monomer, which contributes to increase in $[M]_p$. As the particle number remains constant during the interval II, the polymerization rate R_p is then a constant too (eqn [2a]). Polymerization rate in interval II:

$$R_{\rm p} = \frac{k_{\rm p} \left[\mathrm{M}\right]_{\rm p} N_{\rm p} \tilde{n}}{N_{\rm A}}$$
[2a]

Instantaneous number-average molar mass, M_{n} , in interval II for a 0-1 system with radical entry faster than radical transfer ($\tilde{n} = 0.5$):

$$\overline{M}_{n}^{\text{inst}} = \frac{k_{\text{p}} [\text{M}]_{\text{p}} N_{\text{p}}}{2 R_{\text{i}} N_{\text{A}}} \text{MM}_{\text{m}}$$
[2b]

In eqn [2], k_p is the rate constant of propagation, \tilde{n} the average number of radicals per particle, N_A the Avogadro's number, R_i the initiation rate in the aqueous phase, and MM_m the monomer molar mass. Propagation thus obeys a zeroth order with respect to monomer concentration and not a first order as observed in homogeneous polymerizations and suspension polymerization.

The unique feature of kinetics in emulsion polymerization results from the compartmentalization of the propagating radicals within separate particles. A direct consequence of the compartmentalization is a decreased overall termination rate, that is, a longer radical lifetime, a larger overall concentration of propagating radicals, and thus a much faster polymerization rate than in homogeneous system. One of the most famous and useful theoretical description of the kinetics in emulsion polymerization was established by Smith and Ewart²² who considered several cases, including the very important pseudo-bulk and 0-1 systems. In the former case, the average number of radicals per particle \tilde{n} is well above 1. This occurs when the particle size is sufficiently large or the viscosity inside the particle is sufficiently high (at high conversion), so that two or more radicals can coexist within a single particle without instantaneous termination. This case cannot be distinguished from that of the equivalent homogeneous system, and consequently the polymerization rate is independent of the particle number (no effective compartmentalization effect). In contrast, with particles of sufficiently small size, the entry of an oligoradical into an active particle (i.e., a particle that already contains 1 radical) causes an instantaneous termination reaction. The rate of radical consumption becomes, thus, governed by the rate of entry and not by the termination reaction itself. The particles contain either 1 or 0 radical and this leads to $\tilde{n} = 0.5$ when entry is fast and the exit of radicals is negligible (negligible transfer reactions). This case is applicable to most emulsion polymerizations. When radicals easily escape from the particles (i.e., significant transfer reaction to a small molecule) and undergo fast termination in the aqueous phase, \tilde{n} may become very small, below 0.5. In both situations, the polymerization rate shows a strong dependence on the number of particles, hence the surfactant and initiator concentrations are of critical importance and the compartmentalization effect dictates the kinetics. When radicals easily escape from the particles but reentry into another particle is fast, \tilde{n} is also well below 0.5, but the polymerization rate is little affected by the number of particles, and the compartmentalization effect is actually not effective.

The molar masses of the polymers obtained from emulsion polymerization are significantly larger than those obtained from bulk polymerization, due to a longer lifetime of the propagating radicals resulting from compartmentalization. For a 0-1 system with radical entry faster than radical transfer ($\tilde{n} = 0.5$) and for negligible termination in the aqueous phase, the instantaneous M_n is given by eqn [2b].⁸ It is thus possible to increase simultaneously the average molar mass and the polymerization rate by increasing N_p , whereas in bulk or in suspension polymerization, the molar mass decreases when the rate is increased (by an increase of the initiator concentration). In general, the MMD is broader than in homogeneous systems.

3.14.2.1.2(ii) Particle stabilization

While the stability of the initial monomer-in-water emulsion is not critical, the colloidal stability of the formed particle is in contrast of utmost importance. In most cases, it is ensured by low-molar-mass surfactants, typically anionic and nonionic amphiphilic molecules, which are adsorbed at the particle surface in dynamic equilibrium with the small fraction dissolved in the aqueous phase. When ionic surfactants are used, they contribute to charge the particle surfaces and provide an electrostatic repulsion. The particles are surrounded by an electrical double layer constituted by the counterions of opposite charge, which screens the surface charges and induces the build up of an osmotic pressure responsible for the repulsion. This layer is actually divided in two regions. Close to the interface, the ions are strongly bound to the surface (the so-called Stern layer), whereas at a longer distance, they are more loosely bound and hence more mobile. The latter region is named the diffuse layer, the thickness of which is the Debye screening length. It is larger when the ionic strength in the aqueous phase is lower. Consequently, the electrostatic stabilization of latexes is strongly dependent on the salt concentration and its valency. The repulsion is counterbalanced by attractive forces, namely van der Waals and hydrophobic interactions. The DLVO (Derjaguin, Landau, Verwey, and Overbeek) theory²³⁻²⁶ gives an approximate description of the overall interaction energy between the particles and allows prediction of latex stability.

In some situations, the latex particles are covered with adsorbed hydrophilic polymer chains (either ionic or nonionic), which are swollen with water and expand in the aqueous phase. These polymers contribute to the steric stabilization of the particles through their osmotic pressure. In the absence of adsorption of the hydrophilic polymer at the particle surface, an opposite effect may take place, known as depletion attraction.

Besides the classical low-molar-mass surfactants, various other possibilities have been studied to stabilize the latex particles originating from emulsion polymerization: those can be either water-soluble comonomers and macromonomers, or reactive surfactants^{27–31} or even amphiphilic copolymers.^{32,33} Their advantage is to remain strongly bound to the polymer constituting the particles, either through a covalent bond formed in the radical polymerization mechanism in the case of reactive molecules, or through anchorage of the hydrophobic segment(s) in the case of copolymers. Water-soluble comonomers react with the hydrophobic monomer(s) of the emulsion polymerization, in principle, during the first stages of the reaction and afford amphiphilic random copolymers, which adsorb at the particle surface. In the case of ionic comonomers, the stabilization is mainly electrostatic and possibly steric, depending on the length of the hydrophilic segments. In the case of macromonomers (based predominantly on poly (ethylene oxide) (PEO)), a graft copolymer is formed and induces a steric stabilization. Similarly, the reactive surfactants exhibit a functional group able to participate in one of the various steps of a radical polymerization, but they exhibit an intrinsic amphiphilicity due to the combination of polar and nonpolar parts in their structure and behave as classical surface-active molecules in water. They are called 'inisurfs' when they react as initiators (peroxide or diazoic group), 'transurfs' when they react as chain transfer agents (through a thiol group), or 'surfmers' when they react by copolymerization.²⁷ The latter represent the most important class of reactive surfactants and are now commercial products, based, for instance, on methacrylic or maleic esters. Differently, amphiphilic copolymers do not react in the polymerization process but can be used as stabilizers (the term surfactant may not be appropriate in the absence of surface-active properties) in replacement of the classical surfactants. These copolymers can be prepared by (1) classical radical polymerization (mainly random copolymers and alkali-soluble resins based, for instance, on styrene or methyl methacrylate (MMA) and (meth)acrylic acid), (2) anionic polymerization (diblock or triblock copolymers composed, for instance, of polystyrene or polybutadiene as the hydrophobic block and of PEO or poly(methacrylic acid) as the hydrophilic one), and (3) controlled/living radical polymerization (CRP; i.e., radical polymerization operating through a reversible deactivation of the propagating radicals - see Section 3.14.2.2 for a broad variety of chemical structures). Depending on the chemical structure of the hydrophilic segment(s), they will provide either a steric stabilization or an electrosteric one. With the block copolymers, the structure and thickness of the hydrophilic layer are well defined and the latex particles are often referred to as 'hairy' particles. The primary property of those stabilizers is the strong anchorage at the particle surface, hence impeding their migration during film formation. They may also find advantages during the nucleation step, when their self-assembled structure in water is stable at the timescale of the polymerization. With the so-called frozen micelles, for instance, it was shown that all micelles are nucleated and the final number of particle is then dictated by the initial number of micelles present.^{32,34}

3.14.2.1.2(iii) Emulsion polymerization processes

Batch, semicontinuous, and continuous reactors are used in emulsion polymerization. Typically, these reactors are stirred tank reactors, and the most common operation mode is the semicontinuous one because of its versatility. Because of their large heat transfer area/reactor volume ratio, tubular reactors are an attractive alternative, but they are not often used in emulsion polymerization, principally due to the high risk of phase segregation, fouling, and pipe clogging. Loop reactors (a tubular reactor with high recirculation rate) and pulsed reactors have been used but the main drawback of these tubular reactors is that recipes with high mechanical stability are required to prevent shear-induced coagulation. Tubular microreactors have proven to provide some advantages in homogeneous polymerization (temperature control and polymer microstructure) but they are still in a very preliminary stage of investigation for heterogeneous systems such as emulsion polymerization.

3.14.2.1.2(iii)(a) Batch reactors A batch reactor is a closed system in which the time is the only independent variable. The batch operation can be used for some small production of homopolymers from monomers with a relatively low heat of polymerization. However, the drawbacks associated with this type of operation limit its industrial use: (1) the control of the polymer properties is impracticable; (2) the productivity is low considering the load, unload, and cleaning times; (3) the heat generation rate is high and the control of the reactor temperature is very difficult because all of the monomer is initially charged into the reactor; and (4) the system suffers from batch-to-batch variations due to irreproducible particle nucleation that may jeopardize product consistency. In order to avoid this problem, seeded polymerization may be employed.

Batch reactors are commonly used in research laboratories because of its simplicity and low cost of operation. The composition of the copolymers produced in batch reactors will be dictated by the reactivity ratios of the comonomers and the ratio of their concentration in the polymer particles (Mayo–Lewis copolymer composition equation – see eqn [3] in Section 3.14.2.1.2(iv)). Most of the common monomers employed in emulsion polymerization recipes present different reactivities, and a consequence of this is the compositional drift (nonconstant copolymer composition) produced in batch operation.

3.14.2.1.2(iii)(b) Semibatch reactors In semibatch operation mode, some fraction of reactants (initial charge) is initially charged into the reactor, and the rest of the formulation is continuously fed over some period of time. Most commercial products are manufactured in semibatch reactors. The main characteristic of this process is the great flexibility. Varying the composition and amount of the initial charge, as well as the composition and flow rates of the feeds, both temperature and polymer quality may be controlled. A wide range of products are accessible using this technique that allows tailoring any polymer property, including copolymer composition, MMD, polymer architecture, particle morphology, and PSD. In addition, a large portfolio of products can be produced with a single reactor. The main drawback of this operation mode is the relatively low productivity, which is being compensated by using larger reactors.

In general, the initial charge contains a seed (i.e., preformed latex particles, used principally to avoid the lack of reproducibility of the nucleation stages when the seed is produced *in situ* and for scaling up issues), a fraction of water, surfactant, and initiator. Under some circumstances, certain amount of the monomer(s) can also be present. The rest of the formulation ingredients are added to the reactor at a constant flow rate (or following predefined trajectories in time that can be calculated based on empirical knowledge of the process or on optimization techniques from mathematical models).^{35,36}

3.14.2.1.2(iii)(c) Continuous reactors In continuous operation mode, both inlet and outlet streams flow continuously. The main feature of a continuous stirred tank reactor (CSTR) is the broad residence time distribution (RTD) that is characterized by a decaying exponential function. Due to this broad RTD, it is not possible to obtain narrow PSD using a single CSTR. In addition, CSTRs are prone to suffer intermittent nucleations that lead to multimodal PSDs. This may be alleviated by using a seeding reactor (such as a tubular reactor)

before the CSTR. In steady-state conditions, the properties of the polymer remain constant and hence it is ideal to produce high-tonnage polymers. The broad RTD together with the problem of heat removal in large stirred tanks makes it difficult to achieve high conversions in a single tank. This drawback might be overcome by arranging multiple stirred tanks in series that allow a better heat removal and narrower RTD, which in turn leads to a narrower PSD. CSTRs in series are used for high-tonnage productions such as styrene-butadiene rubber (SBR), but the production of specialty polymers is more challenging because of the difficulties associated with grade transitions.

3.14.2.1.2(iii)(d) Tubular reactors From a safety point of view, tubular reactors are advantageous because they have a large area/volume ratio (the highest values being those obtained in tubular microreactors) and hence the heat removal capacity is higher than that of the CSTR. An important disadvantage of the tubular reactor is the inadequate mixing that can lead to phase separation, reactor plugging, and wall fouling. Several modifications have been performed to improve radial mixing and minimize the associate problems, but to date tubular reactors are not widely utilized for industrial production. The most important modified tubular reactors include loop reactor,^{37,38} pulsed flow reactor,^{41,42}

3.14.2.1.2(iv) Emulsion copolymerization

In most of the cases, latex products are composed of more than one monomer. In copolymerization, two or more monomers are simultaneously built-in into the polymer chains. Emulsion copolymerization allows the production of materials with properties that cannot be obtained by homopolymer latex products or by blending homopolymers. The properties of the materials required are usually dictated by the market. Nowadays, most of them are achieved by combination of more than two monomers in the copolymer product. Typical industrial emulsion polymerization formulations are mixtures of monomers giving hard polymers and monomers leading to soft polymers. Styrene and MMA are examples of monomers giving hard polymers, that is, polymers with a high glass transition temperature (T_g) . Soft polymers, that is, polymers with a low T_{g} , are, for example, formed from *n*-butyl acrylate (BA). The industrial emulsion polymerization formulations (see below) also contain small amounts of functional and specialty monomers such as acrylic and methacrylic acid, or hydroxyethyl methacrylate to impart improved or special characteristics (functionalization) to the latex product.

3.14.2.1.2(iv)(a) Mechanism and kinetics The inclusion of a second (or additional) monomer(s) in the formulation of a homogeneous free radical polymerization greatly complicates the reaction kinetics and brings additional requirements related to the difference in reactivity of the monomers and its impact on the copolymer composition and copolymer sequence distribution. In an emulsion copolymerization, the complexity is even more profound because the heterophasic nature of the polymerization makes aspects such as the partition of the monomers in the different phases to play a significant role in the instantaneous copolymer composition produced and hence in the copolymer sequence distribution. Thus, the classical copolymer

composition equation (so-called Mayo–Levis equation, eqn [3]) for a terminal model of copolymerization also applies in emulsion copolymerization, but the concentration of monomers are now replaced by the concentration of monomer in the polymerization loci, that is, in the polymer particles.

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \quad \text{and} \quad f_1 = \frac{|M_1|_p}{|M_1|_p + |M_2|_p} \quad [3]$$

In eqn [3], F_1 is the instantaneous copolymer composition referred to monomer 1, and r_1 and r_2 are the monomer reactivity ratios for monomer 1 and 2 (terminal model), respectively. During intervals I and II, the concentration of the monomers in the polymer particles are governed by the partitioning of the monomers among monomer droplets, polymer particles, and aqueous phase. In interval III, there are no droplets and the monomer is mostly located in the polymer particles. The concentration of the monomers in the polymer particles depends on the relative values of mass transfer and polymerization rates. Except for poorly emulsified, highly water-insoluble systems, mass transfer is much faster than polymerization rate, and hence the concentration of monomers in the different phases is given by the thermodynamic equilibrium.

For a multimonomer system, the calculation of the concentrations of the monomers in the different phases involves the simultaneous resolution of the thermodynamic equilibrium equations and the material balance equations. Equilibrium equations based on the Morton–Flory–Huggins (MFH) equation⁴³ or on partition coefficients⁴⁴ can be used. For a multimonomer system, the interaction parameters of the MFH equation are not usually available; therefore, the use of the partition coefficients is easier and as accurate as the MFH equations at high solids content (>50 wt.%).⁴⁵ In the case partition coefficients are used, the following system of algebraic equations must be solved (eqns [4] and [5]):

> Equilibrium equation: $K_i^j = \frac{\phi_i^j}{\phi_i^w}$ j = polymer particles, droplets [4]

Material balance equations:

$$\begin{split} \phi_{\rm p}^{\rm p} + &\sum_{i} \phi_{i}^{\rm p} = 1\\ \phi_{\rm w}^{\rm w} + &\sum_{i} \phi_{i}^{\rm w} = 1\\ &\sum_{i} \phi_{i}^{\rm d} = 1\\ V_{\rm p} \phi_{i}^{\rm p} + &V_{\rm d} \phi_{i}^{\rm d} + &V_{\rm w} \phi_{i}^{\rm w} = V_{i}\\ &V_{\rm w} \phi_{\rm w}^{\rm w} = &V_{\rm water}\\ &V_{\rm p} \phi_{\rm p}^{\rm p} = &V_{\rm pol} \end{split}$$
[5]

In eqns [4] and [5], K_i^i is the partition coefficient of monomer *i* between the phase *j* and the aqueous phase; φ_i^j the volume fraction of monomer *i* in phase *j*; the superscripts w, p, and d denote aqueous phase, polymer particles, and monomer droplets, respectively; $V_{p'}$, $V_{d'}$, and V_w are the volumes of monomer-swollen particles, monomer droplets, and aqueous phase, respectively; and V_{iv} , V_{polv} , and V_{water} are the volumes of monomer *i*, polymer, and water, respectively.

3.14.2.1.2(iv)(b) Structured particles Composite polymer particles (particles made out of more than one phase) with



Figure 3 Simulated evolution of the morphology during a seeded semicontinuous experiment. First-stage polymer in gray (spherical grid). Second-stage polymer in green. From left to right, conversion of the second-stage monomer increases indicated by the time caption on top of each figure.

tailored physical properties are of great interest for many industrial applications. Composite latex particles are mainly used as architectural and automotive coatings,⁴⁶ impact modifiers in engineering plastics to improve toughness and impact strength,⁴⁷ opacifiers,⁴⁸ and in hybrid polymer–polymer^{49,50} and polymer– inorganic⁵¹ materials among other high added-value products. Composite latex particles are commonly produced by seeded semicontinuous polymerization where the second-stage monomer(s) is(are) fed into the reactor in a given period of time together with additional initiator, surfactant, and water (if necessary). The conditions are adjusted in such a way that the polymerization is favored inside the existing particles. Figure 3 illustrates the development of the morphology during the seeded semicontinuous reaction.

The position at which the polymer chain is formed depends on the radical concentration profile inside the particle. If the entering radicals are anchored to the surface of the particles, the newly formed polymer chains will be predominantly located in the shell layer. As the concentration of polymer increases, phase separation occurs, leading to the formation of clusters (green particles in Figure 3). Polymerization occurs in the clusters as well as in the polymer matrix; therefore, both the size of the cluster and the number of clusters increase. The resulting system is not thermodynamically stable due to the large surface area associated with the large polymer-polymer interfacial area. In order to minimize the free energy, the clusters migrate toward the equilibrium morphology. During migration, the size of the clusters increases due to (1) polymerization in the clusters, (2) diffusion of polymer into the cluster, and (3) coagulation between clusters. The motion of the clusters is governed by the balance between the van der Waals forces and the repulsion and resistance to flow that arise from viscous drag. The van der Waals forces between the clusters are always attractive whereas the van der Waals forces between cluster and aqueous phase can be attractive (the cluster will be drawn to the surface of the particle) or repulsive (the cluster will be brought toward the center of the particle). In Figure 3, the forces between the cluster (green particles) and the aqueous phase are attractive. It is worth mentioning that the van der Waals forces are proportional to the interfacial tensions. The final morphology heavily depends on the kinetics of the cluster migration.⁵²⁻⁵⁴ Metastable morphologies can be achieved by working under starved conditions (high concentration of polymer in the particles and hence high viscosities), promoting grafting reactions or producing block copolymers in situ (hence reducing the polymer-polymer interfacial tension).⁵⁵

Equilibrium morphologies may be attained if the internal viscosity of the particle is low (low molar mass and low polymer concentration in particles), the polymers are very incompatible (high interfacial tensions resulting in high van der Waals forces), and in very long process times. The equilibrium morphology is the one that minimizes the interfacial energy of the system and depends on the polymer-polymer interfacial tension (σ_{12}) and polymer-water (σ_{13} and σ_{23} for a two-phase system) interfacial tension. Modeling the equilibrium morphology of composite particles for two and three polymer phases has been reported, 56-58 and Figure 4 presents the potential equilibrium morphologies for a two-phase system as a function of the interfacial tensions. For a three-phase system, the number of potential morphologies is too large,⁵⁸ and it is not possible to draw a figure like Figure 4, and furthermore, it is very difficult to accurately compute the equilibrium morphologies without simplifying the potential morphologies.

Most recently, a general method to predict the equilibrium morphology of multiphase systems based on Monte Carlo simulations has been presented.^{59,60} The proposed method reproduces well the equilibrium morphologies calculated by the conventional methods mentioned above for two-phase systems. In addition, it allows the equilibrium morphology of three or more polymer phase particles to be predicted (without any *a priori* assumption of the morphology). **Figure 5** reproduces the three-dimensional equilibrium morphology of composite polymer particles composed by three polymer phases.



Figure 4 Equilibrium morphology of biphasic composite polymer particles (white, polymer 1; black, polymer 2; 3, water).



Figure 5 Equilibrium morphology of a three-phase waterborne polymer particle with a volume ratio $V_1/V_2/V_3 = 0.40:0.40:0.20$ with interfacial tension values $\sigma_{1-w} = 9.51$, $\sigma_{2-w} = 11.57$, $\sigma_{3-w} = 10.54$, $\sigma_{1-2} = 1.50$, and $\sigma_{1-3} = \sigma_{2-3} = 1.23$ mN m⁻¹. Polymers 1, 2, and 3 are represented in gray, light gray, and black, respectively. The water is not shown for clarity. (a) Visualization of the three-dimensional (3D) structure cut at different planes and (b) cross-sectional view of the particle.

3.14.2.1.2(iv)(c) Functionalized particles Some of the monomers used in emulsion polymerization formulations are so-called 'functional monomers' because in addition to bear a double bond (C=C) that covalently links to the polymer backbone, they contain a functional (reactive) group that might impart other properties to the polymer and to the colloidal system. The most common functional monomers for latexes produced in large tonnage are monomers with carboxylic acid and amide functionality, and they are used in small amounts (typically below 5 wt.%).⁶¹ Acrylic acid (AA), methacrylic acid, fumaric acid, and itaconic acid are the most frequently used carboxylic acids. Acrylamide is also often used as a functional monomer. Due to the polarity of these monomers, they are mainly located at the surface of the particles. The COOH group ionizes in water and the degree of ionization depends on the pH of the aqueous phase. In the ionized form (COO⁻), the negative charge of the carboxyl moieties imparts extra stability to the dispersion. In other words, they act as surfactants (see Section 3.14.2.1.2(ii)) with the advantage of being covalently linked to the polymer chains. In addition to the stability provided by these functional monomers, they also impart reactivity. For instance, the presence of carboxyl groups at the surface allows crosslinking reactions with urea-formaldehyde, phenol-formaldehyde, and others of the like. However, the use of these functional monomers might also bring problems such as an increase in the viscosity of the dispersion if excessive water-soluble highmolar-mass polymer is formed in the polymerization. The large partition of these monomers to the aqueous phase and their high reactivity (especially the acrylic ones) in radical polymerization are the main reasons for the production of hydrosoluble material.

Functionalized polymer particles produced by emulsion polymerization are also very attractive for high added-value applications (especially biotechnology) because of the outstanding properties that surface-functionalized polymer latexes offer when used as colloidal supports. Emulsion polymerization is to a great extent the polymerization technique of choice to synthesize the support particles due to the long-term experience and the basic understanding of the fundamental mechanisms controlling the polymerization. In addition, the versatility to carry on the polymerization (seeded batch or semibatch, *ab initio*, etc.) allows for the control of the PSD and particle surface chemistry.⁶² A great deal of work has been done in the past two decades to incorporate functionality to polymer particles, and it has been demonstrated that these particles have potential applications in biomedical and biological applications (tracer, immunoassay, recognition, etc.), drug delivery (cancer treatment), bioelectronics, and biosensors to name a few. Many types of chemical functionalities can be incorporated onto the polymer particles: simple chemical groups or more complex molecular or macromolecular structures able to provide specific recognition of biomolecules or living systems. The functionalization can be achieved by physical and chemical means.⁶³ Physical adsorption of surfactant and polymers has been used to provide functionalization to the particles in addition to steric stability. An example is the functionalization of preformed polymer particles with PEO groups in order to impart hydrophilicity to avoid adsorption of biological compounds (proteins, peptides, etc.) to the particle surface when the particles are used as nanocarriers in the bloodstream.⁶⁴ Functionalization by chemical reaction is preferred because there are a large number of chemical groups that can be easily incorporated at the surface of the particles. The most common way to achieve this goal is by seeded emulsion polymerization (core-shell particles) using a latex of hydrophobic polymer (likely polystyrene) in the first step. Then a shell of the functional polymer is created with monomers bearing carboxylic acid, aldehyde, acetal, chloromethyl, amine, hydroxyl, epoxide, or protected thiol groups.⁶³ Sometimes, the surface functionalization requires hairy layers or polymer brushes with well-defined structure and molar mass along with narrow MMD. The incorporation of this type of structure at the surface of latex particles by conventional free radical polymerization is not an easy task.^{65,66} The advent of CRP (see Section 3.14.2.2) and the possibility to run this method in aqueous phase has allowed and simplified the synthesis of this type of complex particle morphology.67-70 'Click chemistry' has also shown potential to produce functionalized polymer particles.⁷¹

3.14.2.1.2(v) Properties and industrial applications

Emulsion polymers are produced by a complex heterogeneous polymerization mechanism that has been described above. However, this inherent complexity enables the production of polymers with complex architectures and microstructures with a huge application potential. Application properties of latexes depend to a great extent on the polymer architecture that is mostly defined during the polymerization process, namely, in the polymerization reactor. The microstructure of polymer latex includes (see Figure 6) the copolymer composition, monomer sequence distribution, MMD, polymer architecture



Figure 6 Microstructural features of polymers and particles from emulsion polymerization.

(branching, grafting, crosslinking, and gel content), average particle size and PSD, particle morphology, and particle surface functionality.

Copolymer composition has a direct effect on the T_{σ} of the polymer, which determines the minimum film formation temperature (MFFT) of the latex and the application. Copolymer composition also affects properties such as resistance to hydrolysis and durability. MMD has a strong effect on application properties. Thus, for adhesives, it is well known that an appropriate balance of low- and high-molar-mass polymer chains is necessary; low-molar-mass chains impart tack, resistance to peel increases with intermediate-molar-mass chains, and resistance to shear increases with high-molar-mass chains. Polymer architecture defines several final properties too. For instance, gel content above certain values has shown to damage adhesive properties. Surface properties or nature of the functional groups located at the surface of the particles allow many application properties to be tailored, as discussed in the previous section. Relatively small amounts (lower than 5 wt.% based on the polymer) of carboxylic monomers are frequently used in the manufacture of latexes (carboxylated SBR latexes are a clear example). The presence of the carboxylic groups imparts electrostatic stabilization upon neutralization. Another example of surface functionalization is the incorporation of hydroxyl functionality to the surface (using, for instance, hydroxyethyl methacrylate monomer). This functionality allows crosslinking with thermoset coatings by curing with melamine chemistry. Particle morphology enlarges the applications of emulsion polymers. Core-shell particles composed of a rubber-like core and a hard shell are used as impact modifiers for commodity plastics such as PVC and poly(methyl methacrylate). Hybrid polymer-polymer^{49,50,72} and polymer-inorganic latexes⁷³⁻⁷⁵ are emerging as a new class of materials in which the morphology of the particles is a key parameter that affects the potential

properties of these materials. The PSD and particle surface functionality determine the rheology of the latex. Rheology is critical during the polymerization because, to a large extent, it controls mixing and heat transfer. In the synthesis of high solids content latexes, the maximum solids content achievable is controlled by the rheology of the dispersion. Therefore, the control of the PSD is crucial to increase the solids content of a waterborne dispersion.^{76–78} The particle size and PSD also affect the film properties. The smaller the particle size, the better the quality of the film (i.e., gloss).^{79,80}

Half of the polymer latexes synthesized by emulsion polymerization are commercialized as waterborne dispersions and the rest as dry polymer. The main polymer families produced are based on (1) styrene-butadiene, (2) acrylonitrile-butadiene, (3) chloroprene, (4) vinyl chloride, (5) VAc and its copolymers, and (6) acrylic (co)polymers.⁸¹

Styrene-butadiene, acrylonitrile-butadiene, chloroprene, and vinyl chloride emulsion (co)polymers are mainly used in their dried form. Carboxylated SBR, VAc (co)polymers, acrylics, and styrene-acrylic copolymers are used, on the other hand, as binders of formulation for several industrial applications in their dispersed form. **Figure** 7 shows the share of each of these families and the major industrial applications of these latexes.^{11,61}

Paper industry, paints and coatings, adhesive and sealants, and carpet industry cover approximately 80% of the latexes. Other industrial applications where latexes are directly applied are printing inks, automotive coatings, nonwoven fabrics, leather industry, and asphalt modification to name a few.

In the paper industry, the use of polymer dispersions is restricted to surface sizing and paper coating.⁸² Surface sizing means hydrophobizing the surface of the paper sheet to reduce its absorbency. This is achieved using a formulation that includes preferentially starch and the sizing agents that are



Figure 7 Commercial share and main industrial applications of polymer dispersions.

composed of emulsion polymers. The most important emulsion polymers employed are acrylic (co)polymers stabilized by protective colloids. The polymer particles are core-shell type with a hydrophobic core made out of acrylic polymers and a hydrophilic shell formed by the protective colloid, which is either cationic or anionic. Paper coating is the most important surface finishing process for the paper, and the amount of emulsion polymers employed in this process is significantly higher than that used in the sizing process. The goal of the emulsion polymer is not only to bind the pigment particles, but also to secure them at the coating surface and anchor them to the base paper. The coated paper increases the homogeneity of the surface and significantly improves the optical properties such as gloss and brightness. The different emulsion polymers used for coating paper (or board) include SBR, poly(styrene-con-butyl acrylate) copolymers, poly(vinyl acetate), poly(acrylates), poly(ethylene-co-vinyl acetate) copolymers, and in most of the cases those latexes include functional monomers such as acrylonitrile or monomers bearing acid or amide groups.

Decorative and protective coatings (paints) employed about 3 billion liters emulsion polymers in the wet state, and the market is growing at a rate of 3–6% mainly due to the advantages that waterborne polymers present with respect to the traditional solvent-borne polymers (environmentally friendly, easy cleaning, and low toxicity of the solvents). The main application areas are coatings for building, furniture, automobiles, and large industrial structures. Other less important but common use includes removable coatings, and coatings for optical fiber and electronic components.

The latexes are used as binder in complex formulations that comprise a pigment dispersion, the binder (latex), a thickener (rheology control), coalescent agents (which promote film formation), surfactants (which promote stability), a biocide (which prevents microbial attack), defoamer, and neutralizing agents. The volume of solids in the coating formulation is between 40–50% and the volume of polymer is *c*. 83% of the total volume of the dried paint. The first polymers used for coatings were the SBR latexes (with a styrene/butadiene ratio of 65:35). However, nowadays they have been replaced by VAc copolymers, styrene-acrylic copolymers, or pure acrylics. In the case of VAc copolymers, the most used comonomers are BA (VAc/BA = 80:20), Veova (vinyl ester of versatic acid), and ethylene (VAc/E = 90:10). These copolymer latexes exhibit better

performance than VAc homopolymers especially as far as hydrolytic stability and MFFT are regarded, and are predominantly used for interior paints. Styrene-acrylic copolymers (50:50) are more hydrophobic, more water resistant, and have better barrier properties than the VAc copolymer latexes. They are still used in interior paints because of their sensitivity to ultraviolet (UV) light. All acrylic polymer dispersions (for instance, MMA/BA = 50:50) are likely the best in terms of performance, and hence, they are preferred for exterior applications. The other systems (VAc copolymers and styrene-acrylic copolymers) can also be used for exterior applications, but only for low-cost systems. All copolymer systems mentioned above also use specialty comonomers in much lower level than the main components, but they are frequently the ones that provide the performance features to the application. Typical functional monomers are acidic comonomers for stabilization and adhesion, amine-functionalized monomers for adhesion, n-butyl methacrylate (BMA) in BA/MMA copolymers to improve durability, 2-ethylhexyl acrylate (2-EHA) to control hydrophobicity in styrene-acrylic copolymers, and hydroxyethyl methacrylate to provide functionality to acrylic resins.

Adhesives represent the largest market for the emulsion polymers. Pressure-sensitive adhesives (PSAs; including self-adhesive labels and tapes), laminating adhesives, and construction adhesives (including floor covering adhesives, subfloor and wall mastics, sealants and caulks, ceramic tiles adhesives, and polymer-modified mortars) are the applications where most of the emulsion polymers are used. All acrylic copolymers (with large amount of a low T_g acrylic monomer, that is, 2-EHA or BA, and small amounts of a high T_g methacrylate (i.e., MMA)) together with butadiene-rich SBR latexes are mainly used for PSA. The PSAs are formulated using in addition to the latex a tackifying agent, plasticizers, wetting agents, defoamers, and thickeners to adjust the adhesive to the prevailing coating conditions. The SBR latexes need more tackifying agents than the acrylics for the same performance. For the laminating adhesives, polyurethane dispersions are predominant. Adhesives for construction applications use in their formulations non-carboxylated SBR, all acrylic, vinyl-acrylic, styrene-acrylic, and VAc copolymers, depending on the required conditions.

Finally, carpet backing applications use carboxylated SBR latexes with contents in styrene in the 60–70 wt.% range. The carboxylic acid monomers vary from company to company and

the amount is typically lower than 3–5 wt.%. AA, methacrylic acid, itaconic acid, fumaric acid, and acrylonitrile are the most common functional monomers used.

3.14.2.1.3 *Miniemulsion polymerization* 3.14.2.1.3(i) *General principles*

As explained in Section 3.14.2.1.2, in emulsion polymerization an oil-in-water emulsion stabilized by surfactant is polymerized using a free radical initiator. In this process, the nucleation of polymer particles takes place by entry of radicals into micelles (heterogeneous or micellar nucleation) or by precipitation of growing oligoradicals in the aqueous phase (homogeneous nucleation). Although droplet nucleation is possible (by entry of oligoradicals into the micrometer-sized droplets), this is very unlikely because of the large difference in surface area of the monomer-swollen micelles (5-20 nm) with respect to the monomer droplets $(1-10 \,\mu\text{m})$ that favors entry of the oligoradicals in micelles and hence micellar nucleation. Once the particles are formed in emulsion polymerization, the polymer particles undergo substantial growth by polymerization. The monomer required for the polymerization must be transported from the monomer droplets by diffusion through the aqueous phase. This represents, in many cases, a limitation of the emulsion polymerization technique because it is very difficult to incorporate very hydrophobic monomers into the polymer particles due to their limited or negligible diffusion ability. The need for mass transport of monomer through the aqueous phase would be greatly reduced if all (or a large fraction) of the droplets were nucleated. The direct nucleation of the monomer droplets can be enhanced if the droplet size is reduced and the surface area of the droplets is large as compared with that of the micelles. Hence, droplet nucleation should prevail over the other nucleation mechanisms. What is known as 'miniemulsion polymerization' is basically an oilin-water emulsion, in which the size of the monomer droplets has been considerably reduced (50-500 nm) by combining a suitable emulsifier and an efficient emulsification technique and by stabilizing the resulting 'nanoemulsion' (the so-called 'miniemulsion') against diffusional degradation by using a costabilizer (a low-molar-mass hydrophobic compound). Under this condition, the surfactant is adsorbed on the large surface area of the monomer droplets and hence (ideally in a well-formulated miniemulsion) the surfactant that should remain available to form micelles is negligible and micelles are not present. Therefore, if a water-soluble initiator is added to the system and oligoradicals are formed in the aqueous phase, they preferentially enter into monomer droplets that become polymer particles; namely, the main nucleation mechanism is droplet nucleation. The droplet nucleation is a unique feature of the miniemulsion polymerization⁸³ that allows the production of polymers that cannot be produced by any other polymerization in dispersed media technique.84-93 If all the monomer droplets present in the original miniemulsion capture radicals, then all the droplets become polymer particles. This has been taken as an inherent feature of the miniemulsion polymerization, but it hardly takes place in practice.⁹⁴ Namely, in addition to droplet nucleation other nucleation mechanisms such as homogeneous and micellar nucleation as well as droplet coagulation and degradation might also take place.

A miniemulsion formulation includes water, monomer(s), a costabilizer, and the surfactant and initiator systems.

Typically, the procedure to prepare the miniemulsion is as follows: the surfactant system is dissolved in water, the costabilizer is dissolved in the monomer(s) mixture, and both solutions are brought together and mixed under magnetic agitation. The resulting coarse emulsion is converted into a 'nanoemulsion' by applying energy, generally from mechanical devices (rotor-stator systems, sonifiers, and high-pressure homogenizers are the most common ones)⁹⁴ or based on the chemical potential of the components (low energy emulsification methods such as phase inversion temperature).⁹⁵

Among the mechanical devices, the high-pressure homogenizers (Manton–Gaulin homogenizer and microfluidizer) are the most efficient techniques in terms of achieving the smallest droplet sizes.⁹⁶ Both equipments have in common that the coarse dispersions are pressurized using a positive displacement pump, and flow through a narrow gap at high velocity. A strong pressure drop also occurs. **Figure 8** presents a schematic of a high-pressure homogenizer.⁹⁷

In the high-pressure homogenizer, the homogenization is mainly due to extensional forces (shear) with some contribution from cavitation and impact forces. Cavitation occurs because of the strong pressure decrease that makes the vapor pressure of the liquid to exceed the local pressure causing vapor bubbles. When these bubbles implode, shock waves are generated in the liquid that break up the droplets. The impact forces with the walls are not strong because the decrease in the velocity is considerable at the outlet of the valve. The average droplet size decreases and the droplet size distribution (DSD) becomes narrower as the number of passes through the high-pressure homogenizer increases. The effect is more pronounced in the first passes, and it has been found that the number of passes can be considerably reduced if the coarse emulsion is first sonified.⁹⁷

Hexadecane and cetyl alcohol are the most widely used costabilizers, but since these compounds do not polymerize,



Figure 8 Monomer miniemulsion formation in a high-pressure homogenizer.

they contribute to the formation of volatile organic compounds (VOCs) and hence reactive costabilizers (that will covalently attach to the polymer) are preferred. Hydrophobic chain transfer agents, monomers, initiators, or polymers have been used. The role of the costabilizer is to avoid or minimize the degradation of the droplets by diffusion of the monomer from small to large droplets (Ostwald ripening). The stabilization of the monomer droplets against diffusion is governed by the thermodynamics of the system, namely, the chemical potential of the monomer (given by the partial molar Gibbs free energy of monomer) in the monomer droplets in the presence of small amounts of costabilizer. This can be expressed by eqn [6].^{98,99}

$$\frac{\Delta \overline{G_{\rm m}}}{R T} = \ln(\varphi_{\rm m}) + (1 - m_{\rm mh})\varphi_h + \chi_{\rm mh} \ \varphi_{\rm m}^2 + \frac{2\overline{V_{\rm m}}\sigma}{rRT} \qquad [6]$$

In eqn [6], $\varphi_{\rm m}$ and $\varphi_{\rm h}$ are the volume fraction of monomer and costabilizer in the monomer droplets, respectively, $m_{\rm mh}$ the ratio of the molar volume of the monomer $(\overline{V_m})$ and the costabilizer $(\overline{V_h})$, χ_{mh} the interaction parameter, σ the droplet-water interfacial tension, and r the droplet radius. Under maximum swelling equilibrium conditions $\Delta \overline{G_m} = 0$ and eqn [6] can be solved for different costabilizers (by varying $m_{\rm mh}$) and for different sizes of droplets (by varying r). Figure 9 presents these results. A low value of $m_{\rm mh}$ corresponds to a costabilizer with a molar mass much larger than that of the monomer (for instance, a polymer) and higher values correspond to costabilizers with molar masses closer to that of the monomer (i.e., hexadecane). It can be seen that lowmolar-mass costabilizers lead to superswelling in contrast with the modest swelling achieved by a polymer used as a costabilizer. Figure 9 also shows that the larger the droplet, the higher the swelling.

An important issue when formulating a monomer minemulsion is the amount of costabilizer required to keep the miniemulsion stable, at least during the polymerization time.



Figure 9 Effect of the droplet size and type of costabilizer on maximum swelling: $\chi = 0.5$, $\overline{V_m} = 10^{-4} \text{ m}^3 \text{ mol}^{-1}$, $\sigma = 5 \times 10^{-3} \text{ N m}^{-1}$, T = 533 K.



Figure 10 Effect of the volume fraction of costabilizer on the stability of the monomer droplets: $r_{10} = 25 \text{ nm}$, $m_{mh} = 0.5$, $\chi = 0.4$, $\overline{V_m} = 10^{-4} \text{ m}^3 \text{ mol}^{-1}$, $\sigma = 5 \times 10^{-3} \text{ N m}^{-1}$.

The effect of the amount of costabilizer on the stability of a miniemulsion can be predicted by solving eqn [6] for the swelling equilibrium of monomer in the presence of costabilizer when droplets of different sizes coexist, which is typically the case after a homogenization step. For illustrative purposes, $Asua^{94}$ solved the equation for the case with two types of droplet sizes. Figure 10 displays the effect of the costabilizer concentration in the monomer droplets on the stability of the monomer droplets. r_{1e} and r_{2e} are the pseudo-equilibrium droplet radii and r_{10} and r_{20} the droplet radii before diffusional degradation of the small droplet to the large ones.

Figure 10 shows that the droplet stability significantly increases as the amount of costabilizer increases. However, volume fractions above 0.04 only lead to a slight increase in the droplet stability.

It is worth noting that the results presented here are equilibrium values and that monomer diffusion is a kinetic process that might take some time. As the driving force for the monomer diffusion is the difference in chemical potential in the droplets of different sizes, thermodynamic not only affects the final state, but also the rate at which Ostwald ripening occurs.

3.14.2.1.3(ii) Homopolymerization and copolymerization

Miniemulsion homopolymerizations of vinyl chloride, VAc, MMA, BA, styrene, Veova10, dodecyl methacrylate, and stearyl methacrylate have been reported.^{94,100,101} In miniemulsion homopolymerization, once the polymer particles are formed, the process evolves in a similar manner as in interval III of a conventional emulsion polymerization, that is, in absence of monomer droplet phase. The differences in the polymerization and miniemulsion polymerizations can be attributed to the different number of polymer particles formed in each process, which can be substantially different depending on the initiator systems employed.

The situation is more complex when a copolymerization is considered because as two or more monomers are involved and the partitioning of the monomer between the phases might be different, this may lead to variations in the copolymer composition. In emulsion copolymerization, the evolution of the copolymer composition depends, in addition to the reactivity ratios, on the partition of the monomer between the aqueous and polymer particle phases (see Section 3.14.2.1.2(iv)). Furthermore, if the monomer is hydrophobic enough, transport limitations through the aqueous phase might control the concentration of the monomer in the polymer particles. On the other hand, in miniemulsion polymerization, the transport of monomer is reduced to such levels that the incorporation of hydrophobic monomers is favored as compared with conventional emulsion polymerization, and the copolymer compositions achieved in batch miniemulsion copolymerization are closer to those expected from the Mavo-Lewis equation (eqn [3]) under bulk conditions. This trend was experimentally observed by several authors who investigated the copolymer composition produced in batch emulsion and miniemulsion copolymerization using monomers with different water solubilities and reactivity ratios. 102,103

The microstructure (MMD, gel content, branching, and crosslink densities) of the polymer might be affected by the different segregation levels in emulsion and miniemulsion copolymerization. Figure 11 presents the expected evolution of the volume fraction of polymer in the polymer particles as a function of conversion for batch emulsion and miniemulsion polymerization processes. Since miniemulsion polymerization can be roughly approximated to a completely segregated system (no transport of matter between the droplets), each nanodroplet can be considered as a batch reactor in which a bulk polymerization takes place. Therefore, the initial volume fraction of polymer in the polymer particles (at the time of nucleation of the droplet) should be close to zero, and it will increase with conversion. By contrast, in emulsion polymerization the volume fraction of polymer will be that corresponding to the saturation of the particles by monomer (as soon as the particles are formed), and it will remain at the saturation level until the monomer droplet phase is depleted (the conversion at which this occurs depends on the monomer-polymer system). Beyond this point, the volume fraction of polymer will increase



Figure 11 Evolution of the volume fraction of polymer in the particles as a function of conversion for emulsion and miniemulsion polymerization processes.

with the conversion as in the miniemulsion process. This difference in the evolution of the volume fraction of polymer in the polymer particles might have a significant impact on the microstructure. For instance, for the polymerization of acrylate monomers that form long-chain branches (by intermolecular chain transfer to polymer) and eventually gel polymer (insoluble polymer network), if termination by combination is the predominant chain termination event, ^{104,105} then the amount of gel polymer that can be formed by means of a batch miniemulsion polymerization process is smaller than that produced by emulsion polymerization. This was recently reported for the polymerization of 2-EHA and its copolymerization with MMA (2-EHA/MMA = 90:10)¹⁰⁶ and also for the copolymerization of styrene and butadiene.^{107,108}

3.14.2.1.3(iii) Synthesis of hybrid particles

As explained above, droplet nucleation is a unique feature of the miniemulsion polymerization process, and this nucleation mechanism has prompted the discovery of new applications that were not possible by other conventional dispersed phase polymerization techniques. This is in particular the case for the incorporation of highly hydrophobic materials or materials that are unable to diffuse through the aqueous phase (polymers and inorganic particles) to produce waterborne polymerpolymer and polymer–inorganic nanocomposite dispersions.

The efforts to synthesize waterborne hybrid polymerpolymer nanoparticle dispersions are due to the expected synergetic behavior of the positive properties of each polymer phase. Hybrid latexes made of alkyd resins,^{72,92,109,110} polyurethanes,¹¹¹⁻¹¹³ polydimethylsiloxane (PDMS),⁵⁰ polyester,¹¹⁴ and other polymers¹¹⁵ have been reported. The polymer resin can be used as the sole costabilizer, but long-chain acrylates (such as stearyl acrylate) are also used to increase the stability of the monomer miniemulsions. The main polymer phase in the hybrid system is produced *in situ* by polymerization of suitable monomers. Typically, acrylic and acrylic–styrene copolymer formulations are used to take advantage of the weather and water resistance of the acrylic polymers.

For the synthesis of hybrid polymer–polymer latexes by miniemulsion polymerization, the homogenization step is carried out as explained above, but it should be taken into account that the viscosity of the organic phase strongly affects the size of the droplets that can be achieved. Thus, the higher the polymer content in the organic phase, the larger the droplet size will be for the same energy applied because of the higher viscosity of the organic phase.⁹⁷

In most of the cases, limiting conversion was found during the polymerization of the hybrid miniemulsions in batch reactor because the growing radical transferred to the polymer resin that then became a radical sink.^{89,116,117} However, this could be easily overcome working in semibatch mode or by post-polymerizing with suitable redox initiator systems.¹⁰⁹ The morphology of the hybrid particles depends on the compatibility of both polymer phases. The compatibility is enhanced if the acrylic polymer is covalently linked to the polymer resin, that is, if most of the acrylic polymer is grafted onto the resin (acrylic degree of grafting (ADG)) and a large fraction of the resin is also incorporated to the acrylic polymer (resin degree of grafting (RDG)). It has been found that the RDG controls the morphology of the particles. For alkydacrylic hybrids, RDG values greater than 35% are necessary to produce homogeneous particles, provided that the acrylic polymer is almost completely grafted (ADGs above 90%).¹⁰⁹

Hybrid polymer–inorganic nanocomposite latexes have also been synthesized by miniemulsion polymerization. Encapsulation of inorganic material in polymer particles has attracted the interest of scientists working in the field of cosmetics, coatings, adhesives, and in pharmaceutical or biomedical applications. TiO₂, CaCO₃, silica, clay, carbon nanotubes, quantum dots, and magnetite are some examples of nanoparticles that have been incorporated to polymer particles by using miniemulsion polymerization.⁸⁷ In most of the applications, the full encapsulation of the inorganic nanoparticles by the polymer is required (biomedical applications) but in other cases (coatings and adhesives) there is no sufficient proof demonstrating that the encapsulated morphology will provide better properties than other possible morphologies.

The encapsulation of inorganic nanoparticles by means of miniemulsion polymerization requires the following: (1) the nanoparticles to be hydrophobic enough to be dispersed homogeneously in the monomer and costabilizer phase; (2) the formation of monomer nanodroplets with the inorganic material in it; and (3) the polymerization of all (or at least a large fraction) of the nanodroplets avoiding other possible nucleation mechanisms. The success on the encapsulation of the inorganic nanoparticles by miniemulsion polymerization depends on the interplay of several parameters. Thus, the compatibility of the modified nanoparticles and the monomers (nanoparticlemonomer interfacial tension, $\sigma_{nanofiller-monomer}$) and the interaction of the nanoparticle with the aqueous phase (nanoparticle-aqueous interfacial tension, phase $\sigma_{\text{nanofiller-water}}$) are the key parameters to determine the achievable morphologies. Figure 12 presents equilibrium morphologies of hybrid monomer-nanoparticle nanodroplets calculated by means of a Monte Carlo simulation algorithm for different interaction of the nanoparticles with the monomer and water ($\Delta_{nanofiller-monomer}$ and $\Delta_{nanofiller-monomer}$ in Figure 12 are interaction parameters that are proportional to the interfacial tensions). Figure 12(a) shows the equilibrium morphologies achieved with nanoparticles with disklike structure (to mimic clay platelet particles)¹¹⁸ and Figure 12(b) shows the case of nanoparticles with spherical shape (i.e., silica, quantum dots).

The simulation indicates that to encapsulate the inorganic nanoparticle in the monomer droplets, the monomer and nanoparticle should be very compatible (low monomer–nanoparticle interfacial tension) and, on the other hand, the nanoparticles should be very hydrophobic in the case of disklike nanoparticles ($\Delta_{nanofiller-monomer} = 0.9$) and hydrophobic ($\Delta_{nanofiller-water} =$ 0.6-0.9) in the case of spheres. In the other cases (less compatible nanoparticle–monomer system and less hydrophobic nanoparticles), the thermodynamically stable morphologies are armored structures with the nanoparticles preferentially located at the monomer–water interface; when the nanoparticle is very hydrophilic and incompatible with the monomer (large monomer–nanoparticle interfacial tension), the nanoparticle is preferentially located in the aqueous phase.

3.14.2.1.3(iv) Examples of industrial applications

The importance of the miniemulsion polymerization technique relies on the potential to synthesize waterborne polymeric dispersions that cannot be produced by means of conventional emulsion polymerization. The unique feature of the droplet



Figure 12 Equilibrium morphology maps for hybrid monomernanoparticle miniemulsion nanodroplets calculated by means of a Monte Carlo simulation algorithm. (a) Disklike nanoparticles. Reproduced with permission from Micusik, M.; Bonnefond, A.; Reyes, Y.; *et al. Macromol. React. Eng.* **2010**, *4*, 432.¹¹⁸ Copyright Wiley-VCH Verlag GmbH & Co. KGaA. (b) Spherical nanoparticles. Water phase is depicted in light gray, monomer phase in darker gray, and nanofiller in black.

nucleation and the lack of monomer transport during the polymerization have made miniemulsion polymerization very attractive for the development of a new portfolio of products. In addition to the synthesis of hybrid latexes, the applications for which the miniemulsion polymerization is unique with respect to conventional emulsion polymerization are CRP in dispersed systems, catalytic polymerization, ionic polymerizations, polymerization of very hydrophobic monomers, and step-growth polymerization in aqueous dispersed systems. In addition, it offers advantages in other applications such as the synthesis of high solids content latexes (the broad PSDs obtained might help in reducing the viscosities of the latexes and hence increase the solids content) or for process intensification using CSTR or tubular loop reactor (the typical oscillations due to the intermittent micellar nucleation are avoided using miniemulsion polymerization).¹¹⁹

However, the implementation of miniemulsion polymerization in industry is challenging because industry will only adopt this method provided that new and improved materials can be produced and that the technology required to run the process is available at a reasonable cost. The former is true because hybrid alkyd–acrylic coatings and polyurethane–acrylic adhesives with enhanced performance that cannot be synthesized by other polymerization techniques have been recently discovered. The incorporation of inorganic nanoparticles into polymer particles has also been shown, but not all the systems studied at the laboratory scale are ready for commercialization because of the low solids content, reduced range of stability of the dispersions, and the need for complex modifications of the inorganic materials that make the industrialization very challenging.

3.14.2.1.4 Microemulsion polymerization

Microemulsions are thermodynamically stable oil-in-water emulsions, in which the droplet size (10–100 nm) is smaller than that in conventional emulsions (macroemulsions: 1–100 μ m) and miniemulsions (50–500 nm). To prepare a stable microemulsion, large amounts of anionic or cationic surfactants (more than 10–20% in the formulation or at similar levels as the monomer) and short-chain alcohols (e.g., *n*-pentanol) or other cosurfactants are employed.^{120,121} Upon polymerization of the microemulsion with a suitable initiator (either water soluble or oil soluble), polymer latexes with particle sizes in the 10–50 nm range and very high molar masses (>10⁶ g mol⁻¹) can be synthesized.

The mechanisms of particle nucleation and particle growth and hence the kinetics of the microemulsion polymerization are not well understood yet. Although there are common features between microemulsion and emulsion polymerization, the two processes present significant differences in the final products. In contrast to emulsion polymerization, the number of models describing the kinetics and mechanisms of microemulsion polymerization is scarce.¹²²⁻¹²⁷ For a slightly water-soluble monomer such as styrene, the following features are generally assumed: (1) radicals generated in the aqueous phase diffuse predominantly to monomer-swollen micelles; (2) radical termination in the aqueous phase is negligible; (3) radical entry into preformed particles is negligible; (4) termination of radical growth in the particles is predominantly by chain transfer to the monomer followed by desorption of the radicals; and (5) a 0-1 system is assumed for the radical distribution in the particles.

When microemulsion polymerization was first developed in the 1980s, it was seen as a promising technique to produce latexes with very small particle sizes and high molar masses. However, the large amounts of surfactants, namely, the low polymer to surfactant ratios, and the low solids content achievable by this method, have prevented the industrial implementation of this technique. In spite of this limitation, there is a strong interest to obtain nanosized (<50 nm) latexes with high polymer contents (high solids content) and lower surfactant concentrations; ideally without (or with low amounts of) emulsifier. A rough idea of the maximum solids content achievable for narrow unimodal latexes can be obtained by considering the interparticle space (IPS) given by eqn [7]:¹²⁸

$$IPS = 2r\left(\left(\frac{\varphi_n}{\varphi}\right)^{1/3} - 1\right) \quad \text{for} \quad \varphi \le \varphi_n \le 0.64$$
[7]

In eqn [7], *r* is the particle radius, φ_n the maximum packing factor of the monodisperse particles, and φ the volume fraction of the particles. Figure 13 plots the interparticle distance (eqn [7]) as a function of the volume fraction of particles (solids content) for unimodal latexes.¹²⁹ The straight line in the plot



Figure 13 Interparticle spacing vs. volume fraction of particles as a function of particle diameter. The horizontal line represents the safe interparticle distance.

represents an arbitrary safe (i.e., minimum) distance between particles to account for situations that would lead to an excessive increase of viscosity of the dispersion and/or high risk of coagulation. **Figure 13** shows that, for a given volume fraction of the dispersion, the larger the particle diameter, the higher the distance between particles and the higher the solids content that can be reached before the double or adsorption layers of neighboring particles interact (i.e., crossing of the IPS and of the straight line). Therefore, the crosspoints roughly represent the maximum achievable solids content for monodisperse latexes with the given particle sizes.

Xu and Gan¹³⁰ have recently reviewed the attempts made to produce latexes with high solids content and small particle sizes using microemulsion polymerization. The most promising technique is what can be regarded as semibatch microemulsion polymerization. Basically, the approach conin preparing a thermodynamically sists stable microemulsion (using large amounts of surfactant and with the help of a cosurfactant at low solids content, namely, typical microemulsion conditions) that is polymerized in batch up to full conversion. Then, additional monomer is added to the microemulsion to increase the solids content, and hence, reducing the amount of surfactant with respect to polymer of the original microemulsion, and very likely increasing the particle size from that of the original microemulsion. Although it might be viewed as a seeded semibatch emulsion polymerization, there is a fundamental difference with respect to this common process; when the monomer feeding starts, in addition to the seed polymer particles, there are plenty of micelles in this system (in other words, the emulsifier concentration is well above the CMC). The empty micelles compete with the polymer particles for the monomer and radicals, and hence both formation of new particles and growth of the preformed ones in the batch microemulsion take place during the feeding period. Different monomers and different addition strategies have been reported and the most interesting results are presented in Table 1. The results are in agreement with the limitation presented in Figure 13, namely, unimodal

Initial charge: microemulsion?	Particle size (nm)	Polymer/surfactant ratio; type of surfactant	Monomer addition	Solids content (wt.%)	Reference
Yes	<100	15:1; CTAB (cationic)	Winsor I-like	15	131
Yes, M/S = 1:1- 5:1 + 1- pentanol	10–20	7–10:1 (for Sty, BMA, and BA) and 25:1 (for MA); SDS (anionic)	Continuous addition (2–3 h)	10–30 (30 for MA)	132
Yes, M/S = 3:1 (VAc)	$30 \rightarrow 70$	$3:1 \rightarrow 30:1$; Aerosol OT (anionic)	Stepwise; shots every hour (six)	$3 \rightarrow 30$	133
Not given	<40	20:1; SDS (anionic)	Continuous addition (3–5 h)	30-40	134
Yes, M/S = 1:2 (only CTAB)	50-80	15:1; CTAB/PEO-R-MA40 Mixture cationic/nonionic surfmer	Continuous addition (4 h) of monomer and surfmer	10	135
Yes, M/S = 1:2 (BA)	<60	20:1; mixture of SDS/AOT (anionic)	Continuous addition until latex viscosity is gel-like	<30	136
Yes, M/S = 1:2.2 (S)	$26 \rightarrow 45$	3:1; DTAB (cationic)	Stepwise (5 ml every 20 min)	40	137
Yes, M/S = 1:5 (for S, BMA) and M/S = 1:1.25 (for MMA) 1-pentanol	15–60	15:1; CTAB (cationic) or SDS (anionic)	Hollow fiber feeding	<20	138,139
No, micellar solution	25–60	10:; DOWFAX 2A1 (plus acrylamide as cosurfactant)	Continuous addition (includes monomer, DOWFAX, acrylamide)	30–45	140
No, micellar solution (water-soluble initiator, ammonium persulfate)	16–40	18:1; SDS (anionic)	Continuous addition (MMA + 1-pentanol in 1 h)	13–36	141
No, micellar solution (oil-soluble initiator, AIBN)	15–30	160–?/1; SDS (anionic)	Continuous addition (MMA for 1.5 h)	<20	142

 Table 1
 Summary of works that employed semibatch microemulsion polymerization to produce latexes with high solids content, low particle size, and reduced amount of surfactant

M/S, monomer/surfactant; PEO-R-MA40, ω -methoxy poly(ethylene oxide)₄₀ undecyl α -methacrylate.

latexes with particles equal or below 20 nm cannot be produced in volume fractions above 25-28%, unless gel-like or extremely viscous dispersions are allowed, which is not the case for the majority of commercial applications. Using true microemulsion conditions, the best results (highest solids content and lowest particle size with the lowest surfactant concentration) were obtained by Ming et al.¹³² and Ramirez et al.¹³⁶ The former were able to produce poly (methyl acrylate) latexes with solids content of 30 wt.%, number-average particle size of 14.5 nm with broad PSD $(D_v/D_p = 1.5)$, and c. 3 wt.% SDS based on monomer and small amount of 1-pentanol. With less polar monomers (S, BMA, BA, and MMA), they could not reproduce these results: for similar particle sizes, solids contents were below 20 wt.% and larger surfactant concentrations were required. The latter synthesized poly(n-butyl acrylate) latexes with solids content of 30 wt.% and particles size in the 40-55 nm range, with a mixture of SDS and Aerosol OT anionic surfactants at total concentrations of 5 wt.% with respect to monomer. The last three entries of Table 1 are not formally microemulsion polymerization because they do not form a microemulsion (namely, a thermodynamically stable oil-in-water emulsion), although the authors used this name to describe the processes. As shown in the first column, these works started from a micellar solution (rather than from a microemulsion as in the other works in the table) produced with large amounts of surfactant and the monomer (in addition to a cosurfactant, either acrylamide or 1-pentanol in the first two cases, respectively) was slowly fed into the micellar solution. The results reported in the

last entry¹⁴² are interesting because they demonstrated that using small amounts of SDS with an oil-soluble initiator (N,N'-azobisisobutyronitrile (AIBN)) led to very small poly (n-butyl acrylate) latex particles (between 20 and 30 nm) with concentrations of SDS as low as 0.6 wt.% at solids content below 20 wt.%.

In addition to the synthesis of latexes with high solids content and small particle size, in the past decade, microemulsion polymerization has been used to synthesize a wide range of materials. For instance, several works have incorporated inorganic materials such as carbon nanotubes,¹⁴³ ZnO nanoparticles (UV absorption),¹⁴⁴ montmorillonite clay,¹⁴⁵ and quantum dots (luminescence probes)¹⁴⁶ to produce nanocomposites. Furthermore, nanogels,¹⁴⁷ conductive polypyrrole and polyaniline latexes,^{148,149} polyurethanes using immiscible monomers,¹⁵⁰ and polymers in water-in-scCO₂ microemulsions¹⁵¹ have been also prepared by microemulsion polymerization.

3.14.2.1.5 Aqueous dispersion and precipitation polymerizations

3.14.2.1.5(i) Aqueous dispersion polymerization

Dispersion polymerization^{8,12,152–156} is a way of forming polymer particles from an initially homogeneous monomer solution. While the monomer is soluble in the selected solvent, the formed polymer is not and precipitates. In the presence of a stabilizer, this leads to particles. In the vast majority of the situations, the continuous phase is an organic solvent or a mixture of water and alcohol, and the typical particle diameter is in the 200 nm–20 µm range (see Section 3.14.3.1.2). In pure water, there are very few examples and most of them are related to the synthesis of polymer particles able to respond to an external stimulus, such as pH or temperature (for instance, polymers exhibiting a lower critical solution temperature (LCST), such as poly(*N*-isopropylacrylamide) (PNIPAM)). Those may be useful in the domain of biomedical applications and drug delivery.^{157–159}

3.14.2.1.5(ii) Aqueous precipitation polymerization

Precipitation polymerization is a general case of dispersion polymerization in which no stabilizer is added. Although the monomer is soluble in the aqueous phase, the polymer precipitates and forms a second phase. In the typical case of acrylonitrile, the monomer is not a good solvent for the polymer and the polymerization takes place essentially at the polymer-water interface.

3.14.2.2 Controlled Radical Polymerization

3.14.2.2.1 Overview of CRP in aqueous dispersed systems

Since free radical polymerization proceeds with fast self-termination of the propagating radicals and is often dominated by chain transfer to the monomer in emulsion polymerization, it does not allow the synthesis of well-defined polymer chains. In particular, the synthesis of polymers with controlled molar mass, narrow MMD along with well-defined end group and chain structure is almost impossible. Indeed, emulsion polymerization leads to polymers with very high molar masses and sometimes microgels in the case of acrylates, VAc, and butadiene. For some applications, it is highly useful to reduce the chain length using chain transfer agents. Classical molecules such as thiols are often used in the industrial production of latexes. Of lower industrial importance, but with great promises are the catalytic chain transfer (CCT) agents, essentially cobalt-based molecules, which show exceptionally high chain transfer constants and lead to low-molar-mass poly(methacrylic esters) with a terminal double bond.¹⁶⁰⁻¹⁷⁰

A better control of the polymer at the molecular level was made possible with the advent of the CRP techniques.^{84,171-176} CRP is a particular way of performing radical polymerization in which the propagating radicals are subjected to reversible deactivations during the polymerization. They are in equilibrium with dormant chains, in much larger concentration than the radicals themselves. This situation leads to the formation of polymer chains, which exhibit controlled and predictable molar mass (the M_n increases linearly with monomer conversion), narrow MMD (i.e., low polydispersity index (PDI) = M_w/M_n , with M_w the weight-average molar mass), and reactivable end group. Therefore, CRPs allow a high degree of control of polymer microstructure so that the synthesis of structures such as di- and triblock copolymers, star polymers, and comblike graft copolymers can be made. Unlike ionic polymerizations, which sometimes require very low temperatures, rigorous purification of reagents, and careful exclusion of moisture and oxygen, CRP can be conducted under typical conventional free radical polymerization conditions, and do not even require purification of reagents. Several methods have been proposed to reach that goal and all of them can be classified in two main categories according to the mechanism of the deactivation step. The three major types of CRPs are nitroxide-mediated radical polymerization (NMP) (or stable free radical polymerization (SFRP))¹⁷³ and atom transfer radical polymerization (ATRP),^{171,172} which operate by a reversible termination mechanism, and reversible addition-fragmentation chain transfer (RAFT),^{174–176} which operates by a reversible transfer process. All these techniques are well described in the corresponding chapters of this comprehensive. The application of the three major CRP types, as well as more recently developed CRP methods, to aqueous dispersions will be described in this section. It will be shown that the behavior of CRP in aqueous dispersed systems can vary considerably from behavior in bulk or in solution. Challenges arising from partitioning of the mediating species into the aqueous phase, radical exit from particles, and reactions of the mediating species with other components may cause loss of control and/or poor colloidal stability.

The developments of CRP in aqueous dispersed systems have been reported in several review articles,^{88,177-187} which stressed that, although challenging, the target was considered as particularly important due the intrinsic qualities of these processes. There are indeed significant fundamental and practical incentives to conduct CRP in aqueous dispersions. For economic reasons, aqueous dispersions are often the best alternative for large-scale production, providing excellent heat transfer, ease of mixing, process flexibility such as semibatch addition of reagents during polymerization, and ease of handling/transporting the final latex. Recently, it has been shown that important polymer property advantages, such as improved livingness, may also be realized when running CRP in an aqueous dispersion. Moreover, CRP was considered to offer additional advantages than simply controlling the polymer at the molecular level. It can be, for instance, the design of particle composition and morphology, the way to nanostructured organic particles and to hybrid nanocomposites, and so on, for a variety of new potential applications.

3.14.2.2.2 Nitroxide-mediated radical polymerization

In NMP, also known as SFRP, a stable free radical (nitroxide) reversibly terminates propagating macroradicals to yield dormant polymer chains with an alkoxyamine end group (Figure 14). Because the equilibrium favors the dormant species, the propagating radical concentration is most often lower than that in conventional radical polymerization. Under typical polymerization conditions, a dormant chain is activated every $\sim 10^2 - 10^3$ s on average, and the formed macroradical adds \sim 1-5 monomer units prior to deactivation. Deactivation is very fast, at almost diffusion-limited rates, such that the deactivation of a propagating radical occurs $\sim 10^{-4} - 10^{-3}$ s after it is activated. Irreversible termination is ideally minimized although it cannot be completely eliminated. Accumulation of nitroxide is a direct effect of termination (the so-called persistent radical effect (PRE)),¹⁸⁸ and shifts the equilibrium toward the dormant state, thereby suppressing the polymerization rate. Elevated temperatures (~90-135 °C) are necessary to achieve reasonable polymerization rates.

Although several nitroxides have been reported for bulk/solution NMP, 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) and *N-tert*-butyl-*N*-(1-diethyl phosphono-2,2-dimethylpropyl) nitroxide (Figure 15), better known by its trade name 'SG1' (trade name of the Arkema Group), have been most commonly used in aqueous dispersed systems. TEMPO requires higher polymerization temperatures than SG1 (~120–135 °C for TEMPO vs.


Figure 14 Nitroxide-mediated radical polymerization, illustrating reversible activation and deactivation of polystyrene by TEMPO. The activation-deactivation equilibrium constant is defined as $K = k_a/k_d$.



Figure 15 Structure of the nitroxides TEMPO (left) and SG1 (right).

 \sim 90–120 °C for SG1). Other differences between these two nitroxides include their partitioning behavior between aqueous and organic phases, sensitivity to the pH of the aqueous phase, and the stability of the nitroxide at reaction conditions. TEMPO is a more stable radical than SG1, which means it is more prone to accumulation over time. This phenomenon requires another source of radicals, such as those arising from thermal polymerization (in the case of styrene polymerization) or from added initiator, to consume the excess TEMPO. Consequently, polymerization of non-styrenic monomers (e.g., acrylates) is difficult with TEMPO, while it is readily achieved with SG1.

Among the various processes of polymerization in aqueous dispersed systems, nitroxide-mediated suspension polymerizations, where the particle sizes are comparatively large (>1 μ m), have been reported in a few articles only.^{189–193} In general, they behave similarly to bulk polymerization, with the challenges described above not being as prominent as when particle sizes are below 1 μ m, like in miniemulsion and emulsion polymerization, which have been far more studied.

There are limited choices for surfactant at the higher temperatures required for NMP. Sulfates undergo hydrolysis at higher temperatures and are generally not suitable, while sulfonates have excellent hydrolytic stability and do function effectively at elevated temperatures (100-140 °C). The two most commonly used in NMP miniemulsions are sodium dodecyl benzene sulfonate (SDBS) and DOWFAX 8390 (Dow Chemical Inc.) (Figure 16). SDBS is usually available only in a technical grade while DOWFAX 8390 is a mixture of mono- and dihexadecyl disulfonated diphenyloxide sodium salts. Polymerization rates may be significantly influenced by [SDBS].^{194,195} SDBS is able to generate radicals in the presence of ascorbic acid,¹⁹⁶ suggesting additional radical generation is the most likely explanation for the observed effects of [SDBS]. Pan et al.¹⁹⁷ examined the effects of [DOWFAX 8390] on TEMPO-mediated styrene miniemulsions but did not observe notable effects on the rate of polymerization, $M_{\rm p}$, or PDI.



Figure 16 Structure of the surfactants SDBS and DOWFAX 8390, commonly used in high temperature NMP emulsions and miniemulsions.

3.14.2.2.2(i) TEMPO-mediated polymerizations

Initial efforts to conduct TEMPO-mediated NMP in aqueous dispersions logically used an emulsion polymerization approach. While living polymer was obtained, poor colloidal stability and coagulum formation plagued these early attempts.^{88,177} Initially, the reason(s) for the colloidal stability problems was not understood but the underlying causes have recently been elucidated in studies by Pohn et al.¹⁹⁸ and Maehata et al.¹⁹⁹ Pohn et al.¹⁹⁸ simulated the mass transfer of monomer between droplets and seed particles during TEMPO-mediated styrene emulsion polymerization. Simulation results showed that the presence of small particles, which form during the early stages of emulsion polymerization, will (counterintuitively) lead to polymerization occurring preferentially in the large droplets, suggesting that TEMPO-mediated ab initio emulsion polymerizations will not be feasible. By selectively inhibiting polymerization in the monomer droplets using the highly hydrophobic 4-stearoyl-TEMPO, Maehata et al.¹⁹⁹ experimentally demonstrated that droplet polymerization was indeed responsible for the formation of large particles that can lead to coagulum formation. A modified TEMPO-mediated emulsion polymerization process was then developed in which droplet polymerization was suppressed, and was shown to be capable of giving coagulum-free latexes. Another modified SFRP emulsion polymerization process using a nanoprecipitation approach was able to yield a stable latex with mean particle diameters \sim 400–500 nm.²⁰⁰

Miniemulsion polymerization has proven to be robust process for many types of CRP, including TEMPO-mediated NMP. Mathematical modeling of TEMPO-mediated miniemulsion^{201–207} has provided insight into many of the underlying phenomena and how they affect kinetics and polymer properties. A study of interfacial mass transfer of nitroxides predicted that phase equilibrium for [TEMPO] should be maintained.²⁰³ However at larger droplet diameters corresponding to suspension and emulsion polymerizations, the predicted equilibration times are significantly greater, giving rise to the possibility of diffusion-controlled reactions.

For TEMPO-mediated styrene miniemulsions, polymerization rates are nearly independent of the water solubility of the nitroxide even if partition coefficients differ significantly (e.g., TEMPO and 4-hydroxy-TEMPO).²⁰¹ The reason for this surprising result is that thermal autoinitiation of styrene dominates the phase partitioning behavior. In the absence of thermal initiation with monomers such as BA, the rate of polymerization is significantly faster in systems with more water-soluble TEMPO derivatives (4-hydroxy-TEMPO) compared to systems with TEMPO. Zetterlund and Okubo²⁰⁸ corroborated these findings.

TEMPO-scavenging additives can increase polymerization rate, although the role of various additives may be more complex than just simple reaction with nitroxide. Camphorsulfonic acid was used in TEMPO-mediated styrene miniemulsion polymerizations.²⁰⁹ In another way, semibatch addition of ascorbic acid in TEMPO-mediated styrene miniemulsion polymerizations is a powerful technique for enhancing the polymerization rate and achieving high conversions at low reaction times.^{210,211} High conversions (>98%) were obtained in 2–3 h (which is faster than industrial styrene polymerizations) while PDI remained low (<1.3). Livingness was actually higher when the rate was increased, as the reduction in reaction time led to less dead chain formation through disproportionation (i.e., H transfer from the propagating radical to the nitroxide).

Although TEMPO is typically used in the range of ~120–135 °C, it is possible to use temperatures ~100 °C through judicious addition of a nitroxide scavenger such as ascorbic acid.²¹² Although the PDIs were larger than values achieved at higher temperatures, the polymer livingness remained high. An advantage of polymerizing at lower temperatures with TEMPO is that the disproportionation rate is much less.²⁰¹

Most published studies have focused on making narrow MMD with CRP, and far less attention has been given to understanding the behavior of CRP in the presence of crosslinking agents. In conventional bulk polymerization systems, in addition to the desired intermolecular crosslinking, intramolecular crosslinking is also important. Intramolecular crosslinking results in microgel formation and heterogeneous network formation. In CRP, the lower chain lengths (compared to conventional polymerization) result in lower apparent reactivity of the pendent unsaturated sites, which in turn yields more uniform networks without microgel formation that also have greater swelling capability.²¹³ Differences have also been observed, however, between crosslinking behavior in bulk and miniemulsion CRP systems. Okubo and Zetterlund have examined crosslinked styrene-divinylbenzene systems, 214-219 noting distinct differences between bulk and miniemulsion behavior with miniemulsions exhibiting faster kinetics than bulk. Crosslink densities and pendent vinyl group conversion also differed between the bulk and miniemulsion; miniemulsions showed much lower crosslink densities and slower conversion of the pendent vinyl groups. TEMPO is generally not well suited to the polymerization of acrylates or methacrylates, although copolymerizations with styrene are better controlled. Often TEMPO-mediated acrylate homopolymerizations progress with reasonable control to low conversions (<5-10%) and then cease due to TEMPO accumulation as a result of the PRE.¹⁸⁸ Block copolymers (polystyrene-*b*-poly (*n*-butyl acrylate)) made in TEMPO-mediated miniemulsions have been reported.^{220,221} Addition of ascorbic acid enabled high conversion (>99%) in both blocks.²²¹ TEMPO-mediated homopolymerization of BA in bulk²²² and miniemulsion^{222,223} has also been reported where again semibatch ascorbic acid addition (or its oil-soluble derivative, ascorbic acid 6-palmitate) was used.

3.14.2.2.2(ii) SG1-mediated polymerization in miniemulsion

SG1 (Figure 15) is a versatile nitroxide suitable for the polymerization of styrene, acrylates, and even methacrylates (when copolymerized with ~10 mol.% styrene^{224,225} or acrylonitrile²²⁶ to impart livingness to the system). SG1 is an acyclic β -phosphonylated nitroxide with a more favorable equilibrium constant than TEMPO. For highly reactive monomers such as BA, additional SG1 is required to maintain a controlled polymerization.

Farcet *et al.*²²⁷ found that the initial ratio of [SG1]/ [MONAMS] (an SG1-based oil-soluble alkoxyamine) played an important role in determining polymerization rate in the miniemulsion polymerization of BA. [SG1]/[MONAMS] ratios of ~0.035–5 provided good control, with temperature influencing the optimum ratio. Insufficient quantities of SG1 gave higher rates but at the expense of broad MMDs. Excessive quantities of SG1 suppressed the rate. Conversions greater than 70% were reported for $M_n \sim 25–30 \text{ kg mol}^{-1}$ and PDI ~ 1.4–1.6. The observed particle diameters were larger than typically obtained in miniemulsion (400–650 nm) but colloidal stability, a more important concern, was good.

The Charleux laboratory also used a water-soluble SG1-based alkoxyamine, known as MAMA or by its current trade name BlocBuilder MA[®] (Arkema Group)²²⁸ (Figure 17) in SG1-mediated miniemulsion polymerization. BlocBuilder MA® is unique in that it has a carboxylic acid moiety that imparts water solubility when ionized. At pH> \sim 5.5, it exists in the ionized (sodium salt) form while at lower pH it remains in acid form. BlocBuilder MA® also has a higher dissociation rate constant than the oil-soluble MONAMS and does not require additional SG1 to give a controlled polymerization, even for BA. The ionized alkoxvamine is soluble in the aqueous phase, but becomes sufficiently hydrophobic to enter droplets or particles after adding a few monomer units, much like water-soluble initiators in conven-(mini)emulsion polymerization. High initiation tional efficiencies were observed for BA. However, for styrene, initiation efficiencies were low, which was attributed to low oligoradical entry rates from the aqueous phase due to slow aqueous phase styrene polymerization. Addition of small amounts of methyl acrylate (MA) significantly improved the efficiency by increasing the propagation rate of oligomeric radicals in the aqueous phase, yielding a far more effective miniemulsion process. This study provided the framework for subsequent development of SG1-mediated emulsion polymerization.

3.14.2.2.2(iii) SG1-mediated polymerization in emulsion

Unlike TEMPO that is not readily amenable to a true emulsion polymerization process, a seeded emulsion polymerization process using the water-soluble SG1-based alkoxyamine BlocBuilder MA® has been developed.^{229–231} BlocBuilder MA® allows effective aqueous phase initiation, which is key for an emulsion polymerization process. Low-molar-mass seed latex



Figure 17 The SG1-based alkoxyamine BlocBuilder MA® in ionized (a) and nonionized (b) forms, (c) and the difunctional DIAMA.

is first prepared and then swollen with monomer and polymerized to yield final latex particles by chain extension. The use of a seed eliminates monomer droplet formation early in the polymerization and, therefore, prevents droplet polymerization and consequent colloidal instability.

The difunctional derivative DIAMA has also been used in emulsion polymerization (Figure 17),^{230,231} enabling a significant reduction in particle size and narrower distribution compared to latexes prepared using monofunctional BlocBuilder MA®. Polystyrene-*b*-poly(*n*-butyl acrylate)-*b*-polystyrene triblock copolymers were made using the difunctional alkoxyamine, and allowed nanostructured particles to be formed upon internal phase separation.²³² A refined semibatch process shortened overall process time compared to earlier efforts.²³¹

Water-soluble macroalkoxyamines were used in the SG1-mediated surfactant-free, ab initio, batch emulsion polymerization of styrene, BA, 4-vinyl pyridine, 67,68,233 and MMA (with <10% styrene comonomer).²²⁵ They led to amphiphilic block copolymer nanoparticles by simultaneous chain growth and self-assembling in situ. PAA macroalkoxyamines terminated by SG1 were very efficient in particle stabilization, but the initiating efficiency was rather low.^{67,68} Poly(methacrylic acid-co-styrene) macroalkoxyamines (again, small amounts of styrene commoner are required to preserve control and livingness with methacrylate monomers)^{225,234} were used as the first block in the in situ synthesis of amphiphilic block copolymers of poly([methacrylic acid-co-styrene]-b-[methyl methacrylate-costyrene]), with very high crossover efficiency. This method has the advantage of using a single molecule (i.e., the macroalkoxyamine) as the initiator, the control agent, and the stabilizer of the formed particles.

3.14.2.2.2(iv) Compartmentalization in NMP (mini)emulsions

In conventional emulsion polymerization, compartmentalization of the propagating radicals gives higher reaction rates and higher molar masses compared to bulk/solution processes by reducing the termination rate. Initially, it was thought that in reversible termination systems (NMP, ATRP), compartmentalization effects would not exist, although theoretical modeling studies suggested that they may exist at sufficiently small particle size.^{205–207} Maehata *et al.*²³⁵ demonstrated experimentally in TEMPO-mediated styrene miniemulsion polymerizations that particle size effects did exist, influencing both polymerization rate and livingness. Smaller particles showed lower rates of polymerization than larger particles as well as higher livingness. The lower rate in smaller particles likely results from the following: (1) geminate recombination of thermally generated radicals, leading to reduced thermal initiation rates; and (2) enhanced deactivation of propagating radicals with nitroxide (the so-called confined space effect). Enhanced deactivation is also predicted to reduce termination rates and, therefore, to increase livingness in smaller particles. Delaittre and Charleux²³⁶ examined compartmentalization with SG1-mediated emulsion polymerizations, and did not observe effects in the formation of poly(acrylic acid)-b-polystyrene amphiphilic block copolymers. Because SG1 has higher water solubility than TEMPO but more importantly because it exhibits a lower rate constant of recombination with the propagating radicals, it can rapidly diffuse between phases to equilibrate its concentration, and therefore compartmentalization is unlikely to be important.

3.14.2.2.3 Atom transfer radical polymerization

In ATRP (also known as transition metal-mediated polymerization), a halogen atom is transferred from a catalyst–ligand complex to a propagating macroradical (Figure 18). Dormant chains are activated by a transition metal complex in its lower oxidation state (e.g., CuBr/ligand) whereas propagating macroradicals are deactivated by a catalyst complex in a higher oxidation state (e.g., CuBr₂/ligand). The ligand plays a critical role in determining the reactivity of the catalyst complex as well as affecting its solubility in the reaction medium. In dispersed aqueous polymerizations, the ligand should be highly hydrophobic to prevent partitioning of catalyst into the aqueous phase. Of particular concern is loss of the deactivator; Cu(II)



Figure 18 Atom transfer radical polymerization (ATRP) showing activation of Br-terminated polymer chain by Cu(I) complex, and deactivation of propagating macroradical by Cu(II) complex.

species are usually more water soluble than the Cu(I) species that activate dormant chains. Reduction in the concentration of deactivator results in loss of control and significant chain termination. Deleterious reactions of the catalyst are a potential concern in ATRP in aqueous dispersions, and can include hydrogen abstraction (e.g., from monomers or solvents), reaction with monomers containing acid groups, and reactions with anionic surfactants. Unlike NMP, ATRP does not require high temperatures and is much more versatile than NMP in the range of monomers it can polymerize. Important process innovations have occurred in dispersed aqueous phase in recent years. Of special interest is activator generated by electron transfer (AGET) ATRP that has proven to be a versatile and robust system that uses less air-sensitive Cu(II) complexes.²³⁷

A limited range of suitable surfactants exists for dispersed phase ATRP. Anionic surfactants such as sulfates and sulfonates poison the catalyst. Most studies have used nonionic surfactants (Brij 98, PEO₂₀ oleyl ether)^{237–239} or Tween 80 (PEO sorbitan monooleate),^{240–244} although the cationic surfactant cetyltrimethylammonium bromide (CTAB) has been shown to give superior colloidal stability (especially at higher temperatures) and yields smaller particles.²⁴⁵

3.14.2.2.3(i) ATRP in suspension

There are limited reports of ATRP in suspension polymerization,^{246–248} including their use for encapsulating polar organic solvents.^{249–251} As with NMP, suspension polymerizations with larger particle sizes tend to behave similar to bulk polymerizations, with issues such as catalyst partitioning not as problematic as when particle diameters are in submicrometer range.

3.14.2.2.3(ii) ATRP in emulsion

As with NMP, early efforts to conduct ATRP in aqueous dispersions used emulsion polymerization, and employed alkyl halide initiators with Cu(I)/ligand catalyst complexes.^{238–240} Similar to NMP, severe colloidal stability problems were often encountered in emulsion ATRP. Significant difficulties were also observed using reverse ATRP in emulsion,²⁴² although seeded ATRP emulsion polymerization was more successful than *ab initio* polymerizations.^{243,244} A seed latex of poly(*i*-butyl methacrylate) was made by miniemulsion polymerization using CuBr/dNbpy (4,4'-dinonyl-2,2'-dipyridine) with ethyl-2-bromoisobutyrate initiator, and then swollen with styrene and polymerized. Although the polymerizations were controlled, colloidal stability was problematic. Chan-Seng and Georges²⁵² obtained better colloidal stability using a seeded nanoprecipitation technique first developed for emulsion NMP in the ATRP of styrene.

3.14.2.2.3(iii) ATRP in microemulsion

While emulsion ATRP is not a robust process, a new approach using an initial microemulsion polymerization^{253,254} appeared to be considerably more promising. Min and Matyjaszewski²⁵³ extended miniemulsion ATRP to microemulsion using AGET ATRP. Particle sizes of ~40 nm were obtained for polystyrene and poly(methyl methacrylate) latexes. A two-step emulsion polymerization process was subsequently developed, thereby eliminating the need for a miniemulsion process.²⁵⁴ The first stage of the two-step emulsion polymerization process was an AGET microemulsion polymerization, yielding ~30–40 nm particles that were then swollen with monomer and polymerized. Final particle sizes were ~90 nm. While initial experiments used high Brij 98 concentrations (\sim 75 wt.% Brij 98 vs. the monomer), a refined process used only 12 wt.% versus the monomer.

3.14.2.2.3(iv) ATRP in miniemulsion

Conventional (forward) ATRP with bipyridine ligands, a system that works well in bulk and solution, is poorly suited for aqueous systems, primarily because of the sensitivity of the Cu(I) species to air. Reverse ATRP uses Cu(II), which is far more tolerant of exposure to air that occurs when the miniemulsion is created by high shear (e.g., using microfluidization or sonication).^{238,239} High activity, hydrophobic ligands such as CuBr2-tris[2-di (2-ethylhexyl acrylate)aminoethyl]amine (EHA6TREN) or bis 2-pyridylmethyl)octadecylamine (BPMODA) (Figure 19) show much better performance for reverse ATRP in miniemulsion. Catalyst-ligand complexes used in ATRP aqueous dispersions must be fully soluble in monomer, unlike bulk or solution ATRP where heterogeneous catalysts can function effectively. Although reverse ATRP displays much better overall performance than forward ATRP in miniemulsion, there are issues with unpredictable induction periods and mediocre control of molar mass, both arising from variability in the initiation efficiency. Many of the challenges with reverse ATRP were resolved by development of the simultaneous normal and reverse initiation (SNRI) process.

SNRI, like reverse ATRP, uses the less oxygen-sensitive Cu(II) catalyst but addresses the problem of unpredictable initiation efficiency that is experienced with reverse ATRP by employing alkyl halide as the primary initiator. A small amount of free radical initiator is also added (a ~5:1 ratio of alkyl halide to initiator is employed). The activating Cu(I) species is generated *in situ* by reduction of the Cu(II) to Cu(I) as the free radical initiator decomposes. In a series of papers,^{255–257} Matyjaszewski demonstrated the suitability of the SNRI process for polymerization of BMA, BA, and styrene.



Figure 19 ATRP ligands BPMODA and EHA₆TREN, commonly used in ATRP miniemulsions.



Figure 20 Activator generated by electron transfer (AGET) ATRP. Activating species Cu^IBr/L is generated *in situ* by reduction of Cu^{II}Br/L.

In the SNRI process, contamination by homopolymer arising from the free radical initiator prevents synthesis of high-purity block or star polymer structures. AGET ATRP (Figure 20) utilizes a reducing agent to convert Cu(II) to Cu(I), instead of relying on radicals from initiator decomposition.^{237,258} The reducing agent also scavenges oxygen, increasing the tolerance of the system to air. Water-soluble ascorbic acid as a reducing agent is well suited to miniemulsions. Best results were obtained when the ratio of ascorbic acid/Cu(II) varies from ~0.1 to 0.5/1 (ascorbic acid reduces two equivalents of Cu(II)). In the miniemulsion polymerization of BA initiated by ethyl-2-bromoisobutyrate, well-controlled polymerization was obtained with final PDI ~1.2. Linear block and three-arm star copolymers (poly(methyl acrylate)-*b*-polystyrene) were also prepared.

Most publications dealing with ATRP, especially with aqueous systems, have yielded $M_n < \sim 80 \text{ kg mol}^{-1}$, with the typical M_n values being much lower. Simms and Cunningham²⁵⁹ recently showed that ATRP is suitable for preparing much higher molar masses in miniemulsion. Using a redox initiation system (ascorbic acid/hydrogen peroxide) with a CuBr₂/EHA₆TREN (Figure 19) catalyst, they were able to produce poly (*n*-butyl methacrylate) with $M_n \sim 10^6 \text{ gmol}^{-1}$ and PDI ~1.25. Conversions >80% were achieved in ~8 h, with mean particle diameters ~100 nm. The evolution of the MMDs showed excellent livingness, even at $M_n > 800 000 \text{ g mol}^{-1}$ (Figure 21).

3.14.2.2.3(v) Compartmentalization in ATRP

As discussed with NMP, it has been generally believed that compartmentalization effects do not exist in aqueous ATRP dispersions and some studies have shown similar kinetics and MMDs for bulk and miniemulsion experiments.^{255,260} As also reported for NMP, however, compartmentalization can influence the rate of polymerization, the degree of control of the PDI, and the livingness of the polymer formed in aqueous dispersed phase ATRPs. Kagawa et al.²⁶¹ have conducted simulations to explore questions about possible compartmentalization and partitioning effects in dispersed ATRP for CuBr/dNbpy-mediated systems. They predicted compartmentalization effects may be evident for particle diameters <70 nm, resulting in lower polymerization rate but higher livingness. Zetterlund et al.262 simulated compartmentalization for styrene polymerization using CuX/dNbpy (X = Br or Cl) catalyst. They found compartmentalization always improved livingness because of reduced termination (segregation effect). Control was improved as a result of the confined space effect but only for particles that were sufficiently small. The magnitude of compartmentalization effects increased with increasing target molar mass (i.e., fewer chains per particle).



Figure 21 Size-exclusion chromatography traces for the miniemulsion reverse ATRP of *n*-butyl methacrylate. T = 60 °C. Conversion increases from right to left: conversion = 11%, $M_n = 222500 \text{ g mol}^{-1}$, PDI = 1.56; conversion = 23%, $M_n = 345000 \text{ g mol}^{-1}$, PDI = 1.47; conversion = 74%, $M_n = 859000 \text{ g mol}^{-1}$, PDI = 1.24; conversion = 83%, $M_n = 989900 \text{ g mol}^{-1}$, PDI = 1.24. Reprinted from Simms, R. W.;

 $M_n = 989\,900\,\text{g}$ mol⁻⁷, PDI = 1.24. Reprinted from Simms, R. W.; Cunningham, M. F. *Macromolecules* **2007**, *40*, 860,²⁴⁵ with permission from the American Chemical Society.

Thomson and Cunningham²⁶³ simulated the highly active catalyst–ligand system (CuBr/EHA₆TREN) and BMA, with particular focus on the PDI and livingness of the growing chains. They found there is a defined range of particle sizes where the rate of polymerization can be enhanced above that of bulk polymerization while maintaining excellent control, with an expected PDI and degree of termination below that of bulk polymerization. Furthermore, while the polymerization rate is controlled by the equilibrium ratio of Cu(I)/Cu(II) for bulk ATRP, in compartmentalized system, the rate is controlled by enhanced deactivation and also the relative concentration of Cu(I) and Cu(II), which are dependent upon the size of the particles.

Experimental evidence showed compartmentalization in ATRP miniemulsions reduced polymerization rate (confined space effect), and more importantly, improved control over the polymerization²⁶⁴ when the number of chains was small (high target M_n) for the system CuBr/EHA₆TREN-*n*-butyl methacrylate. While in a conventional emulsion polymerization, segregation effects cause an increase in the rate, in ATRP, the confined space effect dominates the kinetics and results in a decrease in rate.

3.14.2.2.4 Reversible addition–fragmentation chain transfer The reversible deactivation process in a RAFT mechanism is governed by a chain transfer reaction between an active macromolecule and a dormant one.^{174-176,265,266} The latter is most generally end-functionalized by a thiocarbonylthio group (from a dithioester, a dithiocarbonate, a dithiocarbamate, or a trithiocarbonate (TTC), Figure 22), and the exchange reaction relies on an addition-fragmentation process. The poly(methacrylic ester)s with a terminal double bond derived from CCT polymerization can also be used, although their reactivity is lower than the thiocarbonylthio counterparts.267 Technically, the polymerization system requires the use of a classical radical initiator decomposing at low to moderate temperature (generally below 100 °C) in conjunction with a RAFT agent, which is consumed in the early stage of the polymerization to create the dormant chains. The latter are also active as macromolecular RAFT agents



Figure 22 Main families of RAFT agents.

throughout the polymerization. Consequently, a linear increase of the M_n with monomer conversion is expected (the number-average degree of polymerization (DP_n) is calculated by the ratio of the initial monomer concentration over the chain transfer agent concentration, multiplied by monomer conversion), along with narrow MMD and the formation of block copolymers by subsequent polymerization of a different monomer. Multistep reactions and/or the use of a multifunctional chain transfer agent allow complex architectures to be elaborated. The polymerization kinetics follow the classical steady-state assumption, meaning that compartmentalization effect is expected to be the same as in classical emulsion polymerization. In some cases, especially with the dithiobenzoate-based RAFT agents, a significant rate retardation effect is often observed.²⁶⁸

The development of the RAFT method in aqueous dispersed systems is quite recent^{88,177-179,181-185,187} and started essentially in miniemulsion polymerization processes. It is only very recently that successful attempts in emulsion polymerization systems have been disclosed. In comparison to miniemulsion and emulsion polymerizations, the suspension process has hardly been applied.²⁶⁹

3.14.2.2.4(i) RAFT in miniemulsion polymerization

In a first approach, RAFT was mainly studied in miniemulsion, because the technique allows the complex nucleation and mass transport processes of an emulsion polymerization to be avoided by preforming monomer droplets that act as nanoreactors throughout the polymerization. The reactivity of the chain transfer agent (i.e., the value of the chain transfer constant) is of primary importance, but its effect on molar mass and MMD should be the same in miniemulsion as in homogeneous systems. The other parameter of highest influence is the water solubility of the chain transfer agent and its partition coefficient between water and the monomer phase. The most hydrophobic transfer agents have been easily used in miniemulsion polymerization, with good control over both the kinetics and the molar masses. Actually, the miniemulsion polymerization process is particularly convenient when the RAFT agent is highly hydrophobic (for instance, a hydrophobic macromolecular RAFT agent),²⁷⁰ and hence, unable to diffuse through the aqueous phase. For more hydrophilic control agents, exit of primary leaving radicals from the particles and termination in the aqueous phase can be an issue, and may lead to rate retardation and poor control over molar masses.²⁷¹ In addition, colloidal stability problems were encountered in some particular examples, mainly with ionic surfactants, and were assigned to a superswelling effect explained by the presence of a large concentration of short chains within the monomer droplets.²⁷² In spite of these difficulties, the miniemulsion process was very successful for RAFT in aqueous dispersed systems and allowed block copolymers to be synthesized with good control over molar mass, MMD, and chain architecture. Special morphologies such as capsules with a liquid core and a well-defined polystyrene shell have been prepared using this method.²⁷³

3.14.2.2.4(ii) RAFT in emulsion polymerization

The development of RAFT in true emulsion polymerization processes was more challenging than in miniemulsion. A general difficulty of RAFT in aqueous dispersed systems, and particularly emulsion polymerization, is related to the need for a radical initiator in conjunction with the RAFT agent. Consequently, it is not always easy to control the locus where reversible transfer will take place, and this may have important and sometimes deleterious consequences on the control over molar mass and MMD. Again, the most important parameters to consider are both the water solubility and the reactivity of the chain transfer agent.

3.14.2.2.4(ii)(a) Low-molar-mass RAFT agents With moderately hydrophobic chain transfer agents (i.e., mainly soluble in the monomer phase but sufficiently water soluble to diffuse from the monomer droplets to the particle, through the aqueous phase) exhibiting low chain transfer constant like dithiocarbonate (also called xanthates), the nucleation step was not modified with respect to a classical radical emulsion polymerization due to the initial formation of long hydrophobic chains. Therefore, the colloidal properties of the latexes



Figure 23 Amphiphilic RAFT agents used in emulsion polymerization.

were good in the presence of a classical surfactant, although control over molar mass and MMD was far from excellent due to the poor reactivity of the chosen control agents. The polymerization was found to be retarded when the amount of xanthate was increased. This result was assigned to an enhanced exit of the primary radicals formed upon transfer in the particles, and to an unexpectedly slow rate of entry of the oligoradicals from the aqueous phase.²⁷⁴ With highly reactive RAFT agents, the emulsion polymerization was more difficult to achieve owing to the fast formation of a large concentration of short oligomers. The latter hampered the nucleation step and led to colloidal instability in the presence of monomer droplets and sometimes very poor control over the chain growth along with severe rate retardation. The conclusion was that droplet nucleation had to be avoided, which motivated further works using either starved-feed conditions or multistep methods (see the following sections). A surface-active RAFT agent, the sodium salt of 2-(dodecylthiocarbonothioylthio)-2-methylpropanoic acid) (TTCA; Figure 23(a)), was further tested²⁷⁵ as TTCA is a widely employed TTC, known for controlling efficiently the polymerization of a large variety of monosubstituted ethylenic monomers276 in homogeneous conditions. In the batch emulsion polymerization, however, the success was limited to specific conditions. In the homopolymerizations of styrene or BMA, the kinetics were either extremely slow (styrene) or the molar masses were not controlled (BMA). In contrast, for the batch emulsion copolymerization of BMA with either BA or styrene, a good control was achieved over both the macromolecular structure of the chains and the colloidal stability of the particles, in the presence or in the absence of additional surfactant.

3.14.2.2.4(ii)(b) Amphiphilic macromolecular RAFT agents in starved-feed conditions or in a two-step method In order to avoid droplet nucleation, a first way was to avoid the presence of droplets by working under starved-feed conditions. An amphipathic asymmetrical trithiocarbonate RAFT agent was used (Figure 23(b)) for the aqueous polymerization of AA in alkaline conditions to form *in situ* a water-soluble oligometic RAFT agent.^{277–280} Then, a hydrophobic monomer was slowly added, and the system led to the formation of amphiphilic block copolymer micelles upon chain extension of the hydrophilic segments in the absence of monomer droplets. These micelles became then

the loci of the next controlled polymerization step performed under starved-feed conditions. Following the same strategy, Božović-Vukić *et al.*²⁸¹ synthesized poly(4-vinyl pyridine) chains in a mixture of toluene and ethanol under RAFT control, and the obtained macromolecular RAFT agent was further used in emulsion polymerization under acidic conditions. In both cases, the characteristics of a controlled polymerization were observed together with good colloidal properties of the formed surfactant-free latexes. The latter were composed of well-defined amphiphilic block copolymers, with a stabilizing hairy layer (core-shell particles) coming from the initially synthesized hydrophilic segments. The method has been well studied for various monomers and various hydrophilic blocks and allowed moreover fundamental studies to be performed on the nucleation step and on the rate of entry of radicals in particles.^{282–284}

To avoid droplet nucleation, another method aimed at locking the RAFT groups within preformed particles before the addition of the hydrophobic monomer in one shot. For this, dibenzyltrithiocarbonate was used as a hydrophobic RAFT agent for the copolymerization of styrene and AA in bulk.²⁸⁵ At incomplete monomer conversion, alkaline water was added slowly to the solution to induce a phase inversion process and hence form living amphiphilic copolymer aggregates swollen with the remaining monomer. Upon a shot addition of styrene, the polymerization was resumed with chain extension of the TTC-functionalized copolymers along with particle growth. The method led to stable latex particles composed of well-defined copolymer chains, but again, it needed several steps to reach the goal.

3.14.2.2.4(ii)(c) Amphiphilic or water-soluble macromolecular RAFT agent in ab initio, batch conditions In the very first works, water-soluble macromolecular RAFT agents were tested in ab initio batch emulsion polymerization, with the idea that the hydrophilic block would chain extend through a transfer reaction and form in situ an amphiphilic block copolymer able to participate in particle stabilization. The technique would be very helpful to replace the low-molar-mass surfactants, which exhibit high mobility and hence deleterious effect in coating applications. With dithiobenzoate as the RAFT group and poly (methacrylic acid)²⁸⁶ or protonated poly(diethylaminoethyl methacrylate)²⁸⁷ or protonated poly(dimethylaminoethyl methacrylate) combined with a PEO segment,²⁸⁸ good colloidal stability was achieved but not the control over molar mass and MMD of the polymer chains forming the particles. Similar results were obtained with dithiocarbonate-functionalized dextran used in the emulsion polymerization of VAc,289 or with TTC-functionalized polyacrylamide in the batch emulsion polymerization of styrene.²⁹⁰ In most cases, the emulsion polymerization kinetics exhibited an induction period, during which formation of the amphiphilic block copolymer was assumed to take place. The latter self-assembled into micelles, in which the emulsion polymerization could progress. In such a situation, control over all the characteristics of the polymer formed in this latter stage is not necessarily a major target, but the method offers a new tool toward surfactant-free emulsion polymerization, which is of high industrial relevance.

In contrast, when PEO-based amphiphilic TTC RAFT agents (PEO-TTC; **Figure 23(c)**) were used in *ab initio*, surfactant-free, batch emulsion polymerization, the reactions were fast and led to good colloidal stability together with excellent control over

molar mass and MMD. These results were fully achieved for the emulsion polymerization of BA²⁹¹ and its copolymerization with MMA over a broad composition range.²⁹² For styrene, the polymerization was rather slow and the control was less efficient. PEO-TTC was shown to react very fast at the early stage of the polymerization, leading to well-defined amphiphilic block copolymer chains and hence self-stabilized, block copolymer particles. In consequence, no PEO chains remained free in the final latex, all of them being covalently bound to the polymer forming the particles. So far, this macromolecular RAFT agent structure can be considered as the most effective for surfactant-free, ab initio, batch emulsion polymerization. Quite recently, a macromolecular RAFT agent composed of AA and PEO acrylate units based on a TTC functional group was shown to lead to nonspherical morphologies in the batch emulsion polymerization of styrene. In particular, very long nanofibers were formed and were composed of poly(acrylic acid-co-PEO acrylate)-b-polystyrene amphiphilic block copolymers self-assembled by polymerization-induced micellization.²⁹³

3.14.2.2.4(iii) RAFT in aqueous dispersion polymerization

The use of hydrophilic macromolecular RAFT agents as both stabilizer and control agent in emulsion polymerization was easily transposed to aqueous dispersion polymerization in which the monomer is completely soluble in the water phase while the corresponding polymer is not. An et al.²⁹⁴ polymerized N-isopropylacrylamide using a water-soluble poly(N,N-dimethylacrylamide) RAFT agent. The polymerization temperature was above the LCST of the newly formed polymer block. Therefore, chain extension led to its precipitation and self-assembling, resulting in the creation of self-stabilized particles. Hydrogel nanoparticles able to swell with a decrease of the temperature were similarly obtained with the additional use of a crosslinker during the dispersion polymerization. Similar temperature-sensitive nanogels of poly(N,N-diethylacrylamide) were prepared using a series of double hydrophilic macromolecular RAFT agents with a PEO first block and a poly(N,N-dimethylacrylamide) second block formed by chain extension of PEO-TTC.²⁹⁵

3.14.2.2.5 Other CRP methods

Besides the most common CRP methods used to control the radical polymerization of vinylic monomers, other techniques have been developed over the time, and have been tested in miniemulsion or emulsion polymerization as well. These methods are described in the corresponding chapters of this comprehensive. They are iodine transfer polymerization (ITP; and the reverse method, RITP), organotellurium-mediated CRP (TeRP), and cobalt-mediated radical polymerization (COMRP).

3.14.2.2.5(i) ITP and RITP in aqueous dispersed systems

The method is based on the reversible exchange of a terminal iodine atom between a propagating radical and a dormant chain.^{296–298} ITP using $C_6F_{13}I$ as a chain transfer agent was shown to be very effective in the miniemulsion polymerization of styrene²⁹⁹ and in the formation of polystyrene-*b*-poly(*n*-butyl acrylate) diblock copolymers.³⁰⁰ More recently, the method allowed original triblock copolymer architectures to be achieved such as poly(vinyl acetate)-*b*-polydimethylsiloxane-*b*-poly (vinyl acetate)^{301,302} and polystyrene-*b*-polydimethylsiloxane-*b*-polydimethylsiloxane-*b*-polydimethylsiloxane-*b*-polydimethylsiloxane-

macromolecular chain transfer agent. In these systems, due to their high water insolubility, the chain transfer agents were used as hydrophobes for the miniemulsion formulation. In contrast, ITP failed in controlling the polymer molar mass in emulsion polymerization due to the incapacity of the chain transfer agents of diffusing from the monomer droplets toward the particles. RITP³⁰⁴ was further developed with the idea of using a classical radical initiator in conjunction with molecular iodine to generate iodinated chain transfer agents in situ.³⁰⁵ Besides its application to the miniemulsion polymerization of styrene,³⁰⁶ it was very convenient for the use in ab initio emulsion polymerization due to the water solubility of iodine and of sodium iodide later used as a precursor.^{298,307} Using RITP in aqueous emulsion, advantage was further taken of the higher reactivity and solubility in water of AA compared to BA to synthesize, in one step, amphiphilic poly(acrylic acid-co-n-butyl acrylate) gradient copolymers able to self-assemble into particles.308

3.14.2.2.5(ii) TeRP in aqueous dispersed systems

The TeRP³⁰⁹ proceeds by the two activation–deactivation processes, namely, thermal dissociation of the C-TeCH₃ terminal bond and degenerative transfer of the terminal –TeCH₃ group. However, when an external source of free radicals is used at low temperature, it only proceeds by degenerative transfer. Okubo *et al.*³¹⁰ used a water-soluble poly(methacrylic acid) with a –Te-CH₃ terminal group to synthesize poly(*n*-butyl acrylate) latex particles by chain extension of the hydrophilic segment in emulsion polymerization. The system resulted in very small particles with controlled polymer chains exhibiting an amphiphilic structure.

3.14.2.2.5(iii) CoMRP in aqueous dispersed systems

Similar to TeRP, CoMRP follows the dual mechanism of reversible termination and degenerative chain transfer.³¹¹ It was applied in suspension^{312,313} and in miniemulsion for the polymerization of VAc and allowed well-defined polymers to be prepared at low temperature (0–30 °C) with quite a fast rate. The miniemulsion process yielded latexes with small particles (diameter of approximately 100 nm) and good stability.³¹⁴ CoMRP is one of the best methods (beside RAFT using a xanthate as a chain transfer agent) to produce poly(vinyl acetate) with controlled molar mass, and its successful implementation to an aqueous dispersed system is an important step.

3.14.2.3 Other Vinyl Polymerization Methods

3.14.2.3.1 ROMP in aqueous dispersed systems

ROMP in homogenous processes (e.g., bulk or solution) is used to manufacture a range of industrially important polymers, including polynorbornene and its derivatives, polycyclooctenes and polydicyclopentadiene. In addition to its established commercial importance, ROMP (and especially functionalized norbornenes) has recently become the subject of intense research interest for applications such as preparing chiral polymers, brush-like peptide-bearing polymers for tissue engineering and drug delivery,³¹⁵ membrane transporters in multicomponent sensors,³¹⁶ antibacterial and hemolytic polymers,³¹⁷ antimicrobial polymers,³¹⁸ and microcellular foams.³¹⁹ Reviews on ROMP are available in the literature.^{320–324}

ROMP is a living polymerization, and as such it enables excellent control of the polymer microstructure, and is well



Figure 24 Principle of ring-opening metathesis polymerization of norbornene.

suited for designing advanced polymers (for applications such as those referenced above) with tailored polymer chain structure (e.g., block, graft copolymers) or functionalized with desired reactive groups for further chemical reaction. The basic ROMP mechanism is shown in Figure 24.

Despite the commercial importance and research interest in ROMP, little has been published on developing an emulsion ROMP process. There is considerable incentive for conducting ROMP in aqueous dispersed systems, including many of the same reaction engineering benefits that have made emulsion and suspension polymerization commercially important processes for free radical polymerization. Aqueous dispersions would eliminate (or greatly reduce) the use of organic solvents, and provide reaction engineering advantages such as facile mixing, heat transfer, residual monomer removal, and product transport. The limited papers that have been published have established the feasibility, in principle, of doing ROMP in aqueous dispersions, but most have been of limited scope and/or were plagued by difficulties such as colloidally unstable dispersions, poor control over particle size and/or molar mass, and low reaction rates.

ROMP has been reported in emulsion, miniemulsion, dispersion, and suspension. Caution should be used in interpreting reported process types in the literature; however, these various processes are not as well defined for nonradical polymerizations as they are for radical polymerizations. In particular, the locus of chain initiation is sometimes ambiguous and the mechanisms of particle nucleation may not be well understood.

3.14.2.3.1(i) Dispersion polymerization

Early ROMP catalysts were intolerant to polar functionality in monomers, resulting in severe catalyst poisoning. Pioneering efforts by Novak and co-workers^{325,326} and Feast and Harrison³²⁷ demonstrated that ruthenium-based catalysts could not only polymerize functional monomers but could do so in an aqueous environment. Novak and Grubbs³²⁵ were able to polymerize functionalized 7-oxanorbornenes under air in a completely aqueous environment using the complex Ru^{II}(H₂O)₆(p-toluenesulfonate)₂. Ruthenium, iridium, and osmium chlorides were used to polymerize 7-oxanorbornenes in water.327 These developments in water-tolerant catalysts led to work in dispersion polymerization first and then other forms of dispersed phase polymerizations (suspension, emulsion, miniemulsion). Booth and co-workers^{328–330} generated a stable latex (<100 nm) in the dispersion polymerization of exo, exo-2, 3bis(methoxymethyl)-7-oxanorbornene. Gnanou and coworkers³³¹⁻³³⁴ further developed the ROMP dispersion polymerization process, and in particular showed the importance of stabilizer design.

3.14.2.3.1(ii) Emulsion and miniemulsion polymerization

Emulsion-type polymerizations for ROMP of norbornene and its derivatives were first reported using hydrates of Ru, Ir, and Os four decades ago.^{335–337} However, polymerization rates were very low. ROMP using water-soluble ruthenium carbene complexes as catalysts was used to polymerize functionalized 7-oxanorbornenes not only in water and methanol, but also in aqueous emulsions.^{338,339} Cationic water-soluble aliphatic phosphines were used in the synthesis of the ruthenium carbene complexes. The polymer polydispersity was low (1.1–1.3), although few details of the dispersed phase polymerization were reported.

Claverie et al.340 reported the ROMP in emulsion of norbornene as well as that of the less strained monomers 1,5-cyclooctadiene and cyclooctene. First-generation (benzylidene-bis(tricyclohexylphosphine)dichlororuthenium) and second-generation (benzylidene[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(tricyclohexylphosphine) ruthenium) Grubbs catalysts used with norbornene yielded stable latexes with minimal coagulum using emulsion polymerization with an anionic surfactant. Fast reaction rates (>80% conversion in less than 30 min) were typical, and molar masses were high, ranging from $\sim 2 \times 10^5$ to $2 \times 10^{6} \,\mathrm{g \, mol^{-1}}$. Mean particle diameters ranged from about 50 to 150 nm. These polymerizations resemble free radical emulsion polymerizations, with aqueous phase initiation and the presence of monomer droplets that act as monomer reservoirs during polymerization. With 1,5-cyclooctadiene and cyclooctene, the Grubbs type 1 and 2 catalysts gave very low yields.340 The more active and faster initiating third-generation Grubbs catalysts (dichloro-di(3bromopyridino)-N,N'-dimesitylenoimidazolino-RuCHPh) are needed for these monomers; however, they are quite hydrophobic and cannot, therefore, be easily used in emulsion polymerization, which requires facile transport of the catalyst through the aqueous phase from monomer droplets to particles. The use of miniemulsion polymerization provided a solution to this problem, since the hydrophobic catalyst could be readily dissolved in the monomer phase (which contained a small amount of toluene) and stable latexes without coagulum formation were reported.

Gnanou's group has extensively explored the use of ROMP in emulsion and miniemulsion in addition to dispersion and suspension.^{332,341} The use of ROMP in tandem with ATRP in miniemulsion has proven to be an effective route for making biphasic or 'Janus particles', consisting of polynorbornene and poly(methyl methacrylate) domains.^{342,343} They were able to use the same ruthenium-based catalyst for both, achieving simultaneous ROMP of norbornene and ATRP of MMA, using miniemulsion polymerization. Stable latexes with minimal coagulum were formed, with mean particle diameters of \sim 200 nm. The polymer polydispersities were typically \sim 1.8, not as narrow as can be achieved in ideal ROMP or ATRP but still reasonable.

3.14.2.3.1(iii) Suspension polymerization

Suspension polymerization was applied to prepare polynorbornene crosslinked beads suitable for use as supports in organic synthesis.³⁴⁴ The monomers used included norbornene, norborn-2-ene-5-methanol, and crosslinking agents including bis(norborn-2-ene-5-methoxy)alkanes, di(norborn-2-ene-5-methyl)ether, and 1,3-di(norborn-2-ene-5-methoxy) benzene. The initial resins, which were unsaturated, were subsequently modified using hydrogenation, hydrofluorination, chlorination, or bromination to yield saturated resins with varying properties. They were reported to be superior to more traditional styrene–divinylbenzene resins due to reduced interference in electrophilic aromatic substitution reactions (e.g., Friedel–Crafts acylation and nitration).

Quémener *et al.*³³² reported the suspension polymerization of both 1,5-cyclooctadiene to yield polybutadiene beads using the organic soluble catalyst (PCy₃)₂Cl₂RuCHPh. High monomer conversions were obtained but colloidal stability was poor using the electrosteric stabilizer poly(diallyl methylammonium chloride), prompting a change to various copolymer stabilizers, of which a graft copolymer (polybutadiene-*g*-PEO) and a macromonomer stabilizer (polystyrene-*b*-PEO) yielded much improved stability. The mean particle diameters were ~20 µm, quite small for suspension polymerization.

3.14.2.3.2 Ionic polymerizations

Cationic polymerization of vinyl monomers is extremely sensitive to water traces as the polymerization proceeds by highly electrophilic propagating carbocations. The polymerization in aqueous dispersed systems is, therefore, an extremely difficult task, not to say an impossible one.³⁴⁵ Nevertheless, attempts have been made using water-tolerant Lewis acids such as $B(C_6F_5)_3$ and ytterbium triflate for the suspension polymeriza*p*-methoxystyrene,^{346–352} its tion of miniemulsion polymerization,³⁵³⁻³⁵⁵ its dispersion polymerization,³⁵⁶ or even its emulsion polymerization³⁵⁷ with presumably an interfacial mechanism. The controlled character of the polymerization was studied. To reach high-molar-mass polymers (i.e., several thousands of $g \mod^{-1}$) instead of oligomers, the polymerization had to be transported inside the monomer droplets, using oil-soluble superacid initiators, namely, 'Lewis acid-surfactant combined catalysts' (LASC).357

The anionic polymerization in aqueous dispersed systems concerns mainly the alkyl cyanoacrylate monomers, which can polymerize spontaneously at a very fast rate in the presence of water. (Nano)particles^{358,359} and nanocapsules^{360–362} were synthesized by emulsion, miniemulsion, or inverse miniemulsion polymerization processes.³⁶³ They mainly find applications in the biomedical domains^{364,365} and received for that reason a huge interest, which makes it impossible to be exhaustive in this chapter.

3.14.2.3.3 Catalytic polymerization

The world production of polymers is about 260 million tons per year and half of the production is made of polyolefins (including low-density polyethylene, high-density polyethylene, linear low-density polyethylene, isotactic propylene, high impact polypropylene, and ethylene-propylene rubbers). Polyolefins compete with other polymer families in most of the markets but their presence in markets where a thin film that adheres on a substrate is required is very limited. These markets are dominated by waterborne polymer dispersions synthesized by emulsion polymerization of styrene, butadiene, (meth)acrylates, and vinyl ether monomers that are more expensive than olefins, which are directly obtained in the steam cracking process. Therefore, there is a strong interest in including olefins as part of the waterborne dispersion formulations. However, this is not an easy task because waterborne dispersions are mostly polymerized by free radical polymerization, which has very limited capability to polymerize olefins and controlling the microstructure of the polymer. Ethylene is polymerized by free radical polymerization but α -olefins are not. Polymerization of ethylene in aqueous phase is possible, but the homopolymer has little application because it is not film forming. The copolymerization with acrylates is challenging because of the very different reactivity ratios ($r_{acrylate} = 13.94$; $r_{ethylene} = 0.01$) and the low solubility of ethylene in water that favors the incorporation of the acrylate. Furthermore, high temperatures and pressure are necessary, which involve high capital investment.

Ziegler-Natta, Phillips, and metallocene catalysts are extensively used to produce polyolefins by catalytic polymerization. These catalysts allow a good control of polymer microstructure and large productivities, but they are based on early transition metals (Ti, Zr, Cr, and V), which are oxophilic, and hence sensitive to water. Therefore, they cannot be used in aqueous systems although some relative success has been recently reported in the polymerization of styrene with metallocene catalysts.³⁶⁶ Late transition metals (Ru, Co, Rh, Ni, and Pd) are much less oxophilic, and hence they may be used in water systems.³⁶⁷ In the past 30 years, a great deal of work has been done to develop late transition metal catalyst to polymerize ethylene and copolymerize it with acrylates in both solvent and aqueous phases.^{368–370} The neutral nickel complexes of [P,O] chelating agents developed by Keim and co-workers^{371,372} were the first ones but only yielded low-molar-mass oligomers. Better yields of the catalyst and higher molar masses were obtained by similar Ni(II)-P,O-based catalysts with a modified ligand.^{373–375} However, they were still not able to copolymerize ethylene with other polar monomers. The cationic versions of Ni and Pd metal complexes of neutral multidentate ligands with nitrogen donor bulky groups were more effective and particularly the Pd(II) catalyst allow the copolymerization with acrylates at weight ratios as high as 25%.376 However, the activity of the catalyst strongly decreased by increasing the concentration of the acrylate monomer.³⁶⁸ Other groups^{377–379} did also report catalysts (based on neutral Ni and Pd complexes with [P,O] ligands) that were able to copolymerize ethylene and acrylates in ethanol and toluene, but molar masses were relatively small $(<10\,000\,\mathrm{g\,mol}^{-1})$ and the incorporation of the acrylate reduced the productivity of the catalyst, which was also modest in most of the cases.

More recently, monometallic palladium catalysts^{380–382} containing a sulfonated phosphine ligand have been developed that are able to homopolymerize ethylene and copolymerize ethylene with acrylates and other polar monomers in both solution and aqueous phase.^{383,384} In solution,³⁸⁵ the activity

of the catalyst for homopolymerization of ethylene was very high and high-molar-mass polyethylene was obtained. The copolymerization with acrylates was possible, but catalyst activity strongly decreased with the degree of incorporation. In aqueous phase,³⁸⁶ both homopolymerization of ethylene and copolymerization of ethylene with acrylates was effective, but for the emulsion polymerization of ethylene, the activity was 20 times smaller and the activity of the catalyst in the emulsion copolymerization of ethylene and MA decreased by a factor of 2 for an incorporation of 2.7 mol.% of acrylate monomer. In both cases, the solids content of the latexes was modest (<8%).

Miniemulsion polymerization has also been used to produce polyethylene dispersions using two families of neutral Ni(II) catalyst originally developed for nonaqueous systems: nickel(II) phosphinoenolato complexes and nickel(II) salicylaldiminato complexes.^{387,388} The water-insoluble catalysts were dissolved in an organic solvent and then miniemulsified. The catalysts were highly active yielding polyethylene latexes with 30% solids and high molar masses. Both molar mass and polymerization rate decreased when the catalysts were used in copolymerization with α -olefins to produce a branched polymer. Latexes with very small particles (10 nm) have been prepared using this family of catalysts in microemulsion polymerization.³⁸⁹ Water-soluble versions of nickel(II) phosphinoenolates³⁹⁰ and salicylaldiminato³⁹¹ complexes did also yield polyethylene latexes with small particles (20 and 4 nm, respectively).

Miniemulsion copolymerizations of α -olefins and ethylene have been carried out using the α -olefin to prepare the miniemulsion (i.e., without using a solvent). Particles with diameters of 50–100 nm and low-molar-mass amorphous polymers were obtained.³⁹²

Sauca³⁹³ recently reported on the use of monometallic palladium catalyst containing a sulfonated phosphate ligand in the homopolymerization of ethylene and copolymerization of ethylene with acrylates and acrylate macromonomers in solution (toluene) and miniemulsion polymerization. Sauca found that in the copolymerization of ethylene with acrylates performed in aqueous systems, the type of surfactant (anionic vs. nonionic) had a strong influence over the polymerization rate, latex stability, and acrylate incorporation. This was attributed to the capability of the surfactant to disperse the entering acrylate. When poly(acrylate) macromonomers were used in the copolymerization of ethylene, it was found that macromonomers synthesized by high-temperature polymerization of acrylate were not incorporated into the polymer backbone whereas macromonomers produced by CRP, in particular those synthesized by ATRP, showed the highest degree of incorporation.

3.14.3 Vinyl Polymerization in Nonaqueous Dispersed Systems

3.14.3.1 Conventional Radical Polymerization

3.14.3.1.1 Inverse emulsion, miniemulsion, and microemulsion polymerizations

Inverse emulsions are water-in-oil emulsions that provide a convenient and commonly used approach for preparing colloidal dispersions of water soluble or hydrophilic polymers, including crosslinked polymers.^{394,395} Water-soluble polymers represent an important class of commercial materials, finding applications as flocculants, thickeners, and drag-reducing agents in a variety of industries, including water and sewage treatment, pulp and paper mills, coatings, paints, and oil recovery. Usually, high-molar-mass polymers are required. Inverse emulsion polymerizations provide the same reaction engineering advantages as most dispersed phase polymerizations, including improved heat transfer, mixing, and low viscosity. The hydrophilic dispersed phase often contains water, in some cases, because the monomers are solids that cannot be readily dispersed in the continuous organic phase (e.g., acrylamide, sodium styrene sulfonate). Addition of water to the final latex induces phase inversion, and the polymer can usually be dissolved without too much difficulty, even at high molar masses. Initiators can be soluble in either phase. Inverse emulsion and miniemulsion polymerizations are kinetically stable, while inverse microemulsions are transparent and thermodynamically stable. Inverse microemulsions have smaller particle size (<40-50 nm) than inverse emulsions or miniemulsions, and contain much higher surfactant levels. The particles in inverse microemulsion latexes can be so small that each particle contains only $\sim 1-10$ polymer chains. Micelles may persist throughout the polymerization that gives rise to an increasing particle number. Inverse miniemulsions are less common, but have recently become important in the CRP of hydrophilic monomers.

Typical oil phases include aromatic and aliphatic compounds such as cyclohexane, heptane, toluene, xylene, isooctane, and paraffin oil. The stabilizer (or emulsifier) plays a critical role in the polymerization and must be chosen carefully, with regard given to monomer(s) selection, polymerization temperature, mixing conditions, and the fraction of monomer in the aqueous phase. In these low dielectric constant hydrocarbon continuous phases, electrostatic stabilization is not feasible and steric stabilization is thus required for inverse emulsions. Unlike oil-in-water emulsions, inverse emulsions require oil-soluble stabilizers. These are usually fatty acid esters of sorbitan (e.g., sorbitan monooleate), PEO derivatives, or triblock polymer based on a PEO midblock with 12-hydroxystearic acid-based esters for the outside blocks.³⁹⁴

Stabilizers are used above the CMC so that micellar nucleation is the predominant mechanism of new particle formation. Free radicals initiate chain growth in the organic phase, where the chains propagate until they reach a critical length and enter either a monomer-swollen micelle or an existing particle. Monomer droplets provide reservoirs that supply the growing particles. Nucleation continues until all micelles are consumed, after which the particles grow until all monomer has been consumed. If water-soluble initiators are used, polymerization in droplets may be significant, depending on droplet size. Inverse microemulsion polymerization, which has very high particle numbers compared to conventional emulsion polymerization, tends to give very high molar masses as chains are not terminated by entry of radicals from the organic phase. The high stabilizer concentration gives rise to a high number of micelles, and, therefore, most newly initiated chains in the continuous phase enter micelles rather than particles. In this case, molar mass is determined by chain transfer to monomer or possibly to the organic phase solvent. While there are similarities between the mechanisms of conventional and inverse emulsion polymerization, the kinetics of inverse emulsion

polymerization are generally more complex and not as well understood.

3.14.3.1.2 Dispersion polymerization

3.14.3.1.2(i) Dispersion polymerization in organic solvents

The preparation of polymeric particles in the 1–10 µm range remains a challenge. Modified emulsion polymerization processes involving the use of multiple, sequential stages can be used to make particles up to \sim 1–2 µm, while microsuspension polymerization becomes increasingly difficult for particles under 10 µm. Dispersion polymerization, however, provides a one-step process for preparing 1–10 µm particles, with monodisperse PSD if desired. Monodisperse particles in this size range have applications in chromatography, instrument calibration standards, xerographic toners, and health sciences. A brief description of dispersion is given below. More detailed reviews are available.^{152–156}

In a dispersion polymerization, the reaction mixture (monomer, initiator, optionally chain transfer or crosslinking agent, stabilizer (surfactant), and solvent phase) is initially homogeneous. The solvent phase is chosen so that monomer(s) is fully soluble but the polymer is insoluble. In the early stages of a dispersion polymerization, free radical initiator decomposes to initiate chains. The chains are initially miscible but when they reach a given length (which depends on the solvent/monomer composition), they precipitate. Individual chains are too small to remain stable, and therefore aggregation of the individual chains into discrete particles occurs until the aggregates reach a particle size that can be stabilized by the available surfactant. Stabilization is steric in nature. (Precipitation polymerization is a similar, related process except no surfactant is added.) The new polymer particles will swell with monomer, although a portion of the monomer remains in the continuous phase. The relative partitioning of the monomer between the particle phase and the continuous phase depends on the thermodynamic properties of monomer, polymer, and solvent. The other components in the formulation (initiator, chain transfer agents, crosslinking agents) will also partition between the phases. The 'critical point' is reached when all of the particles have been sufficiently stabilized by surfactant, after which no new particles are nucleated.

After the critical point is reached, particles continue to grow by different mechanisms. (1) Particles can capture growing oligomeric radicals in the continuous phase. (2) Individual chains that precipitate can aggregate with existing particles. (3) Monomer within the particles polymerizes. Chain initiation in the continuous phase continues throughout the polymerization, but chain initiation also occurs within the particles resulting in two loci of polymerization. If the particle nucleation stage occurs fairly quickly, all particles are nucleated at about the same time and narrow or monodisperse PSDs are more likely. However, solvent and surfactant choice are also critical concerns if monodisperse particles are desired. Variations in solvent composition, solvent/monomer ratio (which affects the overall solvency of the system), monomer polarity, and surfactant type and concentration are all important variables in determining the final PSD. An added complexity of dispersion polymerization is that the solvency of the continuous phase changes continually during polymerization as monomer is consumed.

Although the original early work in dispersion polymerization was conducted in hydrocarbons such as cyclohexane, most subsequent work involved the use of more polar solvents, particularly alcohol-water mixtures. Also popular are mixed solvent-nonsolvents including alcohol-toluene mixtures, alcohol-dimethyl sulfoxide mixture, dimethylformamidemethanol, and dimethylformamide-toluene. Typical polymeric stabilizers include poly(vinyl pyrrolidone) (PVP), poly(vinyl alcohol), poly(hydroxy alkyl celluloses), and PAA.

3.14.3.1.2(ii) Dispersion polymerization in ionic liquids

Ionic liquids have increasingly attracted attention in recent years as alternative solvents for a variety of applications, including catalysis, chemical synthesis, separation processes, dissolution of cellulosics, and synthetic polymers, and as a medium for polymerization. The synthesis of polymer particles in ionic liquids has been reported using techniques such as condensation polymerization, chemical oxidative polymerization, and cationic ring-opening polymerization. Only a few publications have appeared, however, utilizing free radical polymerization to synthesize polymer particles.^{396–398} Polymerization in ionic liquids has been recently reviewed.^{399,400} Attractive properties of ionic liquids include low flammability, low volatility, high boiling points, and good thermal stability in addition to their conductivity. Furthermore, their solubilization properties can be readily tailored by varying the cation and/or the anion. A large number of ionic liquids have been reported for solubilizing polymers.401

Polystyrene particles, polystyrene/poly(methyl methacrylate) composite particles, and polystyrene/PAA core-shell particles were synthesized using dispersion polymerization in the ionic liquids diethyl(2-methoxyethyl)methylammonium bis (trifluoromethanesulfonyl)imide ([DEME][TFSI]) or 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF₄]).^{396,397} Styrene, initiator (AIBN), and surfactant (PVP) are all soluble in the ionic liquid so that the initial reaction medium is homogeneous. The polymer however is insoluble, so that particles are formed as the polymer precipitates in the early stages of polymerization. As with dispersion polymerization in conventional solvents, surfactant choice is critical. The stabilizer must be soluble in the reaction medium but possesses sufficient affinity for the particle surface that it adsorbs onto the surface once polymer chains begin precipitating. Inadequate affinity for the polymer particles will result in the stabilizer residing primarily in the continuous phase and not on the particle surface, during polymerization. Dispersions of ~10% solids with narrowly distributed particles were made at 70 °C. Mean particle diameters were \sim 300–400 nm. Thermal polymerization of the styrene in ([DEME][TFSI]) was also performed at 130 °C in the absence of free radical initiator. Stable dispersions were formed without requiring an autoclave reactor.

PAA particles were made using the ionic liquid *N*, *N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)amide ([DEME] [TFSA]).³⁹⁸ PAA, being a hydrophilic polymer, required both a different ionic liquid and a different surfactant than the hydrophobic polystyrene. PVP, which was an effective stabilizer for polystyrene particles, proved to be ineffective with PAA. However, poly (vinyl alcohol) was able to effectively stabilize PAA particles. Although crosslinking agents were not used in the formulation, crosslinked polymer was obtained, likely as the result of acid anhydride formation although this does not occur in solvents such as hexanes. The ([DEME][TFSA]) could also be reused, an important consideration given the high cost of ionic liquids.

3.14.3.1.2(iii) Dispersion polymerization in scCO₂

CO₂ transforms into a supercritical state at relatively mild conditions ($T_c = 31.1 \circ C$; $P_c = 7.39 \text{ MPa}$), making it suitable for a variety of chemical process applications, including selective separations, chemical syntheses, polymer processing, and polymerizations. It has received extensive attention as a potential alternative solvent for traditional chemical processes that use large volumes of organic compounds. Increasingly stringent environmental regulations on emissions of VOC are driving research into alternative 'greener' solvents. scCO2 has attracted widespread interest for polymerization. The ability to tune the solubility properties of scCO₂ by varying temperature and pressure provides considerable flexibility in designing polymerization processes. scCO2 is inexpensive, inert, nontoxic, and nonflammable with low viscosity and high diffusion rates that facilitate heat and mass transfer. In some cases, homogeneous polymerizations can be conducted in scCO₂; however, for many free radical polymerizations, the vinyl monomers are soluble in the scCO₂ while their polymers have only limited solubility (with the exception of silicon and fluoropolymers that have excellent solubility in scCO₂). Dispersion or precipitation polymerizations are, therefore, commonly used processes Although the solubility of many polymers in scCO₂ is low, the solubility of scCO₂ in polymers is often appreciable, resulting in significant swelling (\sim 5–15%) of the polymer by CO₂ and accompanied by the effects of plasticization including lower T_{g} .

DeSimone et al.⁴⁰² reported the first dispersion polymerization in scCO₂ by free radical polymerization. Using MMA initiated by AIBN at 65 °C and 204 bar, dramatic differences were observed in final conversion and molar mass depending on whether stabilizer was used. In the absence of stabilizer (precipitation polymerization), conversions and rates were low, ranging from $\sim 10\%$ to 40%. However, addition of the fluorosurfactant perfluorooctanoate (PFOA), which is soluble in scCO2, raised conversion to over 90% and allowed molar masses to be increased. Furthermore, the polymer existed as fairly uniform spheres of \sim 1–3 µm in diameter and was recoverable as a free-flowing powder. Although PFOA does not have a block or graft copolymer structure characteristic of most stabilizers, it does function effectively, likely because the backbone has affinity for the particle surface while the fluoroalkyl groups have greater affinity for the scCO₂ phase. PFOA has also been used in polymerizations of styrene and VAc. 403,404

Motivated by the importance of the stabilizer structure on the polymer properties, kinetics, and PSD, numerous studies have examined different types of polymers as stabilizers in $scCO_2$ dispersion polymerization.⁴⁰⁵⁻⁴⁰⁷ In addition to fluorinated homo- and copolymers such as PFOA and its methacrylate analogue, random copolymers, block copolymers, comblike graft copolymers, and reactive macromonomers of varying molar mass and copolymer composition have been used. Fluorinated polymers and silicone polymers (PDMS) are the best choices for the portion of the surfactant with affinity for the $scCO_2$ phase, while the lipophilic moieties used for the anchoring block are often chosen to be same as the monomer being polymerized.

3.14.3.2 Controlled Radical Polymerization

The development of CRP in nonaqueous dispersed systems was envisioned with the aim of controlling simultaneously the polymer chain characteristics along with the colloidal properties of the so-formed polymer particles. However, in comparison with CRP in aqueous dispersed systems, the nonaqueous systems were much less studied, although in the past years the number of articles is in constant progression. Two main types of systems were considered: the classical organic solvents and scCO₂.

3.14.3.2.1 Dispersion polymerization in organic solvent

NMP represents the first CRP technique to be tested in nonaqueous dispersion polymerization.⁴⁰⁸⁻⁴¹¹ The monomer was styrene in all published examples. Although it was possible to control the polymer chain characteristics in terms of molar mass and MMD, the difficulty was to achieve the formation of stable particles at the high temperature needed for NMP (typically above 110 °C). This was related to both the nucleation step and the stability over the course of the polymerization. In general, when stable particles were achieved, the control over the particle size was poor and the PSD was very broad. The solvent type was directly responsible for the quality of the nucleation step: at high temperature and for the initially formed short chains, the solvent may not be appropriate to induce their fast and efficient precipitation. The first stage of the reaction may then mainly take place in solution rather than in dispersion. It was moreover supposed that part of the soluble polymer precipitated when the temperature of the reaction medium was decreased rather than during the polymerization itself. The enhancement of the polymerization rate was further shown to have a positive effect on the PSD.⁴¹¹ Although controlled in term of average molar masses, the polymers exhibited higher PDIs than in bulk, which may possibly be the result of an unfavorable partitioning of the nitroxide in the different phases of the system.

The ATRP of 4-vinylpyridine initiated by a PEO-based macroinitiator was conducted in an ethanol–water mixture in the absence or in the presence of a divinylic comonomer to crosslink the particle core.⁴¹² The system resulted in block copolymer micelles stabilized by the PEO-soluble blocks. To improve the PSD in dispersion ATRP, a two-stage method was applied, starting from a standard free radical polymerization, which allowed the nucleation step to proceed in fast conditions.⁴¹³ The controlled character of the second polymerization step was demonstrated.

Similar to NMP and ATRP, the first articles on RAFT in dispersion polymerization showed that the quality of control along with the PSD was sometimes rather poor.^{414,415} This difficulty was overcome by a delayed introduction of the RAFT agent, after a first step of classical free radical polymerization.^{416–420} At this stage, the nucleation step was over, which guaranteed a narrow PSD throughout the polymerization course. Another strategy also applied in ATRP by the same group⁴¹² was to employ a macromolecular RAFT agent able to play multiple roles in the dispersion polymerization, that is, control agent and stabilizer (providing it is soluble in the continuous phase).⁴²¹ This method led to block copolymers formed *in situ* and able to self-assemble simultaneously to the growth step. In the presence of crosslinker as performed in the quoted study, the system allowed small, core-crosslinked micelles with

narrow size distribution to be obtained in an easy manner. In some situations however, depending most probably on the experimental conditions and type of RAFT group employed, the system was not efficient enough to ensure a good control over the polymer structure, even though the PSD was narrow.^{422,423} The RAFT functional group along with the concentration of the macromolecular RAFT agent was later shown to have a strong influence on the outcome of the dispersion polymerization in terms of both control over the diblock copolymer structure and particle size.^{424,425} Once the difficulties related to the finding of the most appropriate experimental conditions were overcome, the RAFT method was shown to be quite powerful in dispersion polymerization leading to very original block copolymer micelle morphologies such as vesicles and nanotubes.⁴²⁶⁻⁴²⁹

3.14.3.2.2 Dispersion polymerization in scCO₂

The controlled/living heterogeneous radical polymerization in $scCO_2$ has been reviewed quite recently.⁴³⁰ The works are related to precipitation polymerization, that is, in the absence of stabilizer but also dispersion polymerization, in which a CO_2 -philic stabilizer has to be introduced. The latter is usually a polymer, either PDMS or a fluorinated polyacrylate.

The SG1-mediated polymerization of styrene was studied in the presence of a reactive PDMS with attached diazoic initiating groups, in conjunction with free nitroxide. The PDMS being soluble in scCO₂ should play in addition the role of stabilizer. However control over the polymerization was rather poor and the system suffered from stability issues.431 Similar results were obtained when a low-molar-mass initiator was used in the presence of a nonreactive diblock copolymer stabilizer (namely, PDMS-b-poly(methyl methacrylate)), with however better colloidal properties.432 A PDMS-polystyrene-SG1 macroalkoxyamine was further used in similar conditions for the polymerization of styrene, with the advantage of leading to diblock copolymers in situ. The system was then much better controlled in terms of both molar mass and colloidal stability.433 The TEMPO-mediated polymerization of styrene was also studied with either silicon-based or perfluorinated macromolecular stabilizers, also synthesized by NMP.434

Similarly, the ATRP of MMA was studied following various strategies: with fluorinated ligand and fluorinated stabilizer,⁴³⁵ or with a PDMS-Br macroinitiator and a classical ligand,⁴³⁶ or with a fluorinated macroligand playing roles of both ligand and stabilizer.^{437,438} Control over polymerization was rather good in all cases and particle stability was acceptable.

The dispersion polymerization of MMA in scCO₂ was applied using the RAFT method.^{439,440} Although very long induction periods were observed together with rate retardation, the systems were particularly well controlled from the macro-molecular viewpoint, with very narrow MMDs. The use of poly (vinyl alkylate) hydrocarbon surfactants with a RAFT group at the chain end was particularly successful for the synthesis of well-defined PVP particles, due to the good anchoring of the surfactant by chain extension, although no control over the polymerization of vinyl pyrrolidone was achieved.⁴⁴¹

3.14.3.3 Ionic Polymerization of Vinyl Monomers

Nonaqueous dispersed systems (i.e., organic solvents, $scCO_2$, and ionic liquids) can be applied to a much broader range of

polymerization methods than aqueous systems as they can tolerate unstable catalysts and active centers that can be inactivated by water traces. Therefore, ionic polymerizations can be used in such dispersed systems although the number of articles really devoted to the synthesis of stable polymer particles is very scarce as far as vinyl monomers are regarded.

In addition to the living dispersion polymerization of vinyl monomers initiated with *n*-butyllithium^{442,443} or an enolate⁴⁴⁴ in the presence of a steric stabilizer, the anionic polymerization in dispersed systems is also adapted to the synthesis of amphiphilic block copolymers. Indeed, the synthesis of diblock copolymers in a selective solvent that is good for the first block and bad for the second block is a particular situation of dispersion polymerization. In such a situation, self-assembly of the copolymers during the second polymerization step leads to the in situ formation of diblock copolymer micelles. This was actually a method developed for the anionic polymerization of styrene in an aliphatic solvent, using polybutadienyl carbanion as a macroinitiator.445 It was similarly used for the polymerization of divinylbenzene leading to crosslinked particles.446 A very recent work published by Wang et al.447 follows this same principle and provides several examples of polybutadiene-b-polystyrene block copolymer nanoparticles of various shapes and morphologies produced by anionic polymerization in hexane. Other examples of dispersion polymerization can be found in scCO₂ dispersing medium, concerning either anionic⁴⁴⁸ or cationic polymerization systems.^{449–451} Similarly, a few articles describe the cationic polymerization of styrene,⁴⁵¹⁻⁴⁵⁴ the anionic polymerization of MMA,⁴⁵⁵ and its group transfer polymerization⁴⁵⁶ in ionic liquids, a topic which has been well covered by a recent review article.457

3.14.4 Conclusion

As shown in this chapter, polymerization of vinyl monomers in heterogeneous systems covers all types of polymerization chemistries, along with a broad variety of processes. Some of them are widely used in industrial productions. The field remains very active and new systems (to a large extent due to new catalysts and controlling agents being developed) are continually being proposed to improve the polymer structure, particle morphology, surface chemistry, etc. In addition, completely new approaches are regularly reported, demonstrating the dynamic and continually evolving character of the research conducted in this field, where the limits can still be expanded further.

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Biographical Sketches



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3.15 Cationic Polymerization of Nonpolar Vinyl Monomers

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3.15.1	Introduction	501
3.15.2	Fundamentals of Cationic Polymerization	501
3.15.3	Monomers	502
3.15.4	Initiating Systems	502
3.15.5	Solvent Polarity and Temperature	503
3.15.6	Controlled Initiation	504
3.15.6.1	The Inifer Method	504
3.15.6.2	Direct Initiation	504
3.15.6.3	Photoinitiation	504
3.15.7	Living Cationic Polymerization	505
3.15.7.1	Mechanistic and Kinetic Details	505
3.15.7.2	Structure – Reactivity Scales in Cationic Polymerization	506
3.15.7.2.1	Monomers and initiating systems	507
3.15.7.2.2	Additives in living cationic polymerization	507
3.15.8	Functional Polymers by Living Cationic Polymerization	510
3.15.8.1	Functional Initiator Method	510
3.15.8.2	Functional Terminator Method	511
3.15.8.3	Telechelic Polymers	512
3.15.8.3.1	Macromonomers	513
3.15.9	Block Copolymers	515
3.15.9.1	Linear Diblock Copolymers	515
3.15.9.2	Linear Triblock Copolymers	517
3.15.9.2.1	Synthesis using difunctional initiators	517
3.15.9.2.2	Synthesis using coupling agents	517
3.15.9.3	Block Copolymers with Nonlinear Architecture	517
3.15.9.3.1	Synthesis of A _n B _n hetero-arm star-block copolymers	518
3.15.9.3.2	Synthesis of AA'B, ABB', and ABC asymmetric star-block copolymers using furan derivatives	518
3.15.9.4	Block Copolymers Prepared by the Combination of Different Polymerization Mechanisms	518
3.15.9.4.1	Combination of cationic and anionic polymerization	518
3.15.10	Branched and Hyperbranched Polymers	522
3.15.10.1	Surface-Initiated Polymerization – Polymer Brushes	522
3.15.11	Conclusions	522
References		523

3.15.1 Introduction

Cationic polymerization is an important technique for the synthesis of a great variety of useful polymers, some of which cannot be prepared by any other means. Cationic polymerization is performed to produce oligomers and high polymers of considerable technological importance, for example, polyisobutylene (PIB), polybutenes (copolymers obtained from C4 unsaturated hydrocarbons), and butyl rubber (a random copolymer of isobutylene (IB) and isoprene). Together with hydrocarbon resins and poly(vinyl ethers), commercial production exceeds 2 million metric tons per year.

3.15.2 Fundamentals of Cationic Polymerization

Scheme 1 shows the elementary reactions of conventional carbocationic polymerization: initiation, propagation, chain transfer, and termination. Initiation is a two-step event

consisting of ionization and cationization. First, ionization of the initiator I yields the cation I⁺ that in the subsequent step reacts with the monomer M to yield the adduct IM⁺. Propagation involves the repetitive addition of monomer to the growing carbenium ion until a chain-breaking reaction, chain transfer, or termination. In the absence of a deliberately added chain transfer agent, transfer reactions generally involve β-proton elimination to form unsaturated end groups (e.g., with IB) or alkylation of an aromatic ring followed by proton transfer (e.g., with styrenic monomers). In contrast to chain transfer, termination stops the kinetic chain. Termination generally involves ion collapse or transfer of an anionic fragment from the complex counterion. In cationic polymerization, chain transfer is far more important than termination and generally limits the molecular weight. Most reported chain transfers are spontaneous, counterion-assisted processes and zero order in monomer. The rate of both spontaneous and direct transfer to monomer rapidly decreases with decreasing temperature Initiation

$$| \longrightarrow |^+$$

 $|^+ + M \longrightarrow |M|$

Propagation

 $IM^+ + nM - \frac{Hp}{m}$

Chain transfer

$$I(M)_{n}^{+} + A \xrightarrow{h_{tr}} I(M)_{n}M + A$$

 $I(M)_{n}M$

Termination

$$I(M)_n M^+ \xrightarrow{\kappa_t} I(M)_n M(?)$$

Scheme 1 Elementary steps of conventional carbocationic polymerization (anions omitted for clarity). nucleophile, *E* is the electrophilicity parameter of the electrophile, and *s* is a slope parameter, which is in most cases close to unity. Based on the rates of reactions between benzhydryl cations and alkenes, a large number of *N* parameters have been determined by Mayr and co-workers.¹ For the above monomers, these values are listed below:

Accordingly, *N*-vinylcarbazole, ethyl vinyl ether, *p*-methoxystyrene (*p*MeOSt), and α -methylstyrene (α MeSt) are 17 400, 1380, 339, and 37 times more reactive than styrene (St). Due to this very large difference in cationic reactivity, different initiating systems bring about optimum polymerization for different monomers. This also explains why cationic statistical copolymerizations are less useful than the radical counterpart.



due to the high energy of activation for transfer (~20 kJ mol⁻¹) compared to propagation, which proceeds with negligible or no enthalpic barrier. Therefore, many cationic polymerizations are carried out at cryogenic temperatures to suppress chain transfer and obtain high molecular weights.

3.15.3 Monomers

Initiation and propagation take place by electrophilic addition of the monomers to the carbenium ions. Therefore, the monomer must be nucleophilic and its substituents should be able to stabilize the resulting positive charge. As a result, the reactivity of monomers is qualitatively proportional to the electron-donating ability of their substituents, as can be seen below:

3.15.4 Initiating Systems

Cationic polymerization may be induced by a variety of physical methods: high energy radiation, direct or indirect UV radiation, and electroinitiation; and chemical methods: protic acids, Friedel–Crafts acids, and stable cation salts. Most Lewis acids alone are ineffective to bring about polymerization unless adventitious proton sources (e.g., moisture) are present. The most important initiating system from a scientific as well as a practical point of view is the cation donor (initiator)/Friedel–Crafts acid (coinitiator) system. Friedel–Crafts acids (Lewis acids) are able to complex the relatively nucleophilic conjugate bases of Brønsted acids leading to quite stable counteranions. This in turn allows prolonged propagation and leads to high molecular weights. Mixtures of Brønsted acids and Friedel–Crafts acids, therefore, have found many applications for cationic initiation. In place of a proton source, a cation source such as an alkyl halide, ester, or

$$H_{2}C = CH \rightarrow H_{2}C = CH \rightarrow H_{2}C = CH \rightarrow H_{2}C = CH \rightarrow H_{2}C = CH = CH_{3}$$

The reactivity of cationic monomers may be evaluated quantitatively by comparing their nucleophilicity parameter, N. Rates of electrophile–nucleophile combinations can be characterized by a simple equation in Mayr's linear free energy relationship:¹

$\log k = s(N + E)$

where k is the rate constant of electrophile–nucleophile combination, N is the nucleophilicity parameter of the

ether can be used in conjunction with a Friedel–Crafts acid. Initiation with ether-based initiating systems in most cases involves the halide derivative which arises upon fast halidation by the Friedel–Crafts acid, MX_n .

The efficiency of the initiator/coinitiator system depends greatly on the monomer in question. As a general rule, the stability (reactivity) of the initiating cation should be close to that of the propagating chain end. This can be demonstrated by the cationogen efficiency (grams of PIB produced per mol RCl)



Figure 1 The polymerization of IB with various initiating ions in conjunction with (C₂H₅) ₂AlCl (3). PIB, polyisobutylene.

of the alkyl halide/ $(C_2H_5)_2$ AlCl initiating system in the polymerization of IB (Figure 1).² Since initiation involves two subsequent events, that is, ion generation and cationation, species on the two extremes are less active or may be completely inactive, because they form ionic species very slowly and/or in extremely low concentration (primary or secondary alkyl halides) or form ions in high concentration that are, however, too stable to cationate IB (triphenyl methyl halides).

The structure of the initiator influences the initiation step by affecting the rate of ionization and cationation. Ionization is faster and cationation is slower for the more stable cation. It is important to note that back strain, that is, the release of steric strain upon ionization, may contribute significantly to the ease of ionization. Due to the absence of back strain, *tert*-butyl chloride and cumyl chloride are inefficient initiators for the polymerization of IB and α MeSt, respectively. In contrast, the corresponding dimeric chlorides (2-chloro-2,4,4-trimethylpentane (TMPCl)³ and 2-chloro-2,4-diphenyl-4-methylpentane⁴) are excellent initiators.

Since part of the initiator together with the Lewis acid forms the complex counteranion, propagation as well as chain transfer and termination may also be affected by the initiator structure. The activity of an initiating system is also affected by the nature of the Friedel-Crafts (Lewis) acid. This, however, cannot be considered independently of the monomer. While weak Lewis acids such as iodine or zinc halides may be used as coinitiators to polymerize reactive monomers, for example, vinyl ethers or N-vinyl carbazol, they are ineffective to bring about the polymerization of less reactive monomers, for instance, IB or St. Unfortunately, a general and quantitative Lewis acidity scale, which relates acidity and polymerization behavior, does not exist. Based on the C=O stretching frequency difference between 9-xanthone or ethyl acetate and their complexes with metal halides, the following acidity scale can be established:⁵ $ZnCl_2 < SnBr_4 < SnCl_4 < BF_3 < AlCl_3 < TiCl_4 < BCl_3 < SbF_5 < SbCl_5$ < BBr₃. The acidity scale, however, may be different when based on other properties of Friedel-Crafts acids, for example, heat of complex formation with amines. Moreover, the Lewis acidity is ambiguous for some Lewis acids, notably aluminum, organoaluminum, gallium, and titanium halides, which form dimers and dimeric counteranions under polymerization conditions. The dimeric Lewis acids are much stronger than the monomeric equivalents since the negative charge is dispersed more effectively in the dimeric counteranions. Consequently, even when

the dimers are present at very low concentration, initiation and polymerization involve exclusively the dimeric species (the polymerization is second order in Lewis acid). Boron and tin halides are monomeric and therefore the polymerization is first order in Lewis acid. Moreover, the activity of the boron chloride or bromide-based system is greatly solvent dependent, that is, sufficient activity only occurs in polar solvent. In nonpolar solvents where solvation of the counteranion does not promote ion generation, the ionization equilibrium is strongly shifted to the left, and the concentration of cations is extremely small. This results in very low active center concentration and therefore negligible polymerization rates.

3.15.5 Solvent Polarity and Temperature

Solvents of high polarity that are able to solvate the ions generally yield higher polymerization rates. The effect of solvent polarity on the polymerization rate constant is moderate; however, faster ionization and slower termination generally result in higher overall polymerization rates in a more polar solvent. Alcohols, esters, ketones, and so on, however, cannot be used since they react with the cation and/or coinitiator and prevent polymerization. Cationic polymerization, therefore, is carried out mostly in solvents of moderate polarity such as hydrocarbons or chlorinated hydrocarbons. For the selection of solvents relative to polymerization rates and behavior, the dielectric constant and polarizability are of little predictive value. In spite of the similarity of the dielectric constants of CH_2Cl_2 , CH_3Cl , and C_2H_5Cl , these solvents yield quite different IB polymerization rates that decrease in the same order.

The effect of temperature is more complex and the overall effect varies for different monomers. Typical cationic polymerizations of alkenes (IB, St, etc.) proceed with propagation rate constants in excess of $10^7 1 \text{mol}^{-1} \text{s}^{-1.6}$ Such fast bimolecular reactions do not have an enthalpic barrier and for these monomers the propagation rate constant is independent of the temperature. The overall polymerization rate, however, is very much influenced. For IB, St, α MeSt, indene, and some other monomers, the polymerization is faster at lower temperature, that is, the activation energy for the polymerization is apparently negative, due to faster ionization and slower termination at lower temperature.⁷ In cationic polymerization of

vinyl monomers, chain transfer is the most significant chain-breaking process. The activation energy of chain transfer is relatively high; consequently, the molecular weight of the polymer increases with decreasing temperature. Spontaneous, counterion-assisted chain transfer is faster in a less-polar solvent since the transition state is less polar than the ground state. Direct monomer transfer is less affected by solvent polarity since it involves ion–dipole reactions. Intramolecular alkylation, an undesirable side reaction in the polymerization of styrenic monomers and in the polymerization of IB by benzylic initiators, can also be eliminated by lowering the temperature and solvent polarity. However, opposite results were reported for SnBr₄ in the polymerization of α MeSt; for example, intramolecular alkylation occurred using toluene but was absent using CH₂Cl₂.⁸ Evidently, every system has to be examined independently.

3.15.6 Controlled Initiation

Initiation by a carbocation source provides control of the head group (controlled initiation) when used in conjunction with a Friedel–Crafts acid (e.g., $(C_2H_5)_3Al$, $(CH_3)_3Al$, $(C_2H_5)_2AlCl$, TiCl₄, BCl₃ for IB, or I₂ and zinc halides for vinyl ethers) where chain transfer to monomer is absent or negligible or in the presence of a proton trap to abort chain transfer to monomer.⁹ That is, initiation from tertiary, allylic, and benzylic halides gives rise to macromolecules carrying tertiary, allylic, and benzylic head groups. Initiation by halogens results in head groups carrying the halogen. Controlled initiation, however, is achieved only when polymer formation from adventitious protic impurities is also absent or negligible.

Polymer formation from protic impurities can be minimized by increasing the concentration of initiator or can be eliminated by the use of proton traps, for example, 2,6-di-*tert*butylpyridine (DTBP) or similar hindered pyridines (e.g., 2,6di-*tert*-butyl-4-methylpyridine), which exhibit extraordinary specificity toward protons owing to their very high basicity coupled with nonnucleophilicity due to steric hindrance.¹⁰

When using a cation source in conjunction with a Friedel– Crafts acid, the concentration of growing centers is most often difficult to measure and remains unknown. By the use of stable carbocation salts (e.g., trityl and tropylium hexachloroantimonate), the uncertainty of the concentration of initiating cations is eliminated. Due to the highly reproducible rates, stable carbocation salts have been used in kinetic studies. Their use, however, is limited to cationically fairly reactive monomers (e.g., *N*-vinylcarbazole, *p*MeOSt, and alkyl vinyl ethers) since they are too stable and therefore ineffective initiators of less reactive monomers, such as IB, St, and dienes.

3.15.6.1 The Inifer Method

A special case of controlled initiation is the inifer method.¹¹ The word inifer (from *ini*tiator trans*fer* agents) describes compounds that function simultaneously as initiators and as chain transfer agents. Chain transfer to inifer regenerates R^+ . The inifer technique provided the first carbocationic route toward the synthesis of telechelic (α, ω -functional) PIBs¹¹ and telechelic poly(*p*-chlorostyrenes).¹² To prepare telechelic products, chain transfer to monomer must be absent, and with BCl₃ as coinitiator at low temperatures this requirement is fulfilled (Scheme 2).

Initiation

Propagation

Chain transfer to inifer

Termination

 $mC^+ \xrightarrow{k_t} mCX$

 $\infty C^+ + RX \xrightarrow{k_{tr,l}} \infty CX + R^+ -$

 $RX + BCl_3 \longrightarrow R^+ (BCl_3 X^- omitted)$

 $R^+ + C = C \longrightarrow R - C - C^+$

 $R-C-C^+ + C=C \xrightarrow{k_p} \cdots C^+$

Scheme 2 The 'inifer' technique.

3.15.6.2 Direct Initiation

The mechanism of initiation in cationic polymerization using Friedel-Crafts acids appeared to be clarified by the discovery that most Friedel-Crafts acids, particularly halides of boron, titanium, and tin, require an additional cation source to initiate polymerization. Evidence has been accumulating, however, that in many systems Friedel-Crafts acids alone are able to initiate cationic polymerization. The polymerization of IB, for instance, can be initiated, reportedly even in the absence of an added initiator, by AlBr₃ or AlCl₃,¹³ TiCl₄,¹⁴ AlC₂H₅Cl₂,¹⁵ and BCl₃.¹⁶ Three fundamentally different theories have been presented to explain the still controversial existence of direct initiation. Halometalation is proposed by Sigwalt and Olah.¹⁷ In the presence of excess Friedel-Crafts acid, the formed metalloorganic compound may ionize or eliminate HCl, a conventional cationogen. Self-ionization of the Friedel-Crafts acid has been suggested to explain direct initiation.^{14,18} Allylic self-initiation may also explain results with olefins possessing an allylic hydrogen.¹⁹

All three theories imply that the polymerization system is free of protogenic impurities. Although direct initiation by metal halides has been postulated with the above Friedel– Crafts acids, it was proven only for aluminum halides¹⁸ and more recently for BCl₃.¹⁶ With TiCl₄, attempts have been made to observe the corresponding intermediates by ¹H NMR spectroscopy but without success, which was explained by the known instability of the organotitanium compounds.¹⁴ Kinetic investigation of polymerizations by BCl₃²⁰ suggests that initiation is by haloboration according to the Sigwalt– Olah theory. Initiation by I₂ in the polymerization of vinyl ethers can be visualized similarly, that is, a 1,2-diiodide is formed first that is subsequently activated by excess I₂.²¹

3.15.6.3 Photoinitiation

Cationic vinyl and ring-opening polymerization can also be initiated by photoinitiation. Diaryliodonium and triarylsulfonium salt photoinitiators, the two most well-known classes of cationic photoinitiators, can initiate the polymerization of virtually all known monomers polymerizable by cationic mechanism. UV-induced photolysis of these initiators results in both heterolytic and homolytic cleavage of the carboniodine bond, while the heterolytic pathways dominate for triarylsulfonium salts. The reactive species generated may react with solvents, monomers, or impurities to yield protonic acids, which are the true initiators. Onium salt cationic photoinitiators bearing nonnucleophilic anions such as PF_6^- , BF_6^- , BF_4^- ,

or AsF_6^- are most useful, since termination by ion collapse with these anions is slow.

Cationic photoinitiators find applications where a thin film is rapidly cross-linked by exposure to UV light to produce a polymer network. The high rate of cationic cross-linking is ideal for high-speed applications such as coatings, printing inks, and adhesives. Excellent reviews on the discovery, development, recent advances, and applications of cationic photoinitiators have been published.^{22–24}

3.15.7 Living Cationic Polymerization

The discovery of quasiliving polymerization in 1982, where for the first time reversible termination (activation-deactivation) was postulated, heralded the new era of living cationic polymerization, which arrived a few years later. Living polymerizations, which proceed in the absence of termination and chain transfer reactions, are the best techniques for the preparation of polymers with well-defined structure, and, indeed, most of these polymers have been prepared using living polymerization. The resulting model polymers have extensively been used in validation of theories with respect to the properties in solution, melt, and solid states.²⁵ They also have served as excellent standard materials for systematic studies on structure/property relationships of macromolecules, lending an impetus to the major fields of material science and polymer physics. The foregoing activities are made possible by advances in modern synthetic methodologies, combined with state-of-the-art characterization techniques in material science.

The experimental criteria for living polymerizations have been critically reviewed.²⁶ In general, diagnostic proof for the absence of chain transfer and termination can be obtained from both linear semilogarithmic kinetic plot $(\ln([M]_0/[M]))$ vs. time) and linear dependence of number average molecular weight (M_n) versus monomer conversion $(M_n$ vs. conversion). There are no absolute living systems and the careful control of the experimental conditions (counterion, temperature, solvent) is necessary to obtain sufficient livingness to prepare well-defined polymers, especially when high molecular weights are targeted.²⁷ The original author of the seminal paper introducing the concept of living polymers concludes that "we shall refer to polymers as living if their end groups retain the propensity of growth for at least as long a period as needed for the completion of an intended synthesis, or any other desired task".²⁸ This view has been adopted in this chapter.

3.15.7.1 Mechanistic and Kinetic Details

A variety of initiating systems have been described that allow not only controlled initiation but also controlled propagation in the polymerization of vinyl monomers. In these living polymerization systems, chain breaking (chain transfer and irreversible termination) is absent. It is apparent that, due to the extremely rapid propagation, if all chain ends were ionized and grew simultaneously, monomer would disappear at such a high rate that the polymerization would be uncontrollable. The key to living carbocationic polymerizations is a rapid, dynamic equilibrium between a very small amount of active and a large pool of dormant species. For a specific monomer, the rate of exchange and the position of equilibrium depend on the nature of the counteranion in addition to temperature and solvent polarity. Therefore, initiator/coinitiator systems that bring about living polymerization under a certain set of experimental conditions are largely determined by monomer reactivity.

A complete mechanistic understanding of cationic polymerization is fundamental for cationic macromolecular engineering and requires the knowledge of the rate and equilibrium constants involved in the polymerization process. Numerous previous kinetic studies of carbocationic polymerization, however, have generally failed to yield reliable rate constants for propagation (k_p) . This is attributed to uncertainties involved in the accurate determination of the active center concentration, a consequence of our incomplete knowledge of the mechanism due to the multiplicity of possible chain carriers (free ions, ion pairs, and different solvated species) and the complexity of carbocationic reaction paths. Recently, new reaction clock methods have been developed for the determination of rate and equilibrium constants in carbocationic polymerizations.^{29,30} The reaction clock method references the unknown rate constant for the reaction of the intermediate cation to that for a second reaction with a known rate constant, which serves as a 'clock'. In the diffusion clock method, the 'clock' speed is the diffusion limit. These methods have been utilized to determine the rate constant of propagation $(k_{\rm p})$ and the rate (k_i) and equilibrium constant of ionization (K_i) and deactivation (k_{-i}) for IB,³¹ St,³² and ring-substituted Sts.³³⁻³⁶ The results show that previously accepted propagation rate constants³⁷ are underestimated in some cases by as much as 4–6 orders of magnitude. The k_i values for IB and St have also been determined independently by Storey et al.,³⁸⁻⁴⁰ from the average number of monomer units added during one initiation-termination cycle (run number). The reported values agreed remarkably well with those published earlier. Although the reaction clock method has been validated as the propagation rate constant from the reaction clock and conventional measurements yielded similar $k_{\rm p}$ s for 2,4,6-trimethylstyrene (TMeSt) and p-methylstyrene (pMeSt), the close to diffusion-limited $k_{\rm p}$ especially for St and some other styrenic monomers is not universally accepted. For instance, to reconcile the results, Sigwalt and Moreau⁴¹ suggested that cation-nucleophile combinations (including propagation) may involve a two-step reaction: a complexation of the growing carbocation with the nucleophile followed by a unimolecular rearrangement of the complex.

The above studies confirmed the results of prior kinetic investigations with model compounds that the propagation rate constant is independent of the nature of Lewis acid and increases moderately with increasing solvent polarity. In agreement with findings of Mayr⁴² that fast bimolecular reactions (i.e., $k_p^{\pm} > 10^7 \, \text{l mol}^{-1} \, \text{s}^{-1}$) do not have an enthalpic barrier, k_p^{\pm} is independent of temperature for IB, *p*-chlorostyrene (*p*ClSt), St, and *p*MeSt. Although most kinetic investigations have been conducted under conditions where propagation takes place on ion pairs, the propagation rate constant for free ions k_p^+ for IB is reportedly similar to k_p^{\pm} suggesting that free and paired cations possess similar reactivity, and therefore, differentiation between free ions and ion pairs is unnecessary.⁴³

From the k_i , k_{-i} , and k_p values, the sequence of events for an average polymer chain could be ascertained. Using typical concentrations of $[\text{TiCl}_4] = 3.6 \times 10^{-2} \text{ mol } \text{I}^{-1}$ and $[\text{IB}] = 1 \text{ mol } \text{I}^{-1}$ in hexanes/CH₃Cl 60/40 (v/v) at -80 °C the following time intervals (τ) between two consecutive events have been calculated:

$$\tau_{i} = \frac{1}{k_{i}} [\text{TiCl}_{4}]^{2} = 49 \text{ s}$$

$$\tau_{-i} = \frac{1}{k_{-i}} = 2.9 \times 10^{-8} \text{s} = 29 \text{ ns}$$

$$\tau_{p} = \frac{1}{k_{p}} [\text{IB}] = 1.4 \times 10^{-9} \text{s} = 1.4 \text{ ns}$$

Thus, the time interval between two ionizations (activation) is relatively long (49 s). The ionized chain ends stay active for a very short time, only 29 ns before reversible termination (deactivation) takes place, and the polymer end goes back to a dormant, inactive state. Propagation is 20 times faster than deactivation, however (monomer incorporates on average every 1.4 ns), and 20 monomer units are added during one active cycle. This results in a relatively high polydispersity index (PDI) at the beginning of the polymerization that progressively decreases to the theoretical value at complete conversion:⁴⁴

$$\frac{M_{\rm w}}{M_{\rm n}} = 1 + [\mathrm{I}]_0 \frac{k_{\rm p}}{k_{\rm -i}}$$

The above equation, where $[I_0]$ is the total concentration of (active and dormant) chain ends, is valid for unimolecular deactivation (ion pairs); for bimolecular deactivation, the deactivation rate constant should be multiplied by the concentration of the deactivator. The starting [IB] may be decreased to decrease the number of monomer units incorporated during one active cycle and this yields PIB with a lower PDI. For instance, at $[IB] = 0.1 \text{ mol } l^{-1}$, two monomer units are incorporated during one active cycle even at the onset of the polymerization. At $[TiCl_4] = 3.6 \times 10^{-2} \text{ mol } l^{-1}$ and $[IB] = 1 \text{ mol } l^{-1}$, about 4 and 40 min would be necessary for the formation of a PIB with a number average polymerization $DP_n = 100$ and 1000, respectively. For St, under similar conditions, propagation is 60 times faster than deactivation, which results in much higher polydispersities and the complete loss of molecular weight control below $DP_n \sim 60$. Control for low molecular weights can be regained by selecting a weaker Lewis acid (e.g., SnCl₄) compared to TiCl₄.

As indicated in the above examples, for a specific monomer, the rate of exchange and the position of the equilibrium and, to some extent, the zero-order monomer transfer constants depend on the nature of the counteranion in addition to temperature and solvent polarity. Therefore, initiator/coinitiator systems that bring about controlled and living polymerization under a certain set of experimental conditions are largely determined by monomer reactivity.

It is important to note that living polymerization does not require the assumption of special growing species such as stretched covalent bonds or stabilized carbocations, as pointed out by Matyjaszewski and Sigwalt.⁴⁵ In line with this reasoning, identical propagation rate constants were observed in living and nonliving polymerization, indicating that propagation proceeds on identical active centers.⁷

3.15.7.2 Structure – Reactivity Scales in Cationic Polymerization

Due to the ready availability of rate constants for radicalmonomer reactions, it is well established how substituents affect monomer and radical reactivity in radical polymerization. In contrast, rate constants for cation-monomer combinations have been unavailable until very recently, and therefore structure-reactivity relationships in cationic polymerization have been less developed. The relative reactivities of various ring-substituted Sts have been correlated by the semi-empirical Hammett sigma-rho relationship. The validity of this equation, however, was rather limited even for ring-substituted Sts. Monomer reactivity can be accurately correlated using the nucleophilicity parameter, which has been determined for a large number of cationic monomers by Mayr and co-workers. Some electrophilicity parameters of model cations, relevant in cationic polymerization, have also been published by the same group.⁶ In principle, reactivity ratios and cross-propagation rate constants could also be determined based on the linear free energy relationship. However, many cationic homo- and cross-propagations occur with a rate constant > $5 \times 10^7 l \text{ mol}^{-1} \text{ s}^{-1}$, which is outside of the 'linear' domain of the linear free energy relationship as the diffusion limit is approached.

In light of the general view that obtaining reliable reactivity ratios in cationic copolymerization is problematic, a new method has recently been developed for the determination of reactivity ratios and cross-propagation rate constants with the knowledge of k_p . This method utilized terminating copolymerizations, that is, copolymerizations which terminate after a single cross-propagation. This is feasible with a suitable Lewis acid when crossing over from a more reactive monomer to a less reactive one, where rapid and irreversible ion collapse terminates the propagating chain. The cross-propagation rate constants determined this way are listed in Table 1.⁴⁶

Monomer reactivities can be compared against a standard polymer cation in any of the vertical columns. The cross-propagation rate constants of a standard monomer (horizontal rows) provide the scale of cation reactivity. PpClSt⁺ is the least stable cation, due to the electron-withdrawing effect of the Cl group and therefore, it is the most reactive cation in the investigated series. Against 1,3-butadiene (BD) (last row), PpClSt⁺ is 2 times more reactive than PSt⁺, which may be underestimated since BD adds to PpClSt⁺ at close to the diffusion limit. PSt^+ is 62 times more reactive than PIB^+ , and ~ 200 times more reactive than PpMeSt⁺, which reflects the electron-donating effect of the methyl group. The BD row ends here since PpMeOSt⁺ and PαMeSt⁺ are too unreactive against BD. The rows of pMeSt, IB, St, and pClSt complete the comparison for the less reactive cations PpMeSt⁺, PaMeSt⁺, and PpMeOSt⁺. Thus, combining the BD row and for instance the pClSt row, further comparisons can be made. Thus $PpMeSt^+$ is ~ 380 times more reactive than $P\alpha MeSt^+$, which is about 10000 times more reactive than PpMeOSt⁺. From the combination of the data in these two rows PpClSt⁺ is about a billion times more reactive than PpMeOSt⁺ while the reactivity of pMeOSt is only about 800 times higher that that of pClSt. Similarly PpMeSt⁺ is 50–400 times more reactive than $P\alpha MeSt^+$, while $\alpha MeSt$ is only 13 times more reactive than pMeSt. It should be noted here that such differences in reactivities only become effective when diffusion-controlled processes are excluded.

These results are in agreement with previous conclusions that the effect of substituents on carbocation reactivity is much larger than their effect on monomer reactivity.

Monomer	Polymer cation						
pMeOSt αMeSt pMeSt IB St pCISt BD	$\begin{array}{l} {\sf P} {\it p} {\sf MeOSt}^{+12} \\ 7.8 \times 10^3 \\ 1.9 \times 10^2 \\ 2.9 \times 10^1 \\ 2.6 \times 10^1 \\ 1.0 \times 10^1 \end{array}$	$\begin{array}{l} {\sf P}\alpha {\sf MeSt}^{*} \\ {\sf DL}^{a} \\ {\sf 7.7}\times 10^{7b} \\ {\sf 5.9}\times 10^{6} \\ {\sf 1.1}\times 10^{6} \\ {\sf 3.9}\times 10^{5} \\ {\sf 1.1}\times 10^{5} \end{array}$	$\begin{array}{c} {\sf P} {\it p} {\sf MeSt}^{+12} \\ {\sf DL} \\ {\sf DL} \\ {\it 3.0} \times 10^{8c} \\ {\it 7.9} \times 10^{7} \\ {\it 6.2} \times 10^{7} \\ {\it 4.2} \times 10^{7} \\ {\it 3.0} \times 10^{6} \end{array}$	PIB ⁺¹² DL DL T.0 \times 10 ^{8d} 9.1 \times 10 ⁶	PSt ⁺¹² DL DL DL DL DL DL 5.6 \times 10 ⁸	$\begin{array}{c} PpCISt^{+12}\\ DL\\ DL\\ DL\\ DL\\ DL\\ DL\\ DL\\ DL\\ DL\\ 9.4\times 10^8 \end{array}$	
St <i>p</i> CISt BD	2.9×10^{1} 2.6×10^{1} 1.0×10^{1}	$1.1 \times 10^{\circ}$ 3.9×10^{5} 1.1×10^{5}	7.9×10^{7} 6.2×10^{7} 4.2×10^{7} 3.0×10^{6}	9.1×10^{6}	DL DL 5.6×10^8		

 Table 1
 Rate constants (I mol⁻¹ s⁻¹) for cation/monomer reactions in DCM:MeChx (1:1, v:v) at -40 °C

^aDL is abbreviation for diffusion limited.

^bDetermined at -80 °C in DCM:MeChx (1:1, v:v).

^cEstimated value from $k_p = 1 \times 10^9$ in DCM.

Value from hexanes/methylchloride (1:1, v:v).

3.15.7.2.1 Monomers and initiating systems

Since the first reports of living cationic polymerization of vinyl ethers⁴⁷ and IB^{48,49} in the 1980s, the scope of living cationic polymerization of vinyl monomers has been expanded rapidly in terms of monomers and initiating systems. Compared to anionic polymerization, living cationic polymerization can proceed under much less rigorous and much more flexible experimental conditions. The high-vacuum technique is not indispensable, since alternative routes can consume adventitious moisture without terminating the living chains. Nonetheless, rigorous purification of reagents is still required for the best control.

The total number of monomers for living cationic polymerization was estimated to be around 100 in 1994 and it appears that this process has a much broader choice of monomers than the living anionic counterpart.⁵⁰

With a few exceptions, ^{51,52} living cationic polymerization is initiated by the initiator/coinitiator (Lewis acid) binary system. Selection of an initiating system for a given monomer is of crucial importance, since there are no universal initiators such as organolithiums in anionic polymerization. For example, while weak Lewis acids such as zinc halides may be necessary to effect living polymerization of the more reactive vinyl ethers, they are not effective for the living polymerization of the less reactive monomers, such as IB and St. Detailed inventories of initiating systems for various monomers are well described in recent publications.^{25,53,54}

3.15.7.2.2 Additives in living cationic polymerization

Three main categories of additives have been introduced and extensively utilized in the living cationic polymerization of vinyl monomers: (1) Lewis base⁵⁵ (also called 'electron donors $(EDs)^{56}$ or 'nucleophiles'⁵⁷), (2) proton traps,⁵⁸ and (3) salts.⁵⁹ As the different names of the first categories of additives imply, the actual roles of these basic adjuvants and the true mechanisms of enhanced livingness have been longstanding controversies. Higashimura et al.60 proposed the theory of carbocation stabilization by nucleophilic additives through weak nucleophilic interaction. Similar opinion was also expressed by Kennedy et al.53 In contrast to this view, Matyjaszewski57 discussed that these bases only decrease the concentration of active species by reversible formation of onium ions which do not propagate or by complexing with Lewis acids. It has also been proposed by Penczek⁶¹ that these bases may enhance the dynamics of equilibrium between dormant and active species

via onium ion formation, which provides a thermodynamically more favorable pathway from covalent species to cation and vice versa. Unfortunately, no direct evidence for either nucleophilic interaction or onium ion formation has been provided.

Faust *et al.* demonstrated the living polymerization of IB and St co-initiated with TiCl₄ or BCl₃ in the *absence* of nucleophilic additives but in the presence of the proton trap (DTBP), a nonnucleophilic weak base.^{34,62} The addition of nucleophilic additives had no effect on polymerization rates, molecular weights, or molecular weight distributions (MWDs). Thus, it was suggested that the major role of added bases and the sole role of the proton trap is to scavenge protogenic impurities in the polymerization system. While supporting view is emerging,⁶³ the combination of the first and the second additives in one category is still under discussion.

Common ion salts are considered to suppress the ionic dissociation of covalent species and ion pairs to free ions, which are believed to result in nonliving polymerization.³⁴ In light of recent results, which confirmed similar reactivity of free ions and ion pairs, this view may require revision. In addition to the common ion effect, addition of salts can also change the nucleophilicity of counterions by modifying either the coordination geometry⁶⁴ or aggregation degree⁶⁵ of Lewis acids or their complex counterions. The former is the case with SnCl₄ and the latter is the case with TiCl₄ in the presence of tetra-*n*-butylammonium chloride (*n*Bu₄NCl). In both cases, more nucleophilic counterions (SnCl₆ vs. SnCl₅ or TiCl₅ vs. Ti₂Cl₉) are generated and these are reported to mediate the living cationic polymerizations of styrenic monomers^{39,66} and isobutyl vinyl ether (IBVE).⁴⁰

3.15.7.2.2(i) Living cationic polymerization: isobutylene (IB)

IB is the most studied monomer that can only polymerize by a cationic mechanism. The living carbocationic polymerization of IB was first discovered by Faust and Kennedy using organic acetate/BCl₃ initiating system in CH₃Cl or CH₂Cl₂ solvents at -50 to -10 °C.^{23,24} Living carbocationic polymerizations of IB to date are based on BCl₃, TiCl₄, and organoaluminum halide coinitiators. The activity of the BCl₃-based system is greatly solvent dependent, that is, sufficient activity only occurs in polar solvent. In less-polar solvents, the solvation of the counteranion does not promote ion generation and the binary ionogenic equilibrium is strongly shifted to the left. Therefore, the concentration of growing cations is extremely small, resulting in negligible polymerization rates. However, since PIB is poorly soluble in polar solvents at low temperatures, the molecular weights are limited with the BCl₃-based initiating systems.

A wide variety of initiators, organic esters, halides, ethers, and alcohols have been used to initiate living polymerization of IB at temperatures up to -10 °C. The true initiating entity with ethers and alcohols is the chloro-derivative arising by fast chlorination. The polymerization involving the BCl₄ counteranion is very slow, measured in hours, compared to the fast polymerization by protic impurities, and in the absence of proton scavenger, the monomer is consumed mainly by this process. In the presence of proton trap or EDs, similar rates, controlled molecular weights, and narrow MWDs (PDI \sim 1.2) have been reported.³⁷ According to kinetic studies, the polymerization is first order both in respect to monomer and BCl₃.³⁷ The absence of common ion salt effect in polymerizations involving the BCl_4^- counteranion suggests that propagation is mainly via the ion pairs, and the contribution of free ions, if any, is negligible.67

Organic esters, halides, and ethers have been used to initiate living polymerization of IB at temperatures from -90 up to -40 °C. In conjunction with TiCl₄, ethers are converted to the corresponding chlorides almost instantaneously, while the conversion of esters is somewhat slow.³⁴ According to Chen *et al.*,⁶⁸ alcohols are inactive with TiCl₄ alone but have been used in conjunction with BCl₃ and TiCl₄. BCl₃ converts the alcohols to the active chloride, which is activated by TiCl₄. In contrast to Chen *et al.*, Puskas and Grassmuller⁶⁹ reported chlorination of alcohols and initiation by TiCl₄ alone.

Under well-dried conditions, PIBs with controlled M_n s up to \sim 60 000 and narrow MWDs could be prepared in the absence of any additives in nonpolar solvent mixtures and low temperatures.³³ PIBs with $M_{\rm p}$ s up to 150000 and $M_{\rm w}/M_{\rm p}$ s as low as 1.02 have been obtained in the presence of proton trap or Lewis bases. The polymerization is first order in monomer but second order in TiCl₄, due to dimeric counteranions,³³ although first-order dependency was reported at [TiCl₄] < [initiator, I₀].⁷⁰ The consequence of the second-order rate dependence is that although excess of TiCl₄ over the initiator halide is not required to induce polymerization, at low initiator concentrations to obtain high $M_{\rm p}$ acceptable rates are only obtained when high TiCl₄ concentrations (16–36 times $[I_0]$) are used. Living polymerization of IB was also reported with the TiCl₄/TiBr₄ mixed⁷¹ coinitiator that yields mixed $Ti_2Cl_{n+1}Br_{8-n}$ counteranions. By the stepwise replacement of Cl to Br, however, the Lewis acidity decreases, which results in a decreased ionization rate constant and therefore decreasing overall rates of polymerization with decreasing TiCl₄/TiBr₄ ratio.

Organoaluminum compounds have also been employed for the living cationic polymerization of IB using 1,4-bis(1-azido-1methylethyl)benzene/Et₂AlCl/CH₂Cl₂ at -50 °C to produce a living polymerization of IB for $M_n < 50\,000$ where the presence of an ED like DMSO is not necessary.⁷² Another polymerization system based on Et₂AlCl and tertiary alkyl halide initiators has been reported but requires the use of an 80/20 (v/v) nonpolar/polar solvent mixture.⁷³ The first example of Me₂AlCl-catalyzed living polymerizations of IB was presented using conventional tertiary alkyl chloride initiators and 60/40 (v/v) nonpolar/polar solvent mixtures. PIBs were prepared with $M_n = 150\,000$ and $M_w/M_ns = 1.2^{74}$ even in the absence of additives such as proton traps or EDs. The 'living' nature of these polymerizations has been demonstrated at -75 to -80 °C in both 60/40 (v/v) hexane/CH₂Cl₂ and hexane/methyl chloride (MeCl) solvent systems. Recently, the living polymerization of IB was also reported using TMPCl/DTBP/hexanes:MeCl solvent mixtures/–80 °C using Me₂AlCl, Me_{1.5}AlCl_{1.5}, or MeAlCl₂.⁷⁵ With the latter two coinitiators, the polymerization was extremely fast and completed in seconds that necessitated special considerations for reaction control.

3.15.7.2.2(ii) β-Pinene

The first example of living cationic isomerization polymerization of β -pinene was reported with the HCl-2-chloroethyl vinyl ether adduct [CH₃CH(OCH₂-CH₂Cl)Cl] or 1-phenylethyl chloride/TiCl₃(OiPr)-initiating system in the presence of *n*Bu₄NCl in CH₂Cl₂ at -40 and -78 °C.^{76,77} The polymerization was rather slow even at relatively high initiator (20 mM) and coinitiator (100 mM) concentrations. The much stronger Lewis acid coinitiator TiCl₄ induced an extremely rapid polymerization yielding polymers with controlled molecular weight but with broad MWDs. The ¹H NMR analysis of the polymers showed a *tert*-chloride end group, and isomerized β -pinene repeat units with a cyclohexene ring. Copolymerization of β -pinene with IB indicated that the two monomers exhibit almost equal reactivity.⁷⁸

3.15.7.2.2(iii) Styrene (St)

The conventional cationic polymerizations of St suffers from side reactions such as chain transfer by β -proton elimination and interand intramolecular Friedel–Crafts alkylation. Thus, control of the cationic polymerization of St has been considered difficult. The living carbocationic polymerization of St was first achieved by the 1-(*p*-methylphenyl)ethyl acetate/BCl₃-initiating system in CH₃Cl at –30 °C.⁷⁹ The MWD was broad (~ 5–6), most likely because of slow initiation and/or slow exchange between the dormant and active species. Living polymerization of St with controlled molecular weight and narrow MWD was obtained using SnCl₄/1-phenylethyl halides as initiating systems in a nonpolar solvent (CHCl₃)⁸⁰ and solvent mixtures or in polar CH₂Cl₂ in the presence of *n*Bu₄NCl.⁸¹

Living polymerization was also reported with the TMPCl/ TiCl₄/methylcyclohexane (MeChx)/MeCl 60/40 (v/v)/-80 °C system in the combined presence of an ED and a proton trap.⁸² Later studies indicated that the ED is unnecessary and the living nature of the polymerization is not due to carbocation stabilization.⁸³ The living cationic polymerization of St has also been achieved with TiCl₃(OiPr) as an activator, in conjunction with 1-phenylethyl chloride and nBu₄NCl in CH₂Cl₂ at -40 and -78 °C.⁸⁴ The MWDs were narrow throughout the reactions (MWD \sim 1.1). Living St polymerization was also reported with the pMeSt HCl adduct (pMeStCl)/TiCl₄/MeChx/MeCl 60/40 (v/v)/-80 °C in the presence of a proton trap and was found that pMeStCl is a better initiator than TMPCl for St polymerization using TiCl₄ in MeChx/MeCl solvent mixture.⁸⁵ Recently, living polymerization of St was obtained with the system 1-phenylethyl chloride/TiC14/Bu2O in a mixture of 1,2-dichloroethane and hexane (55/45, v/v) at -15 °C.86

3.15.7.2.2(iv) p-Methylstyrene (pMeSt)

Faust and Kennedy⁸⁷ reported the living carbocationic polymerization of *p*MeSt in conjunction with BCl₃ in CH₃Cl and C₂H₅Cl solvents at -30 and -50 °C; however, the MWDs were rather broad (\sim 2-5). TMPCl/TiCl₄-initiated living polymerization of pMeSt in MeChx/MeCl 50/50 (v/v) solvent mixture at -30 °C in the presence of nBu₄NCl and DTBP has been reported by Nagy et al.⁸⁸ Kojima et al.⁸⁹ reported the living cationic polymerization of *p*MeSt with the HI/nBu₄NCl/ZnX₂ system in toluene and CH₂Cl₂ and obtained polymers of fairly narrow MWD. Lin and Matyjaszewski⁹⁰ have studied the living cationic polymerization of St and pMeSt initiated by 1-phenylethyl trichloroacetate/BCl₃ in CH₂Cl₂. Yang et al.⁹¹ studied the living cationic polymerization of pMeSt in the molecular range up to $M_n \approx 5500$, initiated by 1-phenylethyl bromide/SnCl₄-initiating system in CHCl₃ or in CHCl₃/ CH₂Cl₂ solvent mixtures at -27 °C. The polymerization was very slow, even though very high concentrations of SnCl₄ $(0.23 \text{ mol } l^{-1})$ and initiator, 1-phenylethyl bromide $(0.0215 \text{ mol l}^{-1})$, have been used. The $M_{\rm p}$ s of the obtained poly(pMeSt) were in agreement with the calculated values; however, the PDI was relatively high, PDI≈1.5-1.6. Living carbocationic polymerization of pMeSt was also obtained with 1,1-diphenylethylene (DPE)-capped TMPCl/TiCl₄:Ti (IpO)₄-initiating system in the presence of DTBP using hexanes/MeCl or MeChx/MeCl 60/40 (v/v) solvent mixture at -80 °C.92 Very recently, the living carbocationic polymerization of pMeSt was achieved with 1-chloro-1-phenylethane, 1chloro-1-(4-methylphenyl)ethane, and 1-chloro-1-(2,4,6-trimethylphenyl)ethane in conjunction with SnCl₄ as Lewis acid and DTBP as proton trap in CH₂Cl₂ at -70 to -15 °C.¹²

3.15.7.2.2(v) p-Chlorostyrene (pCISt)

Kennedy *et al.* reported the living carbocationic polymerization of *p*ClSt initiated by TMPCl/TiCl₄ in the presence of dimethylacetamide as ED and DTBP as proton trap in MeCl/ MeChx 60/40 (v/v) solvent mixture at -80 °C.^{63,93} Kanaoka *et al.*⁹⁴ obtained poly(*p*ClSt) of a narrow MWD with 1-phenylethyl chloride/SnCl₄-initiating system in CH₂Cl₂ at -15 °C to +25 °C in the presence of *n*Bu₄NCl. The polymerization was somewhat slow. Controlled cationic polymerization of *p*ClSt was also achieved by the alcohol/ BF₃OEt₂ system in the presence of fairly large amount of water.⁹⁵ Recently, for the living polymerization of *p*ClSt, 1-chloro-1-(4-methylphenyl)ethane and *p*ClStHCl adduct was used in conjunction with TiCl₄/DTBP in MeCl/MeChx 40/60 (v/v) solvent mixture at -80 °C.⁹

3.15.7.2.2(vi) 2,4,6-Trimethylstyrene (TMeSt)

In the cationic polymerization of St, one of the major side reactions is indanic cyclization.⁹⁶ Intra- and intermolecular alkylation are absent in the cationic polymerization of TMeSt, which was recognized in an early report on the living polymerization of TMeSt initiated by the cumyl acetate/BCl₃-initiating system in CH₃Cl at -30 °C.⁹⁷ Recently, the living cationic polymerization of TMeSt was initiated by 1-chloro-1-(2,4,6-trimethylphenyl)ethane, a model propagating end, in CH₂Cl₂ at -70 °C and the living polymerization yielded polymers with theoretical molecular weights and very low polydispersity $(M_w/M_n = 1.02-1.1)$.¹⁰

3.15.7.2.2(vii) p-Methoxystyrene (pMeOSt)

The living carbocationic polymerization of *p*MeOSt was first reported with the HI/ZnI₂-initiating system in toluene at – 15 to 25 °C.^{30,98} Living polymerizations were also attained in the more polar solvent, CH_2Cl_2 , with HI/I₂- and

HI/ZnI₂-initiating systems in the presence of nBu_4NX (X = Cl, Br, and I).99 Comparable but less controlled polymerization of pMeOSt has been reported using iodine as an initiator in CCl₄.¹⁰⁰ This system gives rise to long-lived but not truly living polymerization. More recently, pMeOStCl/SnBr₄-initiating system has been used in CH2Cl2 at -60 to -20 °C in the presence of DTBP. The obtained M_{n} s were in good agreement with the calculated ones assuming that one polymer chain forms per initiator. Polymers with $M_{\rm p}$ s up to 120000 were obtained with $M_{\rm w}/M_{\rm p} \sim 1.1^9$ A recent report indicated the controlled cationic polymerization of pMeOSt with controlled molecular weights and relatively narrow MWD (PDI = 1.4) using the pMeOSt HCl adduct (pMeOStCl)/Yb(OTf)3-initiating system in the presence of 2,6di-tert-butyl-4-methylpyridine.¹⁰¹ The authors also claimed the controlled albeit very slow cationic polymerization of pMeOSt in aqueous media using the pMeOStCl/Yb(OTf)3-initiating system. Relatively narrow PDIs (\sim 1.4) were observed and the molecular weights increased in proportion to the monomer conversion. Surfactants,¹⁰² sulfonic acid-based initiators,¹⁰³ and various phosphonic acid initiators¹⁰⁴ were also used for the cationic polymerization of *p*MeOSt in aqueous medium.

3.15.7.2.2(viii) α-Methylstyrene (αMeSt)

The living polymerization of aMeSt was first achieved with the vinyl ether-HCl adduct/SnBr₄-initiating system in CH₂Cl₂ at -78 °C.¹⁰⁵ Controlled polymerization of α MeSt was obtained by the cumyl chloride/BCl₃/-78 °C system in CH₂Cl₂/toluene 1/7 (v/v) solvent mixture in the presence of nBu_4NCl .¹⁰⁶ The living polymerization of aMeSt was also studied at -60 °C using iodine in liquid SO₂/CH₂Cl₂ or liquid SO₂/toluene.¹⁰⁷ The living polymerization of aMeSt has also been established in hexanes/MeCl 60/40 (v/v) at -60 to -80 °C in the presence of DTBP using DPE-capped TMPCl with SnBr₄ or SnCl₄⁴¹ and diphenyl alkyl chloride or HCl adduct of aMeSt dimer with BCl₃ or SnCl₄ coinitiators.^{108–110} Initiation with cumyl chloride, however, is slow relative to propagation, due to the absence of back strain. The living polymerization of p-chloro-aMeSt (pClaMeSt) was achieved using the 1,3dimethyl-1,3-diphenyl-1-chlorobutane/BCl3-initiating system in MeChx/MeCl 60/40 (v/v) at -80 °C.111

3.15.7.2.2(ix) Indene

Chain transfer to monomer via indane formation (intramolecular alkylation), the most important side reaction in the polymerization of St, cannot take place with indene. Therefore, even conventional initiating systems give high molecular weight and negligible transfer at low temperatures. Cumyl methyl ether¹¹² or cumyl chloride¹¹³ in conjunction with TiCl₃OBu or with TiCl₄ and dimethyl sulfoxide as an ED¹¹⁴ initiates living polymerization of indene. Living polymerization is also claimed with TMPCl/TiCl₄-initiating system using hexanes/MeCl 60/40 (v/v)¹¹⁵ and MeChx/MeCl 60/40 (v/v)¹¹⁶ mixed solvents at -80 °C. Thus, polyindene of theoretical molecular weight up to at least 13 000 and narrow MWD ($M_w/M_n \sim 1.2$) can be obtained by the cumyl chloride/ BCl₃-initiating system in MeCl at -80 °C.⁹⁴

3.15.7.2.2(x) N-Vinylcarbazole

There are very few reports available on the living cationic polymerization of *N*-vinylcarbazole, one of the most reactive monomer for cationic polymerization. Living polymerization of *N*-vinylcarbazole was reported in toluene or CH₂Cl₂ solvent system using only HI¹¹⁷ and I₂ as initiator in CH₂Cl₂ and CH₂Cl₂/CCl₄ 1/1 (v/v).¹¹⁸ Living cationic polymers of *N*-vinylcarbazole were synthesized with I₂ at -78 °C in CH₂Cl₂ in the presence of *n*Bu₄NI.¹¹⁹

3.15.7.2.2(xi) Vinyl ethers

Alkyl vinyl ethers are among the most reactive vinyl monomers in cationic polymerization. The pendant alkoxy groups provide the growing vinyl ether carbocation with a high stability. Controlled/living cationic polymerization of IBVE was first discovered with the HI/I2-initiating system.²² The living cationic polymerization of vinyl ethers (CH2=CH-O-R, where $R = CH_3$, C_2H_5 isopropyl, *n*-butyl, isobutyl, *n*-hexadecyl, 2-chloroethyl, benzyl, cyclohexyl, etc.) was first developed by the HI/I2-initiating system and has been reviewed extensively. Subsequently, other weak Lewis acids, for example, ZnCl₂, ZnBr₂, and ZnI₂, have also been employed. A recent review is available.¹²⁰ The living cationic polymerization of *tert*-butyl vinyl ether was achieved by the CH₃CH(OiBu)OCOCH₃/ Et1.5AlCl1.5-initiating system in the presence of THF as 'Lewis base' at -20 °C.¹²¹ However, the polymerization was slow, as close to quantitative yield was reached only in 60 h.

Recently, the living cationic polymerization of tert-butyl vinyl ether¹²² and cyclohexyl vinyl ether (CHVE)¹²³ was accomplished in hexanes/MeCl solvent mixtures at -88 °C using TMPCl capped with 1,1-ditolylethylene (DTE) as initiator and $TiCl_4/titanium$ isopropoxide ($Ti(OiP)_4$) as coinitiators. The process involved capping the initiator, TMPCl, with DTE in the presence of TiCl₄, followed by fine-tuning of the Lewis acidity with the addition of Ti(OiP)4 to match the reactivity of tert-butyl vinyl ether or CHVE. Both polymers exhibited T_gs (88 and 61 °C, respectively) well above the room temperature. Poly (vinyl ether)s with a T_{σ} as high as 100 °C have been obtained in the living cationic polymerization of vinyl ethers with a bulky tricyclodecane or tricyclodecene unit using HCl/ZnCl2 in toluene at -30 °C.¹²⁴ The fast living cationic polymerization of vinyl ethers with SnCl₄ combined with EtAlCl₂ in the presence of an ester as an added base was reported.¹²⁵ The cationic polymerization of vinyl ethers with a urethane group, 4-vinyloxybutyl n-butylcarbamate and 4-vinyloxybutyl phenylcarbamate, was studied with the HCl/ZnCl2-initiating system in CH₂Cl₂ solvent at -30 °C.¹²⁶ The cationic homopolymerization and copolymerization of five vinyl ethers with silyloxy groups, each with a different spacer length, were examined with a cationogen/Et1.5AlCl1.5-initiating system in the presence of an added base. When an appropriate base was added, the living cationic polymerization of Si-containing monomers became feasible, giving polymers with narrow MWD.¹²⁷ The cationic polymerization of 2-[4-(methoxycarbonyl)phenoxy] ethyl vinyl ether, a vinyl ether with a benzoate pendant, was reported to proceed with living/long-lived propagating species with an HCl/ZnCl2-initiating system in dichloromethane at -15 °C.¹²⁸ Hexa(chloromethyl)-melamine/ZnCl₂ was found to be an efficient initiating system for the living cationic polymerization of IBVE in CH₂Cl₂ at -45 °C.¹²⁹ Characterization of the polymers by GPC and ¹H NMR showed that initiation was rapid and quantitative and that the initiator is hexafunctional, leading to six-armed star-shaped polymers. A series of aromatic acetals from substituted phenols were employed as initiators in conjunction with Lewis acids such as AlCl₃, SnCl₄, and SnBr₄ for the cationic polymerization of IBVE.¹³⁰

3.15.8 Functional Polymers by Living Cationic Polymerization

Functional polymers are of great interest due to their potential applications in many important areas such as surface modification, adhesion, drug delivery, polymeric catalysts, compatibilization of polymer blends, and motor oil additives. In addition to the controlled and uniform size of the polymers, living polymerizations provide the simplest and most convenient method for the preparation of functional polymers. However, there are relatively few end-functionalized polymers (polymers with functional groups selectively positioned at the termini of any given polymerization of vinyl monomers, although varieties of end-functionalized polymers have successfully been synthesized in anionic polymerization. There are two basic methods to prepare functional polymers by cationic polymerization:

- 1. initiation from functional initiators; and
- 2. termination by functional terminators.

3.15.8.1 Functional Initiator Method

This method involves the use of functional initiators with a protected or unprotected functional group. When the functional group is unreactive under the polymerization conditions, protection is not necessary. Functional vinyl ethers have extensively been used in the living cationic polymerizations of vinyl ethers and these functional poly(vinyl ethers) can be derivatized to the desired functionality by simple organic reactions. Vinyl ethers carrying a variety of functional pendant groups, in a general form as in **Scheme 3** have been polymerized in living fashion in toluene (or CH_2Cl_2) using HI/I_2 or HI/ZnI_2 systems.¹³¹

Functionalized initiators have been used extensively for St and derivatives to obtain end-functionalized polymers by living cationic polymerization. A series of a-end-functionalized polymers of St and pMeSt were synthesized by living cationic polymerizations in CH2Cl2 at -15 °C initiated with the HCl adducts of CH2=CH(OCH2-CH2X) (X=chloride, benzoate, acetate, phthalimide, and methacrylate) using SnCl4 in the presence of *n*Bu₄NC1.¹³² The living cationic polymerization of aMeSt initiated by HCl adduct of 2-chloroethyl vinyl ether/ SnBr₄-initiating system in CH₂Cl₂ at -78 °C gave terminal functionalities in the products.⁸⁰ The living cationic polymerization of pClSt induced with CH3CH(OCH2CH2Cl)Cl/SnCl4/ *n*Bu₄NCl at 0 °C or room temperature gave living polymers with narrow MWDs, which are a kind of end-functionalized polymers. The authors concluded that a variety of vinyl ethers would lead to end-functionalized poly(pClSt).⁷³ The -CH₂CO₂H and -OH end functionalities have been obtained using the functional initiator method for the living cationic

 $R = OMe, OEt, OAc, (CH_2CH_2O) Et_n [n = 1, 2, 4]$

 $OSi(Me)_3,\,OSi(Me)_2iBu,\,C(CO_2Et)_3,\,O_2CPh$

 $\mathsf{OCH}_2\mathsf{CO}_2\mathsf{Et},\,\mathsf{OC}(\mathsf{O})\mathsf{C}(\mathsf{CH}_3)\mathsf{H}=\mathsf{CH}_2,\,\mathsf{OC}(\mathsf{O})\mathsf{CH}=\mathsf{CH}_2,$

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CH(CH<sub>2</sub>CO<sub>2</sub>Et)<sub>2</sub>, etc.
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Scheme 3 Functional vinyl ethers used for living cationic polymerization.

polymerization of *p-tert*-butoxystyrene.¹³³ A series of end-functionalized polymers of *p*MeOSt were synthesized by the functional initiator method initiated with a functional vinyl ether-HI adduct (X-CH₂CH₂OCH(CH₃)I; X = CH₃COO, (EtOCO)₂CH, and phthalimide)/ZnI₂ in toluene at -15 °C.¹³⁴

Few end-functionalized PIBs have been obtained by using functional initiators. The ester functional initiators 3,3,5trimethyl-5-chloro-1-hexyl isobutyrate and methacrylate have been successfully employed for the living polymerization of IB.¹³⁵ Subsequently, the synthesis of α -carboxylic acid functional PIB was also reported by hydrolysis of the product obtained in the living cationic polymerization of IB using a novel aromatic initiator containing the CH₃OCO- moiety.¹³⁶ While these ester functionalities form a complex with the Lewis acid coinitiator, quenching the polymerization with CH₃OH yields the original ester quantitatively. Initiators containing a cationically unreactive vinyl functionality, for example, 5-chloro-3,3,5-trimethyl-1-hexene and 3-chlorocyclopentene, have been used to prepare PIBs with α -olefin head groups. Following the discovery that the chlorosilyl functionality is unreactive toward Lewis acids or carbocations, a series of novel chlorosilyl functional initiators have been employed in the living cationic polymerization of IB to synthesize well-defined PIBs carrying mono-, di-, and tri-methoxysilyl head group and a tert-chloro end group in conjunction with TiCl₄ in hexanes/MeCl 60/40 (v/v) at -80 °C.¹³⁷ A class of unique epoxide initiators, for example, α -methylstyrene epoxide (MSE), 2,4,4-trimethyl-pentyl-epoxide-1,2 (TMPO-1), 2,4,4-trimethyl-pentyl-epoxide-2,3 (TMPO-2), and hexaepoxisqualene (HES), for the living polymerization of IB in conjunction with TiCl4 has been recently described by Puskas et al.^{138,139} Ring cleavage induced by TiCl₄ produces a tertiary cation that initiates the living polymerization of IB. Upon quenching the polymerization with methanol, PIB carrying primary hydroxyl head group and tert-chloride end group is obtained. During initiation, however, simultaneous side reactions take place. Although these side reactions do not affect the livingness of the polymerization or the functionality of the PIB, they reduce the initiator efficiency to 3% with TMPO-1 and 40% with MSE.

The α -end-functionalized poly(β -pinene) was obtained by living cationic isomerization polymerization in CH₂Cl₂ at -40 °C using TiCl₃(OiPr)/*n*Bu₄NCl and HCl adducts of functionalized vinyl ethers (CH₃CH(OCH₂CH₂X)Cl; X = chloride, acetate, and methacrylate) as initiators carrying pendant substituents X that serve as terminal functionalities.⁵¹

3.15.8.2 Functional Terminator Method

The second method involves end-quenching of living polymers with appropriate nucleophiles. Although this approach appears to be more attractive than the first one, *in situ* end functionalization of the living ends is limited to nucleophiles that do not react with the Lewis acid coinitiator. Because the ionization equilibrium is shifted to the covalent species, the concentration of the ionic active species is very low. Quantitative functionalization can only be accomplished when ionization takes place continuously in the presence of nucleophile. Quenching the vinyl ether polymerization with the malonate anion,¹⁴⁰ certain silyl enol ethers¹⁴¹ and silyl ketene acetals¹⁴² have been successfully used to synthesize end-functionalized poly(vinyl ethers). Alkyl amines,¹⁴³ ring-substituted anilines,¹⁴⁴ alcohols,¹⁴⁵ and water¹⁴⁶ have also been used to quench the vinyl

ether polymerization to synthesize end-functionalized poly (vinyl ethers). Functionalizations by the latter nucleophiles, however, most likely do not entail reactions of the living cationic ends but proceed by SN2 reactions involving the halogen-terminated chain ends.

In the functionalization of living polymers of hydrocarbon olefins, success remained limited up until recently. Although there are various methods available to modify the resulting chloro chain ends, they usually involve a number of steps and are rather cumbersome.

Various nucleophiles, which do not react (or react very slowly) with the Lewis acid, have been used to prepare functional PIBs by in situ functionalization of the living ends. Since these terminators are mostly π -nucleophiles, multiple additions should be avoided. This can be accomplished by employing π -nucleophiles that do not homopolymerize, yielding a stable ionic product or a covalent uncharged product either by rapidly losing a cationic fragment, for example, Me₃Si⁺ or H⁺, or by fast ion collapse. Accordingly, the rapid and quantitative addition of various 2-substituted furans to living PIB⁺ has been observed in conjunction with TiCl₄ as Lewis acid in hexanes/CH2Cl2 or CH3Cl 60/40 (v/v) at -80 °C and with BCl₃ in CH₃Cl at -40 °C.¹⁴⁷ The formation of the stable allylic cation was confirmed by trapping the resulting cation with tributyltin hydride, which yielded PIB with dihydrofuran functionality. Quenching with methanol resulted in the quantitative formation of 2-alkyl-5-PIB-furan. Furan-terminated PIB (2-PIB-Fu) was obtained in quantitative yields in a reaction of PIB+ with 2-Bu₃SnFu in hexanes/CH₃Cl 60/40 (v/v) in the presence of TiCl₄ at -80 °C. Using unsubstituted furan, coupling of two living chain ends as a side reaction could not be avoided. However, thiophene- and N-methylpyrrole-terminated PIB could be obtained by employing unsubstituted thiophene and N-methylpyrrole,¹⁴⁸ respectively.

Allyl telechelic PIBs have been obtained by endquenching with allyltrimethylsilane (ATMS),^{19,149} methallyltrimethylsilane,¹⁹ tetraallyltin, or allyltributyltin.¹⁵⁰ In the functionalization reactions, β -proton abstraction should generally be avoided. Quantitative β -proton abstraction with hindered bases reported recently, however, is a valuable method to produce *exo*-olefin-terminated PIB in one pot.¹⁵¹

A series of end-functionalized polymers of *p*MeOSt were synthesized by quenching the HI/ZnI₂-initiated living poly (*p*MeOSt)⁺ cations with a functional alcohol (HOCH₂CH₂Z; $Z = OOCCH_3$, OOCC(=CH₂)CH₃, and OOCC(=CH₂)H).¹¹⁵

When all dormant chain ends are converted to active ionic species, as in the capping reaction with diarylethylenes,¹⁵² many other nucleophiles, such as NH3 and CH3OH, which also quench the Lewis acid, could be used. In situ functionalization of the living ends by a variety of nucleophiles was recently realized via capping with non(homo)polymerizable diarylethylenes or 2-alkyl furans followed by end-quenching.¹⁵³ The stable and fully ionized diarylcarbenium ion, obtained in the capping of PIBCl or PStCl with DPE, is readily amenable for chain-end functionalization by quenching with appropriate nucleophiles as shown in Scheme 4.¹⁵⁴ Using this strategy, a variety of chain-end-functional PIBs, including methoxy, amine, carbonyl, and ester end groups, have been prepared. It is also notable that, when living PIB is capped with DPE, organotin compounds can also be used to introduce new functionalities such as -H₁ -N(CH₃)₂₁ and furan.¹⁵⁵

Recently, the synthesis of haloallyl functional PIBs (PIBallyl-X, where X = Cl or Br) was reported using the capping



Scheme 4 Synthesis of chain-end-functionalized PIBs.

reaction of living PIB with 1,3-butadiene in hexanes (Hex)/MeCl 60/40 (ν/ν) solvent mixtures at -80 °C¹⁵⁶ with titanium tetrachloride (TiCl₄) or methylaluminum sesquibro-mide (Me_{1.5}AlBr_{1.5}) as a Lewis acid.

Monoaddition of 1,3-butadiene followed by instantaneous halide transfer from the counteranion and selective formation of the trans-1,4-adduct (PIB-allyl-X) was observed in Hex/MeCl 60/40 (ν/ν) solvent mixtures at -80 °C at [1,3-butadiene] ≤ 0.05 mol l⁻¹ ([1,3-butadiene]/[chain end] ≤ 12). Simple nucleophilic substitution reactions on these chloro or bromoallyl functional PIBs allowed the syntheses of end-functional PIBs including hydroxy, amino, carboxy, azide, propargyl, methoxy, and thymine end groups.¹⁵⁷

3.15.8.3 Telechelic Polymers

Telechelic or α, ω -bifunctional and multifunctional polymers carry functional groups at each terminal. Symmetric telechelic or multifunctional polymers can be readily prepared by employing bi- or multifunctional initiators followed by functionalization of the living end as described above.¹⁵⁸

Symmetric telechelic polymers can also be prepared by coupling α -functional living polymer chains using any of the recently discovered coupling agents. Bifunctional silyl enol ethers, such as 1,3-bis{*p*-[1-[(trimethylsilyl)oxy]vinyl]phenoxy}-propane, 1,4-diethoxy-1,4-bis[(trimethylsilyl)oxy]-1,3-butadiene, and 2,4-bis [(trimethylsilyl)oxyl-1,3-pentadiene, are efficient bifunctional coupling agents for the living polymers of IBVE initiated with HCl/ZnC1₂ at -15 °C in CH₂Cl₂ and toluene solvents.¹¹⁶ The di-(1a), tri-(1b), and tetra-(1c) functional silyl enol ethers have

extensively been used with vinyl ethers to obtain functional polymers and block copolymers.¹⁵⁹ As an example, telechelic 4-arm star polymers were obtained by coupling end-functionalized living poly(IBVE) with the tetrafunctional silyl enol ethers (1a).¹⁶⁰



Non(homo)polymerizable bis-DPE compounds, such as 2,2-bis[4-(1-phenylethenyl)phenyl]propane (BDPEP) and 2,2-bis[4-(1-tolylethenyl)phenyl]propane (BDTEP) (2), have been successfully employed in the living coupling reaction of living PIB.^{161,162} It was demonstrated that living PIB reacts quantitatively with BDPEP or BDTEP to yield stoichiometric amounts of bis(diarylalkylcarbenium) ions, as confirmed by the quantitative formation of diaryl-methoxy functionalities



Since 2-alkylfurans add rapidly and quantitatively to living PIB yielding stable tertiary allylic cations, the coupling reaction of living PIB was also studied using bis-furanyl compounds.¹⁶³ Using 2,5-bis[(1-furanyl)-1-methylethyl]-furan (BFPF) (3), coupling of living PIB was found to be rapid and quantitative in hexane/MeCl 60/40 or 40/60 (v/v) solvent mixtures at -80 °C in conjunction with TiCl₄, as well as in MeCl at -40 °C with BCl₃ as Lewis acid. For instance, *in situ* coupling of living PIB, prepared by haloboration-initiation using the BCl₃/MeCl/–40 °C system, with BFPF yielded α,ω -telechelic PIB with alkylboron functionality. After oxidation, this telechelic PIB was converted to α,ω -hydroxyl PIB. The synthesis of α,ω -telechelic PIBs with a vinyl functionality was also achieved by the coupling reaction of living PIB, prepared using 3,3,5-trimethyl-5-chloro-1-hexene as an initiator in the presence of TiCl₄.¹⁶⁴



The α, ω -asymmetric polymers are available by the combination of the functional initiator and functional terminator methods. By the rational combination of haloborationinitiation and capping techniques, a series of α, ω -asymmetrically functionalized PIBs have been prepared.^{165,166} Polymers prepared by haloboration-initiation invariably carry an alkylboron head group,^{42,167,168} which can easily be converted into a primary hydroxy¹⁴² or a secondary amine group.^{140,141} To functionalize the ω -living ends, the functionalization strategy shown in **Scheme 4** is applicable and has been used to incorporate methoxycarbonyl groups as ω -functionality.¹⁶⁹

3.15.8.3.1 Macromonomers

A macromonomer is a macromolecule containing a (co)polymerizable end functional group. Macromonomers have been synthesized by living cationic polymerization using three different techniques: by the functional initiator or functional terminator methods or by chain-end modification.

3.15.8.3.1(i) Synthesis using a functional initiator

This technique is the simplest as it generally requires only one step since the polymerizable function is incorporated via the initiator fragment. Most macromonomers have been prepared with a methacrylate end group¹⁷⁰⁻¹⁷² which is unreactive under cationic polymerization conditions. For instance, the synthesis of the poly(vinyl ether) macromonomer was reported by employing the initiator 4a, which contains a methacrylate ester group and a function able to initiate the cationic polymerization of vinyl ethers. Other vinyl ethers were also polymerized using initiator 4a under similar conditions.¹⁷³

$$H_{2}C = C \begin{pmatrix} CH_{3} & X \\ C = O - CH_{2} - CH_{2} - O - CH - CH_{3} & a: X = I \\ I \\ O & a \end{pmatrix}$$

Poly(ethyl vinyl ether) (PEVE) macromonomers were also prepared using initiator 5 bearing an allylic function.¹⁷⁴ This reactive group remained intact during the polymerization and could be transformed into the corresponding oxirane by peracid oxidation.

Using functionalized initiator **4b**, polystyrene and poly (*p*MeSt) macromonomers bearing a terminal methacrylate¹⁰⁷ could be prepared by living cationic polymerization in CH₂Cl₂ at –15 °C in the presence of SnCl₄ and *n*Bu₄NCl. To preserve the α-end functionality, mixing of the reagents was carried out at –78 °C. When mixing was performed at –15 °C, the functionality was lower than unity, which was attributed to initiation by protons eliminated following intramolecular alkylation. A similar procedure was also used for the synthesis of methacrylate-functional poly(αMeSt).¹⁷⁵

Methacrylate functional PIB macromonomers have been synthesized by living carbocationic polymerization of IB using the 3,3,5-trimethyl-5-chloro-1-hexyl methacrylate (6)/TiCl₄-initiating system in hexane/MeCl 60/40 (v/v).^{110,176} By varying the monomer to initiator ratio, PIBs in the molecular weight range of $2000 - 40\,000\,\mathrm{g\,mol^{-1}}$ were obtained with narrow MWDs and close to theoretical ester functionality.



The polymerization of β -pinene in conjunction with 5/TiCl₃ (O*i*Pr)-initiating system in the presence of *n*Bu₄NCl in CH₂Cl₂ at -40 °C yielded poly(β -pinene) macromonomer with a methacrylate function at the α -end and a chlorine atom at the ω -end.⁵¹ The macromonomers exhibited narrow MWD and the reported functionality was close to unity.

3.15.8.3.1(ii) Synthesis using a functional capping agent

In this method, the polymerizable group is incorporated at the ω -end of the macromolecule by a reaction between a capping agent and the living polymer end.

The sodium salt of malonate carbanions reacts quantitatively with the living ends of poly(vinyl ether)s to give a stable carbon–carbon bond. This reaction was used to functionalize the ends of living poly(IBVE) or poly(benzyl vinyl ether) with a vinyl ether polymerizable end group supported by a malonate ion (end-capping agent 7).¹⁷⁷

$$Na^{+} COOC_2H_5$$

$$Na^{+} COC_2H_2 CH_2 CH_2 O-HC = CH_2$$

$$COOC_2H_5$$
7

A hydroxy function is also able to quantitatively react with the living end of poly(vinyl ether)s, but the resulting acetal end group has poor stability in acidic media; therefore, a proton trap should be added in order to scavenge the protons released during the coupling process. Various end-capping agents with a primary alcohol and a polymerizable double bond were used to produce poly(vinyl ether) macromonomers. Most often, 2-hydroxyethyl methacrylate (HEMA)^{178–181} has been used but other alcohols with an allylic or olefinic group were also employed such as allyl alcohol, 2-[2-(2-allyloxyethoxy)ethoxy] ethanol and 10-undecen-1-ol.

Due to the lower stability of the growing *p*-alkoxystyrene cations and the possibility of several side reactions, some end-capping agents that were successfully used for poly(vinyl ether)s such as sodiomalonic ester and *tert*-butyl alcohol failed to yield end-functional poly(*p*-alkoxystyrene). In contrast, primary and secondary alcohols underwent quantitative reactions to give stable alkoxy terminals. Thus, HEMA and acrylate were used to introduce a polymerizable group at the ω -end.^{108,109} Heterotelechelic poly(*p*MeOSt)s were also prepared by the combination of the functional initiator method and the functional end-capping method. This allowed the synthesis of a poly(*p*MeOSt) macromonomer with one malonate diester at the α -end and one methacrylate group at the ω -end.

In contrast to vinyl ethers and *p*-alkoxystyrenes, quenching the living cationic polymerization of St, in conjunction with SnCl₄ in the presence of *n*Bu₄NCl, with bases such as methanol, sodium methoxide, benzylamine, or diethyl sodiomalonate, led to the terminal chloride instead of the specific end group. This can be explained by the very low concentration of cationic species compared to the dormant C–Cl end group and by the quenching of SnCl₄ with the above Lewis bases. This was overcome by using organosilicon compounds such as trimethylsilyl methacrylate and quantitative functionalization was achieved when the quenching reaction was performed at 0 °C for 24 h, in the presence of a large excess of the quencher and low concentration of the Lewis acid.¹⁸²

Allyl-terminated linear and triarm star PIBs and epoxy and hydroxy telechelics therefrom have been reported by Ivan and Kennedy.¹²⁴ Allyl functional PIBs were obtained in a simple one pot procedure involving living IB polymerization using TiCl₄ as coinitiator followed by end-quenching with ATMS. This method is commercially employed by Kaneka Corp. (Japan) for the synthesis of allyl telechelic PIB, a precursor to moisture curable PIBs. The procedure was based on earlier reports by Wilczek and Kennedy^{183,184} that demonstrated quantitative allylation of PIB-Cl by ATMS in the presence of Et₂AlCl or TiCl₄. Quantitative hydroboration followed by oxidation in alkaline THF at room temperature resulted in –OH functional PIBs, which were used to form PIB-based polyurethanes.¹⁸⁵ Quantitative epoxidation of the double bonds was also achieved with *m*-chloroperbenzoic acid in CHCl₃ at room temperature, giving rise to macromonomers able to polymerize by ring-opening polymerization.

In a similar development utilizing allylsilanes, the synthesis of α -methylstyryl functional PIB macromonomer was reported by the reaction of 2-phenylallyltrimethylsilane with living PIB.¹⁸⁶ The macromonomer, however, displayed low reactivity in cationic copolymerization with IB, which was ascribed to steric hindrance. In contrast, a reactive and unhindered macromonomer was obtained in the reaction of living PIB with 1-(2-propenyl)-3-[2-(3-trimethylsilyl)-propenyl]benzene, where the reactivity of the allylsilyl function is ~ 1000 times higher than that of the α -methylstyryl function.

Furan telechelic PIB macromonomers with well-defined M_n s and narrow MWD were synthesized by end-quenching living PIB with 2-tributylstannylfuran or 2,2-difurylpropane.^{138,187} Three-arm star, furan-functional PIBs were obtained under identical conditions except that 1,3,5-tricumyl chloride was used as initiator. The resulting telechelic PIBs could be efficiently photocured by UV radiation in the presence of a cationic photoinitiator and a divinyl ether reactive diluent.¹⁸⁸ Due to the lower reactivity of thiophene compared to furan, the reaction of unsubstituted thiophene to living PIB resulted in rapid and quantitative monoaddition and quantitative formation of 2-polyisobutylenyl-thiophene.¹⁸⁹

Macromonomers with a terminal non(homo)polymerizable vinylidene group, such as DPE, have gained much attention in recent years. One of the most unique and appealing applications of these types of macromonomers is that they can be used as precursor polymers for a variety of block copolymers with controlled architectures such as ABC-type star-block or comb-type graft copolymers. @-DPE-functionalized macromonomers could be prepared by the addition reaction of living cationic polymers to 'double' diphenylethylenes such as 1,3-bis(1-phenylethenyl) benzene (or meta-double diphenylethylene, MDDPE) or 1,4-bis (1-phenylethenyl)benzene (or para-double diphenylethylene, PDDPE).¹⁹⁰ The addition reaction of living PIB prepared using the TMPCl/TiCl₄/DTBP system in hexane/MeCl 60/40 (v/v) at -80 °C system to 2 equiv. of PDDPE resulted in a rapid and quantitative formation of PIB-DPE macromonomer. as proved by ¹H and ¹³C NMR spectroscopies, without the formation of the coupled product. With MDDPE, larger excess (4 equiv.) was necessary to obtain the monoadduct with negligible amounts of the diadduct.

3.15.8.3.1(iii) Chain-end modification

In this method, the polymerizable function is incorporated by chemical modification of the α - or ω -end group after isolation of the polymer. Although a wide variety of polymerizable groups can be incorporated this way, previously reported methods are generally cumbersome as they involve several steps.^{191–194} A new promising avenue for the preparation of PIB macromonomers takes advantage of the high reactivity of primary chloro- or bromo-functional PIBs in nucleophilic substitution reactions as shown above for the synthesis of functional PIBs. Employing these precursors, acrylate,¹⁹⁵ methacrylate,^{170,196} vinyloxy,¹⁷⁰ and epoxy¹⁷⁰ functional PIBs

with quantitative functionality have been obtained in one-step reactions utilizing inexpensive reagents.

3.15.9 Block Copolymers

Living polymerization is the most effective and convenient method to prepare block copolymers. Synthetic methodologies, however, need to be carefully selected to prepare block copolymers with high structural integrity. In general, block copolymers can be synthesized by sequential monomer addition or by reactions of living or end-functionalized polymer ends. This second method includes the use of macroinitiator for the polymerization of the second monomer and coupling/ linking living and/or end-functional polymer ends.

3.15.9.1 Linear Diblock Copolymers

Living cationic sequential block copolymerization is one of the simplest and most convenient methods to provide well-defined block copolymers. The successful synthesis of block copolymers via sequential monomer addition relies on the rational selection of polymerization conditions such as Lewis acid, solvent, additives, and temperature and on the selection of the appropriate order of monomer addition. For a successful living cationic sequential block copolymerization, the rate of crossover to a second monomer (R_{cr}) must be faster than or at least equal to that of the homopolymerization of a second monomer (R_p) . In other words, efficient crossover could be achieved when the two monomers have similar reactivities or when crossover occurs from the more reactive to the less reactive monomer. When crossover is from the less reactive monomer to the more reactive one a mixture of block copolymer and homopolymer is invariably formed due to the unfavorable R_{cr}/R_{p} ratio. The nucleophilicity parameter (N) reported by Mayr's group might be used as the relative scale of monomer reactivity.197

When the reactivity of the two monomers is similar and steric factors are absent, sequential block copolymerization can be used successfully. Alkyl vinyl ethers have similar reactivity and, therefore, a large variety of AB- or BA-type diblock copolymers could be prepared by sequential block copolymerization. A recent review is available.¹⁹⁸ Typical examples are shown¹⁹⁹ in **Figure 2**.

Hydrolysis of 2-acetoxyethyl vinyl ether or 2-(vinyloxy) diethyl malonate yielded block segments with pendant hydroxyl or carboxyl groups. Most of these syntheses utilized the HI/I_2 - or HX/ZnX_2 (X = halogen)-initiating systems. Within the vinyl ether family, differences in reactivity are relatively small and could be overcome by increasing the concentration of the Lewis acid for the polymerization of the second, less reactive vinyl ether, for instance, in the preparation of poly (IBVE-b-2-acetoxyethyl vinyl ether). Stimuli-responsive diblock copolymers with a thermosensitive segment and a hydrophilic segment have been synthesized via sequential living cationic copolymerization employing Et_{1.5}AlCl_{1.5} as coinitiator in the presence of Lewis base by Sugihara et al.²⁰⁰ The block copolymers consisting of a poly(vinyl ether) block segment with oxyethylene pendants exhibiting LCST-type phase separation in water and a poly-(hydroxyethyl vinyl ether) segment displayed highly sensitive and reversible thermally induced micelle formation and/or physical gelation. Using essentially the same synthetic method, many other vinyl ether-based stimuli-responsive block copolymers (in addition to homoand random copolymers) have been reported by the same research group. A recent review is available.²⁰¹

Similarly, block copolymers of vinyl ethers and *p*-alkoxystyrenes could be prepared by a simple sequential monomer addition.⁷⁴ In contrast, the synthesis of poly(methyl vinyl ether-*b*-St) is more difficult. While methyl vinyl ether (MeVE) smoothly polymerized with the HCl/SnCl₄ system in the presence of nBu_4NCl at -78 °C, for the second-stage polymerization of the less reactive St additional amounts of SnCl₄ and the increase of temperature to -15 °C were necessary.

R ₁	R ₂
nC ₁₆ H ₃₃	CH ₃ , C ₂ H ₅
CH ₂ CH ₂ OH	<i>i</i> C ₄ H ₉ , <i>n</i> C ₄ H ₉ , <i>i</i> C ₈ H ₁₇ , <i>n</i> C ₁₆ H ₃₃
CH ₂ CH ₂ CH ₂ COOH	nC ₄ H ₉ , <i>i</i> C ₈ H ₁₇ , <i>n</i> C ₁₆ H ₃₃
CH ₂ CH ₂ NH ₂	nC ₄ H ₉ , nC ₁₆ H ₃₃
CH ₂ C ₆ H ₅	iC ₄ H ₉
CH_3 or iC_4H_9	OMe



Figure 2 Typical examples of AB- or BA-type diblock copolymers prepared by sequential block copolymerization.

Although structurally different, IB and St possess similar reactivity, and diblock copolymers poly(IB-b-St)⁵⁸ as well as the reverse-order $poly(St-b-IB)^{60,202}$ could be readily prepared via sequential monomer addition. Moreover, identical coinitiator and reaction conditions could be employed for the living cationic polymerization of both monomers. However, while the living PIB chain ends are sufficiently stable under monomer-starved conditions, the living PSt chain ends undergo decomposition at close to $\sim 100\%$ conversion of St.²⁰³ Therefore, IB must be added at \leq 95% conversion of St in order to obtain poly(St-b-IB) diblock copolymers with negligible homo-polystyrene contamination.^{60,204,205} The presence of unreacted St monomer, however, complicates the block copolymerization of IB. The first-order plot of IB, which is linear for homopolymerization, is curved downward for block copolymerization, indicating decreasing concentration and/or reactivity of active centers with time. This is attributed to the slow formation of -St-IB-Cl chain ends (due to the reactivity ratios that are both much higher than unity), which are much less reactive than -IB-IB-Cl.60

In the synthesis of the reverse sequence, poly(IB-*b*-St), it is important to add St after complete polymerization of IB. When St is added at less than 100% IB conversion the polymerization of St will be slow, which again is due to the formation and low reactivity of –St-IB-Cl chain ends. For instance, when St is added after complete polymerization of IB, St polymerization is complete in 1 h. In contrast, when St is added at 94% IB conversion St conversion reaches only ~ 50% in 1 h at otherwise identical conditions.

Living cationic sequential block copolymerization from a more reactive monomer to a less reactive one usually requires a change from a weaker Lewis acid to a stronger one. For instance, the living cationic polymerization of α MeSt has been reported using the relatively mild Lewis acids SnBr₄, TiCl_n(OR)_{4-n}, SnCl₄, or BCl₃ as coinitiators.^{41,80,81,83,84,206} These Lewis acids, however, are too weak to initiate the polymerization of the less reactive IB; therefore the addition of a stronger Lewis acid, for example, TiCl₄ is necessary to polymerize IB by sequential monomer addition. With SnBr₄ or TiCl_n (OR)_{4-n}, however, ligand exchange takes place upon addition of TiCl₄, which results in mixed titanium halides that are too weak to initiate the polymerization of B. Ligand exchange is absent with BCl₃, which also induces living cationic polymerization of α MeSt in MeChx/MeCl 60/40 (v/v) solvent mixture

at -80 °C. Thus, BCl₃ is suitable for the synthesis of poly (α MeSt-*b*-IB) diblock copolymer. Upon addition of IB to the living poly(α MeSt) (P α MeSt) solution, quantitative crossover takes place followed by instantaneous termination (initiation without propagation) and selective formation of P α MeSt-IB₁-Cl.^{85,207} The addition of TiCl₄ starts the polymerization of IB.

The living cationic polymerization of *p*ClaMeSt can also be accomplished under conditions identical to those used for the synthesis of poly(α MeSt-*b*-IB) copolymer.^{86,208} Using the above method, poly(*p*ClaMeSt-*b*-IB) diblock copolymer was also prepared via sequential monomer addition. On the basis of GPC UV traces of the starting *Pp*ClaMeSt and the resulting poly(*p*ClaMeSt-*b*-IB) diblock copolymer, the *B*_{eff} was ~100% and homopolymer contamination was not detected.

Sequential block copolymerization of IB with more reactive monomers such as α MeSt, *p*MeSt, IBVE, or MeVE as a second monomer invariably leads to a mixture of block copolymer and PIB homopolymer. To overcome the difficulty in the crossover step, a general methodology has been developed for the synthesis of block copolymers when the second monomer is more reactive than the first one. It involves the intermediate capping reaction with non(homo)polymerizable monomers such as diarylethylenes and 2-substituted furans.

As shown in Scheme $5^{209}_{,}$ this process involves the capping reaction of living PIB with DPE or DTE, followed by tuning of the Lewis acidity to the reactivity of the second monomer. First, the capping reaction yields a stable and fully ionized diarylcarbenium ion (PIB-DPE⁺)^{210,211} which has been confirmed using spectroscopic methods (NMR and UV/Vis) and conductivity measurements. The capping reaction of living PIB with 1,1-diarylethylenes is an equilibrium reaction, which can be shifted toward completion with decreasing temperature, or with increasing Lewis acidity, solvent polarity, electrondonating ability of *p*-substituents, or concentration of reactants. The purpose of the Lewis acidity tuning, following the capping reaction, is to generate more nucleophilic counterions, which ensure a high $R_{\rm cr}/R_{\rm p}$ ratio as well as the living polymerization of a second monomer. This has been carried out using three different methods: (1) by the addition of titanium(IV) alkoxides $(Ti(OR)_4)$, (2) by the substitution of a strong Lewis acid with a weaker one, or (3) by the addition of nBu_4NCL .

The first and simplest method has been successfully employed in the block copolymerization of IB with $\alpha MeSt$,²¹²



Scheme 5 Synthesis of block copolymers via capping reaction of living PIB with DPE, followed by Lewis acidity tuning and sequential monomer addition.
*p*MeSt,⁶⁶ MeVE,^{213,214} *t*BuVE,⁹⁷ *t*-butyldimethylsilyl vinyl ether,²¹⁵ CHVE,²¹⁶ and *p-tert*-butyldimethylsiloxystyrene (*t*BDMSt).²¹⁷

The substitution of TiCl₄ with a weaker Lewis acid (SnBr₄ or SnCl₄) has also been proven to be an efficient strategy in the synthesis of poly(IB-b- α MeSt)^{41,181} and poly(IB-b-t-BuOSt)²¹⁸ diblock copolymers.

The block copolymerization of IB with IBVE was achieved by Lewis acidity tuning using nBu_4NCl .^{40,219} The addition of nBu_4NCl reduces the concentration of free and uncomplexed TiCl₄ ([TiCl₄]_{free}), and mechanistic studies indicated that when [TiCl₄]_{free} < [chain end], the dimeric counterion, Ti₂Cl₉, is converted to a more nucleophilic monomeric TiCl₅ counterion suitable for the living polymerization of IBVE.

Block copolymerization of IB with MeVE was also carried out using 2-methylfuran or 2-*tert*-butylfuran as a capping agent.^{122,220} However, the crossover efficiency was only ~66% using 2-*tert*-butylfuran and only slightly higher (~75%) when 2-methylfuran was employed as a capping agent under similar condition.

3.15.9.2 Linear Triblock Copolymers

3.15.9.2.1 Synthesis using difunctional initiators

Since soluble multifunctional initiators are more readily available in cationic polymerization than in the anionic counterpart, ABA-type linear triblock copolymers have been almost exclusively prepared using difunctional initiation followed by sequential monomer addition. The preparation and properties of ABA-type block copolymer thermoplastic elastomers (TPEs), where the middle segment is PIB, have been reviewed recently.²²¹

The synthesis of poly(St-b-IB-b-St) triblock copolymer has been accomplished by many research groups.²²²⁻²²⁸ The synthesis invariably involved sequential monomer addition using a difunctional initiator in conjunction with TiCl₄ in a moderately polar solvent mixture at low (-70 to -90 °C) temperatures. As already mentioned at the synthesis of poly(IB-b-St), it is important to add St at $\sim 100\%$ IB conversion. The selection of the solvent is also critical; coupled product that forms in intermolecular alkylation during St polymerization cannot be avoided when the solvent is a poor solvent (e.g., hexanes/MeCl 60/40 (v/v)) for polystyrene.²²⁹ The formation of coupled product is slower in nBuCl or in MeChx/MeCl 60/40 (v/v) solvent mixture; however, to obtain block copolymers essentially free of coupled product, it is necessary to stop the polymerization of St before completion. Detailed morphological and physical properties of poly(St-b-IB-b-St) triblock copolymer have been reported.201,230-233 The two-step sequential monomer addition method has also been employed to obtain poly(pClSt-b-IB-b-pClSt),^{68,234} poly(indene-b-IB-bindene),²³⁵ poly(*p-tert*-butylstyrene-*b*-IB-*b-p-tert*-butylstyrene),²³⁶ poly((indene-co-pMeSt)-b-IB-b-(indene-co-pMeSt)),²³⁷ poly (pMeSt-b-IB-b-pMeSt),²⁰⁴ and poly(styryl-POSS-b-IB-b-styryl-POSS)²³⁸ copolymers.

When the crossover from the living PIB chain ends is slower than the propagation of the second monomer, for example, α MeSt, *p*MeSt, and vinyl ethers, the final product is invariably a mixture of triblock and diblock copolymers and possibly homo-PIB, which results in low tensile strength and low elongation.²³⁹ This slow crossover can be circumvented by the synthetic strategy shown above, utilizing an intermediate capping reaction of the living PIB with diarylethylenes followed by moderating the Lewis acidity before the addition of the second monomer. This method has been successfully employed for the synthesis of poly(*a*MeSt-*b*-IB-*ba*MeSt),²⁴⁰ poly(*p*MeSt-*b*-IB-*b*-*p*MeSt),²⁴¹ poly(*t*BDMSt-*b*-IB-*bt*BDMSt), and poly(*p*-hydroxystyrene-*b*-IB-*b*-*p*-hydroxystyrene) by subsequent hydrolysis,¹⁹² poly(*t*BuVE-*b*-IB-*b*-*t*BuVE)⁹⁷ and poly(vinyl alcohol-*b*-IB-*b*-vinyl alcohol) by subsequent hydrolysis,²⁴² and poly(CHVE-*b*-IB-*b*-CHVE).⁹⁸ Tensile strength of most of these TPEs as well as triblock copolymers reported above were similar to that obtained with poly(St-*b*-IB-*b*-St) and virtually identical to that of vulcanized butyl rubber, indicating failure in the elastomeric domain.

3.15.9.2.2 Synthesis using coupling agents

Although the synthetic strategy using non(homo)polymerizable monomers has been shown to be highly effective for the synthesis of a variety of di- or triblock copolymers, ABA-type linear triblock copolymers can also be prepared by coupling of living diblock copolymers, a general and useful method in living anionic polymerization.

Several coupling agents for living poly(vinyl ethers) and PaMeSt have been reported in cationic polymerization.116,243,244 Synthetic utilization of non(homo) polymerizable diolefins has been first shown for the coupling reaction of living PIB.^{136,245} Using BDPEP or BDTEP or 2,5-bis [1-(2-furanyl)-1-methylethyl]-furan as coupling agent, a rapid and quantitative coupling reaction of living chain end was achieved, independently of the molecular weight of PIB. Kinetic studies indicated that coupling reaction of living PIB by bis-DPE compounds is a consecutive reaction where the second addition is much faster than the first one. As a result, high coupling efficiency was also observed, even when excess BDPEP was used. This coupling agent is, therefore, best suited for the synthesis of ABA triblock copolymers by coupling of living AB diblock copolymers and has been employed to obtain poly(St-*b*-IB-*b*-St)⁶⁰ and poly(α MeSt-*b*-IB-*b*- α MeSt)¹⁸³ triblock copolymers. For the synthesis of poly(St-b-IB-b-St) triblock copolymers, however, the two-step monomer addition method is superior. Since IB must be added at \leq 95% St conversion to obtain living poly(St-b-IB) with negligible PSt homopolymer contamination, the relatively high concentration of unreactive -St-IB-Cl chain ends causes coupling of living poly(St-b-IB) diblocks to be very slow, incomplete even after 50 h.

3.15.9.3 Block Copolymers with Nonlinear Architecture

Cationic synthesis of block copolymers with nonlinear architectures has been reviewed recently.²⁴⁶ (AB)_n-type star-block copolymers, where *n* represents the number of arms, have been prepared by the living cationic polymerization using three different methods: (1) via multifunctional initiators, (2) via multifunctional coupling agents, and (3) via linking agents.

The synthesis using multifunctional initiators has been the most versatile method due to the abundance of well-defined soluble multifunctional initiators for a variety of monomers. Using trifunctional initiators, many groups have prepared three-arm star-block copolymers such as poly (IBVE-*b*-2-hydroxyethyl vinyl ether)₃,²⁴⁷ poly(IB-*b*-St)₃,^{197,248} and poly(IB-*b*-*p*MeSt)₃²¹⁶ star-block copolymers. The synthesis

of eight-arm poly(IB-*b*-St)₈ star-block copolymers was reported,²⁴⁹ using an octafunctional calix[8]arene-based initiator for the living cationic polymerization of IB followed by sequential addition of St. The synthesis of poly (IB-*b*-*p*-(*p*ClSt))₈ star-block copolymer was also accomplished using the previously mentioned method.²⁵⁰ Recently, multi-arm star-block copolymers of poly(IB-*b*-St)²⁵¹ and poly (IB-*b*-*p*-*tert*-butylstyrene)²⁵² copolymers were synthesized by living cationic polymerization using a hexafunctional initiator, HES, which was prepared by a simple epoxidation of squalene.

Novel arborescent block copolymers comprised of rubbery PIB and glassy PSt blocks (arb-PIB-*b*-PSt) are described by Puskas *et al.*²⁵³ The synthesis was accomplished with the use of arb-PIB macroinitiators, prepared by the use of 4-(2-meth-oxyisopropyl)styrene inimer, in conjunction with TiCl₄. Samples with 11.7-33.8 wt.% PSt exhibited thermoplastic elastomeric properties with 3.6-8.7 MPa tensile strength and 950-1830% elongation.

Linking reaction of living polymers has been employed as an alternative way to prepare star-block copolymers. The synthesis of poly(St-*b*-IB) multiarm star-block copolymers was reported using divinylbenzene (DVB), as a linking agent.^{180,254} The synthesis and mechanical properties of star-block copolymers consisting of 5–21 poly(St-*b*-IB) arms emanating from cyclosiloxane cores have been published.^{173,255} The synthesis involved the sequential living cationic block copolymerization of St and IB, followed by quantitative allylic chain-end functionalization of the living poly(St-*b*-IB), and finally linking of these prearms with SiH-containing cyclosiloxanes (2,4,6,8,10,12-hexamethylcyclohexasiloxane) by hydrosilation. Star-block copolymers of poly(indene-*b*-IB) have been prepared using the previously mentioned method.²⁵⁶

3.15.9.3.1 Synthesis of A_nB_n hetero-arm star-block copolymers

The bis-DPE compounds such as BDPEP or BDTEP could be useful as 'living' coupling agents. It was demonstrated that living PIB reacts quantitatively with these coupling agents to yield stoichiometric amounts of bis(diarylalkylcarbenium) ions. Since diarylalkylcarbenium ions have been shown to be successful for the controlled initiation of reactive monomers such as *p*MeSt, α MeSt, IBVE, and MeVE, A_2B_2 star-block copolymers may be prepared by the above method.

As a proof of the concept, an amphiphilic A_2B_2 star-block copolymer (A = PIB and B = PMeVE) has been prepared by the living coupling reaction of living PIB followed by the chain-ramification polymerization of MeVE at the junction of the living coupled PIB as shown in **Scheme 6**.¹³⁷

While the concept of coupling with ω -furan-functionalized PIB as a polymeric coupling agent has been utilized to obtain AB-type block copolymers, it is also apparent that ω -furan-functionalized polymers can be used as living coupling polymeric precursor for the synthesis of hetero-arm star-block copolymers. The synthesis of poly(IB₃-star-MeVE₃) is shown in **Scheme 7**. Tricumyl chloride is reacted with 2-PIB-furan and after tuning of the Lewis acidity the living linked 2-PIB-Fu initiated the polymerization of MeVE.²⁵⁷

3.15.9.3.2 Synthesis of AA'B, ABB', and ABC asymmetric star-block copolymers using furan derivatives

The strategy for the synthesis of AA'B-type star-block copolymers, where A = PIB(1), A' = PIB(2), and B = PMeVE, is illustrated in Scheme 8.¹⁶² First, quantitative addition of ω -furan-functionalized PIB (A'), obtained from a simple reaction between living PIB and 2-Bu₃SnFu, to living PIB (A) could be achieved in hexanes (Hex)/CH₂Cl₂ 40/60 (v/v) at -80 °C in conjunction with TiCl₄. The resulting living coupled PIB-Fu⁺-PIB' was successfully employed for the subsequent chain-ramification polymerization of MeVE. This technique is unique in the ability to control A and A' block lengths independently.

3.15.9.4 Block Copolymers Prepared by the Combination of Different Polymerization Mechanisms

3.15.9.4.1 Combination of cationic and anionic polymerization

The combination of living cationic and anionic techniques provides a unique approach to block copolymers not available by a single method. Site-transformation and coupling of two homopolymers are convenient and efficient ways to prepare well-defined block copolymers.

Block copolymers of IB and methyl methacrylate (MMA), monomers that are polymerizable only by different mechanisms, can be prepared by several methods. The prerequisite for the coupling reaction is that the reactivities of the end groups have to be matched and a good solvent has to be found for both homopolymers and copolymer to achieve quantitative coupling. Poly(IB-*b*-MMA) block copolymers were synthesized by the coupling reaction of two corresponding living homopolymers, obtained by living cationic and group transfer polymerization (GTP), respectively.²⁵⁸

The synthesis of poly(MMA-b-IB-b-MMA) triblock copolymers has also been reported using the site-transformation method, where $\alpha_{,\omega}$ -dilithiated PIB was used as the macroinitiator.²⁵⁹ The site-transformation technique provides a useful alternative for the synthesis of block copolymers consisting of two monomers that are polymerized only by two different mechanisms. In this method, the propagating active center is transformed to a different kind of active center and a second monomer is subsequently polymerized by a mechanism different from the preceding one. The key process in this method is the precocious control of α - or ω -end functionality, capable of initiating the second monomer. Recently, a novel site-transformation reaction, the quantitative metalation of DPE-capped PIB carrying methoxy or olefin functional groups, has been reported.²⁶⁰ This method has been successfully employed in the synthesis of poly(IB-b-tBMA) diblock and poly(MMA-b-IB-b-MMA) triblock copolymers.²⁶¹ In this technique, however, metalation of DPE-capped PIB requires Na/K alloy, as organolithium compounds are ineffective.

A new synthetic route for the synthesis poly(IB-*b*-*t*BMA) developed by combining living carbocationic and anionic polymerizations involves metalation of 2-polyisobutylenyl-thiophene with *n*-butyllithium in THF at -40 °C. The resulting stable macrocarbanion (PIB-T⁻,Li⁺) was successfully used to initiate living anionic polymerization of *t*BMA yielding poly(IB-*b*-*t*BMA) block copolymers.²⁶²



Scheme 6 Living coupling reaction of living PIB with BDTEP and chain-ramification reaction of MeVE for the synthesis of A₂B₂ star-block copolymer.



Scheme 7 Synthesis of poly(IB₃-star-MeVE₃).



AA'B asymmetric star-block copolymer

Scheme 8 Synthesis of AA'B asymmetric star-block copolymer.

The preparation of poly(IB-*b*-MMA or hydroxyethyl methacrylate) block copolymers has also been accomplished by the combination of living cationic and anionic polymerization. First, DPE-end-functionalized PIB (PIB–DPE) was prepared from the reaction of living PIB and PDDPE, followed by the methylation of the resulting diphenyl carbenium ion with dimethylzinc. PIB–DPE was quantitatively metalated with *n*-butyllithium in THF at room temperature and the resulting macroinitiator could efficiently initiate the living polymerization of methacrylate monomers at –78 °C yielding block copolymers with high block efficiency.²⁶³

3.15.9.4.1(i) Combination of living cationic and anionic ring-opening polymerization

Block copolymers containing crystallizable blocks have been studied not only as alternative TPEs with improved properties but also as novel nanostructured materials with much more intricate architectures compared to those produced by the simple amorphous blocks. Since the interplay of crystallization and microphase segregation of crystalline/amorphous block copolymers greatly influences the final equilibrium ordered states, and results in a diverse morphological complexity, there has been a continued high level of interest in the synthesis and characterization of these materials.

Due to the lack of vinyl monomers giving rise to crystalline segment by cationic polymerization, amorphous/crystalline block copolymers have not been prepared by living cationic sequential block copolymerization. Although site-transformation has been utilized extensively for the synthesis of block copolymers, only a few PIB/crystalline block copolymers, such as poly (L-lactide-*b*-IB-*b*-L-lactide),²⁶⁴ poly(IB-*b*- ϵ -caprolactone (ϵ -CL))²⁶⁵ diblock, and poly(ϵ -CL-*b*-IB-*b*- ϵ -CL)²⁶⁶ triblock copolymers, were reported.

The synthesis of poly(IB-b-pivalolactone (PVL)) diblock copolymers was also recently accomplished by sitetransformation of living cationic polymerization of IB to anionic ring-opening polymerization (AROP) of PVL, as shown in Scheme 9.^{267–269} First, PIB with ω -carboxylate potassium salt was prepared by capping living PIB with DPE followed by quenching with 1-methoxy-1-trimethylsiloxy-propene (MTSP), and hydrolysis of ω -methoxycarbonyl end groups. The ω-carboxylate potassium salt was successfully used as a macroinitiator for the AROP of PVL in tetrahydrofuran, leading to poly(IB-b-PVL) copolymers. The same methodology as mentioned above was applied for the synthesis of poly(PVL-b-IB-b-PVL) triblock copolymers, except that a difunctional initiator, 5-tert-butyl-1,3-bis-(1-chloro-1methylethyl)-benzene (tBuDiCumCl), was used for the polymerization of IB in the first step.

The preparation of novel glassy(A)-*b*-rubbery(B)-*b*-crystalline (C) linear triblock copolymers has been reported where A block is $P\alpha MeSt$, B block is rubbery PIB, and C block is crystalline poly (pivalolactone) (PPVL). The synthesis was accomplished by living cationic sequential block copolymerization to yield living



Scheme 9 Synthesis of poly(IB-b-PVL) copolymer by site-transformation.

poly(α MeSt-*b*-IB) followed by site-transformation to polymerize PVL²⁷⁰ In the first synthetic step, the GPC traces of poly (α MeSt-*b*-IB) copolymers with ω -methoxycarbonyl functional group exhibited bimodal distribution in both RI and UV traces, and the small hump at higher elution volume was attributed to P α MeSt homopolymer. This product was fractionated repeatedly using Hex/ethyl acetate to remove homo-P α MeSt, and the pure poly(α MeSt-*b*-IB) macroinitiator was then utilized to initiate AROP of PVL to give rise to poly(α MeSt-*b*-IB-PVL) copolymer.

Complete crossover from living PaMeSt to IB could be achieved by modifying the living PaMeSt chain end with a small amount of *p*ClaMeSt after complete conversion of aMeSt. The poly(aMeSt-*b*-IB) copolymer carrying ω -carboxylate group, obtained from hydrolysis of ω -methoxycarbonyl group of the block copolymer, was used to initiate AROP of PVL in conjunction with 18-crown-6 in THF at 60 °C, to give rise to poly(aMeSt-*b*-PClaMeSt-*b*-IB-*b*-PVL) copolymer.²⁷¹

Recently, the synthesis of poly(IB-*b*-ethylene oxide) diblock copolymer has been reported.²⁷² In the first step, HO-functional PIB was prepared by hydroboration/oxidation of allyl functional PIB, obtained in the reaction of living PIB and ATMS. The ring-opening polymerization of ethylene oxide was

initiated by the PIB alkoxide anion in conjunction with the bulky phospazene t-BuP₄.

3.15.9.4.1(ii) Combination of living cationic and radical polymerization

The scope of block copolymer synthesis by the combination of two different polymerization techniques has been rapidly expanded with the advent of living/controlled radical polymerization. Although block copolymers such as poly(St-b-IB-b-St) could also be prepared by the combination of cationic and atom transfer radical polymerization,^{273,274} the more interesting examples involve monomers that do not undergo cationic polymerization. For instance, the synthesis of poly(IB-b-methacrylic acid) diblocks, poly(methacrylic acid-b-IB-b-methacrylic acid) triblocks, and three-arm star-block copolymers has been reported by Fang and Kennedy,²⁷⁵ by hydrolysis of the corresponding t-BuMA block copolymers. The hydroxyl functional PIBs, obtained by hydroboration/oxidation of allyl functional PIBs, were reacted with 2-bromoisobutyryl bromide to yield a PIB macroinitiator for the atom transfer radical polymerization (ATRP). Radical polymerization of t-BuMA followed by hydrolysis gave the targeted block copolymers.

Block copolymers containing PMeVE and poly(*tert*-Bu acrylate), poly(acrylic acid), poly(Me acrylate), or polystyrene have been prepared by Bernaerts and Du Prez²⁷⁶ by the use of a novel dual initiator 2-bromo-(3,3-diethoxy-propyl)-2-methylpropanoate. In the first step, the living cationic homopolymerization of MeVE is performed with the acetal end group of the dual initiator as initiating site or by the ATRP homopolymerization of *tert*-butyl acrylate from the bromoisobutyrate group of the dual initiator. In the second step in the preparation of block copolymers, well-defined PMeVE-Br and polyp-tBA-acetal homopolymers were employed as macroinitiators, respectively, in the ATRP of several monomers and cationic polymerization of MeVE.

3.15.10 Branched and Hyperbranched Polymers

The synthesis of branched polymers by cationic polymerization of vinyl monomers has been reviewed recently;²²¹ therefore these will be briefly considered here. Star-shaped or multiarm star (co)polymers can be prepared by three general methods:

- 1. Multifunctional initiator method
- 2. Multifunctional terminator method
- 3. Polymer linking method

In the first case, the arms are grown from a single core with a given number of potentially active sites or a well-defined multifunctional initiator. In contrast to anionic multifunctional initiators, well-defined soluble multifunctional cationic initiators are readily available. These multifunctional initiators with three to eight initiating sites have been successfully applied for the synthesis of three- to eight-arm star homo- and block copolymers of vinyl ethers, St and St derivatives, and IB. For example, six-arm star polystyrenes were prepared using initiator with six phenylethylchloride-type functions emanating from a central hexa-substituted benzene ring.²⁷⁷ By subsequent end functionalization, a variety of end-functionalized A_n or (AB)_n (see above) star-shaped structures can also be obtained.

In the second and third cases, first the arms are synthesized and then linked together using either a well-defined multifunctional terminator or a difunctional monomer leading to a cross-linked core. Well-defined star-branched polymers have been obtained by utilizing multifunctional coupling agents with the nucleophilic functions well separated to avoid steric hindrance. For example, high yields were reported in the synthesis of a three- or four-arm star polymers by reacting short poly (IBVE) living polymers with a tri- or tetrafunctional silyl enol ether as multifunctional terminator.²⁷⁸

Difunctional monomers such as DVB or divinyl ether have been found to be efficient in the synthesis of star (co)polymers having a cross-linked core from which homopolymer or block copolymer arms radiate outwards. However, so far only 'core last' method has been reported in cationic polymerization. This method is particularly suited to prepare stars with many arms. The average number of arms per molecule is a function of several experimental and structural parameters.

Graft copolymers by cationic polymerization may be obtained by the 'grafting from' and 'grafting onto' methods and by (co)polymerization of macromonomers. For example, PIB with pendant functionalities could be prepared by copolymerization of IB with a functional monomer such as bromomethylstyrene or chloromethylstyrene in CH_2Cl_2 at -80 °C with BCl₃. An alternate method to obtain initiating sites along a PIB backbone involves the copolymerization with *p*-MeS followed by selective halogenation.²⁷⁹ In subsequent initiation of 2-methyl-2-oxazoline, water-soluble amphiphilic graft copolymers have been obtained.²⁸⁰

Highly branched, the so called 'hyperbranched', macromolecules have recently attracted interest, due to their interesting properties, which closely resemble those of dendrimers. Vinyl monomers with pendant-initiating moieties, for example, 3-(1chloroethyl)-ethenylbenzene, have been reported to give rise to hyperbranched polymers in a process termed 'self-condensing vinyl polymerization'.²⁸¹ Hyperbranched PIBs have been synthesized by cationic copolymerization of 4-(2-methoxyisopropyl)styrene and IB.²⁸² Using a similar approach, the preparation of arborescent block copolymers of IB and St (arb-PIB-*b*-PSt) has also been reported (see above).²²⁸

3.15.10.1 Surface-Initiated Polymerization – Polymer Brushes

Polymer brushes can be generated by the 'grafting to' and 'grafting from' techniques. The 'grafting to' technique, where a living polymer or a suitable end-functionalized polymer is reacted with a reactive substrate, yields limited surface grafting density due to steric hindrance. In contrast, surface-initiated polymerization from a self-assembled initiator on the surface results in high grafting density and film thickness that increases linearly with molecular weight. PSt brushes were prepared on flat silicate substrates by cationic polymerization by Zhao and Brittain.²⁸³ The polymerization of St was initiated from self-assembled monolayers (SAMs) of the cationic initiators, 2-(4-(11-triethoxysilylundecyl)phenyl)-2-methoxypropane in conjunction with TiCl₄. PIB brushes could also be obtained on flat silica surfaces by a similar method employing SAMs of 3-(1-chlorodimethyl-silylmethyl)ethyl-1-(1-chloro-1-methyl) ethylbenzene.²⁸⁴ Initiation from macroscopic surfaces requires the addition of a sacrificial soluble initiator to control the molecular weight of the polymer brush; however, it results in a large amount of unbound polymer. A sacrificial initiator is not necessary when the initiation is from nanoparticles with a large surface area as demonstrated for the surface-initiated polymerization of IB from SAMs on ~ 20 nm silica nanoparticles.²⁸⁵ Due to the high surface area and grafting density $(3.3 \text{ chains nm}^{-1})$, ~4000 polymer chains of $M_{\rm n} = 65000$ were linked to each nanoparticle resulting in \sim 220 nm total particle diameter.

3.15.11 Conclusions

Cationic polymerization is of great theoretical and practical importance. Worldwide production of polymers by cationic vinyl polymerization is estimated at ~ 2.5 million metric tons per year.²⁸⁶ Since the discovery of living cationic systems, cationic polymerization has progressed to a new stage where the synthesis of designed materials is now possible.

The practical importance of cationic macromolecular engineering is wide ranging. Commercialization of new technologies based on living cationic polymerization has already begun. Allyl telechelic curable PIB elastomers (Epion) and poly(St-*b*-IB-*b*-St) triblock copolymer TPEs (Sibstar) are produced by Kaneka Corporation (Japan). Boston Scientific Corp. also commercialized the synthesis of poly(St-*b*-IB-*b*-St) (Translute), which it employs as a polymer drug carrier for paclitaxel-eluting coronary stent systems. Due to recent accomplishments in the simple and economic synthesis of functional PIBs, further industrial developments are predicted in the field of segmented multiblock copolymers (e.g., thermoplastic polyurethanes), especially in applications where transparent, flexible, thermally, chemically, and oxidatively stable, biocompatible, and biostable coatings and adhesives are important.

The rapid advances in this field will lead to useful new polymeric materials and processes that will greatly increase the economic impact of cationic macromolecular engineering.

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Cationic Polymerization of Nonpolar Vinyl Monomers

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525

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Science Series E: Applied Sciences; Puskas, J. E., Ed.; Kluwer Academic

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3.16 Cationic Polymerization of Polar Monomers

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3.16.1	Introduction	527
3.16.2	General Aspects	528
3.16.2.1	Monomer Structure and Reactivity	528
3.16.2.2	Initiators	528
3.16.2.3	Iodine-Mediated Polymerization	529
3.16.2.4	Stereospecific Polymerization	529
3.16.3	Living Cationic Polymerization	529
3.16.3.1	Long-Lived Species	529
3.16.3.2	Living Cationic Polymerization of Alkyl Vinyl Ether: The Breakthrough	530
3.16.4	Design of Initiating Systems for Living Polymerization	530
3.16.4.1	Methods of Living Cationic Polymerization	530
3.16.4.1.1	Nucleophilic counteranion with a weak Lewis acid	530
3.16.4.1.2	Nucleophilic counteranion with a strong Lewis acid and an additive	530
3.16.4.1.3	Other initiating systems	531
3.16.4.2	Early Development of Vinyl Ethers	531
3.16.5	Recent Developments in Living Polymerization	532
3.16.5.1	New Initiating Systems for Vinyl Ethers	533
3.16.5.1.1	Base-assisting living systems with various metal halides	533
3.16.5.1.2	Ultrafast living polymerization	534
3.16.5.1.3	Ligand design for living polymerization	534
3.16.5.1.4	Copolymerization of aromatic aldehydes with vinyl ethers	535
3.16.5.1.5	Heterogeneously catalyzed living polymerization	536
3.16.5.1.6	Metal halide-free system	536
3.16.5.2	New Initiating Systems for Styrene Derivatives	536
3.16.6	New Monomers	538
3.16.6.1	Naturally Occurring Monomers and Their Derivatives	538
3.16.6.2	Vinyl Ether Derivatives	540
3.16.6.3	Diene Monomers	541
3.16.7	Sequence or Shape-Regulated Functional Polymers	542
3.16.7.1	Block Copolymers	542
3.16.7.1.1	Di- and triblock copolymer synthesis via sequential living polymerization	542
3.16.7.1.2	Control of molecular weight distribution and sequence in block copolymer synthesis	544
3.16.7.2	Star-Shaped Polymers	545
3.16.7.2.1	Well-defined functional star polymers	545
3.16.7.2.2	Selective synthesis of star-shaped polymers with narrow molecular weight distributions	547
3.16.7.2.3	Metal nanoparticles stabilized by star-shaped polymers	548
3.16.8	Stimuli-Responsive Polymers	548
3.16.8.1	Thermoresponsive Poly(VE)s with Oxyethylene Pendants and Related Poly(VE)s	548
3.16.8.2	Other Stimuli-Responsive Poly(VE)s	551
3.16.8.3	Stimuli-Responsive Block Copolymers	552
References		554

3.16.1 Introduction

Most of the polar monomers for cationic polymerization have an electron-donating group with a hetero atom whose nonbonding electron pair is delocalized toward the double bond directly or through p orbitals on a phenyl ring. This delocalization enhances the electron density of the double bond in a monomer. Thus, those monomers are classified as highly reactive ones in cationic polymerization. In addition, an electron-donating group stabilizes the growing carbocation; hence high polymers are readily obtained from reactions of polar monomers. The field of cationic polymerization of vinyl monomers is apparently well established, since it has a long history, in which considerable studies had been performed from different aspects.^{1–4} However, almost no progress was made in controlling the polymerization reaction until the 1960s. This difficulty even with polar monomers made polymer chemists believe that suppressing side reactions, such as β -proton elimination, in cationic process would be impossible, since carbocation is inherently unstable and highly active.

The 'common sense' was drastically changed by the discovery of long-lived cationic species in the polymerization of *p*-alkoxystyrene in the late 1970s.^{5,6} Then, long-lived species

were also observed in the polymerization of vinyl ethers (VEs)⁷ and isobutene (IB).⁸ It was in the early 1980s that the first example of living polymerization of alkyl VEs was reported by Higashimura and Sawamoto^{9,10} After this breakthrough, living polymerization of IB was achieved by Faust and Kennedy.^{11,12} Thus, cationic polymerization of polar monomers played a pivotal role in the development of living process. These findings led to intensive investigations on catalyst development for living polymerization and synthesis of well-defined functional polymers.^{13–17}

In the 1990s, precision synthesis of a new class of functional polymers became a main issue, as the catalyst development lost its momentum. For example, various functional block copolymers and star-shaped polymers were prepared from VEs.^{18,19} Of special note is the recent great progress in the precision synthesis of stimuli-responsive polymers of VEs.¹⁹

Living cationic polymerization came to be considered as a tool for preparing well-defined functional polymers around 2000. This fixed image was broken by the recent development of initiating systems for living polymerization of VEs and styrene (St) derivatives.²⁰ Appropriate combinations of simple bases and Lewis acids provided various new systems. A range of metal halides can be employed for living polymerization, in addition to conventional counterparts. The wide selection of Lewis acids permitted characteristic living or controlled polymerization processes, such as ultrafast living polymerization, heterogeneous living polymerization, alcohol-initiated reaction, and controlled alternating copolymerization of an aldehyde derivative with a VE.

3.16.2 General Aspects

3.16.2.1 Monomer Structure and Reactivity

Typical examples of polar monomers in cationic polymerization are VEs, α - or β -methylvinyl ethers (α - or β -MVEs), St derivatives, and *N*-vinylcarbazole (NVC), as shown in **Figure 1**. The reactivity of monomers generally decreases in the following order: NVC>VEs>Sts>alkenes. For St derivatives, a monomer shows higher reactivity if its Hammet's value is negative and smaller. This trend is predicted from the chemical shift in ¹³C NMR of the β -carbon of a monomer. The smaller the chemical shift, the higher the electron density of the double bond and hence the higher the reactivity. For example, a smaller chemical shift is observed with a monomer with an electron-donating group.

The reactivity of alkyl VEs (CH₂=CHOR, R: alkyl) is affected by the structure of their alkyl groups, increasing as the alkyl substituent becomes bulkier: $CH_3 < CH_2CH_3 < CH$ (CH₃)₂ < C(CH₃)₃.²¹ This is attributed to the inductive effect of alkyl groups, in other words, their electron-donating power. The resonance effect would also be important for determining the reactivity. A bulkier substituent is likely to interfere with the delocalization of the electrons on the ether oxygen; hence the resulting carbocation becomes unstable and more active. For functionalized VEs, the reactivity is greatly influenced by the pendant structure even when the functional group is apart from the double bond. For instance, the polymerization rates of typical monomers vary in the following order: $CH_2=CHO(CH_2CH_2O)_nCH_2CH_3>CH_2=CHOR$ (R: alkyl) > $CH_2=CHOCH_2CH_2OCOCH_3$.^{22,23} It is considered that this difference was caused by an intramolecular solvation of the growing active end or Lewis acids with pendant groups.

3.16.2.2 Initiators

The abovementioned polar monomers can be polymerized using a variety of acidic compounds, such as protonic acids (e.g., CF₃COOH, CF₃SO₃H), metal halides (e.g., BF₃OEt₂, SnCl₄, EtAlCl₂), cation-forming salts (e.g., Ph₃C⁺ SnCl₅⁻), halogens (e.g., I₂, IBr), and solid acids (e.g., Al₂(SO₄)₃–H₂SO₄). In general, compounds with weaker acidity can be used for VEs, because of their high reactivity. Most commonly used catalysts are metal halides in recent years.^{20,24}

There have been numerous reports on cationic polymerization using metal halides. However, no clear-cut order of catalyst activity for cationic polymerization was indicated, although it is usually considered that a metal halide with higher Lewis acidity has high polymerization activity. A part of the reason would be that there are many ways to determine Lewis acidity, leading to different orders. The following are some results of Lewis acidity by several methods, which showed variance with their orders.²⁵

1. Thermodynamic method (heat of solution in a basic solvent such as an ether)

 $AlCl_3 > TiCl_4 > SnCl_4 > FeCl_3 > ZnCl_2$

2. Hammett indicator

$$AlBr_3 > AlCl_3 > FeCl_3$$

$$SnCl_4 > SbCl_5 > SbCl_3$$

3. Complex formation with a ketone (wave number shift in infrared (IR) spectra)

 $AlBr_3 \gg FeCl_3 > AlCl_3 > SnCl_4 > TiCl_4 > BF_3 > ZnCl_2 > HgCl_2$

Comparison with catalyst activity for Friedel-Crafts-type reactions is a practical way,²⁵ since there are also many





studies. However, it is still difficult to discuss in detail, although an idea of a general trend can be acquired.

 Formation of an aromatic ketone (toluene to *p*-methylacetophenone)

$$\begin{array}{l} AlCl_3 > SbCl_5 > FeCl_3 > TeCl_2 > SnCl_4 > TiCl_4 > TeCl_4 \\ > BiCl_3 > ZnCl_2 \end{array}$$

- $\begin{array}{l} AlBr_3 > FeBr_3 > SbBr_3 > ZnBr_2 > TiBr_4 > TeBr_4 > MoBr_4 \\ > WBr_5 > HgBr_2 > SnBr_4 \end{array}$
- 5. Isomerization (cyclohexane to methylcyclopentane)

 $\begin{array}{l} AlBr_3 > GaBr_3 > GaCl_3 > FeCl_3 > SbCl_5 > ZrCl_4 \\ > BF_3, BCl_3, SnCl_4, SbCl_3 \end{array}$

6. Deuteration on a phenyl ring with DBr

 $AlBr_3 > GaBr_3 > FeBr_3 > BBr_3 > SbBr_3 > TiBr_4 > SnBr_4$

On the other hand, there are few examples of determining activity orders based on the results of real polymerization reactions. A qualitative order was presented with IB polymerization at -78 °C: BF₃>AlBr₃>TiCl₄>TiBr₄>BCl₃>BBr₃>SnCl₄.²⁶ A more recent example was a thorough investigation on VE polymerization in the presence of an added base (see details in Section 3.16.5.1.1). The activity decreased in the following order: GaCl₃ ~ FeCl₃>SnCl₄>InCl₃>ZnCl₂>AlCl₃~HfCl₄~ZrCl₄> EtAlCl₂>BiCl₃>TiCl₄>>SiCl₄~GeCl₄~SbCl₃.²⁰ This study established a novel index of Lewis acidity for metal halides, and suggested that oxophilicity and chlorophilicity of the electron-deficient central element in a metal halide are decisive factors for determining catalyst activity.

3.16.2.3 Iodine-Mediated Polymerization

Since there are many acidic compounds available as catalysts for cationic polymerization, as mentioned above, it is difficult to review basic investigations with all catalysts because of space limitation. Here, only polymerization with iodine is highlighted, because it is closely related to the production of long-lived species in the polymerization of polar monomers with I₂. Reports on the mechanism of polymerization using iodine appeared in the 1950s. Eley *et al.*^{27,28} proposed π -complex formation of *n*-butyl VE and I₂, which was confirmed by ultraviolet (UV) and IR. Ledwith and Sherrington²⁹ found that a diiodo adduct was generated on mixing a VE with I₂.

The formation of the diiodo adduct was reported with St even in the 19th century. Trifan and Bartlett³⁰ reported St polymerization using I₂ in the 1950s. Giusti and Andruzzi³¹ examined St polymerization with I₂ in 1,2-dichloroethane at 30 °C, and demonstrated that hydrogen iodide (HI) was generated by the elimination of the diiodo adduct of St. It was proposed that the eliminated HI, in turn, added St, and polymerization reaction started by the activation of the resulting C–I bond by I₂. It is interesting that a similar mechanism as that for living polymerization of VEs was already proposed over a decade ago.

3.16.2.4 Stereospecific Polymerization

It has been years since the evidence of stereoregularity in cationic polymerization was reported, that is, the formation of a crystalline polymer in the polymerization of isobutyl VE (IBVE) using BF₃OEt₂ at -78 °C.³² However, the structure of this polymer was not characterized at that time. Later, it was demonstrated that the stereoregularity of that polymer was not as high as expected.³³ Okamura et al.³⁴ reported in 1958 that crystalline poly(IBVE) was obtained even in a homogeneous system in a nonpolar solvent. In the 1950s and 1960s, the possibility of stereospecific polymerization of VEs was examined using various catalysts such as metal sulfate-sulfuric acid complexes,^{35–39} Ziegler-type catalysts,^{40,41} and some metal oxides (e.g., CrO₃).⁴² However, it was not until recently that great progress was made by soluble titanium catalysts with bulky substituents. TiCl₂(OAr)₂ induced stereospecific polymerization to give poly(VE)s with high meso diad values $(\sim 90\%)$.⁴³⁻⁴⁵ This catalyst system is the first example of stereoregulation by the precise design of catalyst ligands in homogeneous systems in cationic polymerization. Other recent studies in homogeneous systems include polymerization using metallocene catalysts with Group 4 metals⁴⁶⁻⁴⁸ and titanium catalysts with tridentate triamine ligands.⁴⁹ Although many attempts have been made, simultaneous achievement of stereoregularity and livingness has never been achieved. A recent study on polymerization of IBVE using iron(II) sulfate, FeSO₄, indicated the possibility of stereospecific living cationic polymerization (see Section 3.16.5.1.5).

3.16.3 Living Cationic Polymerization

3.16.3.1 Long-Lived Species

This section briefly reviews critical researches on controlled polymerization of polar monomers, conducted in the 'pre-living' era. It was then known that higher molecular weight polymers were obtained when a polar solvent was used. This fact suggested that a more dissociated counteranion against the growing carbocation is favorable for smooth propagation. Thus, Higashimura and co-workers examined various acid catalysts for cationic polymerization of St. The survey provided critical clues to design a living polymerization system. The first clue was polymerization with acetyl perchlorate in dichloromethane. In this polymerization, a polymer with a bimodal molecular weight distribution (MWD) was obtained.⁵⁰ The amount of higher and lower molecular weight fractions changed depending on the solvent polarity. The results indicated that polymerization proceeded independently from different types of growing chain ends. Encouraged by this event, polymerization of pmethylstyrene (pMSt) and p-methoxystyrene (pMOS) was also studied using various catalysts. For these monomers, iodine gave polymers with bimodal distributions.⁵¹

Since it was considered less difficult to suppress side reaction in the *p*MOS polymerization due to the stabilization of the growing carbocation, cationic polymerization of *p*MOS was investigated in detail using iodine.⁵ The MWDs of product polymers became unimodal in the polymerization in CCl₄ at 0 °C. A nearly linear relationship was observed between the peak molecular weight of the product polymers and monomer conversion, indicative of polymerization mediated by long-lived active species. At -15 °C, the M_n of product polymers increased in almost direct proportion to monomer conversion after the second feed of *p*MOS.⁶ Moreover, block copolymers with IBVE were obtained under similar conditions, although blocking efficiency was low.⁶ Subsequently, the formation of long-lived growing species in the polymerization of VEs using iodine was reported.⁷ These results were the eye-opening reports and the first clear indication of a high possibility of living cationic polymerization of vinyl monomers.

For comparison, controlled cationic polymerization of IB was also described. Kennedy et al. 52 found that almost no chain transfer occurred in the polymerization of IB with BCl3 in CH₂Cl₂ in the presence of a slight amount of water at -78 °C under high vacuum. Combined with cumyl chloride, BCl₃ induced quantitative polymerization of IB, yielding product polymers with C-Cl bonds at their terminal chain ends.⁵³ Chain transfer reaction was significantly suppressed in the polymerization of α -methylstyrene (α MSt) using cumyl chloride/BCl₃ in CH₂Cl₂/methylcyclohexane (MCH) (25:75) at -50 °C, especially when monomer was added incrementally.⁸ As a result, the product polymers had relatively narrow MWDs ($M_w/M_p = 1.3-1.6$) and the molecular weight increased linearly with monomer conversion in the early stage of the polymerization. In the same paper, an equilibrium between formation and dissociation of the terminal C-Cl growing bonds was first proposed. Better results were obtained in the polymerization with cumyl chloride/TiCl₄ in hexane/CH₃Cl (60:40).⁵⁴ A linear increase in the molecular weight of product polymers against monomer conversion was observed. This first example of controlled (quasiliving) polymerization of IB was a stepping stone to living polymerization of IB.

3.16.3.2 Living Cationic Polymerization of Alkyl Vinyl Ether: The Breakthrough

The system that allowed controlled polymerization of VEs still had a drawback. With the I₂-catalyzed system, slow initiation (addition of a vinyl group with I₂) was responsible for a broad MWD. In order to enhance the rate of the initiating step, hydrogen iodide was employed as an initiator with I₂ as an activator. This combination, in turn, allowed fast quantitative initiation, leading to ideal living cationic polymerization of alkyl VE in hexane at -15 °C (Scheme 1).^{9,10} This system permitted efficient synthesis of homopolymers and block copolymers with very narrow MWDs ($M_w/M_n < 1.1$) for the first time. First, rapid and quantitative addition of HI with the monomer proceeds.⁵⁵ The resulting adduct by itself is not capable of initiating polymerization at least at low temperature. The C–I bond of the adduct is then cleaved by iodine, and the generated carbocation initiates polymerization (Scheme 1).

The stabilization of a counteranion was a key to eliminate chain transfer reaction with the BCl₃ system for IB polymerization. A tertiary ester was used as an initiator for polymerization of IB using BCl₃. Cumyl acetate and 2,4,4-trimethylpentyl acetate induced living polymerization in CH₂Cl₂/hexane at -30 °C.^{11,12}

3.16.4 Design of Initiating Systems for Living Polymerization

3.16.4.1 Methods of Living Cationic Polymerization

Two important requirements have to be fulfilled to achieve living polymerization.²⁴ First, the initiation reaction must be quantitative and fast enough, relative to propagation. To this end, an adduct of a monomer with a protonic acid (**Figure 2**) is generally used as an initiator (cationogen) for VEs, since the resulting cation is similar in structure to the growing chain end. For the same reason, simple protonic acids are often effective for living polymerization. Another requirement is low concentration of unstable free carbocations. The general method of reducing carbocations is to exploit equilibria between active (ionic) and dormant (covalent) species with a hetero atom (**Scheme 2**). The methods of establishing such equilibria can be categorized into two general methods, as will be described below.

3.16.4.1.1 Nucleophilic counteranion with a weak Lewis acid This method is for generating carbocation from a dormant carbon–halogen (often chloride) bond, activated with a weak Lewis acid, such as iodine and zinc halides (Scheme 3). Suitably nucleophilic counteranions capture ionic species fast and effectively to convert them into the dormant counterparts. This method is suitable for polymerization of active monomers including VEs and *p*-alkoxystyrenes.

3.16.4.1.2 Nucleophilic counteranion with a strong Lewis acid and an additive

Control of polymerization can be difficult with a nucleophilic counteranion if a strong Lewis acid is used. An active catalyst would produce more free ionic species, some of which cause side reactions. The addition of an appropriate additive such as a Lewis base and a quaternary ammonium salt into a reaction with a strong Lewis acid shifts the equilibrium to induce living polymerization.

Figure 2 Typical initiators (cationogens) for living cationic polymerization.







Scheme 1 Living cationic polymerization of VEs with HI/l₂.



Scheme 3 Living polymerization using a weak Lewis acid and a nucleophilic counteranion.



Scheme 4 Living polymerization using a strong Lewis acid and an added base.

3.16.4.1.2(i) Added base (Lewis base)

Combinations of various Lewis acids and Lewis bases including esters and ethers permit living polymerization. The role of an added base is to moderate the acidity of a Lewis acid catalyst and to stabilize the growing carbocation by solvation, and thus a suitable equilibrium between the ionic and dormant species is achieved (Scheme 4). A feature of this system is to produce more stable growing ends, compared to other methods. It should also be noted that this system is applicable to a range of monomers: VEs, St derivatives with various reactivities, as well as IB can be polymerized in a living fashion using various types of base-assisting systems.

3.16.4.1.2(ii) Added salt

The addition of a quaternary ammonium salt attains an appropriate equilibrium between the active and dormant species for living polymerization (Scheme 5). The anions of ammonium salts are not necessarily the common ions of the counteranions generated from the initiator and the dormant bond. However, nucleophilic anions (usually halide anions) are required for achieving living polymerization. For example, less nucleophilic anions such as ClO_4^- have no effect on controlling

(M: metal; X, X': halogen; R': alkyl group)

Scheme 5 Living polymerization using a strong Lewis acid and an added salt.

polymerization. Tetraalkylammonium salts ($R_4N^+X^-$, X: Cl, Br, I) are used as added salts, because of solubility in organic solvents. This system is effective for VEs and St derivatives, and is the first initiating system that produced polystyrene with very narrow MWD in cationic polymerization.

3.16.4.1.3 Other initiating systems

A small amount of protons, often generated from the reaction of a Lewis acid and adventitious water in a reaction mixture, may induce undesired and less controlled polymerization. This side reaction is prevented by a proton trap such as 2,6-di-*tert*butylpyridine (DTBP). The nitrogen atom of DTBP captures a proton but is not able to interact with carbocation due to the bulky substituents adjacent to the nitrogen.

A combination of a sulfide and a strong protonic acid induces living polymerization. In this system, a sulfonium salt is produced from a sulfide and the growing carbocation shortly after a protonic acid initiates polymerization. The sulfonium salts are dormant species, which change reversibly into free ionic species (Scheme 6). This initiating system is available only for VE polymerization.

3.16.4.2 Early Development of Vinyl Ethers

The success of the HI/I₂ system suggested the effectiveness of a combination of a nucleophilic counteranion and a relatively mild Lewis acid for living polymerization. Thus, cationic polymerization of alkyl VEs was examined using various protonic acids (or an adduct of a VE with a protonic acid) with weak Lewis acids. Living polymerization was achieved using hydrogen halides^{56–60} and acetic acids^{61,62} in conjunction with zinc



Scheme 6 Living polymerization in the presence of a sulfide.

halides,^{56–60,62} zinc trifluoroacetates,⁶¹ and SnBr₄.⁶⁰ Strong Lewis acids tend to induce nonliving polymerization even if a nucleophilic counteranion is employed, as mentioned above. Living polymerization was also achieved with some strong Lewis acids in the presence of additives, such as Lewis bases and organoammonium salts.

Base (nucleophile)/strong Lewis acid initiating systems for living polymerization were first reported by Aoshima and Higashimura. Organoaluminum halides (Et_xAlCl_{3-x}) combined with esters such as ethyl acetate^{63,64} or cyclic ethers such as 1,4-dioxane^{65,66} permitted living cationic polymerization of VEs in nonpolar solvents such as hexane or toluene at or above 0 °C to yield well-defined polymers with low polydispersity. As a catalyst, EtAlCl₂ or Et_{1.5}AlCl_{1.5} was most suitable for living polymerization. An important feature of this system is that it allows living polymerization of alkyl VEs even at 70 °C,⁶⁴ where it is difficult to obtain polymers from conventional (nonliving) polymerization. Since esters were considered chain transfer agents for cationic polymerization at that time, the living systems in the presence of esters upset conventional wisdom on the field.

The development of various initiating systems permitted living polymerization of not only alkyl VEs but also those with functional groups (Figure 3). In addition to various alkyl VEs, monomers with an ester,^{67,68} an oxyethylene,^{23,69} or an imide^{70,71} side group were polymerized in a living fashion. Hydrolysis or deprotection of pendant functional groups led to well-defined polymers with hydroxy, carboxy, or amino groups (Figure 3).

A tetraalkylammonium salt is able to control equilibrium between the active and dormant species.^{60,72,73} Living polymerization of alkyl VEs was achieved using $SnCl_4$ in conjunction with *tetra-n*-butylammonium chloride in CH_2Cl_2 at -15 °C.⁶⁰ The ammonium salt suppressed the ionization of dormant species, keeping the concentration of ionic species extremely low. Sulfides were also effective for controlling polymerization of VEs using a strong protonic acid as an initiator.^{74,75} For example, triflic acid and dimethyl sulfide (Me₂S) induced

< Alkyl VEs >

living polymerization in CH_2Cl_2 at -40 °C. This system requires no metal halide as a catalyst. Me₂S reacts with the growing carbocation to form a sulfonium salt, which acts as a dormant species.

3.16.5 Recent Developments in Living Polymerization

Various initiating systems were available for polymerizing not only nonpolar monomers such as alkyl VEs and alkyl-substituted Sts but also polar functional monomers. Most Lewis acid catalysts used for living polymerization were metal halides. Thus, polymerization of some monomers with polar functional groups, such as esters and nitrogen-containing functions, was significantly retarded or inhibited,⁷⁶ because of the strong interaction of an electron-rich moiety in a polar group with the electron-deficient central metal of a metal halide. This drawback was a hurdle in the development of various functional polymers from polar monomers. Therefore, more efficient and active initiating systems for functional monomers were eagerly awaited. However, precision synthesis of various functional polymers became a growing interest, instead of catalyst development.

There is much in common between catalysts for cationic polymerization and the Friedel–Crafts and its analogous reactions.² Although the field of Friedel–Crafts reactions has a long history, exploring new catalysts is still a vital area. The purpose of those studies is primarily to realize acylation and/or reactions of substrates with hetero atoms, such as heterocyclic compounds, using a catalytic amount of a Lewis acid. Since a conventional acid, such as AlCl₃, forms the complex with a product and/or a substrate, an equimolar amount of the acid to a substrate is required. Consequently, the main product is often accompanied by significant by-products in industrially used Friedel–Crafts processes. Thus, reactions with various Lewis acids and solid acids^{77–79} have been reported recently.

Metal triflates were the first successful Lewis acids for the catalytic processes of acylation. Efficient acylation was achieved

СН. —СН

$$< \text{Functional VEs} >$$

$$< \text{Functional VEs} >$$

$$CH_2 = CH \qquad CH_2 = CH \qquad CH$$

with a catalytic amount (1–10%) of triflates of Ti,⁸⁰ Hf,^{81,82} Sc,^{83,84} and lanthanides.⁸⁴ Very recently, even metal halides were shown to be effective for acylation and/or alkylation of heterocyclic compounds if those have heavier transition or main-group metals as central metals, including Rh,⁸⁵ Ir,⁸⁵ In,^{86,87} Pt,^{85,88} and Bi.⁸⁹ Thus, weaker interaction of central metals with the carbonyl group or polar functional groups is critical to catalytic processes in addition to sufficient reactivity. This progress suggested that more reactive catalysts could be developed for cationic polymerization of functional mono-

3.16.5.1 New Initiating Systems for Vinyl Ethers

polymerization was losing its appeal in the late 1990s.

3.16.5.1.1 Base-assisting living systems with various metal halides

mers. However, catalyst development for living cationic

The recent rejuvenation of living cationic polymerization of polar monomers started with new polymerization systems for VEs.^{20,90} From the background described above, various metal halides with several main group elements and transition metals were examined, especially in the presence of a Lewis base. The first unexpected example was polymerization of a VE with SnCl₄ in conjunction with an added base.⁹¹ The polymerization was examined using the adduct of IBVE with HCl (IBVE-Cl)/SnCl4 (or 1-(isobutoxy)ethyl acetate (IBEA)-EtAlCl₂/SnCl₄) in toluene at 0 °C in the presence of ethyl acetate.⁹¹ The reaction was accelerated by a factor of $10^3 - 10^5$, depending on the monomer, compared to the system with EtAlCl₂. For example, IBVE polymerization proceeded quantitatively without an induction period within only 2 min, whereas the reaction with EtAlCl₂ took about 2 days under similar conditions. Furthermore, the polymerization was well controlled, giving a polymer with an extremely narrow MWD ($M_w/M_n < 1.05$). This initiating system also catalyzed fast living polymerization of a polar functional VE with an ester or an azo moiety. The polymerization rate for those O- or N-containing monomers was 10³ times larger than the rates using the conventional Et_xAlCl_{3-x} (x = 1 or 1.5)/added base initiating systems.⁹¹

The difference in reactivity is most likely to result from the difference in the hardness of the Lewis acids. Although both SnCl₄ and Al-based Lewis acids are classified as hard acids based on the Hard and Soft Acids and Bases (HSAB) principle,^{92,93} Al-based Lewis acids are harder than SnCl₄.⁹⁴ With basic ingredients in the reaction system, esters or ethers are hard bases, and chloride anions, generated from the growing ends, are around the border-line between hard and soft. Thus, SnCl₄ would interact more weakly with an added base and polar functional groups, compared to its aluminum counterpart, and thus it is easier for SnCl₄ to attack the relatively soft chlorine atom at the growing end. The stability of a counterion was another decisive factor for the high reactivity of the SnCl₄ system. A stable hexa-coordinated anion

with one additional base coordinated is generated from SnCl_4 after it extracts the chlorine atom of the growing end (Scheme 7). On the other hand, an unstable counterion with the tetrahedral structure forms from AlCl_3 .^{90,95} The formation of the stable anion is responsible for the shift of the active–dormant equilibrium toward the active side to raise the concentration of ionic species, leading to fast polymerization. Furthermore, molecular orbital calculations using Gaussian 03 indicated that the Sn system had the activation energy ΔE lower by 10 kcal mol⁻¹ than the Al system.⁹⁵

SnCl₄ is a well-known and conventional catalyst in cationic polymerization, and numerous studies on its polymerization behavior have been reported. Therefore, it is surprising that its combination with an added base exhibited a very different reaction behavior. Thus, investigation extended to other metal halides and monomers that had not been considered suitable for living or controlled cationic polymerization. SnCl₄ was broadly applicable to living polymerization of various monomers: VEs with polar side groups,^{90,91,95} cyclic enol ethers,⁹⁶ and α -MVEs⁹⁷ (see also polymerization of St and its derivatives in Section 3.16.5.2). In the polymerization of α -MVEs, for example, frequent elimination of five acidic B-protons hampered living polymerization under conventional conditions. In fact, EtAlCl₂ produced oligomers at 0 °C even in the presence of an added base.⁹⁷ In sharp contrast, polymers were obtained in good yield at 0 °C using SnCl4, although the molecular weight was low. A lower reaction temperature was found to be good for the precise control of the reaction: living polymerization was achieved with SnCl₄ in the presence of ethyl acetate.⁹⁷ This base-assisting system was also effective for living cationic polymerization of a nonpolar monomer. Living polymerization of tetrahydroindene (THI, i.e., bicyclo-[4.3.0]-2,9-nonadiene) was achieved using SnCl₄ in toluene in the presence of ethyl acetate at -78 °C, producing polymers with narrow MWD $(M_w/M_p = 1.1-1.4)$.⁹⁸ Thus, the SnCl₄/base initiating system significantly accelerated the reaction and/or suppressed side reactions such as oligomerization efficiently, realizing living polymerization of various monomers.

Another target was to reexamine a wide range of metal halides for living polymerization. FeCl₃ is less hard as an acid than the Al-based acids,⁹⁴ and has advantages, such as low toxicity, for industrial use.^{99,100} However, FeCl₃ has never been used for living cationic polymerization of any monomers, although there have been several examples of its use in cationic polymerization of VEs,¹⁰¹ Sts,¹⁰² and dienes.¹⁰³ The combination of FeCl₃ with a Lewis base also allowed fast living polymerization of IBVE. For example, a time period of 15 s was required for quantitative cationic polymerization of IBVE when IBVE-Cl/FeCl₃ was used in toluene in the presence of 1,4-dioxane at 0 °C. In addition, the product polymer had a very narrow MWD ($M_w/M_n = 1.06$).¹⁰⁴



Scheme 7 Dormant and active species in the polymerization using SnCl₄ with a base.

The results with SnCl₄ and FeCl₃ pointed to a possibility that other Lewis acids would induce living polymerization with an added base. The survey revealed that the living polymerization of IBVE proceeded for a variety of Lewis acids (MCl_n; M: Fe, Ga, Sn, In, Zn, Al, Hf, Zr, Bi, Ti, Si, Ge, Sb) in the presence of an appropriate added base, ester, or ether in conjunction with the IBVE-HCl adduct in toluene at 0 °C.¹⁰⁵ All MWDs of the product polymers were very narrow, with polydispersity indices ranging from 1.02 to 1.10. Significant differences were observed with these Lewis acids in terms of polymerization rate. For example, very rapid reactions occurred using some acids, such as FeCl₃, taking in the order of seconds to complete, whereas very slow reactions that took more than a few weeks proceeded with others such as SiCl₄ and GeCl₄. The difference in activity is most likely attributed to the strength of the interaction between the Lewis acid and the chloride anion and/or the basic carbonyl (or ether) oxygen atom of the added base. The stereoregularity of all the product polymers was very similar, and about 70% of dyads in the polymer were meso structure.

The comparison between reactions in toluene in the presence of ethyl acetate at 0 °C gives the following order of polymerization rate:

 $\begin{array}{l} GaCl_3 \sim FeCl_3 > SnCl_4 > InCl_3 > ZnCl_2 > AlCl_3 \sim HfCl_4 \sim \\ ZrCl_4 > EtAlCl_2 > BiCl_3 > TiCl_4 >> SiCl_4 \sim GeCl_4 \sim SbCl_3 \end{array}$

This order is consistent with that of the strength of metal halides for extraction of the chloride anion from trityl chloride in a carbonyl compound, PhCOCl;¹⁰⁶ the amount of cations derived from trityl chloride in the presence of ethyl acetate:

In PhCOCl

$$FeCl_3 > SnCl_4 > ZnCl_2 > TiCl_4 > AlCl_3$$

In ethyl acetate

$$FeCl_3 \sim GaCl_3 > InCl_3 > AlCl_3$$

Some metal halides such as SnCl₄ and ZnCl₂, which interact strongly with a chlorine atom (chloride anion) than with a carbonyl (or ether) oxygen atom, are active, whereas others, including TiCl₄ and AlCl₃, which interact more strongly with the oxygen atom, induce slow polymerization. Thus, the polymerization rate of each metal halide for base-present living cationic polymerization is governed by the balance between the degrees of chlorophilicity and oxophilicity of central metals. The order of polymerization rates does not simply follow that of the chlorophilicity of central elements of metal halides.

Diverse combinations of metal halides and Lewis bases also allowed living/controlled polymerization of monomers with high and poor reactivities. For example, polymerization of NVC was controlled under conditions milder than those of the previous report.¹⁰⁷ The combination of ZnCl₂ with a relatively strong Lewis base, tetrahydrofuran (THF), produced polymers with a narrow MWD ($M_w/M_n \le 1.2$) in toluene at 0 °C.²⁰ Difficult monomers such as vinylcyclohexane (VCH) (see Section 3.16.5.1.3) and an aromatic aldehyde (see Section 3.16.5.1.4) were successfully polymerized in a controlled fashion using GaCl₃, as described below.

3.16.5.1.2 Ultrafast living polymerization

It was reported that the rate of living cationic polymerization of IBVE with Al-based initiating systems was enhanced if the basicity of an added base was reduced.¹⁰⁸ Thus, a weaker base was examined in the polymerization using SnCl₄ and FeCl₃. An alternative weaker base, ethyl chloroacetate, realized very fast polymerization with SnCl₄ in toluene at -78 °C, being completed within 2 s (determined using a high-resolution digital video camera).¹⁰⁹ Moreover, FeCl₃ induced faster polymerization with 1,3-dioxolane, a weaker base than 1,4-dioxane, which was completed in 2–3 s in toluene at 0 °C.¹⁰⁴ In both cases, product polymers had very narrow MWD ($M_w/M_n < 1.1$), irrespective of the monomer conversion.

3.16.5.1.3 Ligand design for living polymerization

Polymerization with some metal pentachlorides was controlled by an added salt, instead of an added base. With NbCl₅ and TaCl₅, addition of a salt (nBu₄NCl) resulted in well-controlled reactions.¹⁰⁵ Among pentachlorides, however, MoCl₅ induced ill-defined polymerization even in the presence of the salt, vielding polymers with broad MWDs.¹⁰⁵ Thus, other additives were examined with MoCl₅. Specifically, oxygen-containing compounds were employed judging from the oxophilicity of molybdenum. An unexpected solution was found with this problem. An alcohol combined with MoCl₅ induced living cationic polymerization of IBVE. For example, MoCl₅ and methanol allowed living polymerization of IBVE in toluene in the presence of ethyl acetate at 0 °C.110 Furthermore, several other metal chlorides were also shown to induce methanol-initiated living polymerization. The Lewis acids examined in the study were classified into three groups in terms of polymerization behavior: those achieving living polymerization (e.g., MoCl₅, NbCl₅, and ZrCl₄), those inducing uncontrolled polymerization (e.g., GaCl₃ and FeCl₃), and those showing no activity (e.g., ZnCl₂ and InCl₃). The exchange reaction between the methoxy group of methanol and the chloride anion of a metal chloride was confirmed in living polymerization systems. This reaction generated HCl, a true initiator, which initiated polymerization. Alcohols that can be used for this purpose are 2-propanol, tert-butanol, and ethylene glycol, in addition to methanol.¹¹¹ ¹H NMR analysis demonstrated that two types of growing ends are formed, depending on the Lewis acid. Only C-Cl dormant terminals were observed with the more oxophilic Lewis acids such as NbCl₅, whereas a rapid equilibrium between the C-Cl ends and acetal structures is involved with Lewis acids oxophilic but less oxophilic relative to NbCl₅. Since some metal halides were able to ionize the C-O bond in an acetal, cationic polymerization was examined with a small acetal compound. 1,1-Dimethoxyethane (DME) with TiCl₄ permitted living polymerization of VEs, pMSt, and p-alkoxystyrenes.112,113

Alcohol-initiated living cationic polymerization was independently reported very recently. Cationic polymerization of IBVE was examined using methanol/BF₃OEt₂ in CH₂Cl₂ in the presence of Me₂S at –15 °C.¹¹⁴ Primary, secondary, and tertiary alcohols induced living polymerization, yielding well-defined polymers (M_w/M_n = 1.1–1.25). *p*-Alkoxystyrenes were also polymerized in a living fashion with this system.

A similar initiating step was established using the acetylacetone (acac)/SnCl₄ initiating system.^{115,116} Acetylacetone reacted readily with an equimolar SnCl₄ in toluene in the presence of ethyl acetate at 0 °C to form a complex species with a proton released. This released proton started polymerization as soon as the monomer was added to the acac/SnCl₄ solution to produce living polymers. It was proposed that acac formed a stable bidentate chelate-type counteranion in the dormant– active equilibrium (Scheme 8). A feature of the systems with alcohols and acac is that simple compounds can be used as initiating agents. It should also be noted that the ligand exchange with methanol or acac that moderates Lewis acidity was a key to achieving living polymerization.

Another recent interesting example is toluene-assisting controlled polymerization of VCH with GaCl₃.¹¹⁷ The cationic polymerization of VCH using GaCl₃ was not controlled in CH₂Cl₂. A catalytic amount of toluene, coordinating with GaCl₃ *in situ*, drastically transformed the reaction behavior into a well-controlled one. A similar initiating system induced well-controlled polymerization of β -pinene (see Section 3.16.6.1).

3.16.5.1.4 Copolymerization of aromatic aldehydes with vinyl ethers

The differing features of the base-assisting catalysts are opening possibilities for living cationic polymerization of new monomers, which had been considered difficult to polymerize in a controlled way. Aromatic aldehydes are difficult to polymerize cationically, and there have only been a few copolymerization studies with St or isoprene, not with VEs. The GaCl₃/base initiating system allowed copolymerization of an aromatic aldehyde with a VE for the first time. A 1:1 mixture of benzal-dehyde (BzA) with IBVE was polymerized using ethanesulfonic acid and GaCl₃ in toluene in the presence of 1,4-dioxane at $-78 \,^{\circ}\text{C}$.¹¹⁸ Copolymerization proceeded smoothly, yielding polymers with narrow MWDs ($M_w/M_n < 1.1$). On the other hand, selective cyclotrimerization occurred using EtAlCl₂. A small amount of cyclic oligomers was also obtained with the GaCl₃ system. Each of the reaction parameters (Lewis acid, solvent, added base, temperature) was essential for achieving controlled copolymerization.

The copolymerization produced no BzA–BzA linkages in any polymer chain, as confirmed by NMR. Accordingly, there are three elemental reactions for propagation: homopropagation and crossover from the IBVE growing end, and the crossover reaction from the BzA active chain end. Thus, the sequence distribution of the two monomers in the polymer chain would be determined by the relative reactivity of the self-propagation and crossover reactions. If an aldehyde is more reactive to the VE cation than a VE monomer, then even alternating copolymerization would proceed. In fact, alternating copolymerization was achieved in the copolymerization of BzA with 2-chloroethyl VE (CEVE) or *p*-methoxybenzaldehyde with IBVE (Scheme 9).¹¹⁹ In both cases, the resulting copolymers had narrow MWDs. The treatment of the product



Scheme 8 Dormant and active species in the polymerization using a complex of acac with SnCl₄.





copolymers with hydrochloric acid under mild conditions yielded cinnamaldehyde selectively.¹¹⁹ Cinnamaldehyde was successfully copolymerized with IBVE in an alternating manner under similar conditions. The product copolymers had only the structure derived from 1,2-addition, and were hydrolyzed into a single aldehyde with a longer conjugation. This is a unique chemical recycle, which creates a new and different aldehyde monomer after copolymerization and degradation (Scheme 9).

Although not involved in propagation, BzA derivatives play a key role in initiating living polymerization of IBVE.¹²⁰ Kamigaito *et al.* reported that cationic polymerization of IBVE was initiated by the carbocation generated from the *in situ* reaction of BzA with trimethylsilyl iodide. This initiation was quantitative and fast enough to allow living polymerization.

BzA was also able to induce living polymerization of trialkylsilyl VE (SiVE), which is regarded as an equivalent of the enol of acetaldehyde.¹²¹ This reaction was catalyzed by a zinc halide, with ZnBr₂ being the most efficient one. The initiation and propagation reactions were aldol-type addition reactions. First, the electron-deficient carbon of the C=O bond, coordinated with ZnBr₂, attacks the electron-rich β-carbon of the VE. Upon this addition, the trialkylsilyl group transfers onto the aldehyde oxygen, and an aldehyde group is generated at the chain end. Thus, this polymerization is called aldol group transfer polymerization (GTP). Hydrolysis of product polymers produced well-defined poly(vinyl alcohol).

This mechanism was applicable to polymerization of dienes.¹²² GTP of 1-butadienyloxy trimethylsilane (CH₂=CH-CH=CH-OSi(CH₃)₃) yielded a diene-type polymer with a narrow MWD through only 1,4-addition.¹²² Hydrogenation and desilylation led to an alternating copolymer of ethylene and vinyl alcohol with low polydispersity.¹²³ Propylene versions were also synthesized via GTP of methyl-substituted dienylox-ysilane monomers.¹²⁴

3.16.5.1.5 Heterogeneously catalyzed living polymerization

Solid catalysts have been of great interest in organic and polymer chemistry for recent years in light of increasing environmental demands. There were several examples of heterogeneous cationic polymerization using solid acids, including metal oxides, heteropoly acids, and ion-exchange resin,^{38,41,125–128} but no living polymerization had been reported. The feasibility of living polymerization of VEs using a solid acid, such as metal oxides, was examined recently.

Aoshima and co-workers first demonstrated that heterogeneous living cationic polymerization of IBVE proceeded using Fe₂O₃ in conjunction with the IBVE-HCl adduct in toluene in the presence of an added base at 0 °C. Ethyl acetate and 1,4-dioxane are effective bases for homogeneous living cationic polymerization of VEs with various metal halides. These bases were also good for a heterogeneous catalyst, Fe₂O₃, and induced living cationic polymerization of IBVE to produce polymers with very narrow MWDs $(M_w/M_n \le 1.1)$.¹²⁹ Furthermore, M_n of the product polymers increased in direct proportion to the monomer conversion. This is the first example of heterogeneously catalyzed living cationic polymerization. Stereoselectivity was of great interest as well as livingness, but the product polymers were similar in steric structure to those obtained in homogeneous systems. Controlled polymerization was attained even at higher temperature (30 °C). Living polymerization was also achieved

using Fe_3O_4 with an added base.¹³⁰ Ga_2O_3 , In_2O_3 , and ZnO were able to induce living polymerization with a base only when an ammonium salt or a proton trap was added.¹³⁰

Facile separation of the catalysts was performed. For Fe₂O₃, it was separated from the reaction mixture by centrifugation. This once-used and retrieved catalyst was able to catalyze living polymerization under the same conditions, yielding a polymer with narrow MWD. The catalyst maintained its reactivity, at least, up to the fifth use to give well-defined polymers with very narrow MWD.¹²⁹ Fe₃O₄ can be separated using a magnet.¹³⁰

Stereospecific cationic polymerization of IBVE using FeSO₄ was investigated under various conditions to aim at the dual control of stereoregularity and molecular weight.¹³¹ An unprecedented reaction was induced with *t*BuOH: the polymerization using the alcohol involved the production of long-lived species, where the MWD curve of the obtained polymer shifted to the higher molecular weight region with the procession of the polymerization. Furthermore, the shift was also observed in the fractionated portions consisting of stereoregular chains. The presence of acetal end structures with the *tert*-butoxy group derived from the used *t*BuOH was confirmed by the ¹H NMR spectrum, which may be responsible for the controlled reactions.

3.16.5.1.6 Metal halide-free system

Metal halide-free systems were reported in the early days: living polymerization of NVC using hydrogen iodide alone,¹⁰⁷ and living polymerization of IBVE using HI with an ammonium salt¹³² or trifluoromethanesulfonic acid with Me₂S.^{74,75} Very recently, Sugihara *et al.*¹³³ and Matsuo *et al.*¹³⁴ independently reported that a HCl/diethyl ether or HCl/1,4-dioxane initiating system induced living cationic polymerization of various VEs in nonpolar solvents such as hexane and toluene.

Another recent example of a metal halide-free system was polymerization using heteropoly acids.^{135,136} Cationic polymerization of IBVE was examined using a Keggin-type heteropoly acid, H₃PW₁₂O₄₀, in CH₂Cl₂ at 0 °C in the presence of various added bases. In the presence of 1,4-dioxane or THF, instantaneous polymerization occurred, and the obtained polymers had very broad MWDs. In contrast, polymerization proceeded in a living fashion in ethyl acetate as a solvent in the presence of Me₂S at –30 °C to give a polymer with a narrow MWD ($M_w/M_n < 1.1$). In addition, the molecular weight of the product polymer indicated that all three protons of H₃PW₁₂O₄₀ initiated living polymerization. The reaction mixtures were heterogeneous because of the very poor solubility of H₃PW₁₂O₄₀ in ethyl acetate. Thus, this is another successful heterogeneous living cationic polymerization.

3.16.5.2 New Initiating Systems for Styrene Derivatives

Recent progress in the living polymerization of St derivatives is symbolized by unique initiating systems. One is controlled polymerization with water-tolerant catalysts as described in Chapter **3.15**, and the other is living polymerization using active and versatile catalysts for various St derivatives (**Figure 4**), which is focused in this section. As for the early development of St derivatives, please refer to Chapter **3.15**. Typical cationogens (initiators) for active polymerization are listed in **Figure 5**.



Figure 4 St derivatives. DPE, 1,1-diphenylethylene; pCISt, p-chlorostyrene; TMSt, 2,4,6-trimethylstyrene; tBOVN, 6-t-butoxy-2-vinylnaphthalene.



Figure 5 Initiators for new living polymerization systems of St derivatives.

Tin-based Lewis acids such as SnCl₄ have been used for living cationic polymerization of Sts as well as their conventional polymerizations, hence the polymerization behavior is well known. However, combinations of SnCl4 with added bases showed a different polymerization behavior from the initiating systems reported before. For example, SnCl₄, coupled with IBEA-EtAlCl₂ as an initiator, induced highly active living polymerization of pMOS in CH₂Cl₂ at 0 °C in the presence of ethyl acetate as an added base.¹³⁷ The reaction was well controlled and was completed within 30 s, producing polymers with quite narrow MWDs (≤ 1.05) and with M_n values increasing in direct proportion to monomer conversion. This initiating system was also operable at higher temperatures. Living cationic polymerization of *p*-tert-butoxystyrene (tBOS) proceeded in toluene even at +40 °C. It was rather surprising that the livingness remained intact during the reaction, since an electron-rich aromatic compound (toluene) and high temperature are considered favorable for Friedel-Crafts side reactions with the growing carbocation.

Another example of a tin-based system for living polymerization of pMOS is the combination of SnBr₄ with DTBP. Well-defined high-molecular-weight polymers (M_n 's up to 1.2×10^5 and $M_w/M_n \sim 1.1$) were obtained using pMOS-Cl/ SnBr₄ with DTBP in CH₂Cl₂ at -60 to -20 °C.¹³⁸

The SnCl₄-based initiating system exhibited versatile performance for living polymerization of Sts with a variety of reactivities. Table 1 summarizes representative results of the polymerization with SnCl₄/added base. Here, the SnCl₄-based system is compared with the EtAlCl₂/added base counterpart for simplification, although other initiating systems are also available for some monomers. In all cases, IBEA-EtAlCl₂ (initiator)/SnCl₄ (activator) and an added base produced polymers with very narrow MWDs ($M_w/M_n = 1.03 - 1.13$), although the rate differences (from 20s to over 200h for completion of the polymerization) were significant.¹³⁹ It should be emphasized that SnCl₄, when combined with a base, is invariably effective for achieving living cationic polymerization of various St derivatives, as opposed to EtAlCl₂, which was not able to induce well-controlled polymerization of all monomers but p-chlorostyrene (pClSt) even in conjunction with an added base. Thus, appropriate combinations of SnCl₄ and Lewis bases are critical to successful living polymerization of not only active monomers but also less reactive counterparts. For instance, phenyl acetate (an added base), less basic than

Monomer Substituent	<i>p</i> MOS OCH₃	tBOS OC(CH ₃) ₃	<i>p</i> MSt CH₃	St H	<i>p</i> AcOSt 0C0CH₃	<i>p</i> CISt CI	αMSt CH ₃ (α)
Living polymerization	5	- (- 5/5	- 0		5 - 5 - 5		- 3()
EtAICI ₂	Х	Х	Х	L	Х	0	Х
EtAICI ₂ /SnCl₄	0	0	0	0	0	0	0
Time (conv. $\sim 90\%$)	20 s	40 s	1.5 h	50 h	120 h	>200 h	1.5 h
$M_{\rm w}/M_{\rm n}$	1.03	1.03	1.13	1.10	1.13	1.12	1.13

 Table 1
 Living cationic polymerization of St derivatives using EtAICl₂/SnCl₄ with added base^a

^aO: living; L: long-lived; X: nonliving. Typical polymerization conditions: $[pMOS]_0 = 0.38 \text{ M}$, $[IBEA]_0/[EtAICl_2]_0 = 4.0/2.5 \text{ mM}$, $[SnCl_4]_0 = 10 \text{ mM}$, $[CH_3COOEt] = 500 \text{ mM}$, in CH_2Cl_2 or toluene at 0 °C.

CH₃COOCH₂CH₃, assisted SnCl₄ to catalyze living polymerization of *p*ClSt in CH₂Cl₂ at 0 °C.¹³⁹

Among the monomers listed in Table 1, cationic polymerization of p-acetoxystyrene (pAcOSt) was rarely investigated, because of its low reactivity. Although its ideal living cationic polymerization has never been reported, controlled polymerization of pAcOSt was achieved using SnCl₄ of high concentration (> 200 mM) combined with H₂O or the water or HCl adduct of pAcOSt (CH3CH-(X)C6H4OCOCH3, X: OH, Cl) in CH₂Cl₂.^{140,141} In those reports, the uniqueness of the polymerization of pAcOSt was suggested: β-proton elimination was suppressed with increasing polymerization temperature.¹⁴¹ A clean reaction was achieved with a similar initiating system at a lower concentration of SnCl₄ even in the absence and presence of an added base.¹⁴² The resulting poly(pAcOSt) was further converted into poly(4-vinylphenol) by alkaline hvdrolysis.142,143 Random and block copolymers of pAcOSt and other St derivatives were also obtained.¹⁴³ The resulting poly(4-vinylphenol) with a narrow MWD underwent sensitive pH-responsive phase separation upon decreasing pH (around pH 10).¹⁴³

St and alkyl-substituted Sts are also in the scope of monomers. The control of St polymerization was attained by adding two different bases (dimethylacetamide (DMA) and Et₂O) $(M_w/M_p = 1.1 - 1.2)^{139}$ when the reaction was conducted with St-Cl/SnCl₄ in CH₂Cl₂ at -15 °C. pMSt was polymerized in a living fashion with IBEA-EtAlCl₂ (initiator)/SnCl₄ (activator) in the presence of a small amount of ethyl acetate (50 mM) in CH₂Cl₂ at 0 °C, resulting in living polymers with very narrow MWDs $(M_w/M_n = 1.1-1.15)$.¹⁴⁴ Incidentally, a base-free system with SnCl₄ and IBEA-EtAlCl₂ yielded fairly controlled polymers $(M_w/M_p = 1.2-1.3)$. Another excellent initiating system is DME-TiCl₄/SnCl₄ with ethyl acetate (an added base) and DTBP (a proton trap).^{112,113} This system also produced finely controlled polymers ($M_w/M_n \sim 1.1$) of pMOS, tBOS, and pMSt in CH₂Cl₂ at 0 °C. A combination of SnCl₄ and a proton trap induced living polymerization of 2,4,6-trimethylstyrene (TMSt) in CH₂Cl₂ at 0 °C, producing well-defined polymers $(M_w/M_p < 1.05)$.¹⁴⁵ This was the highest temperature at which living polymerization of TMSt ever reported.

Ethyl acetate with SnCl₄ was also effective for controlling cationic polymerization of α MSt. Living polymerization of α MSt was achieved using the (CEVE-OAc)–EtAlCl₂/SnCl₄ initiating system with ethyl acetate (0.10 M) in CH₂Cl₂ at -78 °C.¹³⁷ This initiating system permitted the random copolymerization of α MSt with a reactive St derivative at 0 °C, where homopolymerization of *t*BOS, which is more reactive than α MSt, gave random polymers

with narrow MWDs and with M_n values increasing linearly with monomer conversion ($M_n \ge 2.4 \times 10^4$). What is more surprising is that the content of aMSt decreased with decreasing polymerization temperature, which means that the self-propagation of tBOS became faster than the crossover reactions and the αMSt. Sterically hindered self-propagation of 1,1-diphenylethylene (DPE) had never been polymerized to high polymers, only producing a dimer. Copolymerization of DPE with pMSt using SnCl₄ in CH₂Cl₂ at -78 °C proceeded in a living fashion, yielding fairly controlled polymers.¹⁴⁶ This is the first example of (co)polymerization of DPE into highmolecular-weight polymers in the field of cationic polymerization.

The naphthyl group is more susceptible to Friedel–Crafts reactions than the phenyl counterpart. Thus, controlled cationic polymerization of vinylnaphthalene derivatives had never been reported. Very recently, living polymerization was achieved for the first time using a SnCl₄/base initiating system.¹⁴⁷ For example, IBEA–EtAlCl₂ or IBEA–TiCl₄/SnCl₄ polymerized 6-*t*-butoxy-2-vinylnaphthalene (*t*BOVN) in a controlled fashion in CH₂Cl₂ in the presence of ethyl acetate or 1,4-dioxane at –30 °C.

3.16.6 New Monomers

3.16.6.1 Naturally Occurring Monomers and Their Derivatives

Polymer synthesis from renewable resources has recently been of a growing interest from the standpoint of the construction of environmentally benign and sustainable society. For example, Satoh et al. reported cationic polymerization of anethole and isoeugenol (Figure 6) as naturally occurring St derivatives. Cationic copolymerization of these β-MSt derivatives with pMOS was controlled when the alcohol/BF3OEt2 system was used in aqueous media, while no homopolymerization of anethole or isoeugenol proceeded under similar conditions.¹⁴⁸ The M_{n} 's of the copolymers increased in direct proportion to the monomer conversions, and relatively narrow MWDs were attained throughout the reaction. Furthermore, this copolymerization proceeded in an alternating manner, as confirmed by the measurement of monomer reactivity ratios and MALDI-TOF-MS (matrix-assisted laser desorption ionization time-of-flight mass spectrometry) analysis of copolymers of isoeugenol and pMOS. The well-defined phenolic alternating copolymers can be regarded as linear lignin analogues.

 β -Pinene (Figure 6) is one of the main constituents of natural turpentines. Its polymers are used as commercial resins for many applications. Thus its cationic polymerization had



Figure 6 Naturally occurring monomers.

been examined for years, but it was not until the late 1990s that living polymers were obtained. Living cationic isomerization polymerization of β-pinene was first reported with a HCl adduct of CEVE (CEVE-Cl)/TiCl3(iPrO) in conjunction with nBu_4NCl as an added salt in CH_2Cl_2 at -40 to -78 °C.¹⁴⁹ The linear increase in $M_{\rm p}$ against monomer conversion and relatively low polydispersity supported successful living polymerization. ¹H NMR spectra of the product polymers demonstrated that the resulting polymer chain consisted of the initiator-derived (CEVE-type) head group, a tert-chloride tail group, and completely isomerized β-pinene repeat units with cyclohexene rings. Block copolymers, graft copolymers, and end-functionalized polymers were also prepared by this living polymerization system. Living copolymerization with IB was also achieved using St-Cl/TiCl₄:Ti(*i*PrO)₄ (3:1 molar ratio) in conjunction with nBu₄NCl in CH₂Cl₂ at -40 °C.¹⁵⁰ In this case, both monomers were consumed at very similar rates. A new catalyst system for controlled polymerization of β-pinene is the combination of GaCl3 and hexamethylbenzene (1:2 molar ratio), which produced polymers with relatively narrow MWDs ($M_w/M_n < 1.3$) in CH₂Cl₂/1-chlorobutane (7:3) at -78 °C.

For a production version, higher molecular weight polymers are desired. A survey of conventional metal halides revealed that relatively high-molecular-weight polymers ($M_w = 40000-55000$) of β -pinene with an alicyclic structure were produced in the polymerization with EtAlCl₂ or Et_{1.5}AlCl_{1.5} in CH₂Cl₂/ MCH (1:1) at -78 °C.¹⁵¹ This reaction did not proceed in a controlled way. A suitable Lewis acidity and solvent polarity is a key to producing high-molecular-weight polymers. Hydrogenation of the polymers gave terpene-based alicyclic polymers with a high T_g and degradation temperature (>400 °C). The obtained polymers exhibited good properties for optoelectronic materials, such as low dielectric constants, good transparencies, and nonhygroscopicities.

Recently, many studies have been reported on the synthesis, properties, and functions of glycopolymers with sugar moieties, which act as specific biological functional groups,

similar to those of naturally occurring glycoconjugates.¹⁵² The sugar residues of glycopolymers are expected to act as recognition sites between cells due to their multivalent interactions, or those structures could be primary factors controlling the generation of biological functions. Although glycopolymers have been prepared from a few VE derivatives with protected monosaccharide pendants by conventional cationic polymerization, no well-controlled polymers were obtained. Multiple polar groups in the sugar moiety, even if they were protected for cationic polymerization, prevented smooth propagation. Recently, the preparation of well-defined glycopolymers was demonstrated using various living/controlled polymerization techniques such as radical, anionic, and cationic polymerization.¹⁵² In cationic polymerization, Minoda et al.¹⁵³ and Yamada et al.^{154,155} reported living polymerization of carbohydrate-containing VEs, GVE1 and GVE2 (Figure 6). The polymerization of GVE1 and GVE2 was examined using two initiating systems. The CF₃COOH/EtAlCl₂ initiating system with 1,4-dioxane as an added base permitted living cationic polymerization of GVE1 having an acetyl-protected glucose at 0 °C. In contrast, the use of HCl/ZnI2 at -15 °C was found good for the controlled polymerization of GVE2 with an isopropylidene-protected glucose. Thus, homopolymers and various block copolymers with narrow MWDs ($M_w/M_n \sim 1.1$) and controlled molecular weights were prepared. D'Agosto et al. devised the living cationic polymerization of another saccharidic VE (GVE3, Figure 6) using a 1,1-diethoxyethane-Si(CH₃)₃I/ZnCl₂ initiating system. The detailed kinetics were carefully examined using ¹H NMR, dilatometry, and MALDI-TOF-MS.¹⁵⁶ D-Glucosamine-containing glycopolymers with well-controlled structures were also synthesized from monomers protected by acetyl and phthaloyl groups (GAVE, Figure 6) via living cationic polymerization.¹⁵⁷ Living polymerization of GAVE proceeded using an adduct of IBVE with CF₃COOH/EtAlCl₂ in toluene in the presence of 1,4-dioxane (added base), yielding polymers with very narrow MWDs (Mw/ $M_{\rm n} \sim 1.1$). Subsequent quantitative deprotection with hydrazine monohydrate afforded the corresponding water-soluble

polymers with pendant D-glucosamine residues, which had useful characteristics as biotechnological, pharmacological, and medical materials.

3.16.6.2 Vinyl Ether Derivatives

In addition to the sugar monomers described above, various VEs with unique side groups have been targets for controlled polymerization.¹⁵⁸ Takaragi et al.¹⁵⁹ reported fine synthesis of poly(VE)s with pendant cellobiose heptadecanoate residues (1, Figure 7) by cationic polymerization using IBVE-Cl/ZnI₂ in toluene at -15 °C. Polymers with controlled architecture and low polydispersity ratio $(M_w/M_n \sim 1.15)$ were obtained, although the products were accompanied by monomeric and some oligomeric by-products. Their mesomorphic properties were examined using differential scanning calorimetry (DSC), polarization microscopy, and X-ray diffraction. The mesophase of the polymers was quite similar to that of the star-shaped triplet derivative, that is, it was characterized by (1) discotic columns that resulted from a regular stacking of the pendant cellobiose heptadecanoate residues, (2) an extended conformation of each polymer main chain, and (3) three discotic columns. Other advances in living polymerization of VEs with polar functional groups and bulky substituents (Figure 7) are as follows. Namikoshi et al. reported living polymerization of VEs with urethane $(2)^{160}$ and cyclic acetal $(3)^{161}$ groups. Since each monomer has an acid-sensitive polar group, reaction conditions and catalysts were important factors for successful living polymerization. For example, living polymerization of 2 could not be achieved without a judicious choice of substituents adjacent to the urethane nitrogen, the initiating system

(HCl/ZnCl₂), and a lower polymerization temperature (-30 °C). For 3, various initiating systems in conjunction with additives (DTBP and added base) were examined. The cyclic acetal in 3 was shown to be a stable protecting group under living polymerization conditions. Feit and Halak¹⁶² have presented a synthetic route to comb-shaped polymers of VEs with oligooxyethylene carbonate pendant groups (4) by living cationic polymerization using CF_3SO_3H with $S(CH_3)_2$ in CH₂Cl₂ at -23 °C. Fluorine-containing polymers have unique properties such as low surface energy, high contact angle, high biocompatibility, and lipo- and hydrophobicity. Matsumoto et al. achieved living polymerization of a fluorine-containing VE (5), 2-(2,2,2-trifluoroethoxy)ethyl VE, with *n*-butyl VE-Cl/ ZnCl₂. The synthesis of various block copolymers (see Section 3.16.7.1) and the properties of their aqueous solutions were also investigated.¹⁶³⁻¹⁶⁵ Cationic polymerization of fluorine-containing VEs $(CH_2=CHOC_2H_4OC_3H_6C_nF_{2n+1})$: 5FVE $(CH_2=CHOC_2H_4OC_3H_6C_2F_5)$ (n = 2),13FVE $(CH_2=CHOC_2H_4OC_3H_6C_6F_{13})$ (n=6)) was recently investigated in various solvents with an IBEA/Et15AlCl15 initiating system in the presence of an added base.¹⁶⁶ Living polymerization proceeded not only in conventional solvents for cationic polymerization but also in fluorinated solvents such as hydrochlorofluorocarbons, hydrofluorocarbons, hydrofluoroethers, or $\alpha_{\alpha}\alpha_{\alpha}$ -trifluorotoluene. The solvents were also shown to be good for living polymerization of IBVE. The obtained fluorinecontaining polymers underwent temperature-responsive solubility transitions in organic solvents (see Section 3.16.8.1).¹⁶⁶

Cationic polymerization of a VE with a 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) radical (6) was an interesting example,¹⁶⁷ although it was not a living system. The direct



Figure 7 Examples of new functional VE monomers.

polymerization of the radical-containing monomer was conducted using BF₃OEt₂ in CH₂Cl₂ at –25 °C, producing reddish polymers which were soluble in THF, chloroform, *N*,*N*dimethylformamide (DMF), and dimethyl sulfoxide (DMSO). The spin concentration of the obtained polymers was determined by electron spin resonance (ESR) measurement to be 2.75×10^{21} spins · g⁻¹ (100% spin per repeating unit). The spin concentration of the radicals did not decrease even 1 year after polymer samples were stored under aerobic conditions at room temperature. The electrochemical properties of the polymers were examined by cyclic voltammetry measurements. The outstanding stability, the high capacity, and excellent charge/ discharge properties of the polymers of 6 demonstrated a wide range of potential applications as a new power source.

In general, poly(VE)s with linear alkyl chains are usually sticky liquids or gummy materials at room temperature except for those having long alkyl chains. This is a major problem for their use as commodity plastics. One of the solutions is to prepare a polymer from a monomer with a rigid pendant. Living cationic polymerization of a VE containing cyclohexyl (7),^{168,169} 2-adamantyl (8),¹⁷⁰ tricyclodecane (9),^{171,172} or tricyclodecene171 pendant was achieved with VE-Cl (adduct with HCl) or VE-I (adduct with HI)/ZnCl₂ in the presence or absence of nBu₄NI in CH₂Cl₂ at -50 to -30 °C, VE-Cl or VE-I with nBu₄NI in CH₂Cl₂ at -50 to -30 °C, IBEA/Et_{1.5}AlCl_{1.5} with ethyl acetate (added base), or HCl/ZnCl2 in toluene at 0 or -30 °C. The $M_{\rm n}$'s of the product polymers increased in direct proportion to monomer conversion and their MWDs were narrow $(M_w/M_n = 1.03 - 1.1)$. The T_g 's and thermal decomposition temperatures (T_d) of the polymers were 178 and 323 °C for poly(2-adamantyl VE), and 95 and 346 °C for poly(tricyclodecane VE), respectively. These polymers make free-standing films. Thus, diblock copolymers with a stimuli-responsive segment were synthesized for a new class of smart films.^{169,172} The resulting films showed reversible thermoresponsive behavior.

Long alkyl chains and mesogenic groups exhibit stronger interactions, especially in water, compared to other hydrophobic groups. That is why there have been many studies on the self-association behavior of polymers with those groups. VE monomers with a variety of mesogenic substituents (10) were polymerized by HI/I2, HI/ZnI2, CF3SO3H with S(CH3)2, or EtAlCl₂ with added base in CH₂Cl₂, to give narrowly distributed homo-, random, and block (co)polymers.¹⁷³⁻¹⁷⁷ For example, Rodriguez-Parada and Percec175 and Percec and Lee176,177 have systematically studied the effects of the degree of polymerization and the spacer length on the mesogenic phase formation or phase diagrams. Appropriate combinations of Lewis acids with added bases permitted the living cationic polymerization of VEs with a crystalline octadecyl chain (octadecyl VE (ODVE)) or liquid crystalline mesogenic structures (11), to give homopolymers with a narrow MWD and well-defined random and block copolymers with various pendants.¹⁷⁸⁻¹⁸⁰

3.16.6.3 Diene Monomers

Controlled cationic polymerization of linear dienes, such as 1,3-pentadiene, has never been achieved, because frequent side reactions occur such as cross-linking, isomerization, cyclization, and chain transfer reaction (Figure 8). Bennevault-Celton *et al.*¹⁸¹ conducted a series of kinetic studies on the polymerization of 1,3-pentadiene initiated by AlCl₃ in a



Figure 8 Diene monomers. CPD, cyclopentadiene; ND, norbornadiene.

nonpolar solvent. They showed the complexation of propagating species with the polymer at -10 °C, which limited the polymer conversion. The long-lived character of the active centers was observed, as confirmed by deactivating polymerizations with an excess of Me₂S: the formation of sulfonium ion was monitored by ¹H NMR spectroscopy.

In contrast, precise control of molecular weights and MWDs in cationic polymerization was recently achieved using various initiating systems with several cyclic diene monomers such as cyclopentadiene (CPD), THI, and norbornadiene (ND). The cyclic dienes gave rigid main chains of directly linked, unsaturated rings. Their hydrogenated saturated hydrocarbon polymers have attracted much attention as new materials with high T_g 's and low dielectric constants.

CPD is a typical cyclic diene, and its cationic polymerization has been examined with conventional acid catalysts since the 1920s.³ However, the precise control of cationic polymerization of CPD has been difficult, in terms of molecular weights and main-chain microstructure (1,2- and 1,4-enchainments). Ouchi et al.¹⁸² first synthesized poly(CPD) with controlled molecular weights and narrow MWDs with a three-component initiating system consisting of a HCl adduct of CPD or VE (initiator), SnCl₄ (Lewis acid catalyst), and nBu₄NCl, Et₂O or ethyl acetate (added salt or base) in CH₂Cl₂ at -78 °C. The control of regioselectivity of CPD was also examined with various initiating systems.¹⁸³ Weak Lewis acids such as ZnX₂ (X: Cl, Br, I) attained the highest 1,4-content (64, 70, and 76%, respectively), whereas SnCl₄, TiCl₄, and other strong Lewis acids led to less controlled microstructures. More recently, the $pMOS-OH/B(C_6F_5)_3$ initiating system was shown to induce controlled cationic polymerization of CPD under mild experimental conditions such as open air and room temperature.¹⁸⁴ ¹H NMR analysis indicated that the polymerization proceeded via reversible activation of the C-OH bond. It was demonstrated that the regioselectivity of poly(CPD) was influenced by the nature of the solvent. In addition, preliminary results of aqueous suspension polymerization were also presented.

Polymerization of a bicyclic conjugated diene, THI, was examined recently with the aim of synthesizing polymers with novel rigid hydrocarbon backbones consisting of bicyclic structures of five- and six-membered rings. Its hydrogenated product has unique physical and chemical properties and particularly good mechanical, electrical, and optical characteristics. The living cationic polymerization of THI was achieved using the CEVE–HCl/SnCl₄ initiating system in the presence of an added base such as ethyl acetate.^{98,185} The M_n of the obtained polymers increased in direct proportion to the monomer conversion, and the MWDs were narrow throughout the reactions ($M_w/M_n \sim 1.2$). Clean block copolymerization with IBVE

was also demonstrated, yielding di- and triblock copolymers consisting of hard nonpolar THI and soft polar IBVE segments for possible application as a thermoplastic elastomer. The hydrogenation of homopolymer of THI resulted in a saturated alicyclic hydrocarbon polymer with a relatively high $T_{\rm g}$ (220 °C) and a pyrolysis temperature much improved (10% weight loss at 480 °C).¹⁸⁵

The carbocationic polymerization of ND proceeds with transannular rearrangement, where both double bonds are involved. Thus, a product polymer has a rigid and high- $T_{\rm g}$ (~320 °C) tricyclic repeat structure, suitable for thermoplastic applications. Peetz *et al.* examined cationic polymerization of ND using the 2-chloro-2,4,4-trimethylpentane (TMP-Cl)/TiCl₄ initiating system. The use of a proton trap or an added base at – 35 to -60 °C rendered the reaction controlled, and the $M_{\rm n}$ increased linearly with conversion up to approximately 45%.¹⁸⁶ The product polymer chain consisted of approximately equal amounts of exo/exo and exo/endo connected tricyclic repeat units. Furthermore, a set of three-arm star block copolymers, *t*-cumyl(PIB-*b*-PND)₃ and *t*-cumyl (PND-*b*-PIB)₃, were prepared and characterized.¹⁸⁷

3.16.7 Sequence or Shape-Regulated Functional Polymers

3.16.7.1 Block Copolymers

3.16.7.1.1 Di- and triblock copolymer synthesis via sequential living polymerization

The first example of an AB block copolymer with a narrow MWD, prepared by cationic polymerization, was reported in 1984.¹⁰ The synthesis started with the polymerization of IBVE or MVE using the HI/I₂ initiating system in toluene at -35 °C. To the resulting living polymer, a solution of cetyl VE (CVE: CH₂=CH-O-C₁₆H₃₃) or *p*MOS in CCl₄, the second monomer, was added. Then, the polymerization temperature was raised to -15 °C for complete consumption of the second monomer.

The resulting polymers (12 and 13, Figure 9) had narrow MWDs, which shifted toward higher molecular weight without tailing ($M_w/M_n = 1.07$ for the precursor poly(MVE), 1.13 for poly(MVE)-*b*-poly(CVE)). The quantitative blocking efficiency was further confirmed by an extraction experiment with methanol, which demonstrated the absence of the MVE homopolymer. This success spurred the development of the synthesis of a wide variety of block copolymers via sequential living cationic polymerizations and/or an intermediate capping reaction.¹⁸⁸

The sequential addition method for the block copolymer synthesis has the advantage that a reaction can be conducted through easy procedures to attain perfect blocking efficiency and controlled segment lengths. In addition, block copolymer synthesis for VEs is characterized by the reversibility of monomer addition sequences. Various sets of two monomers can be polymerized in no particular order, although adjustment of reaction conditions, additional catalysts, or additives may be required. That is not the case with the block copolymerization of Sts or IB.¹⁸⁸ The success of living polymerization of a variety of functional monomers promoted investigations on the synthesis of block copolymers with pendant polar functional groups including protic versions.

Figure 10 summarizes typical examples of poly(VE)-*b*-poly (VE') AB block copolymers. Higashimura and co-workers successfully synthesized a series of amphiphilic diblock copolymers with pendant hydroxy,^{189–191} carboxy,¹⁹² and amino¹⁹³ groups via sequential block copolymerization of various polar monomers with alkyl VE. Various monomers with protected functional groups were employed and appropriate initiating systems and reaction conditions were carefully chosen. For example, 2-acetoxyethyl VE (AcOVE)¹⁸⁹ or SiVE¹⁹⁰ was first polymerized with HI/I₂ in toluene at -15 or -40 °C, respectively, and an alkyl VE was further polymerized to yield an AB diblock copolymer. Hydrolysis or desilylation of the pendant groups of the obtained block copolymers yielded amphiphilic copolymers. Similar strategies were adopted to







CH₂C₆H₅, Si(CH₃)₂tBu, H, CH₂CH₂Cl, CH₂CH₂OCOCH=CH-C₆H₅

(CH₂CH₂O)_n-CH₃, (CH₂)_n-O-C₆H₄-C₆H₄-X (mesogenic group)

CH₂CH₂-Y (Y: glucose or glucosamine residues)

Figure 10 Poly(VE) diblock copolymers.

prepare other amphiphilic block copolymers with carboxy¹⁹² or amino¹⁹³ groups from monomers with an ester or phthalimide moiety, respectively. These block copolymers were excellent in surface activity to significantly lower the surface tension of the aqueous solutions^{189,192,193} and the interfacial tension of the water/toluene interface.¹⁸⁹ These polymers were the first examples of amphiphilic block copolymers with controlled molecular weight and composition obtained from vinyl-type monomers. Much better control was attained in the polymerization of a VE with a phthalimide when Et_{1.5}AlCl_{1.5} with 1,4-dioxane was employed (see Section 3.16.8.3).⁷¹

Block copolymers with a polyvinyl alcohol (PVA) segment were prepared by the sequential living polymerization of benzyl VE (BnVE)¹⁹⁴ with IBVE by the IBEA/EtAlCl₂ initiating system in the presence of added bases below 0 °C in a nonpolar solvent (toluene or CCl₄). Both acidic and basic conditions ((1) HBr in toluene and (2) Na in liquid NH₃) permitted quantitative debenzylation of the block copolymers, and PVA block copolymers with narrow MWDs were obtained. Another good candidate for a precursor was well-defined polymers consisting of *tert*-butyl VE (*t*BuVE),¹⁹⁵ the bulky butoxy groups of which can be converted into hydroxy groups. Other typical examples of block copolymers obtained by sequential living cationic polymerization consist of poly(CEVE),196 polv (2-vinyloxyethyl cinnamate),¹⁹⁷ liquid crystalline polv (VE), ^{198,199} and glycosidic poly(VE)^{200–204} segments. Their syntheses were performed with a broad array of initiating systems, such as HI/ZnI₂,¹⁹⁶ IBEA/EtAlCl₂,¹⁹⁷ HI/I₂,¹⁹⁸ triflic acid/ (CH₃)₂S,¹⁹⁹ IBVE-Cl/ZnI₂,²⁰⁰ trifluoroacetic acid–IBVE/EtAlCl₂/ 1,4-dioxane,²⁰¹ trimethylsilyl iodide/ZnCl₂,²⁰² and IBEA/ Et_{1.5}AlCl_{1.5}/ethyl acetate.^{203,204}

Block copolymerization of two monomers with much different reactivities is not as straightforward as that of monomers

with similar reactivities, since optimum reaction conditions for living polymerization may differ significantly. This is the case with the synthesis of block copolymers of VE and St derivatives (14. Figure 11). Since most of Sts are far less active than VEs.¹³ the optimum conditions, especially preferred concentrations of Lewis acids, for polymerizations of Sts are too severe for those of VEs. Thus, the first monomer has to be a VE in any combination of a VE and an St derivative. If a styrenic monomer is first polymerized, chain transfer and/or uneven crossover reactions would occur. A relatively simple approach was adopted to preparing block copolymers of VEs and *p*-alkoxystyrenes with HI/ZnI_2 .^{205,206} For efficient blocking, a suitable amount of ZnI_2 (5.0 mM), much larger than that for the first-stage polymerization of IBVE (0.2 mM), was added after the second monomer, $pMOS^{205}$ or $tBOS^{206}$ was added to the reaction mixture. A more devised method was required for the copolymerization of St. With MVE, the polymerization of MVE was first conducted and then that of St, as mentioned above. The HCl/ SnCl₄ initiating system produced living poly(MVE) in the presence of nBu_4NCl at -78 °C, to which the second monomer, St, was added. Immediately after the addition of St, a mixture of SnCl₄ and the salt was added. Although no consumption of St was observed at -78 °C, raising the temperature to -15 °C promoted the St polymerization, producing the target block copolymers quantitatively.²⁰⁷ Without any additional salt, the solution was colored, indicative of side reactions.

Triblock copolymers were also prepared based on a sequential monomer addition method. Amphiphilic ABA-type triblock copolymers with a perfluoro segment (15) (Figure 11) have been prepared by polymerizing AcOVE and a fluorine-containing VE and AcOVE sequentially in CH_2Cl_2 .²⁰⁸ Hydrolysis of the acetyl-protecting groups gave fluorine-containing amphiphilic copolymers. Hashimoto



Figure 11 Block copolymers of VEs with Sts and VE-based triblock copolymers.

et al.²⁰⁹ reported the preparation of new triblock copolymers composed solely of poly(VE) backbones (16) with pendant bulky polycyclic moieties, which behaved as a thermoplastic elastomer. The synthesis started with living polymerization of the bulky VE using HCl/ZnCl₂ in toluene at -30 °C, followed by the polymerization of n-butyl VE (NBVE) and the first monomer. Living polymerization from bifunctional initiators is a facile method for preparing ABA triblock copolymers (17). For example, the trifluoroacetic acid adduct of a divinyl ether was prepared in CCl₄ at 0 °C,²¹⁰ and then it was directly used for the block copolymerization of IBVE and AcOVE. The polymerization was initiated by adding EtAlCl₂ to a mixture of a first monomer, toluene, and 1,4-dioxane (added base). For the sequence of IBVE-AcOVE, the polymerizations of IBVE and AcOVE were carried out at 0 and +40 °C, respectively, while all the reactions were conducted at +40 °C for the reverse order. Subsequent hydrolysis led to ABA amphiphilic triblock copolymers, in which A or B segment was a hydrophilic poly(2hydroxyethyl VE)(poly(HOVE)) chain.

3.16.7.1.2 Control of molecular weight distribution and sequence in block copolymer synthesis

3.16.7.1.2(i) Control of molecular weight distribution in block copolymer synthesis

Polydispersity is a crucial factor for determining polymer properties, and hence its effect on polymer properties is a long-standing subject in various fields, from basic solution studies to functional properties. Hatada *et al.*^{211,212} demonstrated that polymers of uniform molecular weight ($M_w/M_n = 1.00$) exhibited properties clearly different from those of polydisperse polymers. The uniform polymers were obtained by fractionation using supercritical fluid chromatography of living polymers, prepared by common living anionic techniques.^{211,212} Noro *et al.*²¹³ and Lynd and Hillmyer²¹⁴ have reported the polydispersity dependence of the morphology of diblock copolymers in the bulk state, and Terreau *et al.*²¹⁵ have shed light on the effect of polydispersity on the self-assembly of block copolymer vesicles. Judging from these enlightening studies, the design and synthesis of polymers with targeted polydispersity would be an important objective. However, almost no attempt was made to prepare polymers with designed polydispersity via living polymerization.²¹⁶ A novel synthetic strategy was required to synthesize MWD-designed block copolymers.

Diblock copolymers with designed MWDs were prepared by using a continuous living cationic polymerization system, which involves gradual feeding of a polymerization reaction mixture into a terminating agent.²¹⁷ For thermosensitive diblock copolymers of 2-methoxyethyl VE (MOVE) and 2-ethoxyethyl VE (EOVE), the first-stage polymerization was carried out by the usual batch method. For example, living cationic polymerization of the first monomer, EOVE, was conducted in a test tube at 30 °C to give a living polymer $(M_{\rm n} = 1.7 \times 10^4, M_{\rm w}/M_{\rm n} = 1.07)$. To this solution, the second monomer, MOVE (450 equivalent to the growing end), was added, and then the mixture was transferred to a gastight microsyringe. This reaction mixture was added continuously using a syringe pump to methanol during the second stage of polymerization, which yielded an MWD-designed block copolymer, EOVE₁₅₀-*b*-MOVE₄₀₋₄₅₀ (Figure 12; 18, $M_n = 3.1 \times 10^4$, $M_w/M_n = 1.38$, EOVE/MOVE = 1.0/1.7). This polymer had an almost monodisperse thermosensitive EOVE segment and a broadly distributed hydrophilic MOVE counterpart (hydrophilic below 63 °C). The same feeding rate but opposite polymerization sequence afforded another designed polymer, $MOVE_{150}$ -b-EOVE₄₀₋₄₅₀ (19), comprised of an almost monodisperse hydrophilic MOVE segment and a broadly distributed EOVE counterpart $(M_n = 3.1 \times 10^4, M_w/M_n = 1.41, EOVE/$ MOVE = 1.2/1.0).



Figure 12 Concept for controlling MWD of block copolymers.

These resulting polymers were examined in terms of thermosensitive behavior in water. The diblock copolymer EOVE₁₅₀-*b*-MOVE₄₀₋₄₅₀ formed micelles with narrow size distributions in water at 35 °C ($D_{\rm H}$ = 86 nm, $D_{\rm w}/D_{\rm n}$ = 1.05), as observed with diblock copolymers of nearly uniform segment lengths ($D_{\rm H}$ = 59 nm, $D_{\rm w}/D_{\rm n}$ = 1.01) for EOVE₁₅₀-*b*-MOVE₁₅₀ ($M_{\rm w}/M_{\rm n}$ = 1.05). On the other hand, MOVE₁₅₀-*b*-EOVE₄₀₋₄₅₀ with various lengths of the thermosensitive segment formed micelles with a broader size distribution ($D_{\rm H}$ = 114 nm; $D_{\rm w}/$ $D_{\rm n}$ = 1.11).²¹⁷ Thus, the uniformity in the length of the thermosensitive EOVE segment was crucial to the formation of well-defined micelles with narrow size distribution in water.

3.16.7.1.2(ii) Control of sequence in block copolymer synthesis: gradient copolymers

The excellent living nature of base-assisting living polymerization in a semiopen system permitted the synthesis of a variety of gradient copolymers.²¹⁸⁻²²¹ In the synthesis of gradient copolymers, one monomer was added continuously to the solution, where living polymerization of another monomer is taking place. Thermoresponsive gradient copolymers were synthesized by continuously feeding MOVE into a living polymerization reaction mixture of EOVE in the presence of an added base. The product polymers (20, Figure 13) had narrow MWDs $(M_n = 4.5 \times 10^4, M_w/M_n = 1.15, EOVE/MOVE = 260/$ 340). The livingness of the polymerization was confirmed by the linear increase in $M_{\rm p}$ against monomer conversion as well as the clear shift of the MWD curves. The larger ratio of MOVE to EOVE at a longer reaction time (for a longer chain), determined by ¹H NMR, supported the gradient sequence structure in a copolymer chain.²¹⁸

The thermosensitive behavior of aqueous solutions of the product gradient copolymers was studied based on turbidity measurements, dynamic light scattering (DLS), and small-angle neutron scattering (SANS). Copolymers of EOVE and MOVE vary in clouding point depending on the composition. Thus, continuous phase transition along a polymer chain was expected to proceed with increasing temperature. The resulting gradient copolymers of EOVE and MOVE underwent thermally induced micellization in water. The hydrophobic core of a micelle was derived from EOVE-rich segments. Interestingly, monotonous decrease in micelle size with increasing solution temperature was observed with the gradient copolymers (Figure 13).^{220,221} This behavior was clearly different from that of the corresponding conventional block copolymers, the micelles of which in water were constant in size at any temperature. A hydrophobic portion in a chain keeps increasing on heating for the gradient copolymers. This increasing hydrophobic interaction also keeps changing a part of the corona near the

core into a part of the hydrophobic core, resulting in the formation of smaller micelles. Various stimuli-responsive forced gradient copolymers were also synthesized based on the continuous addition method, described above.²¹⁹ The gradient composition of the obtained polymers corresponded well to those determined by a calculation method, even when the monomers had quite different relative reactivity ratios. The product gradient copolymers clearly differed from the corresponding block and random copolymers in terms of thermally or selective solvent-induced self-association behaviors in solution.²¹⁹

3.16.7.2 Star-Shaped Polymers

Well-defined nanoparticles with functional groups, such as dendrimers, have been of great interest in a variety of fields over a couple of decades.^{222,223} Star polymers are also expected to serve as nanoparticles with unique properties. In order to obtain such polymeric nanoparticles, functionalization and precision synthesis of star polymers would be crucial. The synthetic strategies for star polymers fall into three categories: (1) living polymerization from a multifunctional initiator; (2) coupling reaction of linear living polymers with a multifunctional coupling agent; and (3) linking reaction of linear polymers with a divinyl compound.²²⁴⁻²²⁶ These methods of star polymer synthesis were first realized in living anionic polymerization. Since then, living anionic processes permitted the synthesis of a variety of star polymers.²²⁷⁻²²⁹ However, no examples had long been reported on the synthesis of star polymers with pendant polar functional groups since the establishment of the star synthesis in living anionic polymerization. Although methacrylate-type star polymers had already been reported, ^{230–232} those polymers were not treated as functionalized materials at that time.

It was not until 1990 that the synthesis of amphiphilic star-like polymers by free radical polymerization was reported.^{233,234} Star-like polymers were prepared by the simultaneous radical polymerization and grafting-onto reaction from a mixture of a monomer (acrylic or methacrylic acid) and a microgel with vinyl groups, obtained from divinylbenzene and St. Those polymers were functionalized but ill-defined.

3.16.7.2.1 Well-defined functional star polymers

The first examples of well-defined star polymers with polar functional groups were demonstrated using living cationic polymerization.²²⁴ Kanaoka *et al.*²³⁵ successfully synthesized star polymers of alkyl VEs via linking reaction of living polymers with bifunctional VEs (BVEs; Scheme 10). The treatment



Figure 13 Thermoresponsive gradient poly(VE) and its micellization behavior in water.



Scheme 10 Star polymer formation via polymer-linking reaction.

of living polymers of EVE, IBVE, or CVE, prepared with HI/ ZnI₂, with a small amount of a bifunctional VE (BVE) (3–7 equivalent to the growing ends) produced star polymers with fairly narrow MWDs in high yield. The molecular weight and number of arms were governed by the ratio of BVE to the growing ends, the length of arm chains, and/or the concentration of living polymer chains.²³⁵ That was the first example of star polymer synthesis via linking reaction (method (3)) in cationic polymerization.

This success led to the precision synthesis of amphiphilic star block copolymers of VEs with hydroxy²³⁶ or carboxy²³⁷ groups, which were prepared in a similar way (Figure 14). Living block copolymers with ester-containing VEs, obtained by sequential block copolymerization, were used in the linking reaction, instead of homopolymers. Deprotection of the ester

functions yielded amphiphilic star block copolymers with pendant hydroxy or carboxy groups in the arm chains. The segment arrangement in a star molecule can be altered by the order of block copolymerization. The solubility characteristics of the product polymers were greatly affected by the nature of the outer segment, even if its length was short.^{236,237} Inspired by these results, similar amphiphilic star block copolymers with fewer but predetermined number of arms were also prepared based on living polymerization from a multifunctional initiator²³⁸ or coupling reaction of living polymers with a multifunctional terminator.^{239,240}

Following the excellent examples, the syntheses of amphiphilic heteroarm²⁴¹ and core-functionalized²⁴² star polymers were achieved using similar but modified 'arm-first' methods. In the synthesis of heteroarm star polymers, polymer-linking



Figure 14 Amphiphilic star block copolymers.

reaction was first conducted according to the arm-first method described above. Then, a second monomer was polymerized from the active sites in the central cross-linking core.²⁴¹ Core functionalization was attained by simultaneous addition of a bifunctional VE and a polar functional VE in the polymer-linking reaction. Functional monomers are incorporated well in the core if those are similar in reactivity to the divinyl ether employed.²⁴² The resulting amphiphilic star polymers with various architectures were shown to encapsulate small organic compounds efficiently.237,242-244 Amphiphilic star polymers of norbornene derivatives with carboxy groups were also prepared based on living ring-opening metathesis polymerization²⁴⁵ shortly after the first report on hydroxy-containing amphiphilic star polymers by cationic polymerization. Despite these progresses, not many functionalized star polymers were reported before controlled/radical polymerization of vinyl monomers was achieved.

3.16.7.2.2 Selective synthesis of star-shaped polymers with narrow molecular weight distributions

The 'arm-first' linking reaction is one of the most effective methods for preparing star polymers with many arms. Furthermore, functionalization of arms and the core can be conducted in a facile way. However, there was a persistent problem that some amount of starting polymers inevitably remains unreacted,^{225,226,235,245–254} especially when longer starting polymers were involved, in any polymerization mechanism. The conditions that allow high-yield reaction would cause broader MWDs with product polymers. Therefore, a star polymer with a narrow MWD can be obtained only by fractionation of ill-defined products.

This problem was recently overcome using base-assisting living cationic polymerization of VEs. Well-defined star polymers were prepared by linking reaction of living polymers with a divinyl ether based on living polymerization of IBVE using the IBEA/EtAlCl₂ initiating system in hexane in the presence of ethyl acetate at 0 °C.²⁵⁵ The reaction of linear starting living polymers ($M_n = 1.54 \times 10^4$, $M_w/M_n = 1.05$) with 1,4-cyclohexanedimethanol divinyl ether (CHDVE, $r = [CHDVE]_0/[living ends] = 10$) in hexane with ethyl acetate at 0 °C gave star polymers in quantitative yield in 7 h (reaction conditions: [IBVE]_0 = 1.5 M, [IBEA]_0 = 10.0 mM, [EtAlCl_2]_0 = 20.0 mM, [ethyl acetate]_0 = 1.0 M).²⁵⁵ The product

polymers had extremely narrow MWDs $(M_w/M_n = 1.1-1.2)$, compared to star polymers prepared by similar methods. This is the first example of the selective formation of nearly monodisperse star-shaped polymers via a one-pot polymer-linking reaction by any polymerization mechanism. Such clean reactions also proceeded irrespective of the arm length ($DP_n = 50$ -300).²⁵⁵ The $M_{\rm w}$ of the product polymers ranged from 6×10^4 to 30×10^4 , corresponding to arm numbers ranging from 9 to 44. The association of the growing chain ends driven by solvation with the added base, and the more stable growing ends in the base-assisting living cationic process, relative to other living cationic systems, is most likely attributed to this extremely efficient and well-controlled polymer-linking reaction. Well-controlled and nearly quantitative reactions for star polymers were also achieved by devised methods using an anionic process with incremental addition of divinyl compounds²⁵⁶ and radical polymerization using a macromonomer and divinyl compounds.257

Quantitative yield was also observed in the synthesis of thermoresponsive star-shaped polymers that have arms containing oxyethylene side chains.²⁵⁵ The obtained star polymers underwent highly sensitive lower critical solution temperature (LCST)-type phase separation in water, as the corresponding linear polymers do. Star block copolymers with two different thermoresponsive segments showed interesting behavior in phase separation.²⁵⁵ One sharp transition was observed when the outer layer consisted of the higher clouding point chains (21, Figure 15). This star polymer apparently served as a homostar polymer since the properties of the inner layer were concealed by the outer segments. In sharp contrast, a clear two-step transition was observed with the star polymer of the opposite arrangement (22, Figure 15). The transition temperatures correspond to the two segments. In addition, the star block copolymers induced reversible physical gelation in water at a higher concentration.²⁵⁵ A 15 wt.% aqueous solution of 21 caused a sol-gel transition upon cooling. This apparently unexpected transition stems from changes in the diameter of the packed star molecules, driven by the dehydration of poly-(EOVE) segments. A 10% aqueous solution of the star block copolymer 22 underwent rapid physical gelation upon heating. Three-dimensional networks of the star polymers were constructed through intermolecular aggregation of the outer segments.



Figure 15 Thermoreponsive star block copolymers.

3.16.7.2.3 Metal nanoparticles stabilized by star-shaped polymers

Gold nanoparticles (Au NPs) work as catalysts for organic reactions, and have been studied extensively over the world.²⁵⁸ However, ready aggregation of Au NPs in solution had been a problem for practical use. Therefore, the Au NPs should be covered with polymeric or small organic molecules. The fine dispersion (or solution) of Au NPs was obtained according to simple procedures invented by Tsunoyama et al.²⁵⁹⁻²⁶¹ and Sakurai et al.,²⁶² and size dependence of catalytic reactivity was studied in detail with several reactions. However, aggregation of Au NPs during reactions and/or work-up procedures was still a persistent problem in their practical use. This problem was resolved by the use of star polymers consisting of hydrophilic arms and a hydrophobic core.²⁶³ Star poly(2-(2-ethoxy)ethoxyethyl VE) (poly (EOEOVE)) was obtained in quantitative yield within 8 h from the reaction of CHDVE with living EOEOVE polymers, prepared using Et_{1.5}AlCl_{1.5} with 1,4-dioxane in toluene at 0 °C $(DP(arm) = 200, M_w(GPC-MALLS) = 9.4 \times 10^5, M_w/M_p = 1.36)$ 28 arms).²⁶³ The resulting star polymer was soluble in water at room temperature.

Star polymer-protected Au NPs were prepared according to the simple procedures already reported.^{259–262} The reduction of HAuCl₄ was conducted simply by adding NaBH₄ to an aqueous HAuCl₄ solution with the star polymer.²⁶³ The clearness of the resulting brownish solution and a very small absorbance at 520 nm, due to the surface plasmon resonance of the metallic gold clusters, supported the formation of very small Au NPs.²⁵⁹⁻²⁶² Transmission electron microscopy (TEM) analysis demonstrated that most of the resulting particles are less than 4 nm in diameter. Poly(EOEOVE) is a thermoresponsive polymer, which exhibits LCST-type phase separation, as will be discussed in Section 3.16.8.1. The Au-containing star poly(EOEOVE) also underwent LCST-type phase separation in water, being very similar in clouding point to star poly(EOEOVE) by itself. What is special about the Au NPs with star poly(EOEOVE) is that they never underwent negative aggregation even if the polymer was precipitated or phaseseparated.²⁶³ This suggests that a Au particle is located in the central core, being shielded completely by arm chains.

The product particles catalyzed the oxidation of several alcohols in aqueous media under aerobic and mild conditions. For example, benzyl alcohol was transformed quantitatively into benzoic acid in 1 h ([benzyl alcohol] = 16.7 mM, [Au] = 0.33 mM, [KOH] = 50 mM, at 27 °C, in water).²⁶³ It should also be noted that the star-protected particles exhibited

no aggregation at any point during the reaction or even during work-up procedures.²⁶³ This is the first successful example of preventing negative aggregation of Au NP catalysts during reactions.

The thermoresponsiveness as well as excellent durability of the Au NPs led to a facile catalyst reuse system. After the reaction, simple filtration was able to separate the polymer-stabilized catalyst, which was precipitated by raising solution temperature above the clouding point (60 °C) (Scheme 11). The catalyst was able to be reused at least 6 times, maintaining its activity for alcohol oxidation, which proceeded at a very similar rate in each run.²⁶³

Stable palladium nanoparticles were also prepared using thermosensitive VE star polymers.²⁶⁴ The obtained particles were shown to work as a catalyst for the Heck coupling of iodobenzene and ethyl acrylate. A feature of this system is non-necessity of expensive and toxic phosphine ligands. In mechanistic point of view, this zero-valent Pd-mediated reaction would shed new light on how Heck coupling reactions proceed.

3.16.8 Stimuli-Responsive Polymers

Stimuli-responsive polymers are polymers that undergo conformational and/or chemical changes in response to an external stimulus, such as temperature, pH, and magnetic field. Consequently, drastic transformations are induced in the physical properties of those polymers. Thus, stimuli-responsive polymers have been investigated as building blocks of smart materials for a variety of applications.²⁶⁵⁻²⁶⁸ The primary structures of the polymers may be decisive factors for controlling sensitivity and reversibility. The living/controlled radical polymerization of N-isopropylacrylamide (NIPAM) permitted the construction of fine systems with thermosensitivity, encouraging more scientists to study stimuli-responsive polymers. Before the enthusiasm, well-defined poly(VE)s have already demonstrated the importance of controlled primary structures for constructing fine stimuli-responsive systems.¹⁹ Here, we discuss various stimuli-responsive polymers prepared by the living cationic polymerization of VEs.

3.16.8.1 Thermoresponsive Poly(VE)s with Oxyethylene Pendants and Related Poly(VE)s

In the course of the precision synthesis of functional polymers, living polymerizations of VEs with oxyethylene pendants



Scheme 11 Reuse scheme for a Au NP catalyst protected by a thermosensitive star polymer.



Figure 16 A typical example of thermally induced phase separation of poly(OEVE) (x=1, R: C_2H_5) in water (1 wt.%).

$$\begin{array}{c} \underbrace{\left(\begin{array}{c} \mathsf{CH}_2-\mathsf{CH}\right)_n}_n & \mathsf{Poly}(\mathsf{OEVE}) \\ \mathsf{O}\\ \mathsf{O}\\ \mathsf{O}\\ \mathsf{O}\\ \mathsf{A}\\ \mathsf{A}\\ \mathsf{B}\\ \mathsf{C}\\ \mathsf{A}\\ \mathsf{C}\\ \mathsf{$$

Figure 17 Thermoresponsive poly(VE)s for LCST-type phase separation in water.

(Figure 16) were achieved.^{23,69} Later, a series of such polymers (poly(OEVE), Figure 17) were shown to undergo highly sensitive LCST-type phase separation in water,²⁶⁹⁻²⁷¹ as shown in Figure 16. Transparent aqueous solutions of poly(OEVE)s were converted into turbid solutions on heating, with complete transition within 1 °C at a heating rate of 1 °C min⁻¹. The transitions were repeatedly reversible without hysteresis, and no change in clouding point was observed.^{269,272-274} For example, an aqueous solution of poly(EOVE) underwent phase separation sensitively at 20 °C. The phase separation temperature (T_{PS}) of poly(OEVE)s was controllable by varying the length and/or an ω-alkyl group of the oxyethylene pendant.²⁶⁹ A less hydrophobic ω-alkyl group and a longer oxyethylene chain raise the clouding point: aqueous solutions of poly(MOVE) and poly(EOEOVE) underwent phase separation sensitively at 63 and 41 °C, respectively. Small and continuous variations in critical temperature were achieved by regulating the composition of a random copolymer of OEVE with another thermosensitive OEVE, a hydrophilic, or a hydrophobic monomer. For instance, the T_{PS} of a random copolymer of EOVE and MOVE ranges between 20 and 63 °C, depending on its composition. Narrow MWDs were critical to attaining highly sensitive phase transition, because of the molecular weight dependence of $T_{\rm PS}$.²⁶⁹

An appropriate overall amphiphilic balance in a polymer chain may be a key to successful sensitive phase separation. This concept was evidenced by phase separation behavior of a polymer with an alcohol pendant having a fine balance between hydrophilicity and hydrophobicity.²⁷⁵ A hydroxybutyl group is a rearrangement of an ethoxyethyl unit, and is expected to have a similar overall amphiphilic balance. Aqueous solutions of **23** (Figure 17) underwent rapid phase separation at 42 °C.²⁷⁵ The corresponding polymer with branched alcohol pendants showed a lower critical temperature.²⁷⁶ Another type of polymers with fine-tuned amphiphilicity would be random copolymers of hydrophobic

and hydrophilic units.²⁷⁷ A series of copolymers containing hydrophilic (HOVE: CH2=CH-O-CH2CH2OH) and hydrophobic alkyl VE units (24, Figure 17), prepared via base-assisting living cationic polymerization, permitted thermally induced phase separation with high sensitivity and complete reversibility. The T_{PS} of the random copolymers can be varied by altering the composition of HOVE with a hydrophobic VE, or the pendant structure of the hydrophobic VEs. The study also demonstrated that nearly even distribution of two monomers in a polymer chain was the key to realizing such highly sensitive phase separation. In fact, copolymers with both random and block segments exhibited less sensitive phase transitions with obvious hysteresis.²⁷⁷ The use of random copolymers of hydrophilic and hydrophobic monomers is a facile method for achieving thermosensitivity and would be extended to different types of polymers which are usually prepared by other polymerization mechanisms such as anionic and radical polymerizations.

Poly(MVE) is known as a thermoresponsive polymer for a long time.²⁷⁸ Living cationic polymerization of MVE was first achieved using the HI/I₂ initiating system, producing living polymers with narrow MWDs $(M_w/M_n \sim 1.10)$.¹⁰ Block copolymers with $CVE^{10,279}$ and $pMOS^{205}$ were prepared using the HI/I2 and HI/ZnI2 initiating system, respectively. Various well-defined polymers of MVE, such as di- or triblock copolymers (see Section 3.16.8.3), random copolymers, and end-functionalized polymers, were also synthesized with IBVE-Cl/SnCl₄ in conjunction with *n*Bu₄NCl as an added salt in CH₂Cl₂ at -78 °C,²⁰⁷ 1,1-diethoxyethane-Si(CH₃)₃I/ ZnI₂ in toluene at $-40 \,^{\circ}\text{C}_{,}^{280}$ or TMP–DPE-Cl/TiCl₄:Ti(OEt)₄ with DTBP as a proton trap in hexane/CH₂Cl₂ at 0 °C.²⁸¹ Their properties and behaviors in aqueous solution were investigated in terms of micelle formation, self-association, colloidal dispersion, and pressure-enhanced dynamic heterogeneity.

In contrast to the many polymers that exhibit LCST-type phase separation in water, there are a few polymers that induce



Figure 18 Thermoresponsive poly(VE)s for LCST- or UCST-type phase separation in water and organic solvents.

upper critical solution temperature (UCST)-type phase separation.^{282–284} Recently, it was reported that VE polymers with pendant imidazolium salt structures induce sensitive UCST-type phase separation in water.²⁸⁵ The polymers consisting of a poly(VE) main chain and imidazolium salt pendants were prepared via living cationic polymerization of CEVE, followed by nucleophilic substitution of the pendants with an imidazole derivative. The polymers with BF₄ (Figure 18, upper right) exhibited UCST-type phase transition at about 5 °C, whereas those with chloride counteranions were soluble in water.

The imidazolium salt-containing VE polymers also showed unique behavior in organic solvent.²⁸⁶ As with UCST-type phase separation in water, LCST-type phase separation in organic solvent is not straightforward. Although various conventional polymers such as poly(St), poly(IB), poly(acrylic acid), and cellulose derivatives were found to induce LCST-type phase separation,^{287,288} severe conditions, such as a high-pressure system in a sealed cell above the boiling point of a solvent, were inevitable for most of the systems. In sharp contrast, the VE-based polymers realized an LCST-type transition system under mild conditions. The poly([BuIm][Cl]) $(M_{\rm n} = 0.8 \times 10^4, M_{\rm w}/M_{\rm n} = 1.13,$ Figure 18, lower left), soluble in chloroform around room temperature, became phase-separated at 40 °C.²⁸⁶ The opaque solution returned to a clear state again as the temperature was decreased. The transitions were repeatable multiple times without hysteresis. Similar polymers with pyridinium salts also exhibited LCST-type phase separation. The molecular weight, the concentration, and the salt structure dependencies were demonstrated. The hydrogen bonds between polymer pendants and solvent molecules are most likely decisive in achieving this unique phase separation. Heating the solutions weakens the solvent-polymer interaction due to the cleavage of the hydrogen bond, as indicated by DSC and ¹H NMR measurements.

Strong interaction between polymer pendant groups would play a pivotal role in highly sensitive UCST-type phase separation in organic solvents.^{180,289–291} The crystallizing ability of long alkyl chains would endow a polymer with characteristic properties. For example, homopolymers of ODVE (C18 pendant; Figure 18, lower right) and its block copolymers with MVE showed the characteristic solubilities and high emulsion stabilities.²⁸⁰ A series of well-defined polymers of ODVE including homopolymers and random, block, and gradient copolymers were synthesized using base-assisting living polymerization.178-180 Sensitive UCST-type phase separation of homopolymers and random copolymers was observed in various conventional organic solvents with wide-ranging polarities.¹⁸⁰ Calorimetric measurements revealed that the transition with poly(ODVE) is driven by the crystallization of pendant octadecyl chains. Furthermore, aqueous solutions of various copolymers (block, periodic, statistic, and gradient) were converted into gels below 25 °C.^{178,179} The sequence distribution in the copolymers influenced the viscoelastic properties of the product gels significantly.^{178,179} Cholesteryl-^{180,290,291} or biphenyl-containing poly(VE)s with narrow MWDs were also found to undergo sensitive UCST-type phase separation in organic solvents.¹⁸⁰

Fluorine-containing homopolymers (Figure 18, lower right, see also Section 3.16.6.2) and copolymers were other powerful polymers for inducing UCST-type phase separation. For example, poly(5FVE), with C_2F_5 groups, showed sensitive UCST-type phase separation behavior in toluene.¹⁶⁶ It was found that polymers of a C_4F_9 -containing VE (CH₂=CHOC₂H₄OC₃H₆C₄F₉) permitted sensitive UCST-type phase separation not only in various common organic solvents including toluene, chloroform, and acetone, but also in perfluoro solvents.²⁹² Copolymers of 13FVE and IBVE showed UCST-type phase separation in common organic solvents with different polarities depending on their composition, while a homopolymer of 13FVE was insoluble in all nonfluorinated organic solvents.¹⁶⁶

3.16.8.2 Other Stimuli-Responsive Poly(VE)s

An advantage of base-assisting living cationic polymerization is tolerance to various polar functional monomers.²⁰ This strength has allowed selective synthesis of a new family of

well-defined stimuli-responsive polymers such as pH_{-}^{293} photo-,^{76,294,295} solvent-,^{296,297} and pressure-responsive^{298,299} polymers (Figures 19 and 20).^{19,20,270,271} For example, the transmittance of solutions of 25 and 26 having an alkylene



Figure 20 Typical examples of stimuli-responsive behavior of poly(VE)s in water.

group (\geq C5) or a phenylene adjacent to the carboxy group sharply changed at pH 5.6 and 6.5, respectively, whereas their solutions were transparent under nearly neutral or basic conditions.²⁹³ The polymer's pK_a value, the solubility of the polymer, and introduction of hydrophobic units were found to be important for controlling the critical pH. Interestingly, the decrease in pH induced sensitive phase separation of random copolymers **27** and homopolymer **28** in phosphate-buffered saline (PBS) even at pH 7.0, which is exceptionally high for carboxy-containing polymers.

Azobenzene and its derivatives are known as photoresponsive compounds based on cis-trans isomerization by light irradiation. Living cationic polymerization of VEs with azo functions (29) was achieved using various Lewis acids in the presence of an ester as an added base.^{76,294,295} Sensitive and reversible UV- and visible light-induced phase transitions were achieved. For example, random copolymers of thermally responsive and azobenzene units (30) changed their solubility in water by irradiation with UV or visible light at a certain temperature. Other impetus for sensitive phase separation includes the addition of a small amount of water^{271,297} or an organic compound²⁹⁶ and the increase in pressure.^{298,299} Alcohol solutions of silvloxy-containing polymers (31) underwent rapid phase transition on addition of a very small amount of water (as little as 0.1%, Figure 20). Water-induced physical gelation was also achieved with a silvloxy-containing diblock copolymer.271

3.16.8.3 Stimuli-Responsive Block Copolymers

Thermoresponsive poly(OEVE) systems stayed one step ahead of poly(NIPAM) (PNIPAM) systems to study the effects of molecular weight, MWD, and sequence distribution,²⁶⁹ since well-controlled polymerization of NIPAM was not achieved at that time. Thus, the findings with the VE systems were quite important for the understanding of LCST-type phase separation mechanism as well as for further design of stimuli-responsive polymers. Fine structures of stimuli-responsive polymers

would enable the construction of elaborate reversible self-association systems. Thus, multicomponent block copolymers of VEs with thermoresponsive segments were synthesized to examine their thermally induced selfassociation.^{19,20,270,271,300–305} The first example was a diblock copolymer containing a thermosensitive poly(EOVE) segment and a polyalcohol⁶⁷ segment (32), prepared by sequential living cationic polymerization.^{302,303} The diblock copolymer formed micelles with a very narrow size distribution in water above 20 °C, the critical temperature for poly(EOVE), 304,305 as shown in Figure 21. The critical micelle temperature corresponded well to the clouding point of the thermosensitive segment. The obtained micelles dissolved rapidly upon cooling, and this cycle was completely reproducible, yielding micelles of very similar size from the same sample in each cycle. The same polymer induced rapid physical gelation at a higher concentration when the temperature was raised above the critical temperature.³⁰²⁻³⁰⁵ The resulting transparent gel reverted with high sensitivity to the solution state at the same temperature upon cooling, as confirmed by dynamic viscoelasticity measurements. The mechanism of this physical gelation was revealed by SANS studies, DLS studies, and cryo-TEM measurements. The first step was thermally induced micellization into nearly monodisperse spherical micelles with a core of 18-20 nm. The resulting micelles immediately formed a macrolattice with bcc symmetry (Figure 21), which rendered the solution into a physical gel. Controlled primary structures were responsible for sensitive transition in the self-association process. The critical temperature of physical gelation can be determined by the cloud point of a thermoresponsive segment in a diblock copolymer.

Following the thermoresponsive gelation system of diblock copolymers, several reversible gelation systems in response to other stimuli were invented as illustrated in **Figure 22**. The stimuli that cause physical gelation were addition of a selected solvent or compound,^{296,297} cooling,¹⁷⁸ irradiation with UV light,^{76,294,295} pH change,^{71,293} or pressure.^{298,299} Furthermore, stepwise stimuli response or a combination of



Figure 21 Block copolymers of VEs and the mechanism of thermally induced self-association.


Figure 22 Typical patterns of physical gelation of stimuli-responsive diblock copolymers.

different stimuli was examined. Stepwise response was demonstrated using diblock copolymers with two thermosensitive segments^{301,306,307} possessing different $T_{PS'}$ which exhibited characteristic micelle formation and/or physical gelation. Diblock copolymers with two different stimuli-responsive segments were also prepared.71,293 Thermoresponsive ABC triblock copolymers (33) underwent sensitive thermally induced physical gelation (open association) through formation of micelles and subsequently their association by the outer segments. Such ABC triblock copolymers exhibited Weissenberg effects in semidilute aqueous solution.³⁰⁸ Diblock copolymers (34) of an imidazolium-containing segment, for UCST-type transition, and a poly(MOVE) segment, for LCST-type transition, underwent thermally induced gelsol-gel transitions.²⁸⁵ Although Nuyken and Ingrish³⁰⁹ reported similar methods for synthesizing block copoly(VE)s with electrostatically neutral pendant moieties such as pyrrolidonyl, succinimido, pyrazolyl, and imidazolyl groups, no reports were made on phase separation behaviors. The possibilities for application use of the above stimuli-responsive

polymers in many fields have been examined: coating of PET films using thermosensitive diblock copolymers for cell attachment control,³¹⁰ thermosensitive liposomes for drug release,³¹¹ smart films,^{169,172} surface modification by diblock copolymers containing azobenzene,³¹² and surface-modified micelles with carboxy groups.^{313,314}

A variety of well-defined block copolymers of poly(MVE), other typical themoresponsive polymers, were synthesized combined with hydrophilic or hydrophobic segments such as poly(vinyl alcohol),³¹⁵ poly(methyl triethylene glycol VE; TEGVE),^{316,317} poly(IBVE),^{318–320} poly(St),^{207,321} poly(IB),²⁸¹ and poly(ODVE)²⁸⁰ (Figure 23). For instance, diblock copolymers of poly(MVE) and hydrophilic poly(TEGVE) with a narrow MWD were prepared using IBVE-Cl/SnCl₄ with *n*Bu₄NCl in CH₂Cl₂.^{316,317} It was demonstrated that the diblock copolymers were dispersed as single chains in water at room temperature and formed micelles above 50 °C (a unimer–micelle transition). The hydrodynamic radii of the block copolymer micelles with the MVE core ranged from 8.1 to 31 nm (by DLS). The micellization was reversible as

$$\begin{array}{c} -\left(-CH_{2}-CH\xrightarrow{}_{n}b\xrightarrow{}(-R\xrightarrow{}_{m})_{m}\right) = \left(-R\xrightarrow{}_{m}\right) = \left(-R\xrightarrow{}_{m}\right) = \left(-CH_{2}-CH\xrightarrow{}_{m}\right) = \left(-CH_{2}-CH\xrightarrow{}_{m}$$

Figure 23 Poly(MVE) diblock copolymers.

confirmed by ¹H NMR studies at varying temperatures. Di- or triblock copolymers consisting of poly(MVE) and hydrophobic segments have been investigated^{280,322} as nonionic surfactants or thermoresponsive colloidal stabilizers.³²² A series of end-group-modified poly(MVE)s showed the effect of end groups on the phase separation behavior.^{293,323} In addition, such terminal-modified poly(MVE)s were used to prepare precursors for a new class of block, graft, and star-shaped polymers.^{264,293,324}

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3.17 Anionic Polymerization of Nonpolar Monomers

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3.17.1	Introduction to Carbanions, Living Polymerization, and Anionic Polymerization	559
3.17.1.1	Living Polymerization	560
3.17.1.2	General Aspects of Anionic Polymerization	560
3.17.1.2.1	Polymerizability of monomers	560
3.17.1.2.2	Solvents	561
3.17.2	Initiators, Initiation Mechanisms, and Kinetics	562
3.17.2.1	Initiation	562
3.17.2.2	Initiation by Electron Transfer	562
3.17.2.2.1	Alkali metals	562
3.17.2.2.2	Radical anions	562
3.17.2.3	Initiation by Nucleophilic Addition	563
3.17.2.3.1	Alkyllithium initiators	563
3.17.2.3.2	Other organoalkali initiators	563
3.17.2.3.3	Organoalkaline earth initiators	564
3.17.2.3.4	Ate complex initiators	564
3.17.2.3.5	Difunctional initiators	564
3.17.2.3.6	Functionalized initiators	566
3.17.2.4	Initiation Kinetics	566
3.17.2.4.1	Hydrocarbon solution	566
3.17.3	Propagation Kinetics and Mechanisms	568
3.17.3.1	Hydrocarbon Solution	568
3.17.3.1.1	Aggregation of poly(styryl)lithium	568
3.17.3.1.2	Aggregation of poly(dienyl)lithiums	568
3.17.3.1.3	Propagation kinetics for styrene monomers	569
3.17.3.1.4	Propagation kinetics for diene monomers	570
3.17.3.1.5	Relative reactivities of styrene and dienes	570
3.17.3.1.6	Effects of Lewis bases	571
3.17.3.1.7	Effects of ate complexes	571
3.17.3.2	Polar Solvents	572
3.17.4	Chain Termination Reactions	573
3.17.5	Chain Transfer Reactions	575
3.17.6	Stereochemistry	576
3.17.6.1	Polydienes	576
3.17.6.1.1	Hydrocarbon solvents	576
3.17.6.1.2	Polar solvents	578
3.17.6.1.3	Polar modifier effects	579
3.17.6.1.4	Salt and counterion effects	581
3.17.6.2	Polystyrene	582
3.17.7	Copolymerization	583
3.17.7.1	Hydrocarbon Solution	583
3.17.7.1.1	Tapered block copolymers	583
3.17.7.1.2	Counterion effects	585
3.17.7.2	Polar Solvents	586
3.17.7.3	Random Styrene–Diene Copolymers	586
References		587

3.17.1 Introduction to Carbanions, Living Polymerization, and Anionic Polymerization

This chapter describes the general aspects of anionic polymerization of nonpolar vinyl monomers such as styrenes and 1,3-dienes. Anionic polymerization is defined as a chain polymerization in which the active centers are anions, in the form of free ions, paired ions, or aggregated species.¹ An anion will be considered as an atom or group of atoms with a negative charge and an unshared pair of electrons. For styrene and diene monomers, the active centers are carbanions, which can be considered to be the conjugate bases of the corresponding carbon acids as shown in eqn [1]. The stability and reactivity of carbanionic species can be deduced from pK_a values associated with these

equilibria. The more acidic conjugate acids (carbon acids with lower pK_a values) are associated with more stable carbanionic species. The pK_a values for toluene, propene, and diphenylmethane are 43, 42, and 32, respectively.² The corresponding conjugate bases, that is, benzyl, allyl, and diphenylmethyl carbanions, are models for their polymeric analogs involved in initiation and propagation reactions.

$$--C - H - C - C + H^{\odot} - [1]$$

In general, carbanions are associated with a counterion, typically an alkali metal cation. The exact nature of the carbanionic species can be quite varied depending on the structure of the carbanion, counterion, solvent, and temperature.^{3–5} The range of possible species can be described in terms of a Winstein spectrum of structures as shown in eqn [2] for a carbanionic chain end (R⁻).^{3,6} In addition to the aggregated (associated) (1) and unaggregated (unassociated) (2) species, it is necessary to consider the intervention of free ions (5), contact ion pairs (3), and solvent-separated ion pairs (4); Mt⁺ represents a metallic counterion such as an alkali metal cation. In hydrocarbon media, species 1-3 would be expected to predominate. The addition of polar compounds, for example, Lewis bases and polar solvents, tends to shift the Winstein spectrum to the right, that is, toward more reactive, less associated, and more ionic species. It is generally agreed that the carbon-alkali metal bonding is ionic for sodium, potassium, rubidium, and cesium. In contrast, experimental evidence and theoretical studies indicate that the carbon-lithium bond includes some covalent character, that is, it is a semipolar bond;^{3,7} however, there is disagreement about the relative amounts of covalent versus ionic bonding.8

3.17.1.1 Living Polymerization

One of the milestones that led to dramatic advances in the science and technology of anionic polymerizations was the report in 1956 by Michael Szwarc and co-workers^{9,10} that these processes could be described as living polymerizations, that is, they proceed in the absence of the kinetic steps of chain transfer and chain termination unlike most other chain polymerization processes. Living polymerization provides methodologies for the synthesis of polymers with control of the major variables that affect polymer properties including molecular weight, molecular weight distribution, copolymer composition and microstructure, stereochemistry, chain-end functionality, and molecular architecture.^{3,11} This inherent control aspect of living anionic polymerization stimulated tremendous industrial research activity, which led to the development of numerous technologies for the preparation of important commodity and specialty materials.³ Today, anionic polymerization is used for the commercial production of more than 3 million tons of polymers annually, including polybutadiene, polyisoprene, styrene-butadiene rubber (SBR), and styrene-diene-styrene triblock copolymers plus their hydrogenated analogs.¹²

3.17.1.2 General Aspects of Anionic Polymerization

3.17.1.2.1 Polymerizability of monomers

The anionic polymerizability of vinyl monomers cannot be deduced from the thermodynamics of polymerization since almost all vinyl monomers exhibit negative free energies of polymerization; that is, if a suitable pathway exists, the polymerization will proceed spontaneously to form the polymer from the monomer.^{13,14} This is exemplified by the fact that cyclopropane does not undergo anionic polymerization in spite of its high ring strain and exothermic energy of polymerization ($\Delta G = -22.1 \text{ kcal mol}^{-1}$).^{15,16} The proviso that there exists a suitable pathway provides the major limitation on the

$$(RMt)_n \xrightarrow{} n RMt \xrightarrow{} R^-, Mt^+ \xrightarrow{} R^-// Mt^+ \xrightarrow{} R^- + Mt^+$$

$$1 \qquad 2 \qquad 3 \qquad 4 \qquad 5$$

$$[2]$$

Unlike most other chain reaction polymerizations involving low concentrations of transient, reactive intermediates, carbanions and organometallic species are often stable enough to be prepared and characterized independently of the polymerization process. anionic polymerizability of monomers. Thus, for anionic polymerizability, it is generally considered that there must be substituents on the double bond that can stabilize the negative charge that develops in the transition state for the monomer addition step as shown in eqn [3]:

$$R^{-} + CH_{2} \underbrace{\longrightarrow}_{Y} C \underbrace{\bigvee_{Y}}_{Y} \underbrace{\longrightarrow}_{Y} \left[\begin{array}{c} -\delta & -\delta \\ R - \cdots - CH_{2} \underbrace{\longrightarrow}_{Y} C \\ Y \end{array} \right]^{\ddagger} \underbrace{\longrightarrow}_{Y} RCH_{2} C^{-}$$

$$[3]$$

These substituents must also be stable to the reactive anionic chain ends; thus, relatively acidic, proton-donating groups (e.g., amino, hydroxyl, carboxyl, and acetylene) or strongly electrophilic functional groups (e.g., cyano, carbonyl, nitro, and sulfonyl) that react with bases and nucleophiles must not be present or must be protected by conversion to a suitable derivative. In general, substituents that stabilize negative charge by anionic charge delocalization are the substituents that render vinyl monomers polymerizable by an anionic mechanism. Thus, styrene and 1,3-diene monomers readily undergo anionic polymerization. In contrast to the lack of polymerizability of 1-alkenes and other more substituted alkenes, it is noteworthy and unexpected that ethylene is anionically polymerizable in the presence of highly coordinating bases such as N,N,N',N'tetramethylethylenediamine (TMEDA).3,17,18 The propagating primary carbanion in ethylene polymerization is a very reactive species $(pK_3 > 56)^2$ and it has minimal steric requirements. The unreactivity of more substituted alkenes may be associated with the effects of alkyl groups in forming more stable, less reactive pi bonds, less stable carbanions, and more sterically hindered transition states for monomer addition. Although cyclopropane itself is not anionically polymerizable, cyclopropanes with two electron-withdrawing groups on one of the ring carbons, for exam--CO₂R or -CN substitution, undergo anionic ple, polymerization.^{16,19} Another anionically reactive monomer is trimethylvinylsilane (CH₂=CHSi(CH₃)₃) in which the silicon atom with available d-orbitals can stabilize the resulting carbanion.²⁰

Styrene monomers with alkyl, alkoxy, and 3° amine groups undergo controlled, living anionic polymerization.3,21-24 Homologs of styrene, such as vinylnaphthalene, vinylanthracene, and vinylpyrene, are also polymerizable, as expected. 4-Vinyltriphenylamine undergoes living alkyllithium-initiated polymerization to form a polymer of interest as a hole-transport layer in light-emitting diodes.²⁵ The living polymerization of 4-vinylbenzocyclobutene using sec-butyllithium in benzene has been reported.²⁶ For some styrene monomers with potentially groups, anionic reactive functional polymerization can be effected in polar media (tetrahydrofuran (THF)²⁷ or THF/N,N-dimethylacetamide²⁸) at low temperatures $(-78 \degree C)$, for example, 4-(4-(2-isopropenylphenoxy)butyl)styrene²⁷ and 4-cyanostyrene.²⁸ The otherwise limited range of polymerizable styrene-type monomers can be expanded by preparation of monomers with suitable protecting groups for reactive functionalities such as hydroxyl, amine, carbonyl, and carboxyl. The limitations of this methodology, however, are that a new monomer is required for each functional group, the protecting group must be removed after polymerization, and many of these protecting groups are not stable to initiators or carbanionic propagating species and require the use of low temperatures for their controlled polymerization. Examples of substituted styrenes with protected functional groups are shown in Scheme 1. ^{3,21,23,24}

The limited range of conjugated dienes that can be anionically polymerized is shown in **Scheme 2**. There has been renewed interest in the anionic polymerization of 1,3-cyclohexadiene, even though chain transfer and chain termination reactions can occur.^{29–33} 1,3,5-Trienes such as *trans*-1,3,5-hexatriene can be polymerized by alkyllithium-initiated anionic polymerization, but it was not possible to eliminate branching reactions.³⁴ Monoaddition to poly(styryl)lithium (PSLi) was effected by the addition of 1.2 equivalents of *trans*-1,3,5-hexatriene at -10 °C



Scheme 1 Anionically polymerizable styrene monomers with protecting groups.



Scheme 2 Anionically polymerizable 1,3-dienes.

in toluene to form the corresponding diene-functionalized macromonomer. $^{35}\,$

3.17.1.2.2 Solvents

The range of useful solvents for anionic polymerization is limited by the high reactivity (basicity and nucleophilicity) of the initiators and propagating carbanionic chain ends. For styrene and diene monomers, the solvents of choice are alkanes, cycloalkanes, aromatic hydrocarbons, and ethers;^{3,36–38} the use of alkenes has also been described, although some chain transfer can occur, especially at elevated temperatures and in the presence of Lewis bases.³⁹ Aromatic hydrocarbon solvents such as benzene and toluene provide enhanced rates of initiation and propagation relative to the alkanes;⁴⁰ however, chain transfer reactions can occur with alkylated aromatic solvents, for example, toluene and ethylbenzene.^{41,42} A useful alternative is *t*-butylbenzene, which has no reactive benzylic hydrogens and has a much lower freezing point (-58.1 °C) making it useful for low-temperature processes.⁴³

Polar solvents such as ethers and amines react with organometallic initiators, as well as propagating polystyryl and polydienyl carbanions, to decrease the concentration of active centers.^{3,44,45} The rate of reaction with ethers decreases in the order $Li^+ > Na^+ > K^+$. For example, dilute solutions of PSLi in THF at room temperature decompose at the rate of a few percent each minute. Alkyllithium initiators also react relatively rapidly with ethers; the order of reactivity of organolithium compounds with ethers is tertiary RLi>secondary RLi>primary RLi > phenyllithium > methyllithium > benzyllithium.⁴⁴ An approximate order of reactivity of ethers toward alkyllithium compounds is dimethoxyethane>THF>tetrahydropyran>diethyl ether>diisopropyl ether. Tertiary amines can also react with alkyllithium compounds. The importance of these reactions can be minimized by working at lower temperatures (e.g., <0 °C); it is also advisable to use only the minimum amounts of ethers and other Lewis bases required as additives.

3.17.2 Initiators, Initiation Mechanisms, and Kinetics

3.17.2.1 Initiation

An important consideration for the preparation of polymers with well-defined structures and low degrees of compositional heterogeneity is the choice of a suitable initiator. In general, an appropriate initiator is a species that has approximately the same structure and reactivity as the propagating anionic species, that is, the pK_a of the conjugate acid of the propagating anion should correspond closely to the pK_a of the conjugate acid of the initiator is not reactive. If the initiator is too reactive, often side reactions between the initiator and monomer will occur; if the initiator is not reactive enough, then the initiation reaction may be slow or inefficient. The pK_a values for the propagating carbanions in styrene and diene monomers are 43–44;² thus, alkyl organometallic compounds with pK_a values >56 are generally used as initiators.³ Other useful initiators include aromatic radical anions.

3.17.2.2 Initiation by Electron Transfer

3.17.2.2.1 Alkali metals

The direct use of alkali metals and alkaline earth metals as initiators for anionic polymerization of 1,3-diene monomers as first reported in 1910 is primarily of historical interest because these are uncontrolled, heterogeneous processes.⁴⁶ An important milestone in the development of the science and technology of anionic polymerization was the discovery reported in 1956 by Stavely et al.47 at Firestone Tire and Rubber Company that polymerization of neat isoprene with lithium dispersion produced high cis-1,4-polyisoprene, similar in structure and properties to Hevea natural rubber. This discovery led to the development of commercial anionic solution polymerization processes using alkyllithium initiators. It is noteworthy that high 1,4-stereospecificity in anionic 1,3-diene polymerization is only observed for lithium in hydrocarbon solution; high vinyl microstructure predominates with other alkali metals and in polar media.

The mechanism of anionic polymerization of styrenes and 1,3-dienes initiated by alkali metals has been described in detail by Szwarc.⁴⁸ Initiation is a heterogeneous process occurring on the surface of the metal (Mt) by reversible transfer of an electron to adsorbed monomer (M) as shown



Scheme 3 Mechanism of metal-initiated anionic polymerization.

in Scheme 3. The initially formed radical anions (M⁻) rapidly dimerize to form dianions. Monomer addition to these dianions forms adsorbed oligomers that desorb and continue chain growth in solution. Unlike homogeneous anionic initiation processes with organometallic compounds, this heterogeneous initiation reaction continues to generate new active chain ends during the course of the subsequent propagation reactions. Consequently, there is little control of molecular weight, and relatively broad molecular weight distributions have been reported for the soluble polymer obtained from these bulk polymerizations ($M_w/M_n = 3-10$);⁴⁹ a high degree of branching and a high gel content (45%) have also been reported for these processes.^{47,49}

These reactions are useful for the preparation of homogeneous difunctional initiators from α -methylstyrene in polar solvents such as THF. Because of the low ceiling temperature of α -methylstyrene ($T_c = 61$ °C),⁵⁰ dimers or tetramers can be formed depending on the alkali metal system, temperature, and concentration. Thus, the reduction of α -methylstyrene by sodium/potassium alloy in THF produces the dimeric dianionic initiators in THF, while the reduction with a sodium mirror forms the tetrameric dianions as the main products.⁵¹ The structures of the dimer and tetramer correspond to initial tail-to-tail addition to form the most stable dianion as shown in Scheme 4.⁵¹ These dianionic initiators are formed and used in polar solvents such as THF.

3.17.2.2.2 Radical anions

Many aromatic hydrocarbons such as naphthalene and anthracene react reversibly with alkali metals in polar aprotic solvents to form stable homogeneous solutions of the corresponding radical anions as shown in eqn [4].^{4,48} Radical anions can only be formed efficiently in polar aprotic solvents such as THF and glymes.

$$Mt + Ar \longrightarrow Ar^{\bullet-}Mt^{+}$$

$$Mt = Li, Na, K, Rb, Cs$$
[4]

Aromatic radical anions such as sodium naphthalenide react with monomers such as styrene by reversible electron transfer to form the corresponding monomer radical anions as shown in **Scheme 5** (R=H, CH₃). Although the equilibrium between the radical anion of the monomer and the aromatic radical anion lies far to the left because of the low electron affinity of the monomer compared to the condensed aromatic hydrocarbon, this is an efficient initiation process because the resulting monomer radical anions undergo tail-to-tail dimerization reactions with rate constants that approach diffusion control ($k_d = 10^8 - 10^9 \ 1 \text{mol}^{-1} \ \text{s}^{-1}$).⁴⁸ Aromatic radical anions can be used to initiate the polymerization of styrene and 1,3-diene monomers.



Scheme 4 Formation of dimeric and tetrameric dianions by reduction of α-methylstyrene.



Scheme 5 Initiation mechanism with aromatic radical anions.

3.17.2.3 Initiation by Nucleophilic Addition

3.17.2.3.1 Alkyllithium initiators

Although anionic polymerization of vinyl monomers can be effected with a variety of organometallic compounds, alkyllithium compounds are the most useful class of initiators.^{3,44,52,53} A variety of simple alkyllithium compounds are readily available commercially in hydrocarbon solvents such as hexane and cyclohexane. They can be prepared by reaction of the corresponding alkyl chlorides with lithium metal.

Alkyllithium compounds are generally associated into dimers, tetramers, or hexamers in hydrocarbon solution.^{3,44} The degree of association is related to the steric requirements of the alkyl group, that is, the degree of association decreases as the steric requirements of the alkyl group increase.

The relative reactivities of alkyllithiums as polymerization initiators are intimately linked to their degree of association as shown below with the average degree of association in hydrocarbon solution indicated in parentheses after the alkyllithium:^{3,44,52,54}

Styrene polymerization:

menthyllithium (2) > sec-BuLi (4) > i-PrLi (4-6) > i-BuLi > n-BuLi (6) > t-BuLi (4)

Diene polymerization:

menthyllithium (2) > sec-BuLi (4) > i-PrLi (4-6) > t-BuLi (4) > i-BuLi > n-BuLi (6)

In general, the less associated alkyllithiums are more reactive as initiators than the more highly associated species; note, however, that *t*-butyllithium is a poor initiator for styrene, but an excellent initiator for dienes.

Alkyllithium initiators are primarily used as initiators for polymerizations of styrenes and 1,3-dienes. They effect quantitative living polymerization of styrenes and dienes in hydrocarbon solution. *n*-Butyllithium is used commercially to initiate anionic homopolymerization and copolymerization of butadiene, isoprene, and styrene with linear and branched structures. Because of the high degree of association (hexameric) of this initiator, *n*-butyllithium-initiated polymerizations are often effected at elevated temperatures (>50 °C) to increase the rate of initiation relative to propagation and thus to obtain polymers with narrower molecular weight distributions.⁵⁵ The addition of small amounts of Lewis bases such as ethers and amines tends to decrease the degree of aggregation of alkyllithium compounds and accelerate rates of initiation.⁵⁶

sec-Butyllithium is used commercially to prepare styrenediene block copolymers because it can initiate styrene polymerization rapidly compared to propagation so that even polystyrene blocks with relatively low molecular weights (10 000–15 000 g mol⁻¹) can be prepared with stoichiometric control and narrow molecular weight distributions.⁵⁷

3.17.2.3.2 Other organoalkali initiators

In general, the simple organoalkali metal derivatives other than lithium are not soluble in hydrocarbon media. However, higher homologs of branched hydrocarbons are soluble in hydrocarbon media. For example, the reaction of 2-ethylhexyl chloride and sodium metal in heptane produces soluble 2-ethylhexylsodium.⁵⁸ This initiator quantitatively polymerizes butadiene or isoprene to form polymers with observed molecular weights close to the theoretical values (M_n = grams of monomer per mole of initiator), but with relatively broad molecular weight distributions (M_w/M_n = 1.2–1.5).

Cumylpotassium $(pK_a \approx 43 \text{ based on toluene})^2$ is a useful initiator for anionic polymerization of a variety of monomers, including styrenes and dienes. This carbanion is readily prepared from cumyl methyl ether and sodium/potassium alloy in THF, and is generally used at low temperatures in polar solvents such as THF.

3.17.2.3.3 Organoalkaline earth initiators

Both styrene and 1,3-dienes can be polymerized by organoalkaline earth metal compounds, specifically those of magnesium, calcium, barium, and strontium. In general, hydrocarbon-soluble benzyl, 1,1-diphenylalkyl, and triphenylmethyl derivatives have been investigated. For example, dibenzylbarium is not soluble in toluene or diethyl ether, but it is soluble in THF.⁵⁹ The adduct of 1,1-diphenylethylene with dibenzylbarium, that is, bis(1,1,3triphenylpropyl)barium, is soluble in cyclohexane and was used to polymerize styrene. Although the observed $M_{\rm p}$ of polystyrene $(90 \times 10^3 \text{ Da})$ was close to the calculated value $(104 \times 10^3 \text{ Da})$, the observed molecular weight distribution was broad $(M_w/M_p = 1.20)$.⁵⁹ This type of behavior, that is, broad molecular weight distributions, is typical for these initiators for both styrene and butadiene polymerizations and has been ascribed to slow rates of initiation relative to propagation. The structures and initiation efficiencies of a broad series of substituted heteroleptic 2-dimethylamino-α-substituted-benzylcalcium complexes with modified fluorenyl ligands have been investigated; in general, quantitative polymerizations were effected in cyclohexane to provide polystyrenes with near stoichiometric molecular weights but with broad polydispersities $(M_w/M_n \approx 2)$.⁶⁰ Hydrocarbon-soluble n,s-dibutylmagnesium is not an active initiator for styrenes and dienes in cyclohexane.

3.17.2.3.4 Ate complex initiators

Alkyllithium compounds interact with organometallic compounds of different metals (MtR'_n), most notably those of Groups I, II, and III, which behave like Lewis acids, to form mixed organometallic compounds, referred to as 'ate' complexes, 61 schematically represented in the following equation: 61

$$RLi + MtR'_{n} \rightarrow Li^{+}[RMtR'_{n}]^{-}$$
[5]

X-ray and nuclear magnetic resonance (NMR) investigations indicate more complex, stoichiometry-dependent types of structures involving bridging alkyl groups between the two types of metal centers for aluminum, magnesium, and zinc systems as represented in Scheme $6.^{62,63}$

The importance of these mixed organometallic species is that they dramatically attenuate the reactivity of the chain ends so that controlled polymerizations can be effected at higher temperatures and with higher monomer concentrations.⁶⁴

3.17.2.3.5 Difunctional initiators

Aromatic radical anions, such as lithium naphthalene or sodium naphthalene, are efficient difunctional initiators (see Scheme 3). However, the need to use polar solvents for



Scheme 6 Structures of mixed organometallic complexes ('ate' complexes).

their formation limits their utility for diene polymerization since the unique ability of lithium to provide high 1,4-polydiene microstructure is lost in polar media.³ However, a useful, hydrocarbon-soluble, dilithium initiator was prepared by the dimerization of 1,1-diphenylethylene with lithium metal in cyclohexane in the presence of anisole (15 vol.%) as shown in Scheme 7.65 Although the initiator was soluble in this mixture, it precipitated from solution when added to the polymerization solvent (cyclohexane or benzene). Therefore, the dilithium initiator was chain-extended with approximately 30 units of isoprene to generate the corresponding soluble oligomer. This initiator was used to prepare welldefined polystyrene-block-polyisoprene-block-polystyrene and poly (α -methylstyrene)-*block*-polyisoprene-*block*-poly(α -methylstyrene) triblock copolymers with >90% 1,4-microstructure by sequential monomer addition. This was the first demonstration that substituted 1.1-diphenvlalkvllithium compounds (pK, of conjugate acid = 32)² could initiate the polymerization of a 1,3-diene (p K_a of conjugate acid = 43),² which involves the formation of a much less stable allylic anion.

The methodology for the preparation of hydrocarbon-soluble dilithium initiators is generally based on the reaction of an aromatic divinyl precursor with 2 mol of butyllithium. Unfortunately, because of the tendency of organolithium chain ends in hydrocarbon solution to associate and form electron-deficient dimeric, tetrameric, or hexameric aggregates,⁴⁴ most attempts to prepare dilithium initiators in hydrocarbon media have resulted in the formation of insoluble, three-dimensionally associated species. These precipitates are not effective initiators because of their heterogeneous



Scheme 7 Formation of a soluble 1,4-dilithium-1,1,4,4-tetraphenylbutane initiator.

initiation reactions with monomers, which tend to result in broader molecular weight distributions $(M_w/M_n > 1.1)$.⁶⁶

the polybutadiene blocks exhibited relatively high 1,2-microstructure (40–68%).



Soluble analogs of these difunctional initiators have been prepared by the addition of small amounts of weakly basic additives such as triethylamine⁶⁷ or anisole,⁶⁵ which have relatively minor effects on diene microstructure.⁶⁸ Another method to solubilize these initiators is to use a seeding technique, whereby small amounts of diene monomers are added to form a hydrocarbon-soluble, oligomeric dilithium initiating species.^{69,70}

The reaction of *meta*-diisoproprenylbenzene with 2 mol of *sec*-butyllithium has been reported to result in oligomerization to form a mixture of diadduct and multilithium oligomers. Oligomerization occurs because of the relatively low ceiling temperature of this difunctional analog of α -methylstyrene (T_c = 61 °C).⁵⁰ However, the analogous reaction with 2 mol of the more sterically hindered *t*-butyllithium in the presence of one equivalent of triethylamine in cyclohexane at -20 °C has been reported to form pure diadduct without oligomerization

The reaction of pure *m*-divinylbenzene with *sec*-butyllithium in toluene at -49 °C in the presence of triethylamine ([Et₃N]/ [Li] = 0.1) has been reported to produce the corresponding dilithium initiator in quantitative yield.⁷² Polymerization of butadiene with this initiator in toluene at -78 °C produced well-defined polybutadiene with high 1,4-microstructure (87%).

The addition reaction of 2 mol of *sec*-butyllithium with 1,3bis(1-phenylethenyl)benzene (eqn [7]) proceeds rapidly and efficiently to produce the corresponding dilithium species that is soluble in toluene or in cyclohexane.^{52,73} Although this dilithium initiator is useful for the preparation of homopolymers and triblock copolymers with relatively narrow molecular weight distributions, it is necessary to add a small amount of Lewis base or two or more equivalents of lithium alkoxide (e.g., lithium *sec*-butoxide) to produce narrow, monomodal molecular weight distributions.



(eqn [6]).⁷¹ This initiator in the presence of 5 vol.% of diethyl ether has been used to prepare well-defined poly(methyl methacrylate)-*block*-polybutadiene-*block*-poly(methyl methacrylate). Because of the requisite use of diethyl ether to prevent the formation of multimodal molecular weight distributions,

The reaction of multifunctional aryl bromides with several equivalents of *sec*-butyllithium has been used to form multifunctional organolithium initiators that are soluble in hydrocarbon solvent as shown in **Scheme 8**.^{74,75} It should be noted that this procedure requires two extra equivalents of *sec*-butyllithium to



Scheme 8 Synthesis of diaryllithium-based, difunctional initiator.

react with 2 mol of *sec*-butyl bromide formed by lithium-halogen exchange. This initiator was used to prepare triblock copolymers containing polybutadiene center blocks with high 1,4-microstructure and with good tensile properties (>900% elongation, ~30 MPa tensile strength at break).⁷⁴

3.17.2.3.6 Functionalized initiators

Alkyllithium initiators that contain functional groups provide versatile methods for the preparation of end-functionalized polymers and macromonomers.⁷⁶⁻⁷⁸ For a living anionic polymerization, each functionalized initiator molecule will produce one macromolecule with the functional group from the initiator residue at one chain end and the active anionic propagating moiety at the other chain end. However, many functional groups such as hydroxyl, carboxyl, phenol, and primary amine are not stable in the presence of reactive dienvllithium and styrvllithium chain ends. Therefore, it is necessary to convert these functional groups into suitable derivatives, that is, protected groups, that are stable to the carbanionic chain ends and that can be removed readily after the polymerization. Examples of protected functional initiators include the hydroxyl-protected initiators, 1-lithium-6-(1-ethoxyethoxy)hexane, 6-(t-butyldimethylsiloxy)hexyllithium, and 3-(*t*-butyldimethylsiloxy) propyllithium, as well as a primary amine-protected initiator, 4bis-(trimethylsilyl)aminophenyllithium.⁷⁸ A general method for the synthesis of functionalized initiators involves the reaction of substituted 1,1-diphenylethylenes with stoichiometric amounts of sec-butyllithium as shown in eqn [8] (X = functional group).⁷⁹ These hydrocarbon-soluble 1,1-diphenylalkyllithium initiators are useful for the polymerization of styrene and diene monomers.

$$(n-\text{BuLi})_{6} \xrightarrow{K_{d}} 6 n-\text{BuLi}$$
$$n-\text{BuLi} + \text{CH}_{2} \xrightarrow{\text{CH}} \frac{k_{i}}{C_{6}\text{H}_{5}} n-\text{Bu-CH}_{2}\text{CHLi}$$
$$\downarrow C_{6}\text{H}_{5} C_{6}\text{H}_{5}$$

Scheme 9 Mechanism of styrene initiation with *n*-butyllithium in hydrocarbon solution.

dependence on *n*-butyllithium concentration as shown in the following equation:

$$R_i = k_i (K_d / 6)^{1/6} [BuLi]_0^{1/6} [M]$$
 [9]

Since *n*-butyllithium is aggregated predominantly into hexamers in hydrocarbon solution,⁴⁴ the fractional kinetic order dependency of the initiation process on the total concentration of initiator has been rationalized on the basis that unassociated *n*-butyllithium is the initiating species and that it is formed by the equilibrium dissociation of the hexamer as shown in **Scheme 9**.

The kinetic order for *sec*-butyllithium-initiated polymerization of styrene is close to 0.25 in benzene solution; this result is also consistent with initiation by unassociated *sec*-butyllithium, since *sec*-butyllithium is associated predominantly into tetramers in benzene solution.⁴⁴

The frequent coincidence of the degree of association with the fractional kinetic order dependence on initiator concentration supports the postulate that the initiating species is a small amount of reactive monomeric (unassociated) alkyllithium in equilibrium with the much larger concentration of the unreac-



3.17.2.4 Initiation Kinetics 3.17.2.4.1 Hydrocarbon solution

The mechanism of initiation of anionic polymerization of vinyl monomers with alkyllithium compounds and other organometallic compounds is complicated by association and cross-association phenomena in hydrocarbon solvents and by the presence of a variety of ionic species in polar media.^{3,4,48,80} The kinetics of initiation are complicated by competing propagation and the occurrence of cross-association of the alkyllithium initiator with the propagating organolithium.⁵⁴ Thus, only the initial rates provide reliable kinetic data.

Typical kinetics of the initiation reaction of *n*-butyllithium with styrene in benzene exhibit a first-order dependence on styrene concentration and approximately a one-sixth-order tive aggregated species. However, the correctness of this interpretation, that is, direct dissociation to monomeric, unassociated species, has been questioned.³ The experimentally observed energy of activation, for example, 18 kcal mol⁻¹ for *n*-butyllithium initiation of styrene polymerization, ⁸¹ appears to be too low to include the enthalpy of complete dissociation of the aggregates, which is estimated to require approximately 108 kcal mol⁻¹.⁸² An alternative mechanism is the incomplete or stepwise dissociation of the aggregate, for example, as shown in eqns [10]–[13] for hexamers; eqn [12] plus eqn [13] would apply for tetramers.

$$(\text{RLi})_6 \longrightarrow (\text{RLi})_5 + \text{RLi}$$
 [10]

$$(RLi)_6 = (RLi)_4 + (RLi)_2 \qquad [11]$$

$$(\text{RLi})_4 = 2(\text{RLi})_2$$
 [12]

$$(RLi)_2 = 2RLi$$
 [13]

For kinetics in aliphatic solvents, the inverse correspondence between reaction order dependence for alkyllithium initiator concentration and the degree of alkyllithium aggregation is not observed.⁸⁰ In addition, the rates of initiation in aliphatic solvents are several orders of magnitude less than that in aromatic



Figure 1 Typical curves for the appearance of the UV absorption of poly(styryl)lithium. (a) Reaction of 1.09×10^{-3} M *sec*-butyllithium with 5.33×10^{-4} M styrene in benzene solution at 30 °C. (b) Reaction of 1.34×10^{-3} M *sec*-butyllithium with 8.67×10^{-2} M styrene in cyclohexane solution at 40 °C. From Bywater, S.; Worsfold, D. J. *J. Organometal. Chem.* **1967**, *10*, 1; reprinted by permission of Elsevier Science & Technology Journals.

solvents.⁴⁰ Most reaction orders for alkyllithium initiators in aliphatic solvents are close to unity.^{3,80} These results suggest that in aliphatic solvents the initiation process may involve the direct addition of monomer with aggregated organolithium species (eqn [14]) to form a cross-associated species.⁸⁰

$$(\text{RLi})_n + M \longrightarrow [(\text{RLi})_{n-1}(\text{RMLi})]$$
 [14]

The formation of cross-associated species would be expected to complicate the kinetics and lead to variable reaction orders as a function of conversion. The observation of pronounced induction periods as shown in Figure 1 has been ascribed to the enhanced reactivity of the mixed (i.e., cross-associated) aggregated species.⁴⁰ With respect to cross-association effects, it is noteworthy that it has been reported that the rate of exchange of alkyllithium initiators with poly(isoprenyl)lithium is rapid on the NMR timescale in hydrocarbon solution;⁸³ furthermore, exchange among different poly(butadienyl)lithium species is also reported to be rapid on the NMR timescale.⁸⁴ The effects of cross-association of the alkyllithium initiator with the initiated polymeric organolithiums provide at least a partial explanation for the discrepancies reported in the literature for the kinetic order dependencies on alkyllithium initiator concentration;^{3,80} thus, only in the initial stages is it likely that a detailed interpretation of the mechanism is possible or reliable. These results also qualify the often dogmatic assertions regarding the unreactivity of organolithium aggregates.

The actual complexity of these initiation events has been documented by combined ¹H NMR and small-angle neutron scattering (SANS) studies of the *t*-butyllithium-initiated polymerization of butadiene in heptanes at 8 °C, which revealed the presence of coexisting large-scale aggregates ($n \approx 100$; ≤ 1 wt.%) and smaller aggregates during all stages of the polymerization, that is, initiation and propagation.^{85,86} The average degree of aggregation decreased from $n \approx 140$ at the beginning of initiation/polymerization process and leveled off at ~4 with increasing chain length as shown in Figure 2. It was stated that for the lower aggregation numbers, the structure of the



Figure 2 Aggregation number, *N*_{agg}, as a function of degree of polymerization, *D*_p, for *t*-butyllithium-initiated polymerization of butadiene in heptanes at 20 °C. From Niu, A. Z.; Stellbrink, J.; Allgaier, J.; *et al. Macromol. Symp.* **2004**, *215*, 1-15; reprinted by permission of Wiley-VCH Verlag GmbH & Co. KGaA.

aggregates is star-like and in agreement with the traditional mechanism (see 3.17.3.1.4).⁸⁵

The effect of meta and para substituents on the rate of initiation of styrene by *n*-butyllithium in benzene has been investigated.⁸⁷ A plot of the logarithms of the rates relative to that of styrene against the Hammett substituent constants (σ) provided a straight line with a slope (ρ) equal to 1.0. The positive sign of ρ indicates that this initiation reaction is accelerated by electron-withdrawing substituents, as expected for the generation of a negative charge on the developing benzylic chain end during initiation (see eqn [3]). However, the magnitude of this ρ is the same as that for the ionization of substituted benzoic acids in which the substituents cannot directly conjugate with the negative charge, unlike the situation with substituted styrenes. This low value of ρ suggests that little negative charge is built up on the benzylic carbon in the transition state for initiation, implying an exothermic reaction in which the transition state resembles the reactants.88

Lewis bases and alkali metal alkoxides have been used as additives to modify the initiation reaction with alkyllithium compounds. Lewis bases such as ethers and amines, when present in amounts comparable to the initiator concentration, dramatically increase the relative rate of initiation of styrene and diene polymerizations relative to propagation. For example, in the presence of small, stoichiometric amounts of THF, the initiation reaction of styrene with *n*-butyllithium is complete within a few seconds,⁸⁹ compared with approximately 200 min in the absence of Lewis base.⁸⁰ Similarly, analogous initiation of isoprene polymerization in cyclohexane requires hours for completion, but is complete in 15 min in the presence of 10 equivalents of THF.⁹⁰

The effect of lithium alkoxides on alkyllithium-initiated polymerizations is important because these salts are ubiquitously present to some extent as impurities formed by the reactions with oxygen⁹¹ (eqn [15]) and hydroxylic impurities (eqn [16]). In fact, it is common practice to utilize excess butyllithium, that is, more than the stoichiometric amount required to generate the required molecular weight, to scavenge impurities in the solvent and monomer feed.

$$RLi + O_2 \longrightarrow R - R + RO_2R + ROOH + ROH$$
 [15]

$$RLi + ROH \longrightarrow R-H + ROLi$$
 [16]

The effects of lithium alkoxides on the rates of alkyllithium-initiation reactions depend on the solvent, monomer, alkoxide structure, alkyllithium initiator, and ratio of [RLi]/[LiOR'].^{54,80} For *n*-butyllithium initiation of styrene in cyclohexane, the rate of initiation is increased at low relative concentrations of added lithium alkoxide ([BuLi]/ [*t*-BuOLi] < 0.5).⁹² At a ratio of 1:1, the rate is essentially the same as the control without alkoxide; beyond this ratio, the rate decreases continuously with the increasing relative concentration of lithium alkoxide. In aromatic solvents, the initiation rate decreases with increasing relative concentration of lithium alkoxides generally accelerate the rate of initiation by alkyllithiums (*n*-butyllithium and *sec*butyllithium) for isoprene in hexane.^{94,95}

3.17.3 Propagation Kinetics and Mechanisms

Considering the potential complexity of active propagating species based on the Winstein spectrum of carbanionic structures (see eqn [2]), it would be anticipated that the following general rate equation (eqn [17]) would be applicable for anionic polymerization of all styrene and diene monomers that exhibit first-order kinetic dependencies on monomer concentration,

$$R_{\rm p} = -d[M]/dt = \sum k_{ip} C_i^*[M]$$
 [17]

where R_p is the rate of propagation, [M] is the monomer concentration, k_{ip} is the rate of propagation for anionic propagating species *i*, and C_i^* is the concentration of an anionic propagating species *i*. In polar solvents, several different types of ionic species must be considered, that is, ion pairs and free ions; in hydrocarbon solvents, aggregated (associated) and unaggregated (unassociated) species are most important.

3.17.3.1 Hydrocarbon Solution

The mechanism and kinetics of propagation for styrene and diene monomers in hydrocarbon solvents with lithium as the counterion are complicated by chain-end association.3,54,80 However, unlike the kinetics of initiation reactions in organolithium systems, the reaction order dependence of the propagation rate on active center concentration is independent of the identity of the hydrocarbon solvent, aromatic or aliphatic, although the relative propagation rates under equivalent conditions are faster in aromatic versus aliphatic solvents. Because these are living polymerizations, the kinetics of propagation can be investigated independently of initiation so that complications from cross-association with the initiator are absent. In addition, the propagating carbanions are stable species that can be generated quantitatively and independently characterized. Consequently, a variety of techniques have provided detailed characterization of the nature of polymeric organolithium compounds in solution as described in the following sections.

3.17.3.1.1 Aggregation of poly(styryl)lithium

The predominant degree of aggregation of PSLi in hydrocarbon solution has been established as 2 using concentrated solution viscosity, light scattering, and neutron scattering methods.^{96,97} Using concentrated viscosity measurements in the regime where $\eta = KM^{3.4}$ (K is a constant and M is the molecular weight), several groups found that the degree of aggregation for PSLi was 2.0 in benzene and in cyclohexane.^{96,97} These results were confirmed by light scattering measurements. Recent neutron scattering results have provided evidence for the presence of small amounts of higher order aggregates (N > 100) in equilibrium with predominantly dimeric and some tetrameric species.⁹⁸

3.17.3.1.2 Aggregation of poly(dienyl)lithiums

The predominant degree of aggregation of poly(dienyl)lithium chain ends in hydrocarbon solution has been a subject of considerable controversy; predominant degrees of aggregation of both 2 and 4 were reported based on concentrated solution viscosity measurements and light scattering measurements.^{96,97} Fortunately, more recent studies have shown that the predominant degree of aggregation of poly(dienyl)lithium chain ends is 4.^{85,99–103} However, like PSLi, SANS investigations have

revealed the presence of higher order aggregates whose concentration decreases with increasing conversion (molecular weight).86,99,104 Thus, oligomeric poly(butadienyl)lithium in heptane has an average aggregation number (N_{agg}) of ≈ 140 and then with increasing chain length N_{agg} decreases and levels off at values of approximately 4-5.100 From simultaneous measurements of static and dynamic light scattering for cyclohexane solutions of poly(butadienyl)lithium, two relaxation modes were observed and the static structure factor and hydrodynamic radius of the fast relaxing component were interpreted in terms of an unimer-tetramer equilibrium; evidence for the presence of a minor amount (<1 wt.%) of very large aggregates was also presented and the slow relaxation component was attributed to these aggregates.¹⁰¹ A SANS study of poly(isoprenyl)lithium in benzene was interpreted in terms of a final aggregation number of 3.6.¹⁰⁰ Comprehensive viscosity, ⁷Li NMR, and neutron/light scattering studies of poly(butadienyl)lithium in benzene were interpreted in terms of aggregations to form star-like tetramers as the major component.¹⁰³ The major mechanism of exchange between aggregates was assigned to collision of the aggregates to form larger, transient aggregates, rather than dissociation of the aggregates based on the analysis of the viscosity and exchange time data.¹⁰³ In conclusion, although a variety of large-scale structures have been detected for poly(dienyl)lithium chain ends in hydrocarbon solution, the consensus is that the predominant aggregated species has an association number of 4, although poly(butadienyl)lithium seems to exhibit a tendency for higher degrees of aggregation in saturated hydrocarbon solution than in benzene, and higher than that observed for poly(isoprenyl) lithium under the same conditions.

3.17.3.1.3 Propagation kinetics for styrene monomers

The anionic propagation kinetics for styrene (S) polymerization with lithium as counterion are relatively unambiguous. The experimentally observed reaction order dependence on total chain-end concentration, [PSLi]_o, is one-half as shown in the following equation:

$$R_{\rm p} = -d[S]/dt = k_{\rm obs} [\text{PSLi}]_0^{1/2} [S]$$
^[18]

The observed one-half kinetic order dependence on chain-end concentration is consistent with the fact that PSLi is predominantly associated into dimers in hydrocarbon solution. If the unassociated PSLi is the reactive entity for monomer addition, assuming that the aggregate is a dormant species, a simple



Scheme 10 Mechanism of styrene propagation for poly(styryl)lithium.

dissociative mechanism can be invoked (Scheme 10). This mechanism leads to the following kinetic equation:

$$R_{\rm p} = -d[S]/dt = k_{\rm p}[\rm PSLi][S]$$
$$= k_{\rm p}(K_{\rm d})^{1/2}[\rm PSLi]_{\rm o}^{1/2}[S] \qquad [19]$$

By comparing eqn [18] with eqn [19], it can be seen that the observed rate constant for propagation, $k_{obs'}$ is actually a composite of the propagation rate constant, $k_{\rm p}$, and the equilibrium constant for dissociation of the dimeric aggregates, $K_{d_{\ell}}$ raised to the one-half power (eqn [19]). The measurement of the dissociation constants of the aggregates is difficult because of the low concentration of the unassociated species $(K_{\rm d}(\rm est) \approx 10^{-6} - 10^{-7} \, \rm l \, mol^{-1} \, \rm s^{-1})$; thus, it is generally not possible to obtain directly a value for the propagation rate constant $k_{\rm p}$ (see, however, Young et al.,¹⁰⁴ Bywater,¹⁰⁵ and Fetters et $al.^{106}$). With regard to experimental investigations of kinetics, it is important to note that in practice pseudofirst-order kinetics are observed for a given run, since the concentration of active chain ends, [PSLi]_o, is a constant. In contrast to this simple interpretation, the kinetic order dependence on chain-end concentration for propagation of styrene and o-methoxystyrene in toluene with alkyllithium initiators varies from 0.62 to 0.66.106 These results and the presence of higher order aggregates as detected by SANS suggest that the actual mechanism of propagation may be much more complicated than that depicted in Scheme 10 (see, however, Bywater¹⁰⁷). Evidence for the contribution of higher order aggregates (>2) to the propagation kinetics has been reported from a ¹H NMR study of PSLi propagation in cyclohexane.¹⁰⁸

A comparison of the observed propagation rate constants for styrene polymerization with different alkali metal counterions in hydrocarbon solution is shown in Table 1.⁸⁰ Poly(styryl)sodium was presumably associated into dimers since kinetic orders of one-half were observed for the rate dependence on the active chain-end concentration. Poly(styryl)potassium exhibits intermediate behavior; dependence on chain-end concentration was

 Table 1
 Kinetic parameters for styrene propagation in hydrocarbon solvents⁸⁰

Counterion	Solvent	Temperature (°C)	k _{obs} (k _ρ (K _D /n) ^{1/n}) (Imol ^{-1/n} s ⁻¹)
Lithium	Benzene	30	$1.55_{109}\times 10^{-2} \ (1.\times 10^{-2})$
Lithium	Cyclohexane	40	$2.4 imes10^{-2}$
Sodium	Benzene	30	17×10^{-2}
Potassium	Benzene	30	180×10^{-2}
Potassium	Cyclohexane	40	30
Rubidium	Cyclohexane	40	22.5 ^a
Cesium	Cyclohexane	40	19 ^{<i>a</i>}

^aPropagation rate constant presumably for the unassociated species (see eqn [20]); first-order dependence on active chain-end concentration is observed.

one-half order at higher concentrations, but first order at low concentrations. Poly(styryl)rubidium and poly(styryl)cesium exhibit first-order dependencies on chain-end concentrations, which is consistent with unassociated chain ends in cyclohexane. The counterion dependence of the rate of polymerization is $K^+ > Rb^+ > Cs^+ >> Li^+$ in cyclohexane and $K^+ > Na^+ > Li^+$ in benzene. The interpretation of these results is complicated by the fact that the complex observed rate constants (k_{obs}) reflect both the fact that the dissociation constant for the dimers increases with increasing cation size (no association for rubidium and cesium) and also the fact that the requisite energy associated with charge separation in the transition state would be less for the larger counterions. For calibration purposes, the composite rate/equilibrium dissociation constant for styrene propagation in cyclohexane at 40 °C in Table 2 can be used to estimate a polymerization half-life of approximately 15 min, assuming that $[PSLi] \approx 10^{-3} M.$

3.17.3.1.4 Propagation kinetics for diene monomers

The delineation of the mechanism of propagation for isoprene and butadiene in hydrocarbon solution with lithium as counterion in the past has been complicated by disagreement in the literature regarding both the kinetic order dependence on chain-end concentration and the degree of association of the chain ends, as well as by apparent changes in kinetic reaction orders with chain-end concentration.^{3,80} For butadiene and isoprene propagation, reported reaction order dependencies on the concentration of poly(dienvl)lithium chain ends include 0.5, 0.33, 0.25, and 0.167. Kinetic studies of isoprene propagation with lithium as counterion in hydrocarbon solvents showed that the kinetic order dependence on chain-end concentration changed from 0.5 to either 0.25 or 0.17 as the chain-end concentration was varied from 10⁻² to 10⁻⁶ mol l^{-1,3,113,114} Comparison of these kinetic orders with the degrees of association of the poly(dienyl)lithium chain ends had been complicated by the lack of agreement regarding the predominant degree of association of these species in hydrocarbon solution. However, as noted in the previous section, recent evaluation of the association states of poly(dienyl)lithium chain ends in benzene by small-angle neutron scattering, as well as both dynamic and static light scattering, indicates that predominantly tetrameric aggregates are in equilibrium with small amounts of higher order aggregates (n > 100).^{85,99–103} Thus, the 0.25 kinetic order dependence on poly(dienyl)lithium chain-end concentration can be interpreted in terms of the predominantly tetrameric degree of aggregation as shown by the mechanism in Scheme 11.

$$(PDLi)_{4} \xrightarrow{K_{d}} 4 PDLi$$

$$PDLi + D \xrightarrow{k_{p}} PD-DLi$$

$$= k_{p}K_{d}^{1/4}[PDLi]_{o}^{1/4}[D]$$

$$= k_{obs}[PDLi]_{o}^{1/4}[D]$$

Scheme 11 Kinetics and mechanism for poly(dienyl)lithium propagation.

The observation of concentration dependence of the reaction order (increasing from 0.25 to 0.5 when [PILi] $< 5 \times 10^{-5}$ mol l⁻¹) with decreasing concentration of poly(isoprenyl)lithium in benzene can be explained in terms of the intermediacy of a dimeric association state as shown in eqn [20].¹¹³ It is noteworthy, however, that no such concentration dependence was observed in cyclohexane. The rate increased with increasing molecular weight, attributed to an increase in the dissociation constant (see K_d in Scheme 11) with increasing molecular weight.

$$(PILi)_4 \Longrightarrow 2(PILi)_2 \Longrightarrow 4PILi$$
 [20]

In accordance with the identification of large-scale aggregates for poly(dienyl)lithiums, careful, simultaneous investigations of the kinetics and states of aggregation for alkyllithium-initiated polymerizations of dienes have revealed that the kinetic scheme outlined above is oversimplified and not applicable to the initial states of initiation and polymerization. Evidence for the contribution of higher order aggregates (n>4) to the propagation kinetics has been reported from a ¹H and ⁷Li NMR study of poly(butadienyl)lithium propagation in benzene.¹¹⁵

3.17.3.1.5 Relative reactivities of styrene and dienes

The relative reactivities of dienes versus styrenes with lithium as counterion depend on the chain-end concentrations because of the differences in kinetic order dependencies on chain-end concentration. The relative rates of propagation at $[PLi] = \sim 10^{-3}$ M are in the order styrene > isoprene > butadiene. A recent kinetic study in cyclohexane at 40 °C has determined that the composite rate constant for styrene propagation $(k_pK_d^{1/2})$, $k_{ss} = 2.4 \times 10^{-2} l^{1/2} mol^{-1/2} s^{-1}$, while the composite rate constant for isoprene propagation $(k_pK_d^{1/4})$, $k_{ii} = 3.2 \times 10^{-3} l^{1/4} mol^{-1/4} s^{-1}$.¹⁰⁹ However, at $[PLi] \leq \sim 10^{-4}$ M, isoprene propagates faster than styrene.³ The corresponding composite rate constant for butadiene propagation (PBDLi) $(k_pK_d^{1/4})$, $k_{bb} = 0.23 \times 10^{-3} l^{1/4} mol^{-1/4} s^{-1}$ at 30 °C.¹¹⁶

Table 2Equilibrium dissociation constants of organoalkalimetal salts of polystyryl carbanions and the propagation rateconstants for the corresponding ion pairs and free ions in THF at $25 \circ C^{48,110,111,112}$

Counterion	K_{diss}	k±	10 ^{−4} k_
	(×10 ⁷ mol Γ^1)	(I mol⁻¹ s⁻¹)	(I mol ^{−1} s ^{−1})
Li ⁺	1.9–2.2	160	6.5
Na ⁺	1.5	80	
K ⁺	0.7–0.77	~60	
Rb⁺	0.10	~50	6.3
Cs⁺	0.02–0.047	22	

3.17.3.1.6 Effects of Lewis bases

The addition of small amounts of Lewis bases such as ethers and tertiary amines generally increases the rate of propagation in alkyllithium-initiated polymerizations as shown in Figure 3.117 These Lewis bases decrease the average degree of association of the polymeric organolithium aggregates (N) as determined by concentrated solution viscosity measurements.^{3,96,118} Based on concentrated solution viscosity measurements, it was reported that PSLi self-association is virtually absent when [THF]/ [PSLi] = 10, while a ratio of [THF]/[PILi] = 2600 is required to completely eliminate association of poly(isoprenyl)lithium.96,119 In contrast, the addition of stoichiometric amounts of strongly coordinating Lewis bases such as TMEDA and pentamethyldiethylenetriamine can either increase or decrease the reaction rate for alkyllithium propagation of isoprene relative to hydrocarbon solution depending on the chain-end concentration.^{53,120} This situation arises from the different reaction order dependencies on chain-end concentration, that is, ≈0.5 in hydrocarbon solution compared to ≈ 1.0 for the stoichiometric Lewis base complexes. These curves cross at a chain-end concentration $[C^*]$ of 1.2×10^{-3} M; thus, above $[C^*]$, the rate is slower in hydrocarbon solution, but faster below $[C^*]$, as would be expected for the effect of Lewis base addition.¹²⁰

The addition of lithium alkoxides generally decreases the rate of propagation; this is important to note since formation of lithium alkoxides can readily occur in the presence of even small amounts of impurities.³ The addition of other alkali metal alkoxides increases the rate of polymerization in hydrocarbon solution as would be expected if counterion exchange occurred (see Table 2).¹²¹

3.17.3.1.7 Effects of ate complexes

The complexation of alkyllithium initiators with organomagnesium and organoaluminum compounds (ate complexes)¹²² has been shown to dramatically reduce the rate of styrene propagation in cyclohexane as shown in **Figure 4**.^{123–125} For



Figure 3 Effect of tetrahydrofuran (THF) on isoprene polymerization in hexane at 30 °C; $R_{p(THF)}$, polymerization rate in the presence of added THF; $R_{p(hexane)}$, polymerization rate in hexane. From Morton, M.; Fetters, L. J.; Bostick, E. E. *J. Polym. Sci. Part C-1***1963**, 311–323; reprinted by permission of John Wiley and Sons.



Figure 4 Polymerization of styrene initiated by poly(styryl)lithium seeds/*n*,*sec*-dibutylmagnesium: variation of ln([M]₀/[M]) with time for various Mg/Li mole ratios (*T* = 50 °C, cyclohexane). From Desbois, P.; Fontanille, M.; Deffieux, A.; *et al. Macromol. Chem. Phys.* **1999**, *200*, 621–628; reprinted by permission of John Wiley and Sons.

example, the apparent rate constant $\{(R_p/[M]/[PSLi])\}, k_{p,app}, k_{p,app}\}$ decreased from 370 to 61 mol⁻¹ min⁻¹ when two equivalents ([Mg]/[Li] = 2) of *n*, sec-dibutylmagnesium were added to styrene polymerization in cyclohexane at 100 °C.¹²⁴ By the addition of these additives, particularly n.secdibutylmagnesium, it is possible to carry out these polymerizations at elevated temperatures, for example, at $\geq 100 \,^{\circ}$ C, and maintain a linear increase of molar mass with conversion, indicating the absence of chain transfer reactions. The molar masses were in good agreement with the stoichiometric values calculated by assuming that the number of chains corresponds to 1 sec-butyllithium plus 0.7-1 chains initiated by the dialkylmagnesium (the sec-butyl portion). A further advantage of these polymerizations is that control is maintained not only at higher temperatures, but also at higher monomer concentrations, approaching bulk concentrations. Other additives that promote these 'retarded anionic polymerizations' include other metal alkyls such as triethylaluminum and diethylzinc.¹²⁵ The goal of this work was to develop an anionic polymerization process that is competitive with industrial radical processes by effecting polymerization in the absence of solvent and at elevated temperatures.

3.17.3.2 Polar Solvents

A change in the reaction medium from hydrocarbon to polar solvents causes changes in the nature of the alkali metal carbanions, which can be interpreted in terms of the Winstein spectrum of ionic species as shown in Scheme 12.^{3,6} Thus, in addition to the aggregated (1) and unaggregated (2) species that can exist in hydrocarbon solution, in polar solvents it is necessary to consider the intervention of free ions (5), contact ion pairs (3), and solvent-separated ion-pairs (4) as shown in Scheme 12.

In general, as the polarity (dielectric constant) and solvating ability of the medium increase, a transition to more ionic species (a shift in the Winstein spectrum from left to right) occurs. In addition, each different chain-end species can react with the monomer with its own unique rate constant as shown in **Scheme 11**.

In weakly polar solvents such as dioxane (ε =2.21), the kinetics of styrene propagation exhibit pseudo-first-order behavior as illustrated in eqn [21], where k_{obs} is the observed pseudo-first-order rate constant, k_p is the propagation rate constant, and [PS⁻Mt⁺] represents the concentration of carbanionic chain ends that does not change for a living polymerization. The values of k_p can be obtained by plotting k_{obs} versus [PS⁻Mt⁺].

$$-d[S]/dt = k_{obs}[S] = k_p[PS^-Mt^+][S]$$
[21]

The order of reactivity (rate constants in brackets are in units of $1 \text{ mol}^{-1}\text{s}^{-1}$) of alkali metal counterions is Li⁺ [0.9] < Na⁺

 $[3.4-6.5] < K^+ [20-28] < Rb^+ [21.5-34] < Cs^+ [15-24.5].^{48}$ The trend of increasing reactivity with increasing ionic radius, also observed in hydrocarbon solution, has been taken as evidence for contact ion pairs as the reactive propagating species. Similar behavior has been observed for isoprene polymerization in diethyl ether (ε = 4.34); the propagation rate constant assigned to the lithium contact ion pair is $3.2 \, l \, mol^{-1} \, s^{-1}.^{126}$

In more polar solvents such as THF (ε =7.6), a concentration dependence was observed for the plots of k_{obs} versus [PS⁻Mt⁺], that is, k_p exhibits a linear dependence on $(1/[PS⁻Mt⁺]^{1/2})$.^{48,110,111,127} This dependence has been interpreted in terms of the participation of both ion pairs and free ions as active propagating species as shown in **Scheme 13**, where k_{\pm} is the propagation rate constant for the ion pair species, k_- is the propagation rate constant for the free ion, and K_{diss} is the equilibrium constant for dissociation of ion pairs (P $_{\pm}$) to free ions (P $_{-}$).The corresponding rate expression for this system is shown in the following equation:

$$-d[S]/dt = [S](k_{\pm}[P_{+}] + k_{-}[P_{-}])$$
[22]

Assuming that the K_{diss} is small, the concentration of ion-paired species can be assumed to be approximately equal to $[PMt]_{\text{total}}$ and the concentration of free ions can be calculated using the dissociation equilibrium constant as in the following equation:

$$[P_{-}] = K_{diss}^{1/2} [PMt]_{total}^{1/2}$$
[23]

Substituting this expression for the concentration of free ions into the rate equation generates the final rate expression

$$-d[S]/dt = [M] \left(k_{\pm} [PMt]_{total} + k_{-} K_{diss}^{1/2} [Mt]_{total}^{1/2} \right)$$
[24]

or if it is cast analogous to eqn [22], one obtains

$$-d[S]/dt = [M][PMt]_{total}(k_{\pm} + k_{-}K_{diss}^{1/2}/[PMt]_{total}^{1/2})$$
[25]

The corresponding expression for k_p is shown in eqn [26], recognizing that this k_p is only an apparent propagation rate constant (see eqn [21]).

$$k_{\rm p} = k_{\pm} + k_{-} K_{\rm diss}^{1/2} / [\rm PMt]_{\rm total}^{1/2}$$
 [26]

Plots of the apparent propagation rate constant versus $1/[P^-Mt^+]^{1/2}$ are shown in **Figure 5**. From this figure, it can be deduced that the slopes of the lines decrease as the cation size increases from

$$P^{-}, Mt^{+} \underbrace{K_{diss}}_{k_{\pm}} P^{-} + Mt^{+}$$
$$\downarrow k_{\pm}[S] \qquad \qquad \downarrow k_{-}[S]$$

Scheme 13 Participation of ion pairs and free ions for the mechanism of anionic propagation in polar solvents such as tetrahydrofuran (THF).



Scheme 12 Possible reactive entities involved in propagation in polar solvents.



Figure 5 Plots of the propagation constant, k_0 , for salts of living polystyrene in tetrahydrofuran (THF) vs. 1/[LE]^{1/2}. From Szwarc, M. *Adv. Polym. Sci.* **1983**, *49*, 1–177; reprinted with kind permission from Springer Science+Business Media B.V.

lithium to cesium. Since k_{-} is independent of the cation, the variation of the slope with counterion reflects a decrease in K_{diss} as the counterion size increases. This is consistent with independent measures of the dissociation constants for free ion formation from both conductometric and kinetic studies as shown in Table 2. Figure 5 also shows that the intercepts, which represent k_{\pm} , also decrease with increasing cation size. Thus, the order of reactivity of alkali metal counterions in THF is $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$, the inverse of the order observed in the less polar solvent dioxane or in hydrocarbon solution. This order is in accordance with expectations based on cation solvation energies, which decrease with increasing cation size. Values of the propagation rate constant for free styryl anions are relatively insensitive to the solvent; the values for k_{-} are 6.5×10^{4} and 4.0×10^4 lmol⁻¹ s⁻¹ at 25 °C in THF and in dimethoxyethane, respectively.48 Similar results have been obtained for cumylpotassium-initiated polymerization of butadiene in THF; k_{-} had a value of $4.8 \times 10^{4} \, \mathrm{l \, mol^{-1} \, s^{-1}}$ and k_{\pm} was <1 l mol⁻¹ s⁻¹ at 0 °C.¹²⁸ Thus, even though free ions are present in small amounts (see **Table 2**), their contribution to the overall rate of polymerization is significant because of their much higher reactivity.

Although normal Arrhenius behavior was observed for k_{-} , anomalous increases of k_+ with decreasing temperature were observed in polar solvents such as THF and dimethoxyethane (glyme) as shown in Table 3 and these results are plotted in Figure 6.^{110–112} These results have been explained in terms of a temperature-dependent equilibrium between contact and solvent-separated ion pairs as shown in Scheme 14. This equilibrium shifts from the less reactive contact ion pairs (k_c) to the much more reactive solvent-separated ion pairs (k_s) as temperature is decreased because the contribution from the unfavorable (negative) entropy of dissociation $(T\Delta S_{c/s})$ decreases and the enthalpy of dissociation ($\Delta H_{c/s}$) is negative (see **Table 4**). As shown in **Table 4**, the values of k_c and k_s are not very dependent upon the solvent, but the equilibrium constants, $K_{c/s}$ are very dependent on the polarity of the solvent. It is noteworthy that the reactivity of the solvent-separated ion pairs approaches that of the free ions. These results also provide a rationalization for the effect of counterion on k_+ shown in Figure 5. Smaller cations like lithium interact more strongly with the solvent and form significant amounts of more reactive, solvent-separated ion pairs.

3.17.4 Chain Termination Reactions

The categorization of a given polymerization system as living is based on results obtained on the laboratory timescale, that is, the absence of irreversible chain termination or chain transfer reactions occurring within the normal time required to complete the polymerization and carry out any subsequent chemical reactions with the active carbanionic polymer chain ends.^{3,129} In fact, the extent of spontaneous termination reactions in typical alkyllithium-initiated polymerizations of styrene and diene monomers depends on time, temperature, and presence of polar additives.^{3,45,130}

Polymeric organolithium compounds exhibit good stability in hydrocarbon solution at ambient temperatures and for short periods of time at elevated temperatures.^{3,45}

 Table 3
 Ion pair rate propagation constants for anionic polymerization of styrene in THF⁴⁸

e K _{diss}	k	1.
(free ion; M)	(I mol ⁻¹ s ⁻¹)	к _± (I тоГ ⁻¹ s ⁻¹)
1.5	65 000	80
0.947	63 000	21
5.0	16 000	90
0.066	22 000	9
34	3 900	130
0.086	6 200	2.4
160	1 460	250
0.112	1 100	1.0
320	1 030	280
	1.5 (free ion; M) 1.5 0.947 5.0 0.066 34 0.086 160 0.112 320	$\begin{array}{cccc} R_{diss} & R_{-} & R_{-} & \\ (free ion; M) & (I mor^{-1} s^{-1}) \\ \hline 1.5 & 65 000 \\ 0.947 & 63 000 \\ 5.0 & 16 000 \\ 0.066 & 22 000 \\ 34 & 3 900 \\ 0.086 & 6 200 \\ 160 & 1 460 \\ 0.112 & 1 100 \\ 320 & 1 030 \\ \end{array}$



Figure 6 Arrhenius plots of the propagation constants of ion pairs (k_{\pm}) of poly(styryl)sodium in various solvents. The curves approach a common asymptote at low temperatures, interpreted as a linear Arrhenius plot referring to the propagation constant of loose ion pairs ($k_{\pm s}$), and the curves approach again a common asymptote at high temperatures, interpreted as a linear Arrhenius plot referring to the propagation constant of loose ion pairs ($k_{\pm s}$). From Szwarc, M. *Adv. Polym. Sci.* **1983**, *49*, 1–177; reprinted with kind permission from Springer Science+Business Media B.V. DME, 1,2-dimethoxyethane; HMPA, hexamethylphosphoramide; 3-Me-THF, 3-methyltetrahydrofuran; THF, tetrahydrofuran; THP, tetrah



Scheme 14 Participation of both contact and solvent-separated ion pairs for the mechanism of anionic propagation in polar solvents such as tetrahydrofuran (THF).

The principal mode of decomposition is loss of lithium hydride (β -hydride elimination) to form a double bond at the chain end as illustrated in the following equation for PSLi:

$$\begin{array}{c|c} \mathsf{PSCH}_2\mathsf{CH}\text{-}\mathsf{CH}_2\text{-}\mathsf{CHLi} & \xrightarrow{\mathsf{Heat}} & \mathsf{PSCH}_2\mathsf{CH}\text{-}\mathsf{CH}\text{-}\mathsf{CH} + \mathsf{LiH} \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & &$$

PSLi exhibits good stability over the duration of the polymerizations and beyond, that is, days, at ambient temperature in hydrocarbon media. However, at elevated temperatures, it is observed that the initial UV absorption at 334 nm decreases and a new absorption is observed at 450 nm, assigned to a 1,3-diphenylallyllithium species as shown in the following equation:⁴⁵

$$\begin{array}{c} & \overset{\Theta}{\overset{\mbox{Li}^{\otimes}}{\longrightarrow}} \\ \text{PSLi} + \text{PSCH}_2\text{CH-CH} = \text{CH} \longrightarrow \text{PSCH}_2\text{C} & \overset{\Theta}{\longrightarrow} \text{CH} + \text{PSH} \\ & | & | & | \\ & C_6\text{H}_5 & C_6\text{H}_5 & C_6\text{H}_5 \\ \end{array}$$

[28]

The rate constant for spontaneous decomposition was reported to be 4×10^{-5} s⁻¹ at 65 °C in cyclohexane.^{45,131} Analogous decomposition reactions have been observed for poly(styryl) sodium. The rate of decomposition of PSLi in cyclohexane at 150 °C is 0.205 min⁻¹, corresponding to a 3.5 min half-life.¹³² In the presence of two equivalents of *n*,*sec*-dibutylmagnesium at 100 °C, the rate of decomposition of PSLi is 1.9×10^{-5} min⁻¹ while it is 6.4×10^{-4} min⁻¹ in the absence of additive, corresponding to half-lives of 102 and 3 h, respectively.¹³³

The thermal stability of poly(α -methylstyryl)lithium is much lower than that of PSLi. The observed half-lives for spontaneous termination are 5 h and a few minutes at 25 and 60 °C, respectively.¹³⁴ However, the chain ends were stabilized with respect to spontaneous decomposition by the addition of TMEDA. The relative thermal stability of styryl carbanionic chain ends follows the order K⁺>>Na⁺>Li⁺ for the alkali metal counterions.

The carbanionic active centers based on 1,3-butadiene and isoprene with lithium as counterion generally possess good stability in hydrocarbon solvents at ambient temperatures.

 Table 4
 Ion pair rate constants for anionic polymerization of poly(styryl)sodium in ethereal solvents and the equilibrium constant and thermodynamic parameters for ion pair equilibrium⁴⁸

Solvent	k _c	k _s	К _{с/s}	⊿H _{c/s}	∆S _{c/s}
	(1 mol⁻¹ s⁻¹)	(×10 ^{−4} mol ^{−1} s ^{−1})	(25 °C)	(kcal mol ^{−1})	(e.u.)
DME	12.5	5.5	0.13	-5.5	-22.5
THF	34	2.4	2.25 × 10 ⁻³	-6.5	-34
3-Me-THF THP Dioxane	20 10.7 5.5	12.4 5.3	$\begin{array}{c} 5.8\times 10^{-4} \\ 1.3\times 10^{-4} \\ <\!10^{-5} \end{array}$	-5.1 -3.0	-32 -28

DME, 1,2-dimethoxyethane; 3-Me-THF, 3-methyltetrahydrofuran; THF, tetrahydrofuran; THP, tetrahydropyran.

However, poly(dienyl)lithiums undergo complex decomposition reactions upon prolonged storage or heating at elevated temperatures. Poly(butadienyl)lithium in ethylbenzene exhibits an absorption maximum at 300 nm, which gradually decreases in intensity with the formation of absorption tails between 350 and 500 nm.45 Approximately 20% of the active centers were destroyed in less than 3 h at 100 °C in ethylbenzene.¹³⁵ The apparent first-order rate constant for decomposition of poly (butadienvl)lithium in hexane was estimated to be 1.9×10^{-5} s⁻¹ at 93 °C at a chain-end concentration of 2.2 milliequivalents of poly(butadienyl)lithium per 100 g of solution (25 wt.% polymer).¹³¹ The corresponding first-order rate constant for chain-end decomposition of poly(isoprenyl)lithium at 93 °C was estimated to be $6.7 \times 10^{-5} \text{ s}^{-1.131}$ Although the differences are not large, the relative order of increasing stabilities of chain ends toward thermal degradation is poly(α-methylstyryl) lithium << PSLi < poly(isoprenyl)lithium < poly(butadienyl) lithium as estimated by chain-end titration data.

Size-exclusion chromatography (SEC) analyses of the thermal decomposition products of poly(dienyl)lithiums in heptane at 80 °C have shown that the chain-end decomposition is accompanied by formation of species that have double and triple the molecular weight of the original living polymer.¹³⁶ After heating for 46 h at 80 °C in heptane, a 12 wt.% yield of coupled products was observed for poly(isoprenyl)lithium; after heating for 27 h at 80 °C in heptane, a 19 wt.% yield of coupled products was observed for poly(butadienyl)lithium. The reactions shown in **Scheme 15** illustrate the type of reactions proposed to explain the formation of dimeric products.

Evidence also suggests that athermal metalation of the backbone can occur as shown in equation[29]:¹³⁷ compounds.⁴⁴ Living carbanionic polymers react with ether solvents such as THF in a pseudo-first-order decay process and the rate decreases in the order $\text{Li}^+ > \text{Na}^+ > \text{K}^+$. For example, a 10^{-5} M solution of PSLi in THF at 25 °C exhibited a rate of decay of a few percent per minute, but poly(styryl)cesium was found to be exceptionally stable.¹²⁷ Metalation and decomposition reactions can also occur in the presence of amines such as TMEDA.^{138,139}

3.17.5 Chain Transfer Reactions

Chain transfer reactions to polymeric organoalkali compounds can occur from solvents, monomers, and additives that have pK_a values lower or similar to those of the conjugate acid of the carbanionic chain end.³ Relatively few monomers that undergo anionic polymerization exhibit chain transfer to monomers. Chain transfer has been well documented for the anionic polymerization of 1,3-cyclohexadiene. The chain transfer constant $(k_{\rm tr}/k_{\rm p})$ was calculated to be 2.9×10^{-2} at 20 °C and 9.5×10^{-3} at 5 °C in cyclohexane.²⁹ Although chain transfer would be expected for p-methylstyrene, controlled polymerizations can be effected when the temperature is maintained at room temperature or below.¹⁴⁰ The observations of broad molecular weight distributions and a low-molecular-weight tail by SEC analysis have provided evidence for chain transfer during the anionic polymerization of *p*-isopropyl-α-methylstyrene.¹⁴¹

The kinetics of chain transfer to ammonia have been investigated for potassium amide-initiated polymerization of styrene in liquid ammonia at -33.5 °C.¹⁴² The calculated chain transfer constant (k_{tr}/k_p) was 2.34×10^{-4} .

$$PBDLi + P-CH_2-CH \longrightarrow CH_2-P \longrightarrow P-CH-CH \longrightarrow CH_2-P \qquad [29]$$

$$Li$$

It would be expected that this in-chain metalation coupled with elimination of lithium hydride would lead to in-chain diene units which could couple and would have even more reactive allylic hydrogens for further metalation–elimination–coupling sequences that would promote thermal decomposition, branching, and ultimately gel formation.

Polymeric organolithium compounds exhibit limited stability in ether solvents analogous to alkyllithium The chain transfer reaction of PSLi with toluene at 60 °C was investigated during the polymerization of styrene using ¹⁴C-labeled toluene.¹⁴³ The calculated chain transfer constant (k_{tr}/k_p) was 5×10^{-6} . A much larger chain transfer constant $(k_{tr}/k_p = 1.28 \times 10^{-4})$ was found for analogous transfer from toluene to poly(styryl)sodium. In general, alkyllithium-initiated anionic polymerizations of styrenes and dienes should not be carried out in toluene as solvent because of the occurrence of

$$\begin{array}{c} \mathsf{PCH}_2\mathsf{-}\mathsf{CH} & \longrightarrow \mathsf{CH}_2\mathsf{Li} & \xrightarrow{\mathsf{Heat}} \mathsf{PCH} & \longrightarrow \mathsf{CH} & \longrightarrow \mathsf{CH}_2\mathsf{-}\mathsf{CH}_2\mathsf{-}\mathsf{Li} \\ \mathsf{Active, uncoupled} & & \mathsf{Inactive, uncoupled} \\ \mathsf{P'Li} + \mathsf{PCH} & \longrightarrow \mathsf{CH} & \longrightarrow \mathsf{CH}_2\mathsf{-}\mathsf{P'} & & \mathsf{CH}_2\mathsf{-}\mathsf{P'} \\ & & & \mathsf{Active, coupled} \\ \mathsf{PCH} & & \mathsf{CH} & \xrightarrow{\mathsf{CH}_2\mathsf{-}\mathsf{P'}} & \xrightarrow{\mathsf{Heat}} \mathsf{PCH} & \xrightarrow{\mathsf{CH}_2\mathsf{-}\mathsf{CH}_2\mathsf{-}\mathsf{P'}} \\ & & \mathsf{Active, coupled} \\ & & \mathsf{Inactive, coupled} \\ \mathsf{Li} \end{array}$$

Scheme 15 Proposed thermal decomposition reactions for poly(butadienyl)lithium.

chain transfer reactions.¹⁴⁴ After storage of PSLi at room temperature for 72 h, formation of 69% of dead polystyrene chains was observed.¹⁴⁵ Even after 1 day at 20 °C, 13% of the PSLi undergoes chain transfer to toluene.¹⁴⁴ Ethylbenzene exhibits a chain transfer rate constant to PSLi of $2.2 \times 10^{-5} \, \mathrm{l \, mol^{-1} \, s^{-1}}$.¹⁴⁶

Allenes and alkynes are regarded as impurities whose concentration cannot exceed certain minimum levels in monomer feed streams.147 However, these same compounds, especially 1,2-butadiene, are also added as modifiers in alkyllithium-initiated diene polymerizations to prevent thermal branching at higher temperatures via chain termination and/or chain transfer reactions.^{3,147,148} Model studies have suggested that isomerization of 1,2-butadiene to 1-butyne occurs.¹⁴⁹ It was also reported, quite surprisingly, that the addition of 2750 ppm of 1,2-butadiene (5.2 equivalents relative to BuLi) did not affect the conversion/time plot or the molecular weight/time plot for butadiene polymerization initiated by *n*-butyllithium in cyclohexane at 50 °C.¹⁴⁹ These results suggest that the main effect of 1,2-butadiene occurs near the end of the reaction at the elevated temperatures that result from the exothermic nature of these polymerizations, which are often carried out adiabatically. At this time in the reaction, thermal decomposition reactions and metalation reactions would be expected to occur, but these side reactions could be attenuated in the presence of 1,2-butadiene acting primarily as a somewhat less reactive terminating agent. In the presence of Lewis bases such as TMEDA and THF, 1,2-butadiene does affect the conversion/time plots as well as decreases the $M_{\rm p}$ and increases the molecular weight distribution.¹⁵⁰

Chain transfer reactions are promoted by Lewis bases. A chain transfer constant of 0.2 was reported for the telomerization of butadiene initiated by metallic sodium in a toluene/THF mixture at $40 \,^{\circ}$ C.¹⁵¹ Such processes are used for the preparation of liquid rubbers (polybutadienes), with varying amounts of 1,2-microstructure depending on the type and

amount of Lewis base, counterion, and temperature.¹⁵² Significant chain transfer effects have also been reported for alkyllithium-initiated polymerizations using alkenes as solvents.³

3.17.6 Stereochemistry

3.17.6.1 Polydienes

3.17.6.1.1 Hydrocarbon solvents

One of the most important synthetic and commercial aspects of anionic polymerization is the ability to prepare polydienes with high 1,4-microstructure using lithium as the counterion in hydrocarbon solution.^{3,68} The key discovery was reported in 1956 by scientists at the Firestone Tire and Rubber Company that polyisoprene produced by lithium metal-initiated anionic polymerization had a high (>90%) cis-1,4-microstructure analogous to natural rubber.⁴⁷ In general, conjugated 1,3-dienes (CH₂=C(R)-CH=CH₂) can polymerize to form four constitutional isomeric microstructures as shown in Scheme 16. The stereochemistry of the anionic polymerization of isoprene and butadiene depends on the counterion, monomer concentration, chain-end concentration, solvent, temperature, and the presence of Lewis base additives. The effect of counterion on polybutadiene stereochemistry is illustrated by the data in Table 5, which show that lithium is unique among alkali metal counterions in producing polybutadiene with high 1,4-microstructure. Similar results have been reported for the stereochemistry of the anionic polymerization of isoprene (see Table 6) except that the stereochemistry with lithium as the counterion in neat isoprene is 94% cis-1,4 and 6% 3,4 compared with 35% cis-1,4, 52% trans-1,4, and 13% 1,2 for polymerization of butadiene with lithium as counterion. From the data in Table 7, it is possible to delineate the effects of monomer concentration, chain-end concentration,



R = H (butadiene, 1,2- = 3,4); $R = CH_3$ (isoprene)

Scheme 16 Constitutional isomeric structures for repeating units in polydienes.

 Table 5
 Effect of counterion on polybutadiene microstructure for neat polymerizations¹⁵³

		<i>Microstructure</i> (%)			
Counterion	Temperature (°C)	1,4-cis	1,4-trans	1,2	
Lithium	70	35	52	13	
Sodium	50	10	25	65	
Potassium	50 60	15	40 21	40	
Cesium	60	6	35	59	

		Microstructure (%)					
Counterion	Temperature (°C)	1,4-cis	<i>1,4-</i> trans	1,2	3,4		
Lithium	25	94			6		
Sodium	25		45	7	48		
Potassium	25		52	8	40		
Rubidium	25	5	47	8	39		
Cesium	25	4	51	8	37		

 Table 6
 Effect of counterion on polyisoprene microstructure for neat polymerizations^{153,154}

 Table 7
 Microstructure of polydienes in hydrocarbon media using organolithium initiators

Initiator concentration (M)	Solvent	Temperature (°C)	Microstru (%)	icture		Reference
Polyisoprene			1,4- <i>cis</i>	1,4-trans	3,4	
6×10^{-3}	Heptane	-10	74	18	8	155
1×10^{-4}	Heptane	-10	84	11	5	
8×10^{-6}	Heptane	-10	97		3	
$5 imes 10^{-6}$	Heptane	25	95	2	3	156
9×10^{-3}	Benzene	20	69	25	6	157
$5 imes 10^{-6}$	Benzene	25	72	20	8	156
1×10^{-2}	Hexane	20	70	25	5	157
1×10^{-5}	Hexane	20	86	11	3	
3×10^{-3}	None	20	77	18	5	
$8 imes 10^{-6}$	None	20	96		4	
Polybutadiene			1,4- <i>cis</i>	1,4-trans	1,2	
8×10^{-6}	Benzene	20	52	36	12	
5×10^{-1}	Cyclohexane	20	53 ^a		47	158
1×10^{-5}	Cyclohexane	20	68	28	4	157
3×10^{-2}	Hexane	20	30	60	8	
2×10^{-5}	Hexane	20	56	37	7	
$3 imes 10^{-3}$	None	20	39	52	9	
5×10^{-6}	None	20	86	9	5	

^aTotal 1,4-content (cis + trans)

and solvent. The highest *cis*-1,4-microstructure content is obtained in the absence of solvent, that is, with neat monomer, at low concentrations of initiator ($\sim 10^{-6}$ M). High *cis*-1,4-enchainment is also favored by the use of aliphatic versus aromatic solvents at low concentrations of initiator; however, the total amount of 1,4-microstructure (*cis* + *trans*) is relatively insensitive to solvent and chain-end concentration. In general, temperature is not an important variable affecting the microstructure of polydienes prepared in hydrocarbon solution with lithium as the counterion; however, relatively large effects of pressure have been reported, with increasing pressure favoring 1,2-enchainment and decreasing the amount of *trans*-1,4-enchainment for 2,3-dimethyl-1,3-butadiene.¹⁵⁹

A comprehensive hypothesis has been proposed to explain the effects of concentrations of both active chain ends and monomer on polydiene microstructure.¹⁶⁰ Based on studies with model compounds and the known dependence of polydiene microstructure on diene monomer (D) and chain-end concentrations as shown in **Table 6**, the mechanistic hypothesis shown in **Scheme 17** was advanced.

It was proposed that isomerization of the initially formed *cis*-form of the lithiated, active chain (*-cis**) end occurs competitively with monomer addition at each step of the reaction; at equilibrium in hydrocarbon solution, the *trans*-form (*-trans**) is favored.^{155,160} Thus, when the concentration of monomer is high relative to the chain-end concentration, the first-order isomerization of the *cis*-form does not compete effectively



Scheme 17 Stereocontrol mechanism for polydienes with lithium as counterion.

with monomer addition. However, at low concentrations of monomer relative to chain ends, the isomerization does compete and significant amounts of the *trans*-form will be in equilibrium with the *cis*-form.

The kinetic order dependence on the active chain-end concentration is approximately 0.25 for diene propagation, while the kinetic order dependence on the active chain-end concentration is approximately 1 for *cis–trans* isomerization of the chain ends.^{3,80} Thus, while the unassociated chain ends add monomer, isomerization of the chain ends occurs in the aggregated state. Since aggregation is favored by increasing chain-end concentrations, high 1,2-microstructure is observed (47% for butadiene) at high chain-end concentrations ([PBDLi] = ~0.1 M) and high *cis*-1,4-microstructure (86% for butadiene) is obtained at low chain-end concentrations (~10⁻⁶ M).

The microstructure of anionic polymerization of other poly (1,3-diene)s with lithium as counterion in hydrocarbon media is

also predominantly 1,4.³ However, higher amounts of *cis*-1,4microstructures are obtained with more sterically hindered diene monomers. Thus, using conditions that provide polyisoprene with 70% *cis*-1,4-, 22% *trans*-1,4-, and 7% 3,4-microstructure, 2-*i*-propyl-1,3-butadiene and 2-*n*-propyl-1,3-butadiene provide 86% and 91% *cis*-1,4-enchainment, respectively. Both 2-phenyl-1,3-butadiene (92% *cis*-1,4) and 2-triethylsilyl-1,3-butadiene (100% *cis*-1,4) also exhibit high *cis*-1,4-enchainment. High *cis*-1,4-microstructure (98%) was reported for the preparation of poly(1,3-cyclohexadiene) using *n*-butyllithium in cyclohexane.¹⁶¹

3.17.6.1.2 Polar solvents

In polar media, the unique, high 1,4-stereospecificity with lithium as counterion that is observed in hydrocarbon media is lost and large amounts of 1,2-poly(butadiene) and 3,4-poly(isoprene) enchainments are obtained (see **Tables 8** and 9). **Tables 8** and 9 show that there is a tendency

 Table 8
 Effects of polar solvents on polybutadiene microstructure^{162,163}

 Microstructure
 (%)

			(%)			
Solvent	Counterion	Temperature (°C)	<i>1,4-</i> cis	<i>1,4-</i> trans	1,2	
THF	Lithium	0	6	6	88	
THF	Lithium	-78	~0	8	92	
THF	Sodium	0	6	14	80	
THF	Sodium	-78	~0	14	86	
THF	Potassium	0 or –78	5	28	67	
Et ₂ 0	Lithium	0	8	17	75	
Et ₂ 0	Sodium	0	7	23	70	
Et ₂ 0	Potassium	0	11	34	55	
Dioxane	Lithium	15		13	87	
Dioxane	Sodium	15		15	85	
Dioxane	Potassium	15		45	55	
Dioxane	Cesium	15		59	41	
Dioxane	Free ion	15		22	78	

Free ion formation was suppressed for the measurements in THF and Et_2O by the addition of tetraphenylboride salts (triphenylcyanoboron for potassium). THF, tetrahydrofuran.

 Table 9
 Effects of polar solvents on polyisoprene microstructure

			Microstructure (%)				
Solvent	Counterion	Temperature (°C)	<i>1,4-</i> cis	<i>1,4-</i> trans	1,2	3,4	Reference
THF	Lithium	30	12 ^{<i>a</i>}		29	59	164
THF	Sodium	0	11 ^a		19	70	68
DME	Li, Na, K, Cs	15	24–26 ^a		28-33	44–48	165
Et ₂ 0	Lithium	20	35 ^a		13	52	166
Et ₂ 0	Sodium	20	17 ^a		22	61	
Et ₂ 0	Potassium	20	38 ^a		19	43	
Et ₂ 0	Cesium	20	52 ^a		16	32	
Dioxane	Lithium	15	3	11	18	68	163
Dioxane	Potassium	15	4	32	14	50	
Dioxane	Free ion	15	<1	24	32	44	

^aTotal amount of 1,4-microstructure.

DME, 1,2-dimethoxyethane; THF, tetrahydrofuran.

There are several important structural differences for polydienyl anions in polar media versus hydrocarbon solvents: (1) chain ends are generally not associated into higher aggregates in polar media compared to hydrocarbon; (2) the charge distribution of unsymmetrical allylic anions is a function of solvent, counterion, and temperature; (3) the kinetic and equilibrium distribution of chain-end configurations can vary with solvent and counterion; and (4) the distribution of contact ion pairs, solvent-separated ion pairs, and free ions can vary with solvent, counterion, and temperature.

Using the relationship that the ¹³C NMR chemical shift per electron corresponds to 114 ppm per electron, the calculated charge distributions for neopentylallyl-alkali metal (6) and neopentylmethylallyl-alkali metal (7) compounds have been calculated and the results are shown in Table 10.¹⁶⁷

Compounds 6 and 7 can be regarded as models for butadienyl and isoprenyl carbanionic chain ends, respectively. The data in **Table 10** show that while the negative charge is more localized on the α -carbon in hydrocarbon solution for the lithium derivatives, in polar media there is less charge on the α -carbon and more charge on the γ -carbon in all allyl organoalkali compounds. The presence of more negative charge on the γ -carbon provides a partial explanation for the formation of predominantly side-chain vinyl microstructure in polar media; however, lithium with the least charge on the γ -carbon gives the highest 1,2-enchainment and cesium with high charge on the γ -carbon gives the highest 1,4-enchainment. It has been suggested that a highly solvated lithium cation in ether solvents that is situated closer to the α -carbon in the allylic anion may block reaction with monomer at this position and lead to preferential attack at the less hindered γ -position to form 1,2-butadiene units.¹⁶³

Sterically hindered, 2-alkyl-substituted dienes form high 1,4-microstructure in polar media as well as in hydrocarbon media.³ Butyllithium-initiated polymerization of 2-isopropyl-1,3-butadiene in diethyl ether produces a polymer with 81% *cis*-1,4- and 19% *trans*-1,4-microstructure. Similarly, >90% 1,4-microstructure is observed in THF for butyllithium-initiated polymerization of 2-triethylsilyl-1,3-butadiene, 2-trimethoxysilyl-1,3-butadiene, 1-phenyl-1,3-butadiene, 1-pyridyl-1,3-butadiene, and 2-phenyl-1,3-butadiene.

3.17.6.1.3 Polar modifier effects

Small amounts of Lewis base additives in hydrocarbon media can exert dramatic effects on polydiene microstructure as shown by the data in Table 11. Lewis bases that interact most strongly with lithium produce the highest amount of 1,2-microstructure. For example, there is a correlation between the enthalpies of interaction of Lewis bases with polymeric organolithium compounds and the ability of these bases to promote 1,2-enchainment.¹⁷¹ The highest vinyl contents for polybutadiene are obtained with the most strongly coordinating ligands such as the bidentate bases TMEDA and bispiperidinoethane (DIPIP). To obtain significant amounts of vinyl microstructure with weak donor-type bases such as diethyl ether and triethylamine, they must be present in large amounts relative to lithium. In contrast, the strongly coordinating bases produce high vinyl polybutadiene microstructure at low base to lithium atom ratios, for example, R = [base]/[Li] = 1-2.

An important feature of the effect of Lewis base additives on diene microstructure is the fact that the amount of vinyl microstructure generally decreases with increasing temperature as shown in **Table 11** and illustrated in **Figure 7**.^{3,168,172} A simple explanation for the temperature dependence of vinyl

 Table 10
 Calculated charges on allyl carbon atoms of (6) neopentylallyl- and (7) neopentylmethylallyl-alkali metal compounds¹⁶⁷

		Calculated	Calculated charges on allylic carbon atoms				
Counterion	Solvent	α	β	γ	∑(total)		
Neopentylallyl-al	kali metal (6)						
Li	C ₆ H ₆	0.79	-0.13	0.22	0.88		
	THF	0.69	-0.15	0.40	0.94		
Na	THF	0.65	-0.12	0.49	1.02		
К	THF	0.59	-0.11	0.53	1.01		
Rb	THF	0.55	-0.11	0.53	0.97		
Cs	THF	0.51	-0.12	0.52	0.91		
Neopentylmethyl	allyl-alkali metal (7)					
Li	C ₆ H ₆	0.80	-0.14	0.19	0.85		
	THF	0.73	-0.15	0.34	0.92		
Na	THF	0.69	-0.12	0.38	0.95		
К	THF	0.61	-0.09	0.44	0.96		
Rb	THF	0.58	-0.09	0.47	0.96		
Cs	THF	0.54	-0.10	0.45	0.89		

THF, tetrahydrofuran.

		1,2-Microstructure (%)				
Base	[Base]/[Li]	5 °C	30 °C	50 °C	70 °C	Reference
Triethylamine	30		21	18	14	168
	270		37	33	25	
Diethyl ether	12		22	16	14	
	180		38	29	27	
THF	5		44	25	20	
	85		73	49	46	
Diglyme	0.1		51	24	14	
0.9	0.8		78	64	40	
TMEDA	0.6		73	47	30	
	0.4	78				169
	6.7	85				
	1.14		76	61	46	168
DIPIP	0.5	91	50	44	21	170
2	1	99.99	99	68	31	

Table 11 Effects of temperature and concentration of Lewis base on vinyl con	itent of polybutadiene in hexane
--	----------------------------------

DIPIP, bispiperidinoethane; THF, tetrahydrofuran; TMEDA, N,N,N',N'-tetramethylethylenediamine.



Figure 7 Effect of temperature on the microstructure of polybutadiene prepared by *n*-butyllithium-initiated polymerization in cyclohexane in the presence of 1.0 phm (parts per hundred parts of monomer) tetrahydro-furan (THF). From Uraneck, C. A. *J. Polym. Sci. Part A*-

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microstructure, compared to the lack of dependence of microstructure in hydrocarbon media with lithium as counterion, is that high vinyl microstructure is associated with the addition of monomer to a base-coordinated chain end (α -carbon) and this base coordination is reversed (less favorable) at higher temperatures.

The sensitivity of the microstructure to polymerization temperature depends on the Lewis base and the *R* value ([base]/[Li]) as shown in **Table 11**. Although the strongly chelating bidentate bases promote 1,2-polybutadiene microstructure at low temperatures, they generally exhibit a dramatic decrease in their ability to promote vinyl microstructure at elevated temperatures as shown in **Table 11**. This temperature dependence presents a particular problem in high-temperature processes, for example, commercial batch or continuous processes, in which medium vinyl polybutadienes are desired.³

An interesting effect of Lewis bases on diene microstructure is the fact that in the presence of strongly coordinating bases such as TMEDA, 1,2-units are observed for polyisoprene. For example, the microstructure of polyisoprene formed in the presence of TMEDA ([TMEDA]/[Li] = 1) in cyclohexane corresponds to 21% 1,4, 12% 1,2, and 67% 3,4.¹⁷³ The formation of 1,2-units requires the formation of the less stable 1,4-chain end versus formation of the more stable 4,1-chain end as shown in **Scheme 18**. With lithium as counterion in neat monomer or in hydrocarbon solvent, no 1,2-enchainment is detected (see Tables 6 and 7).



Scheme 18 Favored regiochemistry for isoprene monomer incorporation.

Another interesting and surprising phenomenon observed in alkyllithium-initiated polymerization of butadiene in the presence of TMEDA is that cyclization to form in-chain vinylcyclopentane units (up to 60%) is observed when the butadiene monomer is introduced into the reactor at low rates (eqn [30]).^{174,175} Under such conditions, propagation does not

corresponding polymers are higher for polymers with more side-chain vinyl microstructure. For example, the glass transition temperature of polybutadiene is an almost linear function of the % 1,2-configuration in the chain as shown in **Figure 8**.¹⁷⁶ Thus, while *cis*-1,4-polybutadiene has a glass transition temperature of -113 °C, 1,2-polybutadiene has a glass transition temperature



effectively compete with cyclization; similar results are obtained with DIPIP. With respect to the mechanistic requirements for this type of cyclization, it was reported that batch polymerization in THF/TMEDA (92:2, v/v) at 0 °C showed no evidence of these cyclic units although the vinyl content was almost 90%. This reaction forms a relatively unstable 2 ° alkyllithium from a resonance-stabilized allylic lithium, which would appear to be energetically unfavorable. However, it should be noted that this process also converts a π -bond into a more stable σ bond as in any vinyl polymerization. The generality of this cyclization process in monomer-starved systems was demonstrated by showing that significant amounts of cyclization are observed using sodium as counterion in the presence of TMEDA and also with lithium complexed only with THF.

The ability to prepare polydienes with variable microstructures is an important aspect of alkyllithium-initiated anionic polymerization. The main consequence of the change in microstructure is that the glass transition temperatures (T_g) of the of –5 °C.¹⁷⁷ This has practical consequences because polybutadienes with medium vinyl contents (e.g., 50%) have glass transition temperatures (ca. –60 °C) and properties that are analogous to SBR. Analogously, the glass transition temperature of *cis*-1,4-polyisoprene is approximately –71 °C; a polyisoprene with 49% 3,4-enchainment exhibited a $T_{\rm g}$ of –36 °C.¹⁷⁸

3.17.6.1.4 Salt and counterion effects

In contrast to the small effects of added lithium alkoxide observed for diene microstructure, ^{3,179} the addition of other alkali metal alkoxides increases the amount of vinyl microstructure analogous to the microstructure obtained with the corresponding alkali metal counterion. ¹⁸⁰ Thus, the maximum vinyl contents (%) were 67, 48, 55, and 53 for the sodium, potassium, rubidium, and cesium alkoxides, respectively, at *R* values of approximately 1 at 30 °C. ^{3,180} However, the effect of added alkali metal alkoxide decreases with increasing temperature for every alkali metal alkoxide



Figure 8 Variation of the glass transition temperature (T_g) with vinyl (1,2) content for polybutadiene. From Aggarwal, S. L.; Hargis, T. G.; Livigni, R. A.; *et al.* In *Advances in Elastomers and Rubber Elasticity*, Lal, J., Mark, J. E., Eds.; Plenum: New York, NY, 1986; pp 17–36; reprinted with kind permission from Springer Science+Business Media B.V.

analogous to the effect of increasing temperature in the presence of added Lewis bases; for example, at a [Na]/[Li] ratio of 0.5, >60% vinyl polybutadiene was obtained at 30 °C, but <30% at 50 °C.¹⁸⁰

The preparation of high *trans*-1,4-polybutadiene (\geq 80%) is of current interest because it has been reported that these polymers can exhibit strain-induced crystallization analogous to natural rubber.³ One class of initiators that form high trans-1,4-polybutadiene contain barium salts.3,176,181 For example, a polybutadiene with 79% trans-1,4- and 7% vinyl microstructure ($T_g = -91$ °C) was prepared from an initiator from n-butyllithium with 0.5 equivalents of a barium (t-butoxide-hydroxide) salt with 9 mol% hydroxide ion in toluene at 30 °C.¹⁸¹ The trans-1,4-content decreased at higher temperatures. A more recent modification utilizes a catalyst formed from a barium(t-alkoxide-hydroxide) or a barium (t-alkoxide)₂ salt with the complex of a dialkylmagnesium and a trialkylaluminum.^{3,176,181,182} Polybutadienes with 90% 1,4-content were prepared when the ratio of [Ba]/[Mg] was approximately 0.20 and the [Mg]/[Al] ratio was 6 for polymerizations in cyclohexane at 50 °C.¹⁸¹ The trans-1,4-content decreased with increasing temperature, but was as high as 79% even at 80 °C. In contrast to the Ba/Li systems that undergo chain transfer in toluene, the Ba/Mg/Al systems were reported to exhibit the characteristics of a living polymerization. A cyclohexane-soluble initiator system composed of trioctylaluminum, n-butyllithium, and barium 2-ethylhexoxide was shown to produce polybutadiene with controlled structure at useful temperatures (80 °C) with low vinyl content (3-6%) and with variable trans-1,4microstructure (70-90%) depending on the stoichiometry of the reagents.¹⁸³ A similar system comprising a dilithium initiator, barium diethyleneglycol dialkoxide, and triisobutylaluminum has been used to synthesize stereotriblock polybutadiene (high trans-1,4-PB-block-trans-1,4 (55%)-co-cis-1,4(35%)-block-high trans-1,4-PBD).¹⁸⁴

Another initiator system for the preparation of high *trans*-1,4-polybutadiene is based on the complex formed from dibutylmagnesium and potassium *t*-amyloxide (KOAm) in hydrocarbon solvent.^{3,185} *trans*-1,4-Polybutadiene was prepared in variable yields (50–100%) with $[KOAm]/[R_2Mg] \approx 1$, $[KOAm]/[Bu_3MgK] = 1.5-2.3$, and $[KOAm]/[R_3MgNa] = 2.4-10$. High *trans*-1,4-polybutadienes were also obtained with initiators based on a mixture of potassium *t*-amyloxide and *n*-butyllithium ([KOAm]/[RLi] > 4).^{3,186} Two polymer fractions, soluble (high vinyl) and insoluble (high *trans*-1,4), were observed with this initiator as with the corresponding magnesium-based systems.

3.17.6.2 Polystyrene

The homogeneous alkyllithium-initiated polymerization of styrene in hydrocarbon media produces polystyrene with an almost random (i.e., atactic) microstructure.^{3,68} The racemic diad fraction (P_r) was 0.53 for the butyllithium/toluene system.^{3,187} The effects of counterion, solvent, and temperature on polystyrene stereochemistry are shown in Table 12. The principal conclusion from these results is that the stereoregularity of polystyrenes prepared by anionic polymerization is predominantly syndiotactic $(P_r = 0.56 - 0.74)$ and that the stereoregularity is surprisingly independent of the nature of the cation, solvent, and temperature, in contrast to the sensitivity of polydiene stereochemistry to these variables. A report on the effect of added alkali metal alkoxides showed that polystyrene stereochemistry can be varied from 64% syndiotactic triads with lithium t-butoxide to 58% isotactic triads with potassium t-butoxide.190

When small amounts of water were deliberately added to butyllithium in hydrocarbon solution, it was possible to prepare polystyrene with as much as 85% insoluble polymer. The polystyrene formed was insoluble in refluxing methyl ethyl ketone and was identified as isotactic polystyrene by X-ray crystallography.¹⁹¹ Isotactic polystyrene (10-22% crystalline) can be prepared when lithium t-butoxide is added to n-BuLi initiator and the polymerization in hexane (styrene/hexane = 1) is effected at -30 °C.¹⁹² This polymerization becomes heterogeneous and is quite slow (after 2-5 days, 50% monomer conversion; 20-30% conversion to isotactic polymer). The t-butyllithium-initiated polymerization of styrene in the presence of controlled amounts of water yielded polystyrenes with higher overall isotactic content of the unfractionated polystyrene.¹⁹³ Polystyrenes with isotactic triad contents ranging from 65% to 85% were obtained in 5-43% yields using n,secdibutylmagnesium with a potassium alkoxide (1:1) as initiator; however, the highest stereospecificity polymer was obtained in only 5% yield after 48 h at -40 °C in methylcyclohexane.¹⁹⁴

Counterion		Temperature (°C)	Stereochemistry			
	Solvent		mm	mr	rr	Pr
Li	THF	-78	0.10	0.32	0.58	0.74
Toluen		20	0.12	0.37	0.51	0.69
	Toluene	-20	0.13	0.42	0.45	0.66
		20	0.07	0.41	0.52	0.73
К	THF	-78	0.09	0.34	0.57	0.74
Cs	THF	-78	0.14	0.35	0.51	0.69
Na	Toluene	10	0.15	0.40	0.45	0.65
К			0.22	0.37	0.41	0.59
Rb			0.21	0.44	0.35	0.57
Cs			0.24	0.41	0.35	0.56

 Table 12
 Stereoregularity of polystyrenes prepared with anionic initiators^{188,189}

THF, tetrahydrofuran.

Relatively few comonomer pairs undergo anionic copolymerization to incorporate significant amounts of both monomers into the polymer chains.¹⁹⁵ In general, the comonomer that is most reactive (lowest pK_a value for the conjugate acid of the propagating anion)^{2,3} will be incorporated to the practical exclusion of the other comonomer. Comonomer pairs that can be effectively copolymerized include styrenes with dienes and methacrylates with acrylates, that is, comonomer pairs with similar reactivity.

Anionic copolymerizations have been investigated by applying the classical Mayo–Lewis treatment that was originally developed for free radical chain reaction polymerization.^{196,197} The copolymerization of two monomers (M_1 and M_2) can be uniquely defined by the following four elementary kinetic steps (Scheme 19), assuming that the reactivity of the chain end (M_1^- or M_2^-) depends only on the last unit added to the chain end, that is, there are no penultimate effects.

From these four basic kinetic equations, the Mayo–Lewis instantaneous copolymerization equation can be derived:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[m_1] + [m_2])}{[M_2](r_2[m_2] + [m_1])}$$
[31]

where $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$, m₁ and m₂ are the instantaneous monomer concentrations, and d[M₁]/d[M₂] represents the instantaneous copolymer composition. The monomer reactivity ratios, r_1 and r_2 , represent the relative reactivity of each growing chain end for addition of the same monomer compared to crossover to the other monomer. Representative monomer reactivity ratios for anionic copolymerizations are listed in **Table 12**. The applicability of standard copolymerization theory to anionic polymerization has been considered in detail. The equations shown in **Scheme 15** represent an oversimplification solution and there is a spectrum of ion pairs and free ions in polar media.

3.17.7.1 Hydrocarbon Solution

In most copolymerizations, $r_1 \neq r_2$ and one monomer is preferentially incorporated into the initially growing polymer. This leads to depletion of the preferentially incorporated monomer in the feed and the composition of the copolymer formed changes with conversion.¹³ For systems undergoing continuous initiation, propagation, and termination, the resulting compositional heterogeneity is intermolecular, that is, the copolymer formed initially has a different comonomer composition from



Scheme 19 Elementary kinetic steps for anionic copolymerization.

the copolymer formed at the end of the reaction. However, in living anionic copolymerization, all of the compositional heterogeneity arising from the disparity in monomer reactivity ratios is incorporated into each growing polymer chain, that is, the compositional heterogeneity is intramolecular not intermolecular.

3.17.7.1.1 Tapered block copolymers

The alkyllithium-initiated copolymerizations of styrene with dienes, especially isoprene and butadiene, have been extensively investigated and illustrate the important aspects of anionic copolymerization. As shown in **Table 13**, monomer reactivity ratios for dienes copolymerizing with styrene in hydrocarbon solution range from approximately 8 to 17, while the corresponding monomer reactivity ratios for styrene vary from 0.04 to 0.25. Thus, butadiene and isoprene are preferentially incorporated into the copolymer initially. This type of copolymer or a graded block copolymer.³ The monomer sequence distribution can be described by the structures given below:

$$- \left[D \right]_{n} \left[D/S \right] \left[S \right]_{m} - \left[D \right]_{n} \left[D \rightarrow S \right] \left[S \right]_{m}$$

First, there is a diene-rich block; a middle block follows which is initially richer in butadiene with a gradual change in composition until eventually it becomes richer in styrene; a final block of styrene completes the structure. Thus, there is compositional homogeneity between polymer chains, but there is compositional heterogeneity within each polymer chain because of the living nature of these polymerizations and the disparity in the monomer reactivity ratios.

For a typical copolymerization of styrene and butadiene (25:75, wt/wt), the solution is initially almost colorless, corresponding to the dienyllithium chain ends, and the rate of polymerization is slower than the homopolymerization rate of styrene as shown in Figure 9. The homopolymerization rate constants for styrene, isoprene, and butadiene are 1.6×10^{-2} (L/mol)^{1/2} s⁻¹, 1.0×10^{-3} (L/mol)^{1/4} s⁻¹, and 2.3×10^{-4} (L/mol)^{1/4} s⁻¹, respectively.⁸⁰ After approximately 70-80% conversion, the solution changes to orange-yellow, which is characteristic of styryllithium chain ends. At the same time, the overall rate of polymerization increases (inflection point). Although the percent conversion at which the inflection point is observed does not appear to depend on the solvent, the time to reach this percent conversion is quite solvent-dependent, as shown in Figure 9. Analysis of the copolymer composition indicates that the total % styrene in the copolymer is less than 5% up to approximately 75% conversion (see Figure 10);⁵⁴ these incorporated styrene units exist predominantly as isolated sequences.²⁰⁶ When these samples are analyzed by oxidative degradation by ozonolysis, polystyrene segments (corresponding to polystyrene blocks in the copolymer) are recovered only after the inflection point is reached as shown in Figure 11.²⁰⁶ For a 75:25 (wt/wt) feed mixture of butadiene/styrene, it is reported that 72% of the styrene is incorporated into the tapered block copolymer as block styrene.²⁰⁷ The percentage of block styrene increases as the

<i>M</i> ₁	M_2	Solvent	°C	r ₁	r ₂	Reference
Butadiene	Styrene	None	25	11.2	0.04	196
		Benzene	25	10.8	0.04	
		Cyclohexane	25	15.5	0.04	
		Hexane	0	13.3	0.03	
			25	12.5	0.03	
			50	11.8	0.04	
		THF	-78	0.04	11.0	
			0	0.2	5.3	
			25	0.3	4.0	
		Diethyl ether	25	1.7	0.4	
		Triethylamine	25	3.5	0.5	
		Anisole	25	3.4	0.3	
		Diphenyl ether	25	2.8	0.1	
	Isoprene	Hexane	20	2.72	0.42	198
	1,1-Diphenylethylene	Benzene	40	54	~0	199
		THF	0	0.13	~0	
lsoprene	Styrene	Benzene	30	7.7	0.13	200
		Toluene	27	9.5	0.25	201
		Cyclohexane	40	16.6	0.046	202
		THF	27	0.1	9	203
	1,1-Diphenylethylene	Benzene	40	37	~0	204
		THF	0	0.12	~0	
Styrene	1,1-Diphenylethylene	Benzene	30	0.7	~0	205
	,	THF	30	0.13	~0	

 Table 13
 Anionic copolymerization parameters in hydrocarbon solution with alkyllithium initiators

THF, tetrahydrofuran.



Figure 9 Copolymerization of butadiene and styrene in different solvents at 50 °C. From Hsieh, H. L.; Glaze, W. H. *Rubber Chem. Technol.* **1970**, *43*, 22–73; reprinted by permission of the American Chemical Society/Rubber Division.

styrene content in the copolymer increases; thus, 80% block styrene content has been reported for a 67:33 (wt/wt) feed mixture of butadiene/styrene.²⁰⁸

The kinetics of copolymerization provide an explanation for the copolymerization behavior of styrenes with dienes. One useful aspect of living anionic copolymerizations is that stable carbanionic chain ends can be generated and the rates of their crossover reactions with other monomers can be measured independent of the copolymerization reaction. However, it should be noted that in an actual copolymerization the kinetics are complicated by cross-association of the PSLi chain ends (degree of aggregation, 2) with the PBDLi chain ends (degree of aggregation, 4). Two of the four rate constants involved in copolymerization correspond at least superficially to the two homopolymerization reactions of butadiene and styrene, for example, $k_{\rm BB}$ and $k_{\rm SS}$, respectively. The other two rate constants can be measured independently as shown in the following equations:



Figure 10 Styrene incorporation as a function of conversion for copolymerization of butadiene and styrene (75:25) at 50 °C. From Hsieh, H. L.; Glaze, W. H. Rubber Chem. Technol. 1970, 43, 22–73; reprinted by permission of the American Chemical Society/Rubber Division.



Figure 11 Ozonolysis–SEC curves of copolymer samples at various conversions for styrene/butadiene (19.6:80.4 mol.%) copolymerization in toluene at 40 °C: (a) conversion 23.6% (styrene, 1.7 mol.%); (b) conversion 65.6% (styrene, 4.9 mol.%); (c) conversion 75.6% (styrene, 6.9 mol.%); (d) conversion 89.3% (styrene, 13.0 mol.%); and (e) conversion 100% (styrene, 20.6 mol.%). From Tanaka, Y.; Sato, H.; Nakafutami, Y.; Kashiwazaki, Y. *Macromolecules* 1983, *16*, 1925–1928; reprinted by permission of the American Chemical Society.

$$PSLi + butadiene \xrightarrow{k_{SB}} PS-BDLi \qquad [32]$$

$$PBDLi + styrene \xrightarrow{k_{BS}} PBD-SLi \qquad [33]$$

The kinetic results of a number of independent kinetic studies can be summarized as follows for styrene–butadiene copolymerization:^{68,209}

$$k_{\rm SB} >> k_{\rm SS} > k_{\rm BB} > k_{\rm BS}$$

 $(1.1 \times 10^2 \, \mathrm{l} \, \mathrm{mol}^{-1} \, \mathrm{s}^{-1}) >> (4.5 \times 10^{-1} \, \mathrm{l} \, \mathrm{mol}^{-1} \, \mathrm{s}^{-1}) > (8.4 \times 10^{-2} \, \mathrm{l} \, \mathrm{mol}^{-1} \, \mathrm{s}^{-1}) > (6.6 \times 10^{-3} \, \mathrm{l} \, \mathrm{mol}^{-1} \, \mathrm{s}^{-1}).$

This kinetic order contains the expected order of homopolymerization rates, that is, $k_{SS} > k_{BB}$. The surprising result is that the fastest rate constant is associated with the crossover reaction of the PSLi chain ends with butadiene monomer (k_{SB}) ; conversely, the slowest reaction rate is associated with the crossover reaction of the poly(butadienyl)lithium chain ends with styrene monomer (k_{BS}) . Similar kinetic results have been obtained for styrene-isoprene copolymerization.²⁰² It is noteworthy that after oxidative degradation of tapered block copolymers, the molecular weight distributions of the resulting polystyrene blocks are relatively broad, that is, $M_{\rm w}/M_{\rm n} = 1.6 - 1.7$ for $M_{\rm n}(\text{total}) = 18\,000\,\text{g}\,\text{mol}^{-1\,206}$ and $M_{\rm w}/M_{\rm p} = 1.3 - 1.4$ for $M_{\rm p}$ (total) = 200 000 g mol⁻¹.²¹⁰ This is consistent with the expected slow rate of crossover from PBDLi chain ends to PSLi chain ends relative to styrene homopropagation.

3.17.7.1.2 Counterion effects

The counterion also has a dramatic effect on the copolymerization behavior of styrene and dienes.²¹¹ It is particularly noteworthy that the monomer reactivity ratios for styrene ($r_{\rm S}$ = 0.42) and butadiene ($r_{\rm B}$ = 0.30) are almost equal for copolymerization in toluene at 20 °C using a hydrocarbon-soluble organosodium initiator, 2-ethylhexylsodium.^{212,213} Thus, an alternating-type copolymer structure ($r_{\rm S}r_{\rm B}$ = 0.126) would be formed for this system; however, butadiene is incorporated predominantly as vinyl units (60% 1,2). In contrast, initial preferential incorporation of styrene ($r_{\rm S}$ = 3.3; $r_{\rm B}$ = 0.12) is observed for an analogous organopotassium initiator, the 1,1-diphenylethylene adduct of 2-ethylhexylpotassium.²¹¹

Tapered butadiene-styrene copolymers are important commercial materials because of their outstanding extrusion characteristics, low water absorption, good abrasion resistance, and good electrical properties. Tapered block copolymers are used for wire insulation and shoe soles (after vulcanization) as well as for asphalt modification.³

3.17.7.2 Polar Solvents

In polar media, the preference for diene incorporation is reduced as shown by the monomer reactivity ratios in **Table 13**. In THF, the order of monomer reactivity ratios is reversed compared to hydrocarbon media. The monomer reactivity ratios for styrene are much larger than the monomer reactivity ratios for dienes. Thus, although it is apparent that polar solvents such as THF can alter the copolymerization behavior of styrenes and dienes, they have the disadvantage of concurrently increasing the amount of vinyl microstructure for polybutadiene, an undesirable feature.

3.17.7.3 Random Styrene–Diene Copolymers

Random copolymers of butadiene (SBR) or isoprene (SIR) with styrene can be prepared by the addition of small amounts of ethers, amines, or alkali metal alkoxides with alkyllithium initiators in hydrocarbon solution. Random copolymers are characterized as having only small amounts of block styrene content. The amount of block styrene can be determined by ozonolysis²⁰⁶ or more simply by integration of the ¹H NMR region corresponding to block polystyrene segments $(\delta = 6.5 - 6.94 \text{ ppm})$ ²¹⁴ Monomer reactivity ratios of $r_{\rm B} = 0.86$ and $r_{\rm S} = 0.91$ have been reported for copolymerization of butadiene and styrene in the presence of one equivalent of TMEDA ([TMEDA]/[RLi] = 1).²¹⁵ However, the random SBR produced in the presence of TMEDA will incorporate the butadiene predominantly as 1,2-units. At 66 °C using one equivalent of TMEDA, an SBR copolymer will be obtained with 50% 1,2-polybutadiene microstructure.¹⁶⁸ In the presence of Lewis bases, the amount of 1,2-polybutadiene enchainment decreases with increasing temperature. The use of methyl t-butyl ether (MTBE) as a randomizer for styrene-butadiene copolymerizations has been reported. Using an [MTBE]/ [BuLi] molar ratio of 15 at 50 °C in cyclohexane, the monomer reactivity ratios were reported to be $r_{\rm S} = 0.7$ and $r_{\rm B} = 1.84$ and the vinyl microstructure amounted to 21%.216

In general, random SBR with a low amount of block styrene and low amounts of 1.2-butadiene enchainment (<20%) can be prepared in the presence of small amounts of added potassium or sodium metal alkoxides.^{217,218} For example, at 50 °C in the presence of as little as 0.067 equivalents of potassium t-butoxide in cyclohexane, the amount of bound styrene was relatively independent of conversion, in contrast to the heterogeneity observed in the absence of randomizer, that is, tapered block copolymer formation.²¹⁷ The polybutadiene microstructure obtained under these conditions corresponds to about 15% 1,2-microstructure.²¹⁸ Using 0.2 equivalents of hydrocarbon-soluble sodium 2,3dimethyl-2-pentoxide, the monomer reactivity ratios for alkyllithium-initiated SBR were found to be of $r_{\rm B}$ = 1.1 and $r_{\rm S} = 0.1$ ²¹⁹ The resulting copolymer had only 5% block styrene and 18% 1,2-vinyl microstructure. It was found that there is a very narrow compositional window ([RONa]/[RLi]) at



Figure 12 Effect of the molar ratio of [NaOR]/[BuLi] on the % block styrene (blockiness) obtained for copolymerization of styrene and butadiene (25:75, wt/wt) in cyclohexane at 65 °C. From Quirk, R. P.; Zhou, J.-P. *Polym. Mater.: Sci. Eng.* 2001, *84*, 833–834.

which a minimum amount of styrene blockiness was obtained as shown in **Figure 12**.²²⁰ At both lower and higher ratios, significant and unacceptably high levels of block styrene content are formed in the copolymer. It is expected that sodium alkoxide may change the aggregation degree of the organolithium chain ends, may form cross-associated species, and may even exchange counterions with the propagating chain ends. Equilibrium among these active species obviously affects styrene incorporation and diene microstructure.²²⁰ Recent studies have indicated the participation of multicomponent active species (complex cross-aggregates and equilibria between metal-metal exchanged species) depending on the stoichiometry of the mixed initiator.^{221,222}

The effect of dibutylmagnesium and triisobutylaluminum 'retarders' on the copolymerization of neat styrene and butadiene has been investigated at 25 °C.223 Although the monomer reactivity for styrene was relatively constant $(r_{\rm S} = 0.03 \text{ and } 0.04 \text{ at } [R_2Mg]/[RLi] = r = 1 \text{ and } 4, \text{ respectively}),$ the butadiene monomer reactivity ratio was sensitive to the [Mg]/[Li] ratio ($r_B = 9.1$ and 1.9 at $[R_2Mg]/[RLi] = 1$ and 4, respectively). The percentage of 1,2-units in the copolymer increased with increasing molar ratio of [Mg]/[Li] from ~12% at r = 1 to ~33% at r = 4. These results were obtained at 25 °C, however. It would be expected that the amount of vinyl microstructure would decrease at higher temperatures. For triisobutylaluminum, the monomer reactivity ratios reported were $r_{\rm S} = 0.6$ and $r_{\rm B} = 1.1$ for [iBu₃Al]/[RLi] = 0.85. Thus, whereas tapered structures would be formed for the magnesium system, a random copolymer structure would be expected for the aluminum system. In addition, the presence of triisobutylaluminum did not significantly affect the polybutadiene microstructure (13% 1,2-microstructure for $[iBu_3Al]/[RLi] = 0.9$).

Commercial anionically prepared, random SBR polymers (solution SBR) prepared by alkyllithium-initiated polymerization typically have 32% *cis*-1,4-, 41% *trans*-1,4-, and 27% vinyl microstructure compared to 8% *cis*-1,4-, 74% *trans*-1,4-, and 18% vinyl microstructure for emulsion SBR with the same comonomer composition.^{3,224} Solution SBRs typically have branched architectures to eliminate cold flow.^{49,225} Compared to emulsion SBR, solution random SBRs require less accelerator and give higher compounded Mooney, lower heat buildup, increased resilience, and better retread abrasion index.³ Terpolymers of styrene, isoprene, and butadiene (SIBR) have been prepared using a chain of single-stirred reactors whereby the steady-state concentration of each monomer and Lewis base modifier at any degree of conversion can be controlled along the reactor chain.^{3,226–228}

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Biographical Sketch



Roderic P. Quirk, a native of Detroit, Michigan, is a l963 BS chemistry graduate of Rensselaer Polytechnic Institute (Troy, NY). He received his MS (l965) and PhD (l967) degrees in organic chemistry at the University of Illinois (with professor David Y. Curtin), followed by 2 years of postdoctoral research with professor E. M. Arnett at the University of Pittsburgh (Mellon Institute). He was a faculty member in the Chemistry Department at the University of Arkansas from 1969 to 1978. He joined the University of Akron as professor of polymer science in 1983 after 5 years as a senior research scientist at Midland Macromolecular Institute (now Michigan Molecular Institute) in Midland, MI. His research interests are in synthetic organic polymer chemistry with emphasis on anionic polymerization, chain-end functionalization reactions, and synthesis of new block, cyclic, and branched polymers. He is author of more than 300 professional publications including 4 books and 32 patents. He was awarded a fellowship from the Japanese Society for the Promotion of Science (1990) and was a visiting professor at Tokyo Institute of Technology (1990); the Institut Charles Sadron, CNRS, Strasbourg, France (1991); the Universite Bordeaux, France (1998); and University of the Basque Country, San Sebastian, Spain (2005). In 1996, he was appointed Kumho Professor of Polymer Science and also Distinguished Professor of Polymer Science. He served as Chair in the Department of Polymer Science (1995–1998) and as Interim Director of the Institute of Polymer Science and Polymer Science.

3.18 Anionic Polymerization of Protected Functional Monomers

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3.18.1	Introduction	591
3.18.2	Functional Styrene Derivatives	592
3.18.2.1	Styrene Derivatives with Hydroxyl Groups	592
3.18.2.2	Styrene Derivatives with Other Functional Groups	596
3.18.2.3	New Protective Strategy for Functional Styrene Derivatives: Use of Protected Functionalities Showing	
	Electron-Withdrawing Characters	600
3.18.2.4	Anionic Polymerization Behavior of Styrene Derivatives Possessing Benzyl Ether Skeletons	603
3.18.2.5	Styrene Derivatives Possessing Silanol Functions	606
3.18.3	Functional 1,3-Butadiene Derivatives	608
3.18.4	Functional (Meth)acrylate Derivatives	611
3.18.4.1	(Meth)acrylic Acids	612
3.18.4.2	Functional Methacrylate Derivatives	613
3.18.5	N-Isopropylacrylamide	617
3.18.6	Concluding Remarks	618
References		619

3.18.1 Introduction

Although many living/controlled polymerization systems have been developed via different mechanisms in the last 25 years, the living anionic polymerization of styrene, 1,3-butadiene, or isoprene is still the best living polymerization system from the following points of view.¹⁻³ First, molecular weight can be precisely controlled over a wide range from 10³ to even 10⁶ g mol⁻¹. Second, molecular weight distributions are nearly monodisperse, with M_w/M_p values being 1.05 or even smaller. Finally, the resulting living anionic polymers have chain-end carbanions which are highly reactive, but stable under appropriate conditions. Such molecular characteristics as well as reactivity and stability of chain-end carbanions are ideally suited for the synthesis of well-defined architectural polymers such as block copolymers, graft copolymers, comb-like polymers, star-branched polymers, dendrimer-like hyperbranched polymers, and more complex branched polymers.

A major and serious drawback of such living anionic polymerization systems is the intolerance to most of the highly useful functional groups such as hydroxyl, mercapto, amino, formyl, acyl, and carboxyl groups. Monomers substituted with such functional groups cannot be directly subjected to anionic polymerization, because they normally would participate in termination or chain transfer reaction under the conditions of anionic polymerization where highly reactive carbanions (initiators and propagating chain-end anions) are always present. Only limited functional styrene derivatives were reported to undergo living anionic polymerization until the beginning of 1980s. The successful examples are para-substituted styrene derivatives with alkyl,^{4,5} aryl,⁶⁻⁹ alkoxy,¹⁰⁻¹² dimethylamino,¹³ trimethylsilyl (TMS),¹⁴ triphenylgermyl,¹⁵ and triphenyltin groups.¹⁶ The results are not surprising, since these functional groups are sufficiently stable toward highly reactive carbanions in organic chemistry.

In order to overcome this longstanding problem, Nakahama and co-workers^{17–20} introduced a protective strategy into the living anionic polymerization of functional monomers. The strategy involves the following three reaction steps as illustrated in Scheme 1: (1) the functional group is masked by an appropriate protective group to convert it to the stable form under the conditions of anionic polymerization; (2) the resulting protected functional monomer is subjected to living anionic polymerization; and (3) the protective group is removed to regenerate the original functional group after the polymerization. In this strategy, there are two strict requirements. First, the protected functionality must be completely stable during the course of the living anionic polymerization. Second, the protective group must be quantitatively removed under mild conditions. In the case of polymers, even a small amount of residual protected functionalities in the polymer chain is impossible to be removed from the original functional groups regenerated, since both functionalities are together in the same polymer chain. The second requirement is more complex than that of low-molecular-weight compounds, which can allow several isolation techniques such as distillation, recrystallization, sublimation, and chromatography.^{21,22} Throughout this chapter, the importance of the choice of the protective group that satisfies the abovementioned requirements in achieving the living anionic polymerization of protected monomers with protected functionalities is discussed. As will be described in detail later, the success of this protective strategy in conjunction with living anionic polymerization enormously broadens the range of functional groups that can be applied to the living anionic polymerization and extends further the synthetic capability and flexibility of the living anionic polymerization.

Although the proper choice of initiator and polymerization conditions is essential for the living anionic polymerization of methyl methacrylate (MMA), the polymerization can be sufficiently controlled to afford the best class of living anionic polymers in terms of predictable molecular weight up to several $10^5 \text{ g} \text{ mol}^{-1}$ and narrow molecular weight distribution (M_w / M_n < 1.05) at the present time.^{1,2,23-25} The chain-end anion of the resulting living polymer is a delocalized enolate anion, which has low electron density due to the electron-withdrawing



Scheme 1 Protection and living anionic polymerization of functionalized styrene derivatives.

carbonyl group. Therefore, the enolate anion is less reactive than the carbanions generated from styrene and diene monomers, and hence it can coexist with the side chain methyl ester function. However, the enolate anion is generally categorized as one of the highly reactive anions and it readily reacts with most of the functional groups mentioned above. Therefore, similar to the living anionic polymerization of functional styrene and 1,3-diene monomers, functional groups must be masked by protective groups prior to the anionic polymerization of functional methacrylate monomers.

This chapter will first focus on the development of the living anionic polymerization of protected functional styrene and diene monomers since the middle of 1980s. In the later parts, the living anionic polymerization of protected functional (meth)acrylate derivatives will be described. In addition, living anionic polymerization of a protected N-isopropylacrylamide (NIPAM) having a similar anionic polymerizability as that of MMA will be discussed. Since we have observed some interesting behaviors in the anionic polymerization of specific protected functional monomers, which cannot be predicted from the chemistry of protective groups in organic synthesis, these will be introduced in Sections 3.18.2.3 and 3.18.2.4. These are the lowered reactivity of living polymers derived from styrene derivatives carrying electron-withdrawing protective groups and the nonpolymerizability of styrenes possessing benzyl ether skeletons.

3.18.2 Functional Styrene Derivatives

The range of solvents that can be used for the living anionic polymerization of styrene is limited due to the highly reactive anionic initiators and the propagating chain-end carbanions. The solvents of choice are mainly aliphatic and aromatic hydrocarbons and ethers. Typically, the following two polymerization conditions are used in the living anionic polymerization of styrene. In the first condition, the polymerization is carried out in nonpolar hydrocarbon media such as cyclohexane, benzene, toluene, and similar hydrocarbons at room temperature or higher temperature from 40 to even 80 °C. In such hydrocarbon media, various organolithium (RLi) compounds such as *n-*, *sec-*, and *tert*-butyllithiums (BuLi) are employed as anionic initiators because of the solubility and commercial availability.²⁶ In general, the initiators and propagating chain-end anion are more or less aggregated in hydrocarbon media and the dissociated forms produced via equilibrium are active species capable of polymerizing styrene.

The other system is the polymerization carried out in polar ethereal media at temperatures lower than -40 °C to avoid the undesirable side reaction of media with anionic initiators and chain-end anions. The condition in tetrahydrofuran (THF) at -78 °C is among the most employed system. In polar media, not only RLi but also organosodium and organopotassium compounds can be used as initiators. Furthermore, radical anion complexes formed by aromatic hydrocarbons and alkali metals are often used as difunctional initiators. In the propagating chain-end anion in polar media, there is equilibrium among several ion pairs and a free ion, each of which can participate in the propagation reaction.

The polymerization systems in nonpolar media are superior to those in polar media from industrial viewpoints including simple procedure, moderate polymerization rate, expandable reaction scale, ease of solvent purification, and energy saving. However, the anionic polymerizations of protected functional styrene derivatives are mostly carried out under the conditions in THF at -78 °C because of the insolubility of polystyrenes carrying polar functional groups in hydrocarbon media and intolerance of protective functionalities toward the initiators and propagating chain-end anions at higher temperatures. The possible choice of any initiators having different countercations is an additional advantage in the polar media.

3.18.2.1 Styrene Derivatives with Hydroxyl Groups

The first successful example of the protective strategy in conjunction with living anionic polymerization is the synthesis of well-defined poly(4-hydroxylstyrene) (or poly(4-vinylphenol)) (poly(1)) by the living anionic polymerization of



Figure 1 Monomers 1 and 1a–1c.



Scheme 2 Anionic polymerization of 1a and deprotection of poly(1a).

4-(*tert*-butyldimethylsilyloxy)styrene (1a) (Figure 1), a silyl ether-protected styrene monomer, followed by quantitative removal of the silyl protective group of the resulting poly(1a), as illustrated in Scheme 2.^{27–29} The phenolic hydroxyl group ($pK_a = 10$) of 1 was first protected by a sterically hindered *tert*-butyldimethylsilyl (TBDMS) group and the resulting protected styrene, 1a, was subjected to anionic polymerization with lithium naphthalenide in THF at –78 °C (Table 1). Soon after

Table 1Anionic polymerization of 1a–1g and 2a in THF at -78 °Cfor 0.5–1 h

Monomer	Initiator	<i>M</i> _n calcd (g mol ⁻¹)	<i>M</i> _n obsd ^a (g mol ⁻¹)	M _w /M _n
1a	Li-Naph ^b	10 000	11 000	1.05
1a	K-Naph ^c	20 000	20 000	1.07
1a	<i>sec</i> -BuLi/α-MeSt ^d	45 000	51 000	1.03
1b	K-Naph/α-MeSt ^e	20 000	20 000	1.07
1c	K-Naph/α-MeSt	17 000	18000	1.08
1f	K-Naph/α-MeSt	33 000	35 000	1.05
1g	K-Naph/α-MeSt	12 000	14 000	1.09
2a	<i>sec</i> -BuLi/α-MeSt	10 000	12 000	1.02
2a	Li-Naph/α-MeSt ^f	19000	20 000	1.07
2a	Li-Naph/α-MeSt	31 000	33 000	1.05

^aMeasured by VPO.

^dOligo(α-methylstyryl)lithium.

^eOligo(α-methylstyryl)dipotassium.

^{*f*}Oligo(α -methylstyryl)dilithium.

the addition of 1a to the initiator, an orange-red color developed, strongly indicating the formation of the propagating chain-end of polystyryl anion generated from 1a. The color remained visually unchanged at -78 °C even after 24 h, but disappeared instantaneously by quenching with degassed methanol. A polymer was obtained in 100% yield.

The ¹H and ¹³C nuclear magnetic resonance (NMR) spectra of the resulting polymer revealed the disappearance of vinyl protons and carbons and the presence of signals corresponding to the backbone chain and the TBDMS group. Thus, the vinyl polymerization of 1a quantitatively proceeded and the TBDMS group remained as such during the polymerization. The size-exclusion chromatographic (SEC) profile exhibited a symmetrical sharp monomodal distribution, with the M_w/M_n value being 1.1. The M_n value determined by vapor pressure osmometer (VPO) agreed well with that calculated from the monomer to initiator ratio. These results clearly demonstrated that the TBDMS ether-protected monomer, 1a, underwent anionic polymerization to afford a stable living polymer in THF at -78 °C. Thus, the phenolic hydroxyl group of 1 was completely protected by the TBDMS ether form to achieve the living anionic polymerization.

The living anionic polymerization of **1a** was successfully carried out with various anionic initiators such as *sec*-BuLi, cumylpotassium, lithium and potassium naphthalenides, oligo(α -methylstyryl)dilithium, and oligo(α -methylstyryl)dilotassium. There was an immediate color change to either orange red (Li⁺) or dark red (K⁺) in each polymerization system. The polymerization was rapid and complete within a few minutes in THF at –78 °C. The results are summarized in **Table 1**. As expected, all initiators were effective to

^bLithium naphthalenide.

^cPotassium naphthalenide.

quantitatively yield poly(1a)s with predictable molecular weights and narrow molecular weight distributions. Similar to styrene, no polymerization of 1a occurred with Grignard reagents (C_6H_5MgCl and $C_6H_5CH_2MgCl$), LiAlH₄, and potassium *tert*-butoxide. Accordingly, 1a is similar to styrene in anionic polymerizability.

The sequential block copolymerization of **1a** with styrene efficiently proceeded to afford an objective AB diblock copolymer, poly(**1a**)-*block*-polystyrene, with well-defined structures. This success further confirms the living nature of the anionic polymerization of **1a**. Similarly, a well-defined BA diblock copolymer, polystyrene-*block*-poly(**1a**), was synthesized by reversing the sequence of monomer addition, namely styrene followed by **1a**. Thus, the possible crossover copolymerization indicates that the electrophilicities of **1a** and styrene as well as the nucleophilicities of both living polymers are very similar.

Although the TBDMS protective group of poly(1a) was stable in aqueous and alcoholic solutions under neutral conditions, it was readily and quantitatively cleaved to give poly(1) by treatment with either 2 N HCl in aqueous THF or $(C_4H_9)_4$ NF in THF at room temperature (Scheme 2). ¹H and ¹³C NMR signals corresponding to the TBDMS groups disappeared after the deprotection, clearly indicating the complete removal of the protective groups. Unfortunately, the resulting poly(1) could not be directly measured by SEC in THF, since a significant tailing to a lower molecular weight side was always observed, due to the strong interaction between the phenolic hydroxyl group and the SEC column. Therefore, the poly(1) was first converted to poly(4-benzoyloxystyrene) by treatment with benzoic anhydride and subjected to SEC measurement. As expected, a narrow monomodal peak eluted at a reasonable molecular weight region, similar to that of the original poly (1a), was observed. This also supports that the poly(1) herein obtained must be narrowly distributed in molecular weight. The poly(1a) has a solubility very similar to that of polystyrene, while the poly((1) shows a nearly opposite solubility. It was soluble in methanol, ethanol, pyridine, 1,4-dioxane, and THF, but insoluble in benzene, toluene, p-xylene, cyclohexane, carbon tetrachloride, chloroform, and water.

The successful synthesis of well-defined poly(1) by the protective strategy in conjunction with living anionic polymerization, as illustrated in **Scheme** 1, has opened the way to the tailored synthesis of a variety of well-defined functional polymers.^{27–31} Similar to the TBDMS protective group, robust thexyldimethylsilyl²⁰ and triisopropylsilyl groups²⁰ were also effective to protect the hydroxyl function of 1 to achieve the living anionic polymerization of the corresponding silyl-protected monomers (1b and 1c) (Table 1). In contrast, the protection with less hindered TMS, triethylsilyl, and even isopropyldimethylsilyl groups failed under the same conditions. Thus, the choice of silyl protective group is critical and important to realize living anionic polymerization.

In the chemistry of protective groups, ethers and acetals are also often employed as protective groups of phenolic hydroxyl function under highly basic conditions.^{21,22} In practice, the living anionic polymerization of the ether- or acetal-protected monomers **1d–1g** (Figure 2) was possible under the same conditions in THF at –78 °C.^{6–8,20} On the other hand, quantitative removal of such protective groups was rather difficult compared to the corresponding low-molecular-weight analogs, and required the drastic acidic conditions in which cross-linking often occurred.

5-Vinyl-1,3-benzodioxole (2a) (Figure 3), an acetal-protected catechol monomer, was successful in undergoing living anionic polymerization in THF at -78 °C with oligo(α -methylstyryl) lithium or oligo(α -methylstyryl)dilithium (Table 1).³² The cyclic acetal moieties of poly(2a) were completely cleaved to give a poly(4-vinylcatechol), poly(2), by treating with boron tribro-mide–dimethyl sulfide complex in 1,2-dichloroethane (Scheme 3). The resulting poly(2) was first soluble in various solvents, such as methanol, THF, *N*,*N*-dimethylformamide (DMF), and 1,4-dioxane, but became insoluble in all the solvents along with coloration, probably due to the oxidation reaction.

The success of the protective strategy prompted us to extend the strategy to styrene derivatives with alcoholic hydroxyl groups ($pK_a = 16$). The hydroxyl groups of 4-(2-hydroxyethyl)styrene (3) and 4-(3-hydroxypropyl) styrene (4) were protected by TBDMS group, followed by







Scheme 3 Deprotection of poly(**2a**).



Figure 2 Monomers 1e-1g.



Figure 4 Monomers 3, 3a, 4, and 4a.

polymerization of the resulting TBDMS anionic ether-protected monomers, 3a and 4a (Figure 4).^{33,34} The two monomers underwent anionic polymerization in THF at -78 °C, similar to living poly(1a), to form poly(3a) and poly(4a) with predictable molecular weights and narrow molecular weight distributions, as shown in Table 2. The TBDMS protective groups were quantitatively cleaved by treatment with (C₄H₉)₄NF in THF. Interestingly, less hindered isopropyldimethylsilyl (3b), triethylsilyl (3c), and even TMS protective groups (3d) were capable of protecting the hydroxyl group of 3 (Figure 5). This is in sharp contrast to the case of 1 mentioned above and can be explained by the fact that

Table 2Anionic polymerization of 3a–3d, 6a, and 7a–7e in THFat -78 °C for 0.5–20 h

Monomer	Initiator	<i>M</i> ncalcd (g mol ⁻¹)	<i>M</i> nobsd ^a (g mol ⁻¹)	M _w /M _n
3a	<i>n</i> -BuLi/α-MeSt ^b	20 000	22 000	1.05
3a	K-Naph/α-MeSt ^c	26 000	23 000	1.10
3b	K-Naph/α-MeSt	55 000	54 000	1.11
3c	<i>n</i> -BuLi/α-MeSt	11 000	12 000	1.06
3c	K-Naph/α-MeSt	16000	13 000	1.13
3d	K-Naph/α-MeSt	23 000	20 000	1.12
3d	Li-Naph ^d	28 000	25 000	1.13
6a	<i>sec</i> -BuLi/α-MeSt	27 000	24 000	1.04
6a	Li-Naph/α-MeSt ^e	18 000	16000	1.09
6a	K-Naph/α-MeSt	13 000	15 000	1.15
7a	sec-BuLi	31 000	33 000	1.08
7a	<i>sec</i> -BuLi	70 000	82 000	1.13
7b	<i>sec</i> -BuLi	11 000	9 400	1.08
7c	<i>sec</i> -BuLi	20 000	16 000	1.07
7d	<i>sec</i> -BuLi	40 000	42 000	1.04
7e	<i>sec</i> -BuLi	32 000	31 000	1.04

^aMeasured by VPO, ¹H NMR (end-group analysis), SEC, and static light scattering. ^bOligo(α-methylstyryl)lithium.

^cOligo(α -methylstyryl)dipotassium.

^dLithium naphthalenide.

^eOligo(α-methylstyryl)dilithium.



Figure 5 Monomers 3b–3d.

phenolate anion is a better leaving group than alcoholate anion in the silvl ether cleavage reaction by anionic species.

Surprisingly, the TBDMS-protected group was not effective to protect the hydroxyl function of 4-hydroxymethylstyrene (5).²⁹ Indeed, a TBDMS ether-protected monomer, 4-(*tert*butyldimethylsilyloxy)methylstyrene (5a), was not anionically polymerized with any anionic initiators, which included *sec*-BuLi, lithium naphthalenide, oligo(α -methylstyryl)dilithium and oligo(α -methylstyryl)dipotassium (Figure 6), although these initiators promote the living anionic polymerization of not only 1a, 3a, and 4a, but also styrene. Since the result indicates the importance of further development of the protective strategy in the living anionic polymerization, this will be discussed in detail in Section 3.18.2.4.

As mentioned above, the cyclic acetal of 2a was capable of protecting two phenolic hydroxyl groups under the conditions of living anionic polymerization. Similarly, cyclic acetals and orthoesters were observed to successfully protect diols and triols. For instance, anionic polymerization of an orthoester-protected styrene monomer, 4-[(4-(4-vinylphenyl)butoxy) methyl]-1-methyl-2,6,7-trioxabicyclo[2.2.2]octane (6a), proceeded in a living manner in THF at -78 °C (Figure 7).³⁵ The resulting polymers possessed predictable molecular weights and narrow molecular weight distributions (Table 2). Thus, the protection of triol by the cyclic orthoester form was effective under the conditions of living anionic polymerization. The orthoester-protected functionality was quantitatively removed to form a poly(6) carrying a triol function by mild acidic hydrolysis (pH 4) and the subsequent basic hydrolysis (Scheme 4)

One particular case is the cyclic acetal protection of four hydroxyl groups of monosaccharide derivatives. Several new cyclic acetal-protected styrene derivatives with 1,2:5,6-di-O-isopropylidene moiety, **7a–7e** (Figure 8), were synthesized and anionically polymerized in THF at –78 °C with *sec*-BuLi, oligo(α -methylstyryl)lithium, or lithium and potassium naphthalenides.^{36,37} These protected styrene monomers underwent anionic polymerization without difficulty to quantitatively afford stable living polymers. After quantitative removal of the cyclic acetal protective groups with 1 N HCl, a



series of well-defined water-soluble polystyrenes substituted with monosaccharide residues were obtained. The polymerization results are summarized in Table 2.

Thus, the protective strategy in conjunction with living anionic polymerization successfully works to afford well-defined functional polystyrenes substituted with alcoholic and phenolic hydroxyl groups, diols, and triols. The silyl ether-, cyclic acetal-, and orthoester-protected functionalities are effective for this purpose. This strategy may possibly be applied to other useful functional styrene derivatives and will be discussed in the next section.

3.18.2.2 Styrene Derivatives with Other Functional Groups

The protective strategy using TBDMS group was also adaptable to 4-mercaptostyrene (8) and 4-(2-mercaptoethyl)styrene (9).³⁸ The resulting TBDMS thioether-protected styrene monomers, 8a and 9a (Figure 9), were successful in undergoing living anionic polymerization in THF at -78 °C (Table 3). Both poly(8a) and poly(9a) with well-defined structures were

quantitatively obtained. The TBDMS thioether-protected functionalities were stable under neutral to basic conditions, but were readily cleaved to quantitatively regenerate the thiol functions by treatment with either 0.9 N HCl in aqueous 1,4-dioxane or $(C_4H_9)_4NF$ in THF at room temperature (Scheme 5). However, the resulting deprotected polymers were not stable and became insoluble due to the formation of S–S linkage among polymer chains by thiol oxidation. It is therefore difficult to isolate and characterize soluble poly(8) and poly(9) even when polymers are handled with great care under nitrogen or inert gas atmosphere. This suggests that it is better to cleave the TBDMS thioether-protected functionalities just before their use.

Since amines are sufficiently acidic to anionic initiators such as RLi, they must be protected prior to anionic polymerization. A less sterically hindered TMS group was enough to protect the amines of 4-aminostyrene (10) and 4-(2-aminoethyl)styrene (11) and the resulting TMS-protected monomers, 10a and 11a, were subjected to anionic polymerization in THF at -78 °C (Figure 10).³⁹⁻⁴¹ The polymerization mixtures were always colored orange-red, and the coloration disappeared immediately by quenching with degassed methanol. The yields of polymers were quantitative in both cases. The molecular weights measured by VPO agreed well with the calculated values and narrow molecular weight distributions were obtained (Table 3). These results and the red coloration of the polymerization system clearly showed that both TMS-protected monomers, 10a and 11a, were anionically polymerized to afford living polymers and their Si-N bonds were sufficiently stable to chain-end anions in THF at -78 °C for 24 h.



Scheme 4 Deprotection of poly(6a).



Figure 8 Monomers 7a-7e.



Figure 9 Monomers 8, 8a, 9, and 9a

 Table 3
 Anionic polymerization of 8a, 9a, 10a, 11a, 12a, 13a, 14e, 15b, 16a, and 17a in THF at -78 °C for 0.5 h

Monomer	Initiator	<i>M</i> ncalcd (g mol ⁻¹)	<i>M</i> nobsd ^a (g mol ⁻¹)	M _w /M _n
8a	K-Naph/α-MeSt ^b	20 000	14 000	1.13
9a	<i>n</i> -BuLi	53 000	67 000	1.03
10a	Li-Naph ^c	42 000	53 000	1.12
10a	K-Naph ^d	24 000	21 000	1.21
11a	<i>n</i> -BuLi/α-MeSt ^e	40 000	41 000	1.13
12a	<i>sec</i> -BuLi/α-MeSt ^e	77 000	98 000	1.07
12a	K-Naph/α-MeSt	25 000	25 000	1.04
13a	<i>sec</i> -BuLi/α-MeSt	21 000	20 000	1.07
14e	K-Naph/α-MeSt	39 000	40 000	1.07
15b	K-Naph/α-MeSt	38 000	39 000	1.08
16a	Cumyl-K/α-MeSt ^f	82 000	80 000	1.06
17a	K-Naph/DPE ^g	33 000	35 000	1.05

^aMeasured by VPO, ¹H NMR (end-group analysis), SEC, and static light scattering. ^bOligo(α-methylstyryl)dipotassium.

^dPotassium naphthalenide.

 $eOligo(\alpha-methylstyryl)lithium.$

[/]Oligo(α-methylstyryl)potassium.

^g(1,1,4,4-Tetraphenylbutanediyl)dipotassium

The TMS-protected functionalities were readily cleaved under slightly acidic conditions (pH ~ 6) (Scheme 6). It should be mentioned that the resulting polymers must be handled and stored under a nitrogen atmosphere, or else they will readily absorb CO_2 to become insoluble. The amine-functionalized polystyrenes thus obtained were not directly analyzed by SEC due to significant tailings to lower molecular weight sides. This is possibly due to the strong interaction of the regenerated amines with carboxylic acid functions on the SEC column, which were formed by oxidation. Therefore, these polymers were converted to the corresponding benzoylated polymers by treatment with benzoic anhydride in pyridine and subjected to SEC measurement. The SEC profiles exhibited sharp monomodal peaks eluted at reasonable molecular weight regions.

The acidic hydrogen of ethynyl (-C=CH) function ($pK_a = 25$) of 4-ethynylstyrene (12) was protected with TMS group to successfully achieve living anionic polymerization of the resulting 4-(trimethylsilyl)ethynylstyrene (12a) in THF at -78 °C (Figure 11 and Table 3).^{42,43} Under such conditions, the silylethynylphenyl part remained intact and did not participate in the polymerization. Similarly, 4-(4-trimethylsilyl-3-butynyl)styrene (13a), a TMS-protected monomer of 4-(3-butynyl)styrene (13), underwent living anionic

^cLithium naphthalenide.



 $(CH_2 - CH)_n \qquad (CH_2 - CH)_$

Scheme 5 Deprotection of poly(**8a**).

polymerization to quantitatively afford a well-defined polymer (a predictable molecular weight and a narrow molecular weight distribution).⁴⁴ However, the chain-end anion of poly(**13a**) was gradually deactivated after the conclusion of the polymerization, possibly due to proton abstraction from acidic methylene group adjacent to $-C=C-SiMe_3$ bond. Fortunately, the deactivation could be completely suppressed by lowering the polymerization temperature to -95 °C.

The TMS protective group was quantitatively deprotected by treatment with $(C_4H_9)_4$ NF in THF at room temperature (**Scheme 7**). SEC profiles of the resulting poly(12) and poly (13) exhibited narrow monomodal distributions similar to those of the original poly(12a) and poly(13a), respectively. Thus, TMS group is capable of protecting the active ethynyl hydrogen of 12 in addition to hydroxyl and amine functions. Since ethynyl and the related C=C bonds have been recently used in 'click reaction' with azides to prepare block copolymers, star-branched polymers, and even hyperbranched

Scheme 7 Deprotection of poly(12a).

polymers,^{45–47} well-defined ethynyl-functionalized homopoly (12) and block copolymers containing poly(12) segment are attractive precursory polymers for this purpose.

Needless to say, the electrophilic aldehyde function of 4-formylstyrene (14) must be protected prior to anionic polymerization. The most suitable protected functionality for aldehydes may be the acyclic and cyclic acetals that are stable to highly reactive basic reagents and nucleophiles. Indeed, a styrene *para*-substituted with D-glucose (7a), whose diol functions were protected as cyclic acetals, successfully underwent living anionic polymerization, as mentioned in Section 3.18.2.1. The cyclic acetal-protected functionalities were sufficiently stable in THF at -78 °C, but were readily cleaved to quantitatively regenerate the diol functions under mild acidic hydrolysis.

Similar to the protection of diol as the cyclic acetal, the aldehyde function of 14 was also protected as acyclic and cyclic acetals in the opposite direction and the resulting



Figure 10 Monomers 10, 10a, 11, and 11a.









Figure 12 Monomers 14 and 14a–14e.

acetal-protected monomers, 14a-14d, were subjected to anionic polymerization (Figure 12).48 Surprisingly, however, no polymerization of such protected monomers took place with any of the anionic initiators, including n-BuLi, sec-BuLi, lithium and potassium naphthalenides, $oligo(\alpha-methylstyryl)$ dilithium, oligo(α-methylstyryl)disodium, and oligo (α-methylstyryl)dipotassium, in THF at -78 °C or with sec-BuLi in benzene at 30 °C. Thus, the cyclic acetal protective group, which was effective to protect diol function, failed to protect the aldehyde function of 14. Similarly, the protection of 4-acetylstyrene (15) as a cyclic acetal was not successful (Figure 13).⁴⁹ Anionic polymerization of a protected monomer, 15a, did not occur at all. Since the same undesirable side reaction would occur in the anionic polymerization of the TBDMS ether-protected monomer, 5a mentioned above, these polymerization systems will be discussed in Section 3.18.2.4.

Aldehydes can be protected as *N*,*N*-acetals, which are stable to highly basic reagents such as RLi. Therefore, the aldehyde function of 14 was treated with *N*,*N'*-dimethylethylenediamine to convert it to a *N*,*N*-acetal-protected styrene (14e).⁵⁰ Unlike the oxygen analogues, 14e was anionically polymerized without problem to afford a living polymer, which was stable in THF at –78 °C even after 24 h (Table 3). The protective group was quantitatively removed by acid hydrolysis with 2 N HCl in THF (Scheme 8). The SEC trace of the poly(14) thus obtained





showed a narrow monomodal molecular weight distribution. Unfortunately, this effective *N*,*N*-acetal protection could not be used for the protection of **15** due to the inability of *N*,*N'*-dimethylethylenediamine to react with ketones. Instead, the acetyl group of **15** was successfully protected as a TBDMS enol ether derivative, **15b**.⁴⁹ The resulting protected monomer **15b** was observed to undergo living anionic polymerization (**Table 3**). Similar to TBDMS ethers, the TBDMS enol ether was readily cleaved to quantitatively regenerate the original acetyl group under mild conditions (0.5 N HCl or (C₄H₉)₄NF in THF) (**Scheme 9**).

Carboxylic acids are usually protected as esters, amides, and hydrazides. However, these protected functionalities readily react with RLi used as anionic initiators. On the other hand, 4,4-dialkyl-2-oxazolines are stable to highly reactive basic reagents such as Grignard reagents (RMgX) and RLi. An oxazoline-protected monomer, 2-(4-vinylphenyl)-4,4-dimethyl-2-oxazoline (16a) for 4-vinylbenzoic acid (16), was indeed demonstrated to undergo living anionic polymerization in THF at -78 °C with either sec-BuLi or potassium naphthalenide (Figure 14 and Table 3).^{51,52} Unlike low-molecular-weight analogs, harsh conditions were required for quantitative removal of the oxazoline protective group from the resulting polymer (3 N HCl at 100 °C for 3 h, followed by 20% NaOH at 100 °C for 6–10 h) (Scheme 10). Protective groups for 16 that could be easily cleaved will be introduced in the next section. Interestingly, the oxazoline protective group is also effective to protect a carboxylic functionality of 4-vinyl-a-methylcinnamic acid (17), possessing α , β -unsaturated carbonyl moiety. Anionic polymerization of 2-[1-methyl-2-(4-ethenylphenyl)ethenyl]-4,4-dimethyl-2-oxazoline (17a) and subsequent deprotection gave a well-defined poly(17) in quantitative yield.⁵³

As discussed in this section, most of the important functional groups can satisfactorily be protected to successfully achieve the living anionic polymerization of the corresponding protected functional styrene derivatives. The protective group and protected functionalities stable to RLi compounds are basically usable for the protective strategy herein developed





Figure 14 Monomers 16, 16a, 17, and 17a.



Scheme 10 Deprotection of poly(16a).

and indeed most of them are fitted for this purpose. However, the anionic polymerization of certain styrene monomers protected as TBDMS ether and acetal forms failed under the same conditions, although their protected functionalities were stable to RLi and the related anionic species. These particular cases will be described in detail in Section 3.18.2.4.

The substituted styrene monomers with protected functionalities herein introduced are almost similar to styrene in anionic polymerization behavior. For instance, highly reactive anionic initiators, such as RLi compounds, alkali metal naphthalenides (radical anion complexes), cumylpotassium, and living oligomers of α -methylstyrene with Li⁺, Na⁺, and K⁺ as countercations, are required to initiate the polymerization of such protected styrene monomers. No appreciable polymerization takes place with Grignard reagents (RMgX and R₂Mg), LiAlH₄, sodium hydride, potassium tert-butoxide, and living anionic polymers of alkyl methacrylates and ethylene oxide. The resulting living anionic polymers of these protected functional styrene monomers have reactivities very similar to that of living anionic polymer of styrene and can initiate the polymerization of styrene, α-methylstyrene, 1,3-butadiene, isoprene, 2-vinylpyridine, alkyl methacrylates, N,N-dialkylacrylamides, and ethylene oxide. The living anionic polymers are sufficiently stable in THF at -78 °C after 24 h, but are gradually deactivated on raising the temperature to room temperature.

As mentioned before, the living anionic polymerization of styrene is possible not only in THF at -78 °C but also in hydrocarbon media at room temperature. Currently, however, the anionic polymerizations of most protected functional monomers have not yet been examined in hydrocarbon media. Therefore, they should be explored in detail under such conditions, which is important from industrial viewpoints.

3.18.2.3 New Protective Strategy for Functional Styrene Derivatives: Use of Protected Functionalities Showing Electron-Withdrawing Characters

Esters can be generally used as a protective group for carboxylic acids in many organic syntheses.^{21,22} However, it is considered that the carboxylic acid moiety of 16 cannot be protected as esters under the conditions of anionic polymerization because they readily react with anionic initiators such as RLi and living polystyrene. In fact, no appreciable anionic polymerization of methyl, ethyl, and allyl 4-vinylbenzoates occurred. Surprisingly, the anionic polymerization of tert-butyl 4-vinylbenzoate (16b) proceeded with potassium naphthalenide in THF at -95 °C to quantitatively afford the polymer (Figure 15).⁵⁴ As soon as 16b was mixed with potassium naphthalenide, a dramatic color change from dark green to red was observed and the resulting red color remained visually unchanged, indicating the formation of the living polystyryl anion derived from 16b. The resulting polymer was observed to possess a predictable molecular weight and a narrow molecular weight distribution (Table 4). All of the results clearly demonstrate the occurrence of the living anionic polymerization of 16b.

The quantitative anionic polymerization of **16b** was also possible at -78 °C. The polymerization lasted for 30 min and the polymer obtained exhibited a narrow molecular weight distribution. The distribution, however, became multimodal with time, with ester attack by the chain-end anion occurring at -78 °C. Thus, the polymerization temperature is very critical in the polymerization of **16b**.

The *tert*-butyl ester was cleaved to quantitatively regenerate the carboxylic acid by treatment with a 1:1 mixture of $(CH_3)_3SiCl$ and sodium iodide in a mixed solvent of $CHCl_3$ and acetonitrile at room temperature (Scheme 11). Since the



Figure 15 Monomers 16b–16e.

Table 4Anionic polymerization of 16b–16h, 14f–14i, and 18 in THFat -78 °C for 0.5–24 h

Monomer	Initiator	<i>M</i> ncalcd (g mol ⁻¹)	<i>M</i> _n obsd ^a (g mol ⁻¹)	M _w /M _n
16b ^b	Cumyl-K/α-MeSt ^c	63 000	59 000	1.18
16c	Ph ₂ CHK ^d	21 000	20 000	1.06
16d	Ph ₂ CHK	26 000	32 000	1.04
16e	K-Naph/DPE ^e	12000	13 000	1.12
16f	Li-Naph/α-MeSt ^f	17 000	14 000	1.06
16f	Cumyl-K/α-MeSt	48 000	48 000	1.08
16g	K-Naph/α-MeSt ^g	21 000	20 000	1.06
16h	K-Naph/α-MeSt	37 000	38 000	1.11
14f	K-Naph/α-MeSt	33 000	29 000	1.07
14g	K-Naph/α-MeSt	22 000	24 000	1.06
14h	Li-Naph/α-MeSt	10 000	9400	1.09
14i	Ph ₂ CHK	28 000	29 000	1.04
18	<i>n</i> -BuLi/TMS ₂ DPE ^{<i>h</i>}	99 000	122 000	1.09
18	Cumyl-K ⁱ	24 000	27 000	1.06

^aMeasured by VPO, ¹H NMR (end-group analysis), SEC, and static light scattering. ^bAt –95 °C.

^cOligo(α-methylstyryl)potassium.

^dDiphenylmethylpotassium.

e(1,1,4,4-Tetraphenylbutanediyl)dipotassium.

^fOligo(α-methylstyryl)dilithium.

^gOligo(a-methylstyryl)dipotassium.

^h1,1-Bis(4'-trimethylsilylphenyl)hexyllithium

[/]Cumylpotassium.

poly(16) thus obtained showed an asymmetric SEC peak with a long tailing eluted at relatively low-molecular-weight regions due to the strong interaction with SEC columns, the re-esterification of the carboxylic acid with diazomethane to convert to methyl ester was carried out in order to examine the molecular weight and molecular weight distribution by SEC. The SEC profile of the resulting methyl ester polymer, poly (methyl 4-vinylbenzoate), clearly exhibited a narrow monomodal distribution, similar to that of the original poly(16b).

Sterically bulkier 2,6-diisopropylphenyl (16c), 2,6-di(tertbutyl)-4-methylphenyl (16d), and 2,6-di(tert-butyl)-4-methoxyphenyl esters (16e) were more effective to protect the carboxylic acid of 16.55 These ester-protected styrene monomers, 16c-16e, underwent living anionic polymerization without any side reaction in THF even at -78 °C. The resulting living polymers were stable for 24 h under such conditions. Polymers with predictable molecular weights and narrow molecular weight distributions $(M_w/M_n < 1.1)$ were quantitatively obtained. The success of postpolymerization and the sequential block copolymerization with tert-butyl methacrylate (tBMA) further supports the living nature of the polymerization of 16c-16e. Thus, tert-butyl and sterically bulkier phenyl esters satisfactorily protect the carboxylic acid function of 16 to enable the living anionic polymerization of their ester-protected monomers.

As mentioned above, the resulting living polymers quantitatively initiated the polymerization of the same ester-protected styrenes (postpolymerization) as well as tBMA. It was, however, observed that the living polymers could not initiate the polymerization of isoprene, a-methylstyrene, and styrene, all of which were polymerized with living anionic polystyrene under the same conditions (Figure 16). Thus obviously, the living anionic polymers of the ester-protected styrene monomers, 16b-16e, are lower in nucleophilicity than the living anionic polymers of living polystyrene. The lower reactivity of the chain-end anion can be elucidated by reducing the electron density on the anion via strong electron-withdrawing effect of ester carbonyl group. We initially thought that the success of the living anionic polymerization of 16b-16e was attributed to protection with sterically bulkier tert-butyl or aryl moieties. However, lowering the reactivities of the chain-end anions by electron-withdrawing character of ester carbonyls may also play an important role in suppressing ester attack by the propagating chain-end anions, thereby achieving the living anionic polymerization. Therefore, the use of ester-protected functionalities for living anionic polymerization involves two factors:







Figure 16 Crossover reaction of living poly(16b) with various monomers.



the steric demand of protected functionality, and the reduced reactivity of chain-end anion.

In the same sense, *N*,*N*-dialkylamides can be used to protect the carboxylic acid of **16**. Indeed, tertiary amide-protected styrene monomers, *N*,*N*-diethyl- (**16f**) and *N*,*N*-diisopropyl-4-vinylbenzamides (**16g**), were anionically polymerized to afford stable living anionic polymers in THF at -78 °C (**Figure 17** and **Table 4**).^{56,57} Unfortunately, these tertiary amide-protected functionalities were robust and difficult to cleave even under harsh conditions. N-(4-Vinylbenzoyl)-N'methylpiperazine (16h), as an easily cleavable tertiary amide-protected styrene monomer, was newly designed, synthesized, and subjected to anionic polymerization.⁵⁸ As expected, 16h underwent living anionic polymerization without difficulty and the tertiary amide functionality was quantitatively cleaved under the conditions with 6 N HCl at 80 °C or by treatment first with methyl iodide, then sodium ethoxide, followed by acid hydrolysis as shown in Scheme 12.⁵⁹ Thus, a certain tertiary amide function may also be used as a suitable protective group for 16. Since these N_{i} N-dialkylamide moieties themselves are proved to react with RLi as well as living polystyrene, lowering the reactivity of the chain-end anion by strong electron-withdrawing amide carbonyl group is essential to achieve the living anionic polymerization of 16f-16h.

Aldehydes react with amines to form *N*-alkyl- or *N*-arylimines. The resulting imines are readily cleaved to regenerate the original aldehydes by mild acidic hydrolysis. However, imines cannot be used as protective groups under



Scheme 12 Deprotection of poly(16h).



Figure 18 Monomers 14f-14i.

the conditions of anionic polymerization, because they readily react with RLi compounds and living anionic polystyrene. Nevertheless, *N*-cyclohexyl-*N*-(4-vinylbenzylidene)amine (14f), an *N*-alkylimine-protected styrene monomer, was successful in undergoing living anionic polymerization in THF at –78 °C (Figure 18 and Table 4).⁶⁰ The resulting living polymer carrying electron-withdrawing CH=N-R moiety was stable after 24 h under such conditions. A polymer with a predictable molecular weight and a narrow molecular weight distribution was quantitatively obtained. In contrast to lowmolecular-weight analogs, stronger acidic condition, 3 N HCl in THF, was required for quantitative cleavage of the *N*-cyclohexylimine-protected functionality to regenerate poly (14) (Scheme 13).

Sterically bulkier *N*-isopropyl (14g), *N*-tert-butyl (14h), and 2,6-diisopropylphenyl imines (14i) are also effective protected functionalities and can be used to achieve living anionic polymerization. ^{61,62} The *N*-methyl derivative was also polymerized under the same conditions, but broadening of the molecular weight distribution occurred gradually after the conclusion of the polymerization. Thus, a less hindered *N*-methyl group was not effective to protect the aldehyde function of 14. Obviously, after the polymerization, the nucleophilic attack of chain-end anion toward CH=N bond occurred gradually. Once again, for protection of the aldehyde function of 14 as *N*-alkyl- (or aryl) imines for anionic polymerization, both steric bulkiness of *N*-substituent and lowering the reactivity of chain-end anion are essential.

Interestingly, the living anionic polymerization of 4-cyanostyrene having a strong electron-withdrawing cyano group (18) was successful under the conditions in THF at -78 °C (Figure 19 and Table 4).⁶³⁻⁶⁶ Although a cyano group is not a protective group, it can be quantitatively converted to both amine and carboxylic acid by LiAlH₄ reduction and hydrolysis with HCl. Therefore, poly(18) is equivalent to poly(4-aminomethylstyrene) and poly(4-vinylbenzoic acid) (poly(16)). Thus, a procedure combining the living anionic polymerization of 18 with suitable reactions will offer an





Figure 19 Monomer 18.

excellent synthetic route for both amine and carboxyl functional polymers with well-defined structures.

Ċ≡N

18

 $CH_2 = CH$

In summary, the development of protective groups and/or protected functionalities with electron-withdrawing characters herein introduced considerably broadens the range of protective groups applicable to the living anionic polymerization.^{67–70} Indeed, esters, *N*,*N*-dialkylamides, *N*-alkylimines, and *N*-arylimines could be used to protect the carboxyl and aldehyde functions of styrene monomers. Throughout the crossover block copolymerization study, the resulting living anionic polymers were found to be less reactive than living polystyrene but almost comparable in reactivity to living poly (2-vinylpyridine).

3.18.2.4 Anionic Polymerization Behavior of Styrene Derivatives Possessing Benzyl Ether Skeletons

As mentioned in Section 3.18.2.1, 4-hydroxystyrene, 1, as well as 4-(2-hydroxyethyl)styrene, 3, and 4-(3-hydroxypropyl)styrene, 4, could be protected as TBDMS ethers to successfully achieve the living anionic polymerization of the TBDMS ether-protected styrene monomers 1a, 3a, and 4a.^{27–29,33,34} Accordingly, TBDMS group effectively protected both phenolic and alcoholic hydroxyl groups toward the highly reactive anionic initiators and chain-end anions. On the other hand, surprisingly, the hydroxyl protection of 4-hydroxymethylstyrene, 5, with TBDMS group failed to serve the same purpose. In practice, the TBDMS ether-protected monomer, 4-(tert-butyldimethylsilyloxy) methylstyrene (5a), was not polymerized with any of the anionic initiators, which can initiate the polymerization of 1a, 3a, and 4a as well as styrene. A characteristic red color of the initiator solution of $oligo(\alpha-methylstyryl)dilithium, oligo$ (α-methylstyryl)disodium, or oligo(α-methylstyryl)dipotassium disappeared instantaneously on mixing with 5a. No polymer or only small amounts of insoluble polymers were obtained from the polymerization systems.

In contrast to the polymerization result of **5a**, the corresponding *meta*-isomer, 3-(*tert*-butyldimethylsilyloxy)



Figure 20 Monomers 19 and 19a.

	Table 5	Anionic polym	erization of	19a in THF	at –78 °C	for 0.5	h
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Monomer	Initiator	<i>M</i> ncalcd (g mol ⁻¹)	<i>M</i> nobsd ^a (g mol ⁻¹)	M _w /M _n
19a	K-Naph/ α -MeSt ^b	11 000	10 000	1.08
19a 19a	LI-Naph/ α -MeSt ^d <i>n</i> -BuLi/ α -MeSt ^d	44 000	45 000	1.15

^aMeasured by VPO.

^bOligo(α -methylstyryl)dipotassium.

^cOligo(α-methylstyryl)dilithium.

^{*d*}Oligo(α -methylstyryl)lithium.

methylstyrene (19a), was successfully polymerized with oligo (a-methylstyryl)dilithium under the same conditions in THF at -78 °C (Figure 20 and Table 5).²⁹ An orange red color immediately developed on mixing the initiator with 19a and remained unchanged even after 24 h. A polymer with a predictable molecular weight and a narrow molecular weight distribution was quantitatively obtained. The addition of styrene to the polymerization system of 19a gave the well-defined objective block copolymer poly(19a)-block-polystyrene. These results clearly demonstrate that the anionic polymerization of 19a proceeds in a living manner. Furthermore, the stability of TBDMS ether was confirmed by the fact that benzyl TBDMS ether synthesized as a model compound was stable and remained intact with sec-BuLi and poly(styryl)lithium in THF at -78 °C for 24 h. These results strongly indicate that the parasubstituted TBDMS ether is responsible for the problem associated with the anionic polymerization of 5a.

Based on the above results and the anion-induced rearrangement previously reported by Moss *et al.*,⁷¹ the following reaction pathway, as illustrated in Scheme 14, is proposed to account for what is happening in the anionic polymerization of 5a.²⁹ At first, a few monomers are successively added to sec-BuLi used as an initiator. Then, the chain-end anion may undergo rapid intramolecular rearrangement, followed by a 1,6-elimination reaction of a tert-butyldimethylsilanolate anion to generate very reactive p-xylylene intermediate. Subsequently, the coupling reaction between such *p*-xylylene intermediates and/or the addition reaction of the anion to a tetraene part of the xylylene would occur to form trace amounts of insoluble polymer at the early stage of the polymerization. The proposed reaction pathway is applicable for only the parasubstituted derivative and possibly the ortho-isomer, and it cannot be extended to the corresponding meta-isomer, because the compound showing the chemical formula of *m*-xylylene is not present. Thus, the different behavior of para- and metasubstituted styrene monomers in the anionic polymerization may be explained by this reaction pathway. As shown in Scheme 14, para-benzyl TBDMS ether skeleton induces anion rearrangement. This is also confirmed by the success of the living anionic polymerization of para-TBDMS ether-protected styrene monomers, 3a and 4a, where the tertbutyldimethylsilyloxyl group is separated by two or three methylene chains from the phenyl ring.

The methyl and tert-butyl ether-protected monomers, 5b and 5c (Figure 21), were not anionically polymerized under the same conditions.²⁰ Thus, the protection of 5 by ethers was also not effective for the anionic polymerization. A similar 1,6-elimination reaction may be induced by the skeleton of para-alkyl benzyl ethers. Furthermore, acetal-protected 4-formylstyrene, acetal-protected 4-acetylstyrene, and orthoester-protected 4-vinylbenzoic acid monomers, 14a-14d, 15a, and 16i (Figure 22),^{48,49,72} behaved similar to the abovementioned TBDMS ether- and ether-protected monomers in the anionic polymerization. No appreciable







Scheme 14 Proposed reaction pathway for the anionic polymerization of 5a.



Figure 22 Monomers 14a–14d, 15a, and 16i.



Figure 23 Monomers 20a, 21a, and 22a.

polymerization of such monomers occurred with any of the anionic initiators, including RLi, alkali metal naphthalenides, and oligo(α -methylstyryl)alkali metals. All these styrene monomers possess *para*-TBDMS or alkyl benzyl ether skeletons as common-featured structures.

On the other hand, all the corresponding *meta*-isomers, **20a**, **21a**, and **22a** (Figure 23 and Table 6), underwent living

Table 6	Anionic po	lvmerization	of 20a-25a	in TH	- at -78	°C for	0.51
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Monomer	Initiator	<i>M</i> _n calcd (g mol ⁻¹)	<i>M</i> _n obsd ^a (g mol ⁻¹)	M _w /M _n
20a	Cumyl-K/α-MeSt ^b	31 000	29 000	1.13
20a	K-Naph/α-MeSt ^c	16000	14 000	1.14
21a	K-Naph/α-MeSt	15 000	15 000	1.09
22a	Cumyl-K ^d	7 200	12 000	1.05
23a	K-Naph/α-MeSt	19000	20 000	1.09
24a	<i>sec</i> -BuLi/α-MeSt ^e	37 000	44 000	1.06
24a	K-Naph/α-MeSt	14 000	12 000	1.09
25 a ^{<i>t</i>}	Li-Naph/α-MeSt ^g	19000	20 000	1.04
25 a ^f	K-Naph/α-MeSt	16 000	15 000	1.06

^aMeasured by VPO.

^bOligo(α-methylstyryl)potassium.

^cOligo(α-methylstyryl)dipotassium.

^dCumylpotassium.

^eOligo(α-methylstyryl)lithium.

^fAt -40 °C

^gOligo(α-methylstyryl)dilithium.

ditions.48,72 In addition, the para-substituted styrene monomers with acetal- or orthoester-protected functionalities, 7d, 7e, 23a, 24a, and 25a (Figure 24), 36,37,48,72 were successfully polymerized to give stable anionic living polymers in THF at -78 °C. Polymers with predictable molecular weights and narrow molecular weight distributions were quantitatively obtained. The polymerization results of 23a, 24a, and 25a are also summarized in Table 6. In these styrene monomers, the protected functionalities are separated by two or more methylene chains from the phenyl rings and there are no para-alkyl benzyl ether skeletons. Their acetal and orthoester moieties were cleaved by mild acidic hydrolysis to quantitatively regenerate aldehydes, ketones, and carboxylic acids. Their living anionic polymers are similar in reactivity to the living polymers introduced in Section 3.18.2.2 and living polystyrene. Accordingly, these living polymers can initiate the polymerization of styrene, α -methylstyrene, 1,3-butadiene, isoprene, 2-vinylpyridine, and alkyl methacrylates, yielding the objective block copolymers with well-defined structures.

anionic polymerization without difficulty under the same con-

Interestingly, poly(19a) was easily converted to poly(3-bromomethylstyrene) and poly(3-iodomethylstyrene) bv treatment with a 1:1 mixture of (CH₃)₃SiCl/LiBr and (CH₃) ₃SiCl/NaI, respectively (Scheme 15).^{73,74} Quantitative conversion was confirmed by ¹H and ¹³C NMR analyses. The SEC profiles of both polymers exhibited narrow monomodal distributions eluted at expected molecular weight regions which were almost the same as that of the starting poly(19a). These polymers are the first successful well-defined poly(halomethylstyrene)s, which possess precisely controlled molecular weights and narrow molecular weight distributions as well as highly reactive benzyl bromide and benzyl iodide functions in all monomer units. A well-defined poly(3-chloromethylstyrene) was also prepared by treatment of poly(19a) with BCl_3 . However, small amounts (<5%) of high-molecular-weight polymers, with molecular weights double that of the parent polymers, were often but not always produced. The resulting poly(3-halomethylstyrene)s are attractive as precursors for the preparation of comb-like polymers and graft copolymers by







Scheme 16 Polymer reaction of poly(3-bromomethylstyrene).

reaction with other living anionic polymers. Under the conditions in THF at temperatures lower than -40 °C, 100% grafting efficiency was achieved, resulting in highly dense comb-like polymers (Scheme 16).^{73,74} This subject is beyond the scope of this review and has been covered elsewhere.²⁰

3.18.2.5 Styrene Derivatives Possessing Silanol Functions

Silanol (\equiv Si-OH) is an important function that readily reacts with hydroxyl groups, carboxylic acids, and oxides present on inorganic compounds and metals to form organic-inorganic and organic-metal hybrid materials. Therefore, functional silanol compounds, the so-called 'silane coupling agent', can modify inorganic and metal surfaces, thereby increasing their adherence to organic polymers. As is known, free silanols are extremely labile and difficult to isolate because of the ready formation of Si–O–Si bonds. For this reason, they are generally stored as alkoxysilanes, which can be hydrolyzed *in situ* to generate silanol-containing species as occasion demands. Accordingly, alkoxysilanes can be regarded as protected functionalities of silanols.

Because of the instability of silanols, polymers possessing free silanols can hardly be present. In Section 3.18.2.1, Si–O–C linkages in silyl ethers are demonstrated to be stable under the conditions of anionic polymerization and to be quantitatively cleaved by mild acidic hydrolysis. This suggests that alkoxysilane-protected styrene monomers can also be anionically polymerized in a living manner and the resulting polymers are equivalent to free silanol-functionalized polymers.¹⁸ These polymers are useful and versatile functional polymers capable of reacting with inorganic compounds and metals to form hybrid materials. The success of the living anionic polymerization of alkoxysilane-protected monomers makes it possible to design and precisely synthesize well-defined hybrid materials.

In order to examine the possibility of alkoxysilanes as protected functionalities for silanols, 4-(ethoxydimethylsilyl) styrene (26a) was newly prepared and subjected to anionic polymerization (Figure 25).⁷⁵ On mixing potassium naphthalenide with 26a, a red color developed immediately, indicating



Table 7	Anionic polymerization of 26a-26f in THF at -78 °C for
0.5 h	

Monomer	Initiator	<i>M</i> _n calcd (g mol ⁻¹)	<i>M</i> _n obsd ^a (g mol ⁻¹)	<i>M</i> _w/ <i>M</i> _n
26a 26b 26c 26d 26e 26e 26f	K-Naph/α-MeSt ^b K-Naph/α-MeSt K-Naph/α-MeSt K-Naph/α-MeSt K-Naph/α-MeSt <i>n</i> -BuLi/α-MeSt ^c	25 000 22 000 16 000 30 000 32 000 49 000	27 000 21 000 17 000 29 000 33 000 44 000	1.10 1.07 1.09 1.07 1.07 1.08

^aMeasured by VPO.

^bOligo(α-methylstyryl)dipotassium.

^cOligo(α-methylstyryl)lithium.

the formation of polystyryl anion generated from 26a, and remained unchanged for 24 h in THF at -78 °C. A polymer was obtained in 100% yield. The resulting polymer was found to possess a predictable molecular weight and a narrow molecular weight distribution (Table 7). A sequential block copolymerization of 26a, followed by addition of styrene, resulted in a well-defined AB diblock copolymer. Thus, the living anionic polymerization of 26a was successfully carried out.

The ethoxysilyl group of poly(26a) is stable in alcoholic and aqueous solutions under basic conditions, but can be cleaved immediately under acidic conditions to afford an insoluble cross-linked polymer due to the formation of Si-O-Si bonds among the polymer chains (Scheme 17). Both 4-(diethoxymethylsilyl)styrene (26b) and 4-(triethoxysilyl)styrene (26c) were also successful in undergoing living anionic polymerization under the same conditions.⁷⁵ Similarly, 4-(dimethylisopropoxysilyl)styrene (26d) underwent living anionic polymerization.⁷⁶ The resulting poly(26d) is much more robust to moisture and alcohols and can be stored for a few years even in the air without cross-linking. The living anionic polymerization of the methoxysilyl derivative (26e) also proceeded without difficulty, but the resulting polymer was labile and became insoluble in spite of handling it with great care.

4-[(Diethylamino)dimethylsily]styrene (26f) having Si-N bond was observed to undergo living anionic polymerization with oligo(α -methylstyryl)lithium in THF at -78 °C.⁷⁷ The aminosilane-protected functionality was stable under basic conditions, but was readily cleaved by acid treatment, followed by the formation of Si–O–Si bonds. As a result, the polymer became insoluble.

The results (M_n and M_w/M_n values) of the resulting polymers are also summarized in **Table** 7. These polymers are precisely controlled in molecular weight and narrowly distributed in molecular weight. The living anionic polymers are similar in reactivity to anionic living polystyrene and, therefore, a variety of block copolymers can be synthesized based on the combination of living anionic polymers with styrene, α -methylstyrene, isoprene, and 1,3-butadiene.

Lee et al.^{78,79} successfully prepared a series of nanoscale porous membranes and glucose sensors by using the microphase-separated structure of an ABA triblock copolymer, poly(26d)-block-polyisoprene-block-poly(26d). As illustrated in Scheme 18, the poly(26d) microdomains were first fixed by cross-linking under the acidic condition, followed by subsequent etching with ozone to remove the polyisoprene microdomains, resulting in porous membranes whose nanostructures reflected the original microphase structures. Figure 26(a) shows the surface morphology of a thin film of the original triblock copolymer, poly(26d)-block-polyisopreneblock-poly(26d), measured by transmission electron microscopy (TEM). After acidic cross-linking and following ozonolysis of the thin film, the scanning electron microscopy (SEM) analysis of the surface (Figure 26(b)) and cross section (Figure 26(c)) revealed the formation of a continuous microporous membrane. Interestingly, the original morphology and domain size were maintained in the cross-linked microporous membrane. This is a pioneering work in the field of nanodevice preparation using block copolymers, and has been extensively studied and developed in recent years.80-83

As discussed above, the strategy of living anionic polymerization of a variety of styrene derivatives carrying protected functional groups successfully expands the range of monomers amenable to the anionic polymerization. 1,1-Diphenylethylenes are typical candidates for this purpose, although they are categorized into α -phenyl-substituted styrene derivatives showing nonpolymerizability under anionic conditions.^{2,20,84} In fact, various 1,1-diphenylethylenes possessing protected functional groups were synthesized and employed



Scheme 17 Polymer reaction of poly(26a).



Scheme 18 Cross-linking and ozonolysis of block copolymer.



Figure 26 Electron micrographs. (a) Transmission electron microscopy of a thin film of poly(26d)-*block*-polyisoprene-*block*-poly(26d) cast from methyl isobutyl ketone (MIBK); (b) scanning electron microscopy (SEM) of the surface of cross-linked microporous membrane; (c) SEM of cross section of cross-linked microporous membrane.

for the end-functionalization reactions (Figure 27).^{20,84–88} All the protective groups used for styrene derivatives were applicable to 1,1-diphenylethylene derivatives bearing functional

groups. The various end-functionalized polymers were synthesized by using protective methods and particular 1,1-diphenylethylene reactivity, such as 'the termination methods' (Scheme 19) and 'the initiation methods' (Scheme 20). Furthermore, the chemistry of 1,1-diphenylethylene allows the precise synthesis of other well-defined architectural polymers involving chain-multifunctionalized polymers, star-branched polymers, densely branched polymers, and dendritic branched polymers. This topic is not within this review and has been reviewed by Hirao *et al.*⁸⁹⁻⁹²

3.18.3 Functional 1,3-Butadiene Derivatives

As mentioned in the preceding section, the protective strategy in conjunction with living anionic polymerization was successfully established as a novel methodology for the synthesis of



Figure 27 Functional 1,1-diphenylethylene derivatives.

End-functionalized polymer



Anionic living polymer





Scheme 20 Synthesis of end-functionalized polymer by initiation method.

functional polystyrenes and their block copolymers with well-defined structures. In principle, the protective strategy can be applied to all other monomers amenable to living anionic polymerization. Among such monomers, functional 1,3-butadiene derivatives are selected as the next target monomers, since 1,3-butadiene monomers are similar in anionic reactivity to styrene monomers and the living chain-end anions have reactivities roughly comparable to that of living polystyrene.^{1,2} Accordingly, the protective groups and/or protected functionalities usable for functional styrene derivatives can be basically employed for the protection of functional 1,3-butadiene monomers.

The living anionic polymerization of 1,3-butadiene and isoprene is industrially important for the production of various synthetic elastomers, thermoplastic elastomers, and styrenebutadiene rubbers (SBRs). In addition, numerous alkyl- and aryl-substituted 1,3-diene monomers have been subjected to anionic polymerization to develop new elastomers. Unfortunately, the anionic polymerization of functional 1,3-butadiene derivatives has not attracted much attention due to their synthetic difficulties. As limited examples, the anionic polymerizations of 2-trimethylsilyl-1,3-butadiene93,94 and a series of 2-dialkylaminomethyl-1,3-butadiene monomers^{95,96} were previously reported. However, both polymerizations were not well controlled in terms of molecular weight and molecular weight distribution. Recently, a new interesting monomer, 2-(1-adamantyl)-1,3-butadiene (27), having a sterically bulky adamantyl group was synthesized





and subjected to anionic polymerization (Figure 28).^{97,98} This 1,3-butadiene monomer was readily polymerized in a living manner with *sec*-BuLi either in cyclohexane at 40 °C or in THF at -30 °C. Surprisingly, the microstructure of the poly (27) obtained even in polar THF is predominantly regulated in the 1,4-addition mode (88%, 1,4-*cis/trans* = 72/16), while the major structures of poly(1,3-butadiene) and polyisoprene are well known to be mainly 1,2- and 3,4-modes under the same conditions. Thus, a bulky rigid adamantyl substituent dramatically influenced the microstructure. Currently, the anionic polymerization of protected functional 1,3-butadiene monomers has not been reported except for the case of alkoxysilane-protected 1,3-butadiene derivatives.

As mentioned in Section 3.18.2.5, the silanol functions of styrene monomers could be protected as alkoxysilanes to achieve the living anionic polymerization. Similarly, the anionic polymerization of alkoxysilane-protected 1,3-butadiene monomers, 2-trimethoxysilyl-1,3-butadiene (28a) and 2-triisopropoxysilyl-1,3-butadiene (28b), was



carried out in THF at -78 °C with oligo(α -methylstyryl) dilithium, oligo(α-methylstyryl)disodium, or oligo (α-methylstyryl)dipotassium (Figure 29).^{99–101} The polymerizations of 28a and 28b were observed to proceed in a living manner to quantitatively afford the polymers with predictable molecular weights and narrow molecular weight distributions, as shown in Table 8. Thus, methoxyand isopropoxysilane-protected functionalities were stable to the anionic initiators and chain-end anions, but were readily cleaved to regenerate silanols, followed by self-condensation to form Si-O-Si bonds under acidic conditions (Scheme 21). By this treatment, the polymers immediately became insoluble due to cross-linking among the polymers.

The living nature of the anionic polymerization of 28a and 28b was also demonstrated by the success of postpolymerization and the sequential block copolymerization of 28a or 28b

Table 8 Anionic polymerization of 28a-28f in THF at -78 °C for 24-160 h

Monomer	Initiator	<i>M</i> _n calcd (g mol ⁻¹)	<i>M</i> _n obsd ^a (g mol ⁻¹)	M _w /M _n
28a 28b 28c 28c 28d 28e 28f	K-Naph/α-MeSt ^b K-Naph/α-MeSt Li-Naph/α-MeSt K-Naph/α-MeSt Li-Naph ^d K-Naph/α-MeSt Cumul-K ^e	14 000 36 000 21 000 18 000 12 000 13 000	14 000 31 000 19 000 16 000 10 000 13 000	1.11 1.11 1.08 1.13 1.17

^aMeasured by VPO.

^bOligo(α-methylstyryl)dipotassium.

^cOligo(α-methylstyryl)dilithium.

^dLithium naphthalenide.

^eCumylpotassium.

with 2-vinylpyridine as a second monomer. On the other hand, these living polymers could not initiate the polymerization of isoprene at all in THF at -78 °C. This suggests that their propagating anions are less reactive than those of living polyisoprene and polystyrene, which are capable of initiating the polymerization of isoprene. Possibly, electron charges on the chain-end anions may be accepted to a certain extent by an empty π -orbital of silicon, thereby lowering the reactivity of the chain-end anions.

Interestingly and importantly, the polymerizations of 28a and 28b proceeded exclusively in the 1,4-addition mode in polar THF (Figure 30 and Table 9). The ratio of *E*/*Z* configuration of the C=C bond was 7/3 in the poly(28a), while the geometry of the C=C bond in the 1,4-repeating unit was perfectly regulated to E configuration corresponding to cis configuration in the poly(28b), regardless of the difference of the countercation (Li⁺, Na⁺, and K⁺). Thus, the living anionic polymerization of 28b proceeded with not only regiospecificity but also stereospecificity. To the best of our knowledge, this is the first successful living anionic polymerization in which chain configuration is perfectly controlled. A detailed discussion of the microstructures of poly(2-trialkoxysilyl-1,3-butadiene)s is reported elsewhere.¹⁸

Similarly, four 2-((N,N-dialkylamino)dimethylsilyl)-1,3-butadiene monomers, 28c-28f (Figure 29), underwent living anionic polymerization in THF at -78 °C.¹⁰² The resulting polymers were controlled in molecular weight and narrowly



Figure 30 Microstructures of poly(28a) and poly(28b).





Table 9 Microstructures of polymers of 28a–2	of 28a-28f
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	Conditions		Microstructures (%) ^a				
Polymer	Counterion	Solvent	1,4-E	1,4-Z	1,2	3,4	
Poly(28a)	Li⁺	THF	90	10	0	0	
Poly(28a)	K+	THF	73	27	0	0	
Poly(28b)	Li+	THF	100	0	0	0	
Poly(28b)	K+	THF	100	0	0	0	
Poly(28c)	Li+	THF	57	27	16	0	
Poly(28c)	K+	THF	58	25	17	0	
Poly(28c)	Li+	Heptane	16	84	0	0	
Poly(28d)	K+	THF	56	34	10	0	
Poly(28d)	Li+	Heptane	30	70	0	0	
Poly(28e)	K+	THF	61	27	12	0	
Poly(28e)	Li ⁺	Heptane	32	68	0	0	
Poly(28f)	K+	THF	60	31	9	0	
Poly(28f)	Li ⁺	Heptane	100	0	0	0	

^aMeasured by ¹H and ¹³C NMR.

distributed in molecular weight as summarized in **Table 8**. The living polymer of **28c** was observed to be similar in reactivity to living poly(**28a**) and poly(**28b**) by the sequential block copolymerization with isoprene, styrene, or 2-vinylpyridine. As can be seen from **Table 9**, the polymers produced in THF possess high 1,4-contents (77–91%). The *E*/*Z* ratios varied to a certain extent by the *N*-substituent and the countercation of the initiator, while 100% 1,4-*E* configuration was observed in the polymers obtained with *sec*-BuLi in heptane. Since the resulting polymers were observed to react *in situ* with silica particles, their homopolymers and copolymers with 1,3-butadiene and isoprene are expected to be new functional elastomers capable of reacting with silica particles and possibly inorganic materials and metal surfaces.

It may also be possible to synthesize various polymers of functional 1,3-butadienes and their block copolymers with 1,3-butadiene and isoprene simply by employing the successful protective strategy developed in the living anionic polymerization of functional styrene monomers, although this has not been realized at the moment. The resulting poly(functional 1,3-butadiene)s are important materials as they can provide additional functionalities to the present synthetic elastomers.

3.18.4 Functional (Meth)acrylate Derivatives

Although the anionic polymerization of alkyl (meth)acrylate monomers, mainly MMA and tBMA, has been studied for a long time, the living anionic polymerization is not straightforward.^{23–25,103–106} In general, ester carbonyls are not stable and occasionally react with anionic initiators and/or the propagating chain-end anions. Among them, the intramolecular self-condensation between propagating chain-end enolate anions and the carbonyl group present at the antepenultimate monomer unit, the so-called backbiting termination, is the most serious side reaction, particularly observed at the final stage of the polymerization. In the case of acrylate monomers, an α -proton abstraction reaction of monomer and/or polymer main chain with anionic species is also a significant side reaction to often terminate the polymerization. In addition, the exothermic rapid propagation and partially aggregated propagating species may cause broadening of the molecular weight distributions.

The proper choice of initiator, countercation, solvent, and polymerization temperature is essential to realize the living anionic polymerization of alkyl (meth)acrylate monomers.^{23–25,103–110} In general, sterically hindered π -stabilized initiators, such as 1,1-diphenylhexyllithium (n-BuLi and 1,1-diphenylethylene), 1,1-diphenyl-3-methylpentyllithium (sec-BuLi and 1,1-diphenylethylene), diphenylmethyllithium (Ph₂CHLi), diphenylmethylsodium (Ph₂CHNa), and diphenylmethylpotassium (Ph₂CHK), are useful initiators. These polymerizations must be carried out in polar media like THF at temperatures lower than -40 °C. A number of additives that are effective to control the polymerization have been found in the last 20 years.^{23-25,111-116} Such additives include LiCl, LiClO₄, LiOC(CH₃)₃, KOC(CH₃)₃, lithium 2-(2-methoxvethoxy)ethoxide, and crown ethers. For instance, the molecular weight distribution of poly(MMA) becomes significantly narrow (M_w/M_p) value from around 1.2 to 1.05 or even smaller) by the addition of LiCl in the polymerization of MMA with 1,1-diphenyl-3-methypentyllithium in THF at -78 °C.¹¹² It is possible to achieve the living anionic polymerization of tert-butyl acrylate (tBA) in THF at -78 °C with LiCl.¹¹¹ The M_w/M_n values of the resulting poly(tBA) were reduced from 2.6 (without additive) to 1.1 in the presence of LiCl.

Several binary initiator systems have also been developed. Ozaki et al.¹¹⁷ and Ishizone et al.¹¹⁸ demonstrated that the use of Et₂Zn was very effective to control the polymerization of alkyl (meth)acrylates with Ph₂CHK in THF at -78 °C. With this system, polymers with predictable molecular weights and narrow molecular weight distributions $(M_w/M_p \le 1.1)$ were quantitatively produced, while the polymerization could not be well controlled in the absence of Et₂Zn, resulting in polymers with multimodal distributions. Et₂Zn with a weak Lewis acid character may possibly coordinate with the chain-end anion to reduce the reactivity and offer bulkiness. Moreover, the coordination by Et₂Zn may dissociate the aggregated chain-end anion to a single active species. The undesirable backbiting termination reaction might be prevented by both reduced reactivity and steric bulkiness of the coordinated chain-end anion, thus achieving controlled polymerization. A similar effect was observed by the addition of R3B, R3Al, and the modified reagent from R₃Al with 2,6-di(*tert*-butyl)phenol.^{23-25,119,120} With the above living polymerization systems, molecular weight can be precisely controlled up to several 10⁵ g mol⁻¹ in the anionic polymerization of MMA, tBMA, and possibly alkyl methacrylate monomers. Also, extremely narrow molecular weight distributions are attained, with $M_{\rm w}/M_{\rm n}$ values being 1.1 or even smaller.

It should be noted that tBA is currently the only acrylate monomer that undergoes living anionic polymerization to afford polymers with up to a few 10^4 g mol^{-1} or higher M_n values under suitable conditions.^{111,118,119} This means that it is necessary to synthesize functional *tert*-alkyl esters of acrylic acid, as shown in **Figure 31**, in order to achieve the living anionic polymerization of protected acrylate



Figure 31 Plausible functional *tert*-alkyl esters of acrylic acid.

monomers. Unfortunately, the living anionic polymerization of other alkyl acrylate monomers has not been well developed at the present time. Accordingly, the protective strategy in conjunction with living anionic polymerization focuses on only functional alkyl methacrylate monomers except for the synthesis of a well-defined poly(acrylic acid) via the poly(tBA) obtained by living anionic polymerization.

Since living chain-end enolate anions generated from methacrylate monomers are less reactive than those (carbanions) generated from styrene monomers, living anionic polymerization of the following functional methacrylate derivatives can be achieved without protection in THF at -78 °C with the use of the above initiator systems: glycidyl methacrylate, 121-123 3-ethyl-3-(methacryloyloxymethyl)oxe-2-(1-aziridinyl)ethyl methacrylate,¹²⁴ tane, allyl methacrylate, 125 2-chloroethyl and 2-bromoethyl methacrylates,¹²⁶ 2-(perfluorobutyl)ethyl methacrylate,¹²⁷ 2,2,2trifluoroethyl methacrylate,¹²⁷ 6-[4-(4-cyanophenyl)phenoxy] hexyl methacrylate,¹²⁸ 6-[4-(4-methoxyphenyl)phenoxy]hexyl

methacrylate,¹²⁹ and 3-(3,5,7,9,11,13,15-heptaisobutylpentacyclo[9.5.1.^{3,9}1^{5,15}1^{7,13}]oxtasiloxan-1-yl)propyl methacrylate (POSSMA) (**Figure 32**).¹³⁰ Needless to say, such functional groups cannot be tolerated under the living anionic polymerization of styrene monomers.

3.18.4.1 (Meth)acrylic Acids

Esters are often used as protected functionalities for carboxylic acids. As mentioned above, alkyl methacrylate monomers, MMA and tBMA, undergo living anionic polymerization to afford the corresponding polymers having ester functions as side chains, which can be regarded as ester-protected poly (methacrylic acid)s. Unfortunately, the hydrolysis of poly (MMA) was not straightforward under the alkaline conditions that cleave low-molecular-weight methyl esters. On the other hand, the complete cleavage of tert-butyl ester function of poly (tBMA) was readily achieved under acidic conditions such as HCl in aqueous 1,4-dioxane at 85 °C, p-toluenesulfonic acid in toluene at 80 °C, or (CH₃)₃SiI (or a 1:1 mixture of (CH₃)₃SiCl and NaI) in acetonitrile/chloroform at room temperature, resulting in poly(methacrylic acid) (poly(29)) in 100% yield (Scheme 22).^{131,132} The resulting poly(29) was quantitatively converted to poly(MMA) by treating with diazomethane in order to re-examine the molecular weight and molecular weight distribution by SEC. SEC analysis of the resulting poly (MMA) showed a narrow molecular weight distribution and a predictable molecular weight, clearly indicating that the resulting poly(29) is well defined in chain structure, similar to the



Figure 32 Functional methacrylates capable of living anionic polymerization.



Scheme 22 Deprotection of poly(tBMA).



Figure 33 Monomers 29a–29d.

original poly(tBMA). Interestingly, the poly(tBMA) segment of poly(MMA)-*block*-poly(tBMA) could be chemoselectively cleaved by treatment with $(CH_3)_3SiI$ at room temperature, resulting in poly(MMA)-*block*-poly(29).

Similarly, a well-defined poly(acrylic acid) (poly(**30**)) was readily prepared by the living anionic polymerization of tBA, followed by quantitative cleavage of *tert*-butyl ester function under acidic conditions.

Trimethylsilyl- (29a), 1-ethoxyethyl-, (29b), 1-butoxyethyl-(29c), and 1-*tert*-butoxyethyl methacrylates (29d) were reported as alternative protected derivatives of 29 (Figure 33).^{133–136} These protected functionalities are designed to be cleaved more easily than *tert*-butyl ester under mild conditions. All monomers, 29a–29d, underwent living anionic polymerization with the use of π -stabilized bulky initiators, such as 1-phenyl-1- α -naphthylhexyllithium and 1,1-diphenylhexyllithium, in THF at lower temperatures (–20 to –78 °C). As expected, the protected functionalities were readily and quantitatively cleaved under mild acidic conditions at room temperature. Moreover, poly(29b) was easily deprotected as such by thermolysis to afford a pure poly(29) in 100% yield (Scheme 23), thus without the need for a purification step.¹³⁷

3.18.4.2 Functional Methacrylate Derivatives

2-Trimethylsilyloxyethyl methacrylate (31a) (Figure 34), whose hydroxyl function was protected as a TMS ether, was



Scheme 23 Deprotection of poly(29b).

anionically polymerized in a living manner under conditions similar to those employed in the living anionic polymerization of MMA.^{138,139} The TMS ether of poly(**31a**) was not stable and was gradually cleaved during the precipitation of the polymer. It was completely cleaved by adding a few drops of 2 N HCl to polymer solution, resulting in the quantitative formation of poly(2-hydroxyethyl methacrylate) (poly(31)). Since there is a strong interaction between SEC column and the resulting poly(31), similar to poly(1) and poly(3) having hydroxyl groups, a long tailing is always observed in the SEC trace. Therefore, the poly(31) was converted to poly (2-benzyloxyethyl methacrylate) by treatment with benzoic anhydride and characterized by SEC, VPO, and NMR. The benzoylated polymer was observed to possess a predictable molecular weight with a narrow molecular weight distribution. The results of a series of polymerizations are summarized in Table 10.

Similar to styrene derivatives carrying hydroxyl groups, the OH function of 31 can be protected as TBDMS ether, acetal, and vinyl ether. The living anionic polymerization of the resulting protected monomers, 2-(tert-butyldimethylsilyloxy)ethyl methacrylate (31b),¹³⁹ 2-(methoxymethoxy)ethyl methacrylate (31c),¹³⁹ and 2-vinyloxyethyl methacrylate (31d),¹⁴⁰ proceeded smoothly in THF at -78 °C with 1,1-diphenyl-3methylpentyllithium in the presence of LiCl. Unlike the above TMS ether of poly(31a), these protected functionalities are sufficiently stable during the isolation step and characterization process. The characterization results indicate that the polymers are well controlled in molecular weight and molecular weight distribution as summarized in Table 10. The protected functionalities were quantitatively cleaved by treatment with 2 N HCl in aqueous 1,4-dioxane solution. The TBDMS ether was also cleaved by $(C_4H_9)_4NF$ to regenerate the hydroxyl function (Scheme 24). Interestingly, the chemoselective cationic



Figure 34 Monomers 31a-31d.

Monomer	Initiator	Additive	<i>M</i> _n calcd (g mol ⁻¹)	<i>M</i> _n obsd ^a (g mol ⁻¹)	M _w /M _n
31a	<i>sec</i> -BuLi/DPE ^b		15 000	16000	1.52
31a	<i>sec</i> -BuLi/DPE	LiCl	19 000	19000	1.10
31b	<i>sec</i> -BuLi/DPE		11 000	9 500	1.22
31b	<i>sec</i> -BuLi/DPE	LiCl	83 000	87 000	1.01
31c	<i>sec</i> -BuLi/DPE	LiCl	25 000	24 000	1.07
31d	<i>Sec</i> -BuLi/DPE	LiCl	20 000	23 000	1.12
32a	<i>n</i> -BuLi/DPE ^c	LiCl	26 000	26 000	1.03

 Table 10
 Anionic polymerization of 31a–31d and 32a in THF at -78 °C for 1 h

^aMeasured by VPO.

^b1,1-Diphenyl-3-methylpentyllithium.

^c1,1-Diphenylhexyllithium.

polymerization of vinyl ether moiety of **31d** was achieved to result in poly(vinyl ether) bearing methacryloyl side chain.¹⁴¹

Poly(31) has attracted considerable attention over the years because of practical biomedical applications such as contact lenses, coating of surgical sutures, hydrogels, and hemodialysis membranes.^{142,143} The success of the living anionic polymerization of protected monomers, 31a-31d, opens the way to newly design well-defined amphiphilic block copolymers with more potential applications. A series of block copolymers of 31a with styrene, α -methylstyrene, 4-octylstyrene, or isoprene were synthesized and their surface structures and environmental movements were characterized in detail by TEM, X-ray photoelectron spectroscopy (XPS), and contact angle measurements.^{144–146} The surface reconstruction was clearly observed by changing the outer environment. Specially designed AB diblock copolymers, polysilane-*block*-poly(**31**)¹⁴⁷ and poly (1,1-diethylsilacyclobutane)-*block*-poly(**31**),^{148,149} and ABC triblock terpolymers, poly(2-perfluorobutyl)ethyl methacrylate-*block*-poly(tBMA)-*block*-poly(23)¹²⁷ and poly (2,3-dihydroxypropyl methacrylate)-block-poly(31)-block-poly (29),¹⁵⁰ were synthesized and purposely used as desired. It should be noted that poly(31) is highly hydrophilic and hygroscopic, but not soluble in water except for lowmolecular-weight oligomers.

The acetal-protected monomer, (2,2-dimethyl-1,3dioxolan-4-yl)methyl methacrylate (**32a**), whose two hydroxyl functions were protected as a cyclic acetal, enabled the living anionic polymerization in THF at -78 °C with 1,1-diphenyl-3-methylpentyllithium/LiCl (**Figure 35** and **Table 10**).^{151,152} The cyclic acetal-protected functionality was cleaved by treatment with 1 N HCl, quantitatively yielding water-soluble poly (2,3-dihydroxylpropyl methacrylate) (poly(**32**)) (**Scheme 25**).

Recently, Ishizone *et al.*¹⁵³ synthesized new methacrylate monomers bearing oligo(ethylene glycol) units, 33 and 34, which are designed to offer the water solubility of the resulting



Figure 35 Monomers 32 and 32a.

polymers. Their ω-hydroxyl functions were protected as TBDMS ethers and the resulting protected monomers, 33a and 34a, were subjected to anionic polymerization in THF at -78 °C with 1.1-diphenyl-3-pentyllithium/LiCl (Figure 36). As expected, both monomers underwent living anionic polymerization, and well-defined water-soluble polymers were quantitatively obtained after removal of TBDMS groups with $(C_4H_9)_4NF$ in THF at room temperature (Scheme 26). The same research group reported the synthesis of a series of well-defined water-soluble polymethacrylates bearing oligo (ethylene glycol) alkyl ethers, 35-40, by the living anionic polymerization of the corresponding monomers (Figure 37).^{154–158} The resulting polymers showed reversible cloud points varying from 4 to 68 °C, depending on the length of oligo(ethylene glycol) unit and ω -alkyl functionality. The polymerization results of 33a, 34a, and 35-40 are listed in Table 11.

Kitayama *et al.*¹⁵⁹ reported the anionic polymerization of a methacrylate monomer bearing a sterically bulky phenol moiety, 3-(3',5'-di-*tert*-butyl-4'-hydroxyphenyl)propyl methacrylate (**41**) (Figure 38). Surprisingly, the polymerization was successfully achieved without protection of the phenol function under the particular conditions in toluene at -78 °C in the presence of sterically hindered alkylaluminum compounds, giving the corresponding polymer in 60–90% yield. Although the molecular weight distribution was relatively narrow ($M_w/M_n = 1.1-1.3$), the observed molecular weight was significantly higher than the calculated value, indicating the low initiation efficiency (30–40%). It is thus interesting and indicative that two bulky *tert*-butyl groups may provide a sufficient steric hindrance for the protection of phenolic hydroxyl group during the anionic polymerization.

As mentioned before, the ethynyl acidic proton of 4-ethynylstyrene (12) was successfully protected by a TMS group to achieve living anionic polymerization of a TMS-protected monomer (12a). Since the terminal proton of ethynyl function ($pK_a = 25$) is sufficiently acidic even in the anionic polymerization of methacrylate monomer, it must be protected to carry out the anionic polymerization of methacrylate monomers bearing ethynyl function. The terminal ethynyl proton of 2-propynyl methacrylate (42) was protected with a TMS group and the resulting TMS-protected monomer, 2-(3-trimethylsilyl)propynyl methacrylate (42a), was subjected to anionic polymerization under the conditions in THF at -78 °C with







Scheme 25 Deprotection of poly(32a).



Figure 36 Monomers 33, 33a, 34, and 34a.

the binary initiator system such as 1,1-diphenyl-3 methylpentyllithium/LiCl and Ph₂CHK/Et₂Zn (**Figure 39**).¹⁶⁰ Under such conditions, **42a** was anionically polymerized in a living manner to quantitatively afford the polymers with controllable molecular weights and narrow molecular weight distributions (M_w / M_n < 1.1) (see **Table 12**). Thus, the TMS group is effective for the protection of the terminal acidic ethynyl proton of **42**. Furthermore, the polymerization was not disturbed by the presence of the active methylene protons adjacent to the C=C bond.

The TMS protective group was quantitatively removed by treatment with K_2CO_3 in THF/methanol or $(C_4F_9)_4NF$ in THF at room temperature (Scheme 27). The SEC trace of the poly (42) shifted to a low-molecular-weight side, while the molecular weight distribution remained narrow. Relatively surprisingly, 42 having an acidic proton (-C=CH) was anionically polymerized without TMS protection under the same conditions, yielding poly(42) in 100% yield. However, the SEC trace of the resulting polymer was monomodal with a tailing to a low-molecular-weight region, the M_w/M_n value being 1.24. Abstraction of terminal ethynyl proton might occur during the anionic polymerization, although it was not predominant. Both 2-butynyl (43) and 3-pentynyl methacrylates (44) having inner C=C functions and no acidic terminal protons were anionically polymerized to quantitatively afford polymers with predictable molecular weights and narrow molecular weight distributions. These results again show that the less reactive enolate anions can coexist with the active methylene protons adjacent to C=C moiety. The results are listed in Table 12.



Table 11Anionic polymerization of 33a, 34a, and 35–40 in THFat -78 °C for 2–24 h

			44	14 . 1 . 13	
Monomer	Initiator	Additive	/// _n caicd (g mol ⁻¹)	/// _n obsd" (g mol ⁻¹)	M _w /M _n
33a	<i>sec</i> -BuLi/DPE ^b	LiCI	20 000	22 000	1.05
33a	<i>sec</i> -BuLi/DPE	LiCI	48 000	63 000	1.03
33a	Ph₂CHK ^c	Et ₂ Zn	7 600	7 500	1.03
34a	<i>sec</i> -BuLi/DPE	LiCI	17 000	17 000	1.08
34a	Ph ₂ CHK	Et ₂ Zn	13 000	13 000	1.06
35	<i>sec</i> -BuLi/DPE	LiCI	19000	21 000	1.04
36	<i>sec</i> -BuLi/DPE	LiCI	11 000	16 000	1.09
36	Ph ₂ CHK	Et ₂ Zn	15 000	16 000	1.05
37	Ph ₂ CHK	Et ₂ Zn	18 000	18 000	1.09
38	<i>sec</i> -BuLi/DPE	LiCI	12 000	15 000	1.04
38	Ph ₂ CHK	Et ₂ Zn	14 000	17 000	1.04
39	<i>sec</i> -BuLi/DPE	LiCI	12 000	14 000	1.04
39	Ph ₂ CHK	Et ₂ Zn	11 000	11 000	1.04
40	Ph ₂ CHK	Et ₂ Zn	10 000	8 900	1.07

^aDetermined by ¹H NMR (end-group analysis).

^b1,1-Diphenyl-3-methylpentyllithium.

^cDiphenylmethylpotassium.

As mentioned before, silanols were satisfactorily protected as alkoxysilanes during the anionic polymerization of styrene derivatives (26a–26d). 3-(Trimethoxysilyl)propyl methacrylate (45a), which is commercially available as a silane coupling agent, is a typical methoxysilane-protected methacrylate monomer (Figure 40).¹⁶¹ The anionic living polymerization of 45a was successfully carried out under conditions similar to those









Figure 39 Monomers 42, 42a, 43, and 44.

Table 12	Anionic	polymerization	of	42a,	43,	and	44	in	THF
at -78 °C for	1 h								

Monomer	Initiator	Additive	<i>M</i> _n calcd (g mol ⁻¹)	<i>M</i> _n obsd ^a (g mol ⁻¹)	<i>M</i> _w ∕M _n
42a 42a 42a 43 43 43 44	sec-BuLi/DPE Ph ₂ CHK ^c sec-BuLi/DPE Ph ₂ CHK sec-BuLi/DPE Ph ₂ CHK sec-BuLi/DPE Ph ₂ CHK	LiCI LiCI Et ₂ Zn LiCI Et ₂ Zn LiCI Et ₂ Zn	22 000 38 000 11 000 24 000 11 000 11 000 12 000	23 000 47 000 11 000 26 000 12 000 13 000 15 000	1.04 1.04 1.08 1.09 1.06 1.08 1.09

^aDetermined by ¹H NMR (end-group analysis).

^b1,1-Diphenyl-3-methylpentyllithium.

^cDiphenylmethylpotassium.

employed in the polymerizations of other methacrylate monomers, yielding poly(45a) with a predictable molecular weight and a narrow molecular weight distribution. Unfortunately, the poly(45a) thus obtained was not stable during the polymer handling and characterization process and became cross-linked despite handling it with great care. Labile and sensitive methoxysilyl function of 45a can be converted to ethoxysilyl and bulkier isopropoxysilyl groups by the exchange reaction of the corresponding alcohols in the presence of a catalytic amount of p-toluenesulfonic acid. These new methacrylate monomers, 45b and 45c, also underwent living anionic polymerization. As expected, the resulting polymers were stable during polymer handling and characterization processes, but were readily cleaved under acidic conditions, yielding insoluble cross-linked polymers. The polymerization results of 45a-45c are summarized in Table 13.

The living anionic polymers of protected functional methacrylate monomers herein introduced are very similar in reactivity and stability to those of MMA. Accordingly, these living polymers can initiate the polymerization of MMA, tBMA, and other protected functional methacrylate monomers, resulting in block copolymers with tailored chain structures. Complete crossover block copolymerizations among these methacrylate monomers are possible. Furthermore, living anionic polymers of styrene, α -methylstyrene, isoprene, and 1,3-butadiene initiate the polymerization of protected functional methacrylate monomers to afford well-defined AB diblock copolymers. In order to avoid ester carbonyl attack by the chain-end anions, the living anionic polymers should be end-capped with 1,1-diphenylethylene

 Table 13
 Anionic polymerization of 45a-45c in THF at -78 °C for 1 h

Monomer	Initiator	Additive	<i>M</i> _n calcd (g mol ⁻¹)	<i>M</i> _n obsd ^a (g mol ⁻¹)	M _w /M _n
45a 45b 45c 45c	<i>n</i> -BuLi/DPE ^b <i>n</i> -BuLi/DPE <i>n</i> -BuLi/DPE <i>n</i> -BuLi/DPE	LiCI LiCI LiCI LiCI	9 600 9 900 24 000 50 000	8 200 9 200 26 000 58 000	1.05 1.03 1.02 1.02

^aMeasured by VPO.

^b1,1-Diphenylhexyllithium.





 $\begin{array}{cccc} CH_3 & CH_3 & CH_3 & CH_3 \\ CH_2 = C & CH_2 = C & CH_2 = C \\ COOCH_2CH_2CH_2Si(OMe)_3 & COOCH_2CH_2CH_2Si(OEt)_3 & COOCH_2CH_2CH_2Si(OPr^i)_3 \\ \hline \end{tabular}$

Figure 40 Monomers 45a-45c.

prior to block copolymerization to reduce the reactivities as well as increase the steric bulkiness.

Since several highly stereoregular poly(alkyl methacrylate)s have been synthesized in recent years by designing initiator, countercation, solvent, additive, and polymerization temperature,^{24,162–164} one can expect to synthesize functional methacrylate polymers in which not only molecular weight and molecular weight distribution but also stereoregularity is well controlled.

3.18.5 N-Isopropylacrylamide

The living anionic polymerization of a series of N,N-dialkylacrylamides was successfully achieved under the conditions in THF at -78 °C with π -stabilized bulky initiators such as triphenylmethylcesium (Ph₃CCs) and Ph₂CHK.¹⁶⁵⁻¹⁶⁹ Polymers with controlled molecular weights and somewhat narrow molecular weight distributions ($M_w/M_n = 1.1-1.2$) were quantitatively obtained under such conditions. Kobayashi *et al.*¹⁶⁶⁻¹⁶⁸ and Ishizone *et al.*¹⁶⁹ reported that the binary initiator systems effective in the polymerization of methacrylate monomers are also effective in controlling the polymerization of N,N-diethylacrylamide in molecular weight, molecular weight distribution, as well as stereoregularity.

In contrast to the living anionic polymerization of N,N-dialkylacrylamides, N-alkylacrylamides were not anionically polymerized under the same conditions because of the proton abstraction from the acidic amide moieties ($pK_a = 25$ -26). Alternatively, the hydrogen transfer polymerization was often induced.¹⁷⁰ Therefore, the amide proton must be protected to enable the exclusive vinyl polymerization. Among N-alkylacrylamide monomers, NIPAM (46) is the most often used monomer, since its polymer (poly(46)) is of vast interest for a wide range of practical applications, such as hydrogels, drug delivery devices, biomedical uses, and permeation membranes, due to its hydrophilic, water-soluble, and thermoresponsive $(T_c = 32 \text{ °C})$ characteristics. Over the last 10 years, several living/controlled radical polymerization systems of 46 have been developed, which enable control of molecular weight and molecular weight distribution of poly(46) $(M_w/M_n < 1.3)$.^{171–176} Some interesting amphiphilic block copolymers containing poly(46) segment were also synthesized by these systems.

Kitayama *et al.*¹⁷⁷ synthesized a TMS-protected 46, O-trimethylsilyl-*N*-isopropylacrylamide (46a) (Figure 41), and anionically polymerized it with *tert*-BuLi in the presence of trialkylaluminum in toluene. Although the highly isotactic poly(46) (m = 97%) was obtained (Figure 42), the polymerization could not be controlled well in terms of molecular weight and molecular weight distribution. The TMS protective group was labile and was easily removed under mild acidic conditions to afford the objective poly(46) quantitatively.







Figure 42 Stereoregularity of poly(46).

Surprisingly, the resulting highly isotactic poly(46) was insoluble in water, while a commercially available atactic poly(46) (m/r = 50/50) prepared by radical polymerization was water-soluble.^{178–180}

Soon after, Ishizone and Ito^{181–183} synthesized a new acetalprotected monomer, *N*-methoxymethyl-*N*-isopropylacrylamide (46b), whose amide proton was protected with a more robust methoxymethyl group, and anionically polymerized 46b in THF at –78 °C with the use of various binary initiator systems. These include 1,1-diphenyl-3-methylpentyllithium, Ph₂CHLi, Ph₂CHK, and Ph₂CHCs in combination with either Et₂Zn or LiCl. With the use of these systems, the polymerization of 46b proceeded in a living manner to afford the poly (46b)s with predictable molecular weights and narrow molecular weight distributions ($M_w/M_n < 1.1$) (Table 14). The living nature of the polymerization of 46b was further confirmed by the success of the sequential block copolymerization of 46b with *N*,*N*-diethylacrylamide.

The methoxymethyl group was stable during the polymer isolation and characterization process, but was completely cleaved by treatment with 2 N HCl in aqueous 1,4-dioxane at room temperature (Scheme 28). The SEC trace of the poly(46) thus obtained shifted toward a lower molecular weight region maintaining a monomodal and narrow distribution $(M_w/$ $M_{\rm p}$ = 1.08), similar to that of the original poly(46b) ($M_{\rm w}$ / $M_{\rm n}$ = 1.06). The stereoregularity of the resulting poly(46)s strongly depends on the initiator system employed. Syndiotactic-rich polymers (r = 75-83%) were obtained by the polymerization with 1,1-diphenyl-3-methylpentyllithium/ Et₂Zn and Ph₂CHLi/Et₂Zn systems. On the other hand, the polymerization with Ph2CHLi/LiCl gave isotactic-rich poly (46)s (m = 75 - 78%). Rather surprisingly, atactic poly(46)s (r = 50%) were synthesized by using a Ph₂CHK/Et₂Zn system in the polymerization.

Table 14	Anionic polymerization of 46b in THF at -78 °C
for 1–20 h	

Initiator	Additive	<i>M</i> ncalcd (g mol ⁻¹)	<i>M</i> nobsd ^a (g mol ⁻¹)	M _w /M _n	Tacticity (%) (m/r)
sec-BuLi/DPE sec-BuLi/DPE sec-BuLi/DPE sec-BuLi/DPE Ph ₂ CHK ^c Ph ₂ CHK	Et ₂ Zn Et ₂ Zn LiCl Et ₂ Zn	11 000 11 000 16 000 11 000 10 000 23 000	15 000 12 000 18 000 14 000 11 000 23 000	2.06 1.11 1.13 1.19 1.25 1.10	57/43 23/77 17/83 85/15 69/31 50/50
Ph ₂ CHK Ph ₃ CK ^d	Et ₂ Zn Et ₂ Zn	52 000 11 000	67 000 11 000	1.06 1.07	48/52 51/49

^aMeasured by ¹H NMR (end-group analysis).

^b1,1-Diphenyl-3-methylpentyllithium.

^cDiphenylmethylpotassium.

^dTriphenylmethylpotassium.



Scheme 28 Deprotection of poly(46b).

The stereoregularity of poly(46) significantly affects the water solubility, T_{ci} and glass transition temperature (T_{σ}). Both atactic and syndiotactic poly(46)s are water-soluble, while isotactic polymers (m > 69%) are insoluble in water. Figure 43 shows the relationship between T_c values and molecular weights $(M_{\rm n} = 3600 - 48000 \,{\rm g \, mol^{-1}}).$ The atactic polymers $(M_{\rm n} > 6600 \,{\rm g \, mol^{-1}})$ showed sharp $T_{\rm c}$ values around 32 °C, which are almost the same as those of poly(46)s obtained by radical polymerization. A small effect of molecular weight distribution on the sensitivity (ΔT) was observed in such atactic polymers with comparable molecular weights. For instance, the ΔT value of anionically polymerized poly(46) $(M_{\rm n} = 48\,000\,{\rm g\,mol^{-1}}, M_{\rm w}/M_{\rm n} = 1.07, r = 52\%)$ was 0.6 °C and, on the other hand, the radically polymerized poly(46) $(M_{\rm n} = 42\,000\,{\rm g\,mol^{-1}}, M_{\rm w}/M_{\rm n} = 4.2, r = 50\%)$ showed ΔT of 1.8 °C. The aqueous solution of a poly(46) with a slightly *m*-rich configuration (m = 58%) became cloudy at 20 °C $(T_c = 28 \text{ °C})$, and once again isotactic-rich polymers (m > 69%)were insoluble in water.¹⁷⁸⁻¹⁸⁰ In contrast, syndiotactic-rich polymers trended to show T_c values higher than 32 °C and the highest T_c value obtained was 37 °C for the sample with r = 83%.

Isotactic-rich polymers showed T_g values between 115 and 122 °C, while atactic polymers presented slightly higher T_g at around 130 °C. On the other hand, the T_g 's of syndiotactic-rich polymers were observed at 143–148 °C, and were apparently higher than those of isotactic and atactic polymers. The



Figure 43 Transmittance vs. temperature curves obtained for 0.2 wt.% aqueous solution of atactic poly(**46**)s ($m/r \sim 50/50$) synthesized with Ph₂CHK/Et₂Zn. (a) $M_n = 3600$, $M_w/M_n = 1.12$; (b) $M_n = 6600$, $M_w/M_n = 1.12$; (c) $M_n = 48000$, $M_w/M_n = 1.07$; (d) $M_n = 42000$, $M_w/M_n = 4.20$ (obtained with azobisisobutyronitrile (AIBN)).

observed effect of tacticity on T_g is consistent with the tendency reported in the stereoregular poly(MMA).

In summary, well-defined poly(46) was synthesized by the methoxymethyl protection of 46, followed by the living anionic polymerization of the protected monomer, 46b. Poly(46)s having M_n values up to 48 000 g mol⁻¹ and M_w/M_n values of less than 1.1 were obtained. Since the living nature of the anionic polymerization of 46b is demonstrated, the syntheses of a variety of new amphiphilic and thermosensitive block copolymers and other architectural polymers with well-defined structures are expected. In addition, it was found for the first time that the stereoregularity of poly(46) significantly influences water solubility, T_{cr} and T_g . Such information may be very important for the future molecular design and practical applications of poly(46).

3.18.6 Concluding Remarks

This chapter presents the versatile synthetic strategy of various functional polymers with well-defined chain structures via living anionic polymerization of protected functional monomers. The framework of monomers amenable to this strategy includes styrenes, 1,3-butadienes, alkyl (meth)acrylates, and acrylamides. This strategy consists of the following three steps: (1) the protection of functional groups of monomers; (2) living anionic polymerization of the protected functional monomers; and (3) deprotection of the protective groups from the resulting polymers. Two criteria of stability of the protective groups during the anionic polymerization and quantitative removal of the protective groups after the polymerization are strongly required for the success of this strategy. A number of functional groups, such as OH, SH, NH₂, CHO, COCH₃, COOH, C≡CH, ≡SiOH, and CONHR moieties, are protected by suitable protective groups tolerant to the anionic species. The resulting polymers before and/or after deprotection possess the (protected) functional groups in all monomer units as well as predictable molecular weights, narrow molecular weight distributions, and sometimes highly regulated tacticity or microstructure. A variety of tailored block copolymers containing functional polymer segment are also successfully synthesized by the sequential copolymerization of protected functional monomers. The electron-withdrawing protective groups, such as COOR, CONR₂, CH=NR, and C=N groups, play an important role in stabilizing the propagating carbanions during the polymerization. Not only the stability of the protective group but also the structure of the protected functional monomer is

essential for the attainment of this strategy if intramolecular rearrangement of the benzyl propagating anion occurs. The formation of a wide variety of anionic living polymers derived from styrenes, 1,3-butadienes, alkyl (meth)acrylates, and acrylamides allows the tailored synthesis of new end-functionalized polymers and special architectural polymers including macrocyclic, comb, graft, star-branched, Y-shaped, H-shaped, and even star-linear block polymers. In particular, nonpolymerizable 1,1-diphenylethylene derivatives carrying functional groups are very useful tools for the iterative synthesis of star-branched polymer and dendritic star-branched polymer. Thus, the success of this synthetic strategy, the living anionic polymerization of protected functional monomers, certainly expands the possibility of future molecular design and practical applications of well-defined functional polymers.

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3.19 Anionic Polymerization of Polar Vinyl Monomers

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3.19.1	Introduction	623
3.19.1.1	Types of Polar Vinyl Monomers	624
3.19.1.2	Side Reactions in Alkyl (Meth)acrylate Polymerization	624
3.19.1.3	Initiators for (Meth)acrylate Polymerization	625
3.19.1.3.1	Monofunctional anions	626
3.19.1.3.2	Di- and multifunctional anions	627
3.19.2	Mechanism of the Anionic Polymerization of Alkyl (Meth)acrylates	627
3.19.2.1	Polymerization in Polar Solvents	627
3.19.2.1.1	Propagation via solvated contact ion pairs	627
3.19.2.1.2	Studies on oligomerization of MMA	629
3.19.2.1.3	Aggregation of enolate ion pairs and their equilibrium dynamics	629
3.19.2.1.4	Effect of dynamics of the association equilibrium on the MWD	631
3.19.2.1.5	Improved initiating systems for alkyl (meth)acrylate polymerization	632
3.19.2.2	Modification of Enolate Ion Pairs with Ligands: Ligated Anionic Polymerization	632
3.19.2.2.1	Lewis base (σ -type) coordination	633
3.19.2.2.2	Lewis acid (µ-type) coordination	633
3.19.2.2.3	σ - μ -Type coordination	636
3.19.2.3	Metal-Free Anionic Polymerization	636
3.19.2.3.1	Group transfer polymerization	636
3.19.2.3.2	Tetraalkylammonium counterions	638
3.19.2.3.3	Phosphorous-containing counterions	639
3.19.2.4	Polymerization in Nonpolar Solvents	640
3.19.2.4.1	μ-Type coordination	641
3.19.2.4.2	σ - μ -Type coordination	642
3.19.2.5	Coordinative Anionic Initiating Systems	642
3.19.2.5.1	Aluminum porphyrins	642
3.19.2.5.2	Metallocenes	643
3.19.3	Anionic Polymerization of Other Acrylic Monomers	644
3.19.3.1	N,N-Dialkylacrylamides	644
3.19.3.2	(Meth)acrylonitrile	645
3.19.3.3	Vinyl Ketones and Acrolein	646
3.19.4	Anionic Polymerization of Other Polar Vinyl Monomers	647
3.19.4.1	Polymerization of Vinylpyridines	647
3.19.4.1.1	Complexities in anionic polymerization of vinylpyridines	647
3.19.4.1.2	Controlled homo and block copolymerization	648
3.19.4.2	Polymerization of Cyanostyrenes	650
3.19.5	Conclusions	651
References		651

3.19.1 Introduction

The synthesis of polar vinyl polymers of well-defined molecular weight with narrow molecular weight distribution (MWD) draws significant importance due to their wide applications in the areas of mechanical, biological, and materials science and engineering.^{1–7} Polymers with predictable molecular weight and tailored functionalization of chain-ends can be made if a polymerization follows a termination- and transfer-free process and the reactivity of propagating chain-ends remains active for chain extension or for suitable functionalization.⁸ Uniform polymer growth can be ensured when only one type of propagating species is present in the system.⁹ If multiple species exist in a polymerization system, then their dynamics of interconversion should be faster than the rate of propagation to form narrow MWD polymers. These conditions are met perfectly in ionic, especially anionic polymerization and to some extent in recently developed controlled radical polymerization methods.^{10–20}

A good understanding of anionic polymerization of hydrocarbon monomers such as styrene, α -methylstyrene, and dienes (in particular, 1,3-butadiene and isoprene) in apolar and polar solvents has been achieved through numerous kinetic and mechanistic studies.^{21–23} Polar vinyl monomers, on the other hand, exhibited significant challenges associated with side reactions.

3.19.1.1 Types of Polar Vinyl Monomers

α-Olefins with electron-withdrawing substituents are, in general, called polar vinyl monomers (**Figure 1**).^{3,24} The substituents stabilize the anionic chain-end. The most important polar vinyl monomers that are polymerizable via anionic initiators can be classified as (1) alkyl (meth)acrylates, (2) *N*,*N*-dialkyl(meth)acrylamides, and (3) vinylpyridines (**Figure 1**).³ Since some of their polymers, in particular poly (methyl methacrylate) (PMMA), are commercially very important, their polymerizations have been investigated in greater detail with respect to both kinetics and stereochemistry.^{4,7} Other monomers which are anionically polymerizable with limited control over the polymerization are (meth)acrylonitrile, vinyl ketones, (meth)acrolein, vinyl sulfones, and α-olefins or styrene derivatives with other electron-withdrawing groups, such as –NO₂ and –CN.

Polar vinyl monomers that contain labile hydrogen such as (meth)acrylic acid, hydroxyethyl methacrylate, and (meth)acrylamide cannot be used directly for anionic polymerization as they can act as a terminator via proton transfer to the reactive anions. They can be subjected to anionic polymerization only after appropriate protection of these functional groups into nonreactive groups toward anions, for example, by esterification or silylation.^{25–28} A detailed list of protected monomers is given in various reviews.^{23,27}

3.19.1.2 Side Reactions in Alkyl (Meth)acrylate Polymerization

The anionic polymerization of styrene and dienes proceeds in an ideal manner without termination and transfer reactions and the living chain-ends retain their reactivity for further polymerization.^{29,30} However, anionic polymerization of polar monomers often proceeds with side reactions either during the initiation or in the propagation. Early studies on the mechanism of (meth)acrylate polymerization in toluene and in tetrahydrofuran (THF) revealed that a large percentage of initiators did not participate in the polymerization and the MWD of the synthesized polymers was very broad and deviated significantly from the Poisson distribution.^{31–36} The low initiator efficiency was attributed to several side reactions accompanying initiation and propagation (Scheme 1).

The complexities of anionic polymerization of alkyl (meth) acrylates are primarily due to their high reactivity toward anions and their susceptibility to various modes of reaction with anions (Scheme 1). A significant amount of initiator destruction reaction is evident when reactive anions whose nucleophilicity is much higher than that of the chain-end are used for the polymerization.³⁷ Thus, the initiation of alkyl (meth)acrylates with classical initiators like butyllithium (BuLi) is not a straightforward method for initiation as it leads to a broad MWD with a low conversion due to initiator



Figure 1 Some polar vinyl monomers that can be polymerized using carbanions.
(a) Initiator destruction



Scheme 1 Major side reactions in the anionic polymerization of MMA. (a) Initiator attack onto the monomer ester group and (b) backbiting intramolecular termination.

destruction reaction with the carbonyl group of monomers.^{29,38,70} The reaction of the ester carbonyl group in alkyl (meth)acrylates with highly reactive anionic initiators leads to the elimination of a less reactive alkoxide. The reaction of initiator with the carbonyl group of the monomer produces a new monomer, vinyl ketone, and an unreactive alkoxide. The formed vinyl ketone can add to the anionic methacrylate chain-end forming a chain-end with lower reactivity, further complicating the process.^{39,40}

Many authors confirmed the occurrence of several other side reactions experimentally.^{31-33,41-45} Wiles and Bywater^{38,46,47} reported the formation of considerable amounts of lithium methoxide in *n*-butyllithium (*n*BuLi)-initiated polymerization of methyl methacrylate (MMA) in toluene. In all the termination reactions, methoxide expulsion is common. Most of the methoxide is generated during initial stages of the polymerization, that is, by attack of the monomer.^{38,47,48} However, this is also due to the fact that the linear trimer is least sterically hindered to undergo the backbiting reaction (see below). Hatada et al.^{39,40} have detected the incorporation of the initiator fragment in the polymer chain by ¹H NMR by polymerizing deuterated monomer using undeuterated initiator. They found that the polymer and the oligomer of MMA-d₈ produced in toluene using nBuLi as an initiator had about one butylisopropylphenyl ketone unit per chain.^{49–54} The side reaction involved with the initiator can be suppressed if the initiator either resembles the propagating center (i.e., ester enolate) or is sterically hindered for an approach to the ester group (see below).^{55–57}

The reaction of the propagating anion with a carbonyl group of another polymer chain leading to chain coupling is rarely observed. Any such intermolecular chain coupling would lead to a high-molecular-weight fraction in the final product, which has not been detected so far.⁵⁸

The attack of the propagating enolate anion to the antepenultimate ester carbonyl group is the major secondary reaction identified, forming cyclic β -ketoester-terminated polymers.^{41,42,59} The presence of the backbiting reaction producing cyclic β -ketoester in the case of MMA polymerization has been confirmed using IR spectroscopy as a distinct band at

 1712 cm^{-1} (Scheme 1(b)).⁵⁹ In the case of acrylates, the keto group of the backbiting product forms an enol which is immediately deprotonated by a second enolate anion, forming an unreactive cyclic keto-enolate.^{34,35}

Evidence for termination of chain growth by transfer of a hydrogen in α -position to an in-chain ester group to the chain-end of poly(alkyl acrylate)s was seen in some cases where the obtained polymers had olefinic unsaturation.³³

3.19.1.3 Initiators for (Meth)acrylate Polymerization

The reactivity of the initiator and the stabilization of the resulting propagating enolate anions significantly affect the overall kinetics of the polymerization. Therefore, the reactivity of anionic initiators toward polar vinyl monomers and the control of the polymerization are strongly dependent on the choice of initiator and the polarity of the reaction medium.⁷

Any carbanion with nucleophilicity higher or approximately equal to that of the propagating anionic center can be used as initiator in the polymerization of polar vinyl monomers. The pK_a of the corresponding protonated species is a rough measure of nucleophilicity. However, the use of highly reactive carbanions, in particular BuLi, as initiators in the polymerization of alkyl (meth)acrylates and other polar vinyl monomers can lead to side reactions with the polar group of the monomer (see Scheme 1(a)). To suppress the side reactions associated with the polar functionality, sterically hindered and delocalized carbanions are used as initiators in the anionic polymerization of polar vinyl monomers (Figure 2; structures 1-7, and 13-19).³⁷ In addition, ester enolates (Figure 2; 10, 11) and dialkylamides (Figure 2; 12) have been successfully used. The initiation and polymerization are often performed in the presence of ligands to control the kinetics and to produce polymers with narrow MWD. The reactivity of carbanions is governed by several factors such as the type of counter cation with which it is associated, the concentration, the presence of any other associating species, and the polarity of solvent in which the reaction is conducted.^{60–65}

(1) Monofunctional anionic initiators



Figure 2 Various types of anions used as initiators for the anionic polymerization of alkyl (meth)acrylates and other polar vinyl monomers.

3.19.1.3.1 Monofunctional anions

Several resonance-stabilized carbanions have been successfully used for the polymerization of alkyl (meth)acrylates (Figure 2).^{29,36,37,66-84} 1,1-Diphenylhexyllithium (DPHLi), the addition product of *n*BuLi or *sec*-BuLi and 1,1-diphenylethylene (DPE), a nonpolymerizable monomer, has been used as an efficient initiator for methacrylates since it has a matched nucleophilicity and high bulkiness. It produces polymers with controlled molecular weight and moderately narrow MWD in THF at -78 °C (Scheme 2).³⁷ Wiles and Bywater³⁷ used DPHLi for the polymerization of MMA in toluene. Although the polymerization was not controlled, the amount of lithium methoxide formed was lower when compared to the *n*BuLi-initiated polymerization. The same reaction when conducted in polar solvent at -78 °C proceeds in a controlled manner and produced narrow MWD PMMAs.⁸⁵

Reactive macroanions, such as polystyryl anions, also attack the carbonyl group of MMA. This effect was minimized by first adding DPE, leading to a chain-end with reduced nucleophilicity.66,67 Similarly, diphenylmethyl68 and triphenylmethyl69 anions have been used effectively for MMA polymerization. Other nucleophilic anions like $oligo(\alpha-methylstyryl)$ and cumyl anions with sodium or cesium worked efficiently and produced PMMA with narrow MWD.^{70,86-88} Fluorenyllithium was successfully used as initiator in 1,2-dimethoxyethane (DME) at -60 °C for MMA polymerization.⁷¹ However, its initiation is slow compared to propagation. When the fluorenyl anion is used with larger counterions, for example, 9-methylfluorenylsodium, it leads to a higher initiation rate.⁷⁰ Other aromatic-stabilized initiators, such as diphenyl, trityl, and benzyl anions, have been used for the polymerization of polar vinyl monomers.^{29,36,72,73} Grignard reagents have been used as initiators for the controlled



Scheme 2 Initiation of MMA using DPHLi as initiator.

Ester enolates, in particular alkyl α -lithioisobutyrates, were introduced as initiators for MMA polymerization in polar and nonpolar solvents by Lochmann and Lím⁵⁵ and Lochmann *et al.*^{56,57} As these initiators can be considered as a model for the propagating species in the anionic polymerization of alkyl (meth)acrylate, the rate of initiation and propagation was expected to be similar, which, in turn, should lead to polymers with narrow MWD. However, the ester enolate-initiated polymerization of MMA exhibited low initiator efficiency, attributed to the presence of a higher degree of aggregation in both polar and nonpolar solvents.^{48,57}

3.19.1.3.2 Di- and multifunctional anions

Difunctional carbanionic initiators are useful for the synthesis of ABA-type triblock copolymers using sequential monomer addition. The synthesis of difunctional initiator in polar solvent is carried out using the coupling of radical anions resulting from the monomers such as styrene, DPE upon reaction with the sodium, or potassium naphthalide radical anion. Szwarc^{30,89} first used this type of initiators to synthesize homo- and triblock copolymers of styrene and dienes. The synthesis of difunctional initiators in pure hydrocarbon solvent is difficult due to poor solubility. Difunctional organolithium initiators based on 1,3-bis(1-phenylethenyl)benzene (PEB) and *m*-diisopropenylbenzene (DIPB) have been studied thoroughly in the literature.^{74–78} The contributions from eminent groups such as Szwarc, Quirk, Schulz, Fetters, Höcker, and others have significantly enhanced the knowledge in the development of difunctional alkyllithium initiators based on DPE.74-76,90-91

Yu *et al.*^{77,80,81} and Ladd and Hogen-Esch⁷⁹ have developed difunctional initiator from the adduct of DIPB with *sec*butyllithium (*s*-BuLi) or *tert*-butyllithium (*t*-BuLi) for the synthesis of ABA triblock copolymers consisting of polybutadiene and PMMA or polystyrene. These initiators work efficiently in polar solvents. A major problem associated with plurifunctional alkyllithium initiators in hydrocarbon media is their strong aggregation, which makes them insoluble and inefficient for the polymerization. When these initiators are used in nonpolar solvents, it is necessary to have small quantities (~3–10 vol.%) of polar solvents such as THF, diethylether, or triethylamine for complete bifunctional initiation. Hofmans and Van Beylen⁹⁸ have used π -complexing nonpolar additives such as durene and tetraphenylethylene to form hydrocarbon-soluble difunctional initiators for triblock copolymer synthesis.

The formation of difunctional alkyllithium initiator from the adduct of *s*-BuLi and PEB in nonpolar solvent enabled the synthesis of H-shaped polymers, regular combs, centipedes, and barbwires.^{99–104} Quirk and Tsai^{105,106} prepared a trifunctional alkyllithium initiator based on 1,3,5-tris(1-phenylethenyl) benzene and used it for the synthesis of three-arm star polymers in benzene. Three-arm star polymers exhibiting multimodal distributions were obtained due to the intermolecular aggregation of initiator rendering initiation incomplete or slow. The addition of a polar solvent such as THF (THF/Li = 20) to the initiator solution in benzene produced three-arm star polymer with narrow MWD.¹⁰⁷

Matmour *et al.*^{82–84} have used halogen–lithium exchange method to synthesize several soluble multifunctional anionic

initiators. Tri- and tetra-functional aryl carbanions have been prepared and used successfully for the synthesis of star polymers in the presence of alkoxide additive.⁸²

3.19.2 Mechanism of the Anionic Polymerization of Alkyl (Meth)acrylates

Solvent polarity largely affects the reactivity and nature of the propagating species.^{45,108,109} It was shown by Löhr and Schulz^{86,87} and Mita *et al.*¹¹⁰ that the anionic polymerization of MMA proceeds with or without detectable termination in THF at -65 °C using Na⁺ or Cs⁺ as counterions. In nonpolar solvents such as toluene the propagating enolate ion pair aggregates strongly and exists in a slow equilibrium with aggregates of distinctly varying equilibrium constants leading to complex kinetics and gelation.^{111–113} Aggregation is significant even in polar solvents like THF. It is important to modulate the equilibrium dynamics of propagating enolate ion pairs in alkyl (meth)acrylate polymerization using external additives such as Lewis acids or Lewis bases in both polar and nonpolar solvents to obtain proper control of the polymerization. The details will be discussed in the following sections.

3.19.2.1 Polymerization in Polar Solvents

3.19.2.1.1 Propagation via solvated contact ion pairs

First mechanistic investigations of a living polymerization of MMA were published by Roig *et al.*,^{45,109} Löhr and Schulz,^{86,87} and Mita *et al.*¹¹⁰ using sodium, or better cesium, counterions in THF at low temperature. The Mainz group studied the effect of different counterions (Li⁺, Na⁺, K⁺, and Cs⁺)^{70,86,88,114–116} and found a strong dependence of propagation rate constant on the counterion size (except for K⁺ and Cs⁺; **Figure 3**). Their results



Figure 3 Dependence of propagation rate constant on the interionic distance, *a*, in the anionic polymerization of MMA in THF at $-100 \degree C.$ ¹¹⁶ Reprinted with permission from Wiley-VCH.

suggest that the active species involved in MMA polymerization is presumably a contact ion pair.

For larger counterions, like Cs^+ , dissociation into free anions and cations was observed at very low concentrations.^{86,87} However, the dissociation constants are much lower than those of polystyryl ion pairs and the contribution of free anions to polymerization is negligible in most cases, except for [Na⁺,222], that is, the sodium ion encaged by cryptand 222, which has a large interionic distance (see Figure 3).¹¹⁵

Müller showed a linear dependence of the propagation rate constant on the reciprocal interionic distance, *a*, of ion pairs in the anionic polymerization of MMA in THF at -100 °C (**Figure 3**). The deviation of Na⁺ and K⁺ was attributed to a preferential peripheral solvation by THF leading to higher reaction rate than normally expected. The rate constants and the activation parameters of anionic polymerization of MMA in various solvents using different counterions were also determined (**Table 1**).

 Table 1
 Rate constants and activation parameters of the anionic polymerization of MMA in various solvents with different counterions

Counterion	E _a , kJ mol⁻¹	<i>log</i> A	k _p ^{223К} I mol ^{−1} s ^{−1}	References
In THF				
Cs⁺	19.5	7.3	860	88
K+	19.3	7.2	750	116
Na ⁺	18.3	7.0	800	88,117
Li ⁺	24.0	7.4	100	116
In DME				
Cs⁺	15.1	6.8	2680	108
Na ⁺	13.8	6.5	2550	108
Li+	21.4	6.0	16	108
In tetrahydrop	vran (THP)			
Na ⁺	21.5	7.5	480	118
In toluene				
Li+	(23)	(5)	(0.7)	119

Solvent polarity and counterion size largely influence the rate of polymerization and affect the tacticity of the polymers.¹¹² At higher temperatures, in THF the termination reactions gain in importance as indicated by the deviation from first-order kinetics, broadening of MWD, and the generation of alkali methoxide.¹¹⁰

In polar solvent, such as DME using benzyl-oligo-(α -methylstyryl)sodium as initiator, MMA polymerization proceeded without termination reactions. The first-order time-conversion plots were linear even at 0 °C and the obtained PMMA showed narrower MWD when compared with the polymer obtained in THF. Thus, the polymerization of MMA exhibits a good control in polar solvents such as THF and DME.⁸⁷

Glusker *et al.* and Schulz *et al.* suggested that the polymerization is controlled due to the absence of intramolecular solvation of the counterion. In highly solvating media such as DME, the counterion is externally solvated with solvent and thereby intramolecular termination via backbiting reaction is suppressed at low temperature.^{31,32,88,108} It was suggested that only one kind of active species is involved in MMA polymerization, which they assigned as a peripherally solvated contact ion pair (Scheme 3). Solvent-separated ion pairs were not observed due to a much stronger bond between the enolate oxygen and the counterion.

Intramolecular solvated species (a) and (b) facilitate chain termination by backbiting reaction in solvents of low polarity. In solvents of higher solvating power, like DME, the equilibrium shifts toward the solvated ion pair (c). In solvents of medium polarity such as THF, the external solvation of the counterion may exist in competition with intramolecular solvation (a and b). The low amount of termination reaction in DME in comparison to THF was, therefore, attributed to low concentration of structure (b), which is a precursor for the intramolecular termination giving a cyclic structure.

The use of DME as solvent increases the external solvation of the ion pairs, due to its bidentate structure. The rate of polymerization of MMA is high in DME, as compared to THF, when using Na^+ as counterion due to increased interionic



Scheme 3 Intramolecular and peripheral solvation of counterion in MMA polymerization.

distance in the ion pair as a result of the external solvation. However, smaller rate constants are obtained for Li⁺ counterion in DME compared to THF (Table 1). This was attributed to the efficiency of the Li⁺ counterion to strongly coordinate with the enolate anion and to DME, which makes the incoming monomer difficult to displace DME in the solvated contact ion pair, leading to a decreased rate constant of the polymerization.

3.19.2.1.2 Studies on oligomerization of MMA

Ester enolates of alkyl isobutyrates are models of the growth center in the anionic polymerization of MMA. Lochmann *et al.*^{55,120} prepared several alkyl *a*-lithioisobutyrates as models and studied their initiation with MMA. They investigated the decomposition products of lithiated dimer, trimer, and tetramer of MMA in THF at 25 °C.¹²¹ Surprisingly, the lithiated MMA dimer formed cyclic trimer and methyl isobutyrate via a disproportionation mechanism. Lithium *tert*-butoxide (*t*BuOLi) had a pronounced effect on the product distribution of the oligomerization of MMA.^{56,57,122}

The rate constants of polymerization and cyclization and the equilibrium constant of polymerization of MMA were reported by Müller *et al.*⁴⁸ and Lochmann *et al.*¹²³ using methyl α -lithioisobutyrate (MIBLi) as initiator in THF. The rate constants significantly depend on the degree of polymerization (**Figure 4**). The rate constant of the reaction of MIBLi with MMA, k_i , was higher than that of the subsequent propagation steps, k_p . Treatment of MIBLi with an equimolar amount of MMA formed 60% of dimethyl α,α,α' -trimethylglutarate (dimer) along with higher boiling products. Similarly, when 2 mol of MMA react with MIBLi, it was found that cyclic trimers, *cis*- and *trans*-forms of 2,4,6,6-tetramethylcyclohexanone-2,4-dicarboxylic acid dimethyl ester, along with small amounts of dimers and oligomers were formed (**Scheme 4**). Size exclusion chromatography (SEC) eluogram of the oligomeric



Figure 4 Dependence of the rate (k_i) and equilibrium (K_i) constants of polymerization on the chain length (i).⁶⁸ Reprinted with permission from Wiley-VCH.

sample prepared from the reaction of MIBLi and MMA in a flow-tube reactor showed the presence of a large fraction of cyclic trimer. This showed that the effect of penultimate carbonyl coordination of active centers is very pronounced leading to side reactions in the anionic polymerization of MMA.

3.19.2.1.3 Aggregation of enolate ion pairs and their equilibrium dynamics

Alkali enolates do not only exist as reactive ion pairs (peripherally solvated in polar solvents) but also form aggregates of low reactivity, depending on the polarity of the reaction medium as described in the Fuoss–Winstein spectrum.^{60–65,124–126} Even in polar solvents, aggregated ion pairs exist in dynamic equilibrium with nonaggregated ones (Scheme 5). The reactivity and aggregation of an anion is governed by various factors such as the charge density of the anion, the nature of counterion, the interionic distances, the dielectric constant, and the donating properties of the solvent.¹²⁷ The existence of aggregated ion pairs even in solvating media, such as THF, is in strong contrast to the polymerization of nonpolar monomers, where aggregates are only found in nonpolar solvents.

Thus, anionic polymerization of alkyl (meth)acrylates can propagate via aggregated ion pairs of lower reactivity and nonaggregated (unimer) ion pairs of higher reactivity. The dynamics of aggregation/de-aggregation greatly influences the control of alkyl (meth)acrylate polymerization as outlined below.

The rate of an ideal living polymerization process free from termination and transfer reactions should follow pseudo-first-order kinetics. In such a process, the number of active centers, $[P^*]$, remains constant provided the polymerization proceeds with a single active species, or faster interconverting species and the rate of initiation should be faster or at least equal to the rate of propagation, that is, $k_i \ge k_p$:

$$[P^*] = \sum \left[P_i^* \right] = \text{const.}$$
 [1]

Thus, the rate of polymerization has a first-order dependence on monomer concentration and is represented as

$$R_{\rm p} = -\frac{d[M]}{dt} = k_{\rm p} \times [M] \times [P^*] = k_{\rm app} \times [M]$$
^[2]

where k_{app} is an 'apparent' pseudo-first-order rate constant. The integration of eqn [2] gives

$$\ln \frac{[M]_0}{[M]_t} = k_p \times [P^*] \times t = k_{app} \times t$$
[3]

$$k_{\rm p} = \frac{k_{\rm app}}{[P^*]} = \text{const.}$$
 [4]

However, the experimentally measured propagation rate constant, $k_{p,exp}$, of the MMA polymerization for Li⁺ and Na⁺ counterions was found to decrease with increasing concentration of active centers, $[P^*]$ (Figure 5).¹²⁸ The participation of dissociated free enolate ion pairs in the propagation was ruled out as the addition of common ion salt had no significant effect on the rate constants in THF in the concentration range measured. Thus, the behavior was attributed to the coexistence of associated and nonassociated contact ion pairs propagating at two different rates.

Müller *et al.*^{48,128–131} found that the propagation rate constant of associated ion pairs, $k_{a'}$ is much smaller than that of the nonassociated ion pairs, k_{\pm} , in alkyl (meth)acrylate



Scheme 5 Different mesomeric structures of the ion pair and its aggregation in the anionic polymerization of MMA.

polymerization (Scheme 6). The aggregation of chain-ends was further confirmed by quantum-chemical calculations of ester enolates as models of chain-ends.¹⁰³

The apparent rate constant of propagation, k_{app} , is determined by the rate constants of ion pair, k_{\pm} , the associates, k_{a} , and the fraction of nonaggregated species, α (eqns [5]–[7])

$$k_{\text{app}} = [P^*] \left\{ \alpha \times k_{\pm} + \frac{1}{2} \times (1 - \alpha) \times k_a \right\}$$
$$= [P^*] \left\{ \frac{1}{2} \times k_a + \left(k_{\pm} - \frac{1}{2} \times k_a \right) \times \alpha \right\}$$
[5]

and the fraction of nonassociated ion pairs, α , is given^{130,132} by

$$\alpha = \frac{[P_{\pm}^{*}]}{[P^{*}]} = \frac{(1 + 8K_{\rm A}[P^{*}])^{1/2} - 1}{4 \times K_{\rm A}[P^{*}]}$$
[6]

where K_A is the equilibrium constant of association. When the contribution of aggregated chain-ends to the total rate is small, $k_a[(P^*)_2] \ll k_{\pm}[P^*_{\pm}]$, eqn [5] becomes,

$$k_{\rm app} \approx k_{\pm}[P_{\pm}] = \alpha k_{\pm}[P^*] = k_{\pm} \times \frac{\left(1 + 8K_{\rm A} \times [P^*]\right)^{1/2} - 1}{4K_{\rm A}}$$
 [7]



Figure 5 Dependence of the observed propagation rate constant, k_p , on the effective initiator concentration and the equilibrium constants of association, K_A , in the anionic polymerization of MMA using methyl alphasodium isobutyrate (MIBNa) as initiator in THF at -43 °C.¹²⁸ Reprinted with permission from the American Chemical Society.



Scheme 6 Equilibrium between ion pairs and associated ion pair.

For a limiting case of high chain-end concentration, where K_{A} ·[P^*] \gg 1, eqns [6] and [7] become

$$\alpha = \frac{1}{\sqrt{2K_{\rm A} \times [P^*]}} \propto [P^*]^{-1/2}$$
[8]

$$k_{\rm app} = \frac{k_{\pm}}{\sqrt{2K_{\rm A}}} \sqrt{[P^*]}$$
[9]

which leads to a reaction order of 0.5 with respect to $[P^*]$. For low chain-end concentrations, $K_{\Lambda^*}[P^*] << 1$, the aggregated ion pairs disappear ($\alpha \approx 1$) and $k_{app} \approx k_{\pm} \times [P^*]$, leading to a reaction order of unity with respect to $[P^*]$.

In fact, kinetic experiments of polymerization of MMA with lithium counterion in THF at -65 °C showed that the reaction order changes from 0.58 to 0.75 in the concentration range from 2.5 to 0.12 mM,¹³¹ allowing for the determination of k_{\pm} and $K_{\rm A}$ and proving that the aggregation is an important factor in the polymerization of alkyl (meth)acrylates in polar solvent. Further, the fractional reaction order was confirmed by Baskaran¹⁵² who obtained a reaction order of 0.53 for the polymerization of MMA using DPHLi as initiator in THF at 20 °C.

3.19.2.1.4 Effect of dynamics of the association equilibrium on the MWD

The rate of interconversion between associated and nonassociated ion pairs in alkyl (meth)acrylate polymerization has a profound effect on the MWD of the polymer synthesized. Although the reactivity of aggregated lithium enolate chain-ends is much lower than that of the nonassociated ones, a slow rate of the interconversion equilibrium between active species would allow both species to participate in propagation at two different rates. This leads to the formation of two different populations of polymers with a broad or bimodal MWD depending on the dynamics of the equilibrium. Broad or even bimodal MWD was obtained in the polymerization of various (meth)acrylates with lithium counterion at -65 °C (Figure 6). Kunkel et al.¹³¹ attributed the two peaks in the MWD of poly(tert-butyl acrylate) (PtBA) to the propagation of aggregated and nonaggregated enolate chain-ends. They also showed that the high polydispersity is not due to termination but to the slow association phenomena. Figini^{134,135} and others¹³⁶⁻¹⁴² have shown that, for a

Figini^{134,135} and others^{136–142} have shown that, for a two-state mechanism, a slow exchange between various active (or between active and dormant) species leads to a broadening of the MWD as given in eqn [10]:

$$PDI = \frac{M_{w}}{M_{n}} = \left(\frac{M_{w}}{M_{n}}\right)_{Poisson} + U_{ex} \approx 1 + U_{ex}$$
[10]

where U_{ex} is an additional nonuniformity that depends on the rate of exchange relative to the rate of propagation. The excess term, U_{ex} is given by

$$U_{\rm ex} \cong \frac{2\langle n \rangle}{\overline{DP_n}} \tag{[11]}$$

where $\langle n \rangle$ is the average number of monomer additions between two exchange processes, averaged over the whole polymerization process, and DP_n is the number-average degree of polymerization. At a given conversion, *n* is identical to the ratio of the rates of polymerization, *R*_p, and association, *R*_A,¹³¹

$$n = \frac{R_{\rm p}}{R_{\rm A}} = \frac{k_{\pm} \times [M] \times [P_{\pm}^*]}{k_{\rm A} \times [P_{\pm}^*]^2} = \frac{k_{\pm} \times [M]}{k_{\rm A} \times [P_{\pm}^*]}$$
[12]

where k_{\pm} is the rate constant of ion pair, k_A is the rate constant of association, and $[P_{\pm}^*]$ and [M] are the concentrations of active



Figure 6 MWD obtained in the polymerization of MMA (·····, PDI = 1.3), *t*BMA (····; PDI = 1.1), and *t*BA (·····; PDI = 7.9) initiated by MIBLi in THF at -65 °C.¹³¹ Reprinted with permission from Wiley-VCH.

species and the monomer, respectively. Averaging of 'n' over the monomer concentrations up to a given monomer conversion, $x_{p'}$ gives

$$\langle n \rangle = \frac{k_{\pm}}{2k_{\mathrm{A}} \times [P_{\pm}^*]} \times \left([M] + [M]_0 \right) = \frac{k_{\pm} \times [M]_0}{2k_{\mathrm{A}} \times [P_{\pm}^*]} \times (2 - x_{\mathrm{p}}) \quad [13]$$

Introducing $\overline{DP}_n = [M]_0 x_p / [P*]$ and combining with eqn [11] leads to

$$U_{\rm ex} = \frac{k_{\pm}}{\alpha k_{\rm A}} (2/x_{\rm p} - 1)$$
[14]

and eqn [10] becomes

$$\frac{M_{\rm w}}{M_{\rm n}} = 1 + \frac{k_{\pm}}{\alpha k_{\rm A}} (2/x_{\rm p} - 1)$$
 [15]

For full monomer conversion $(x_p = 1)$, eqn [15] becomes

$$\frac{M_{\rm w}}{M_{\rm n}} = 1 + \frac{k_{\pm}}{\alpha k_{\rm A}}$$
[16]

Thus, it is required to have high rates of association and high conversions to obtain polymers with narrow MWD in a polymerization system involving associated and nonassociated active species.

Kunkel *et al.*¹³¹ determined all the rate constants involved in this process for three different monomers. They showed that the broad MWD obtained in the polymerization of *tert*-butyl acrylate (*t*BA) is only due to the fact that both the rate constants of association and dissociation are comparable to those for MMA polymerization, but that the rate constant of propagation is 50 times higher than that of MMA.

The concept of slow equilibria between various active and dormant species was later elaborated in more detail (including nonequilibrium initial conditions) and generalized to other kinds of exchange processes by Litvinenko and Müller.^{132,143–146} These calculations have been useful for understanding various other living/controlled processes, like group transfer polymerization (GTP) and controlled radical polymerization.

3.19.2.1.5 Improved initiating systems for alkyl (meth) acrylate polymerization

Several new initiating systems have been identified in the last two or three decades for the living polymerization of alkyl (meth)acrylates.⁷ There are three main approaches employed

for achieving a living polymerization of alkyl (meth)acrylates, which can reduce the rate of termination, enabling it to work at higher temperatures up to room temperature:

- Use of various σ-type (Lewis base) and μ-type (Lewis acid) ligands that can form complexes with the counterion or with the propagating ion pair. This can lead to faster aggregation dynamics of the ligand-complexed ion pairs.
- (2) Initiators with nonmetal counterions. This class includes Group Transfer Polymerization (GTP) with silyl ketene acetals (silyl ester enolates) as initiators and 'metal-free anionic polymerization' using initiators with, for example, tetrabutylammonium and phosphorous-containing counterions. This suppresses aggregation of ion pairs.
- (3) Coordinative anionic systems involving aluminum porphyrin and lanthanocene initiators. This eliminates the ionic character of the propagating enolate and provides control of the polymerization through coordinative monomer insertion.

All of these initiating systems enhance the livingness of the (meth)acrylate polymerization to varying degrees to suppress secondary reactions and achieve living polymerization that enables manipulations of active chain-ends such as chain extension, block copolymerization, and functionalization. In addition, they moderate the position and the dynamics of the association equilibrium. Some details of the polymerization of (meth)acrylates using these new initiating systems are outlined below. More detailed results were reviewed by Baskaran.⁷

3.19.2.2 Modification of Enolate Ion Pairs with Ligands: Ligated Anionic Polymerization

The equilibrium dynamics of propagating ester enolate ion pairs in alkyl (meth)acrylate polymerization in both polar and nonpolar solvents can be modified favorably in the presence of coordinating ligands. Several new ligands capable of coordinating with either the cation or the enolate ion pairs were reported in the literature (Scheme 7). In general, the coordination of ligands with enolate ion pairs can enhance the rate of interconversion between aggregated and nonaggregated chain-ends and thereby alter the kinetics of propagation



Scheme 7 Various ligands used for the modulation of kinetics through coordination with enolate ion pair in anionic polymerization of alkyl (meth) acrylates. (1) σ -type, (2) μ -type, and (3) σ , μ -type ligands.

and to some extent suppress the side reactions.^{68,73,111,115,133,147–160} Wang *et al.*¹⁶¹ have classified the coordination of ligands with enolate ion pairs into

- σ-type coordination with Lewis bases like crown ethers,^{149,150} cryptands,¹¹⁵ or tertiary amines;^{73,152–154}
- (2) μ-type coordination with Lewis acids like alkali alkoxides,^{162–165} lithium halides,^{131,148,166} lithium perchlorate (LiClO₄),^{111,167} aluminum alkyls,^{156–159} boron alkyls,¹⁶⁰ and zinc alkyls;⁶⁸ and
- (3) σ,μ-type coordination with alkoxyalkoxides,^{133,168–170} aminoalkoxides,¹⁷¹ and silanolates.¹⁷²

3.19.2.2.1 Lewis base (σ -type) coordination

The coordination of σ -type ligands, such as various 'tertiary diamines' (linear and cyclic), and cyclic ethers provides improved living character to alkyl (meth)acrylate polymerization through peripheral solvation depending on the steric factor and the number of coordination sites that are present in the ligand.^{73,152,153} The influence on the propagation and termination reaction varies with the strength of ligand coordination. Anionic polymerization of MMA in the presence of *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA) and cyclic polyamine (1,4,8,11-tetramethyltetraazacyclotetradecane, TMTCT) is known to stabilize the propagating species and in some cases suppress the termination reaction at –20 °C in THF (Figure 7).

The addition of TMEDA was shown to increase the stability of the active centers of MMA polymerization in THF using the monomer resumption method¹⁵³ and in kinetic studies.^{73,152} The reaction order with respect to active chain-ends concentration is 0.5, indicating that chelation of the lithium cation does not effectively perturb the aggregation state of the enolate ion pair (Figure 8).

No significant difference in the rate of the polymerization was observed in the presence and in the absence of TMEDA at -20 °C. It was assumed that the chelation only replaces the THF molecules in the dimeric enolate ion pair retaining the peripheral coordination with lithium during propagation (Scheme 8).



Figure 7 Effect of chelation in MMA polymerization initiated by DPHLi in THF at -20 °C. Experiments were performed using a flow-tube reactor: [DPHLi] 1.4×10^{-3} m l⁻¹, [MMA]₀ = 0.2 m l⁻¹.¹⁷³



Figure 8 Reaction order with respect to initiator concentration for the polymerization of MMA with TMEDA-chelated Li⁺ counterion in THF at -20 °C (■) with TMEDA and (□) without TMEDA.^{73,152} Reprinted with permission from Wiley-VCH.

Pyridine has been used as a ligand. However, if a reactive initiator is used, it can metalate the ligand and further complicate the anionic polymerization. For example, McGrath *et al.* reported that the polymerization of MMA with *n*BuLi in pyridine or in a pyridine–toluene-mixed solvent leads to metalation of pyridine ring which acts as initiator and generates monodisperse PMMA at -78 and -20 °C (Scheme 9).^{85,154,174} ¹H NMR showed the presence of the dihydropyridine end group in the polymer, indicating that the actual initiator is not the alkyllithium but its adduct with pyridine (Scheme 9, A). In THF a hindered alkyllithium initiator must be used to maintain molecular weight control.

Various 'crown ethers' were used as ligands for the Na⁺ counterion in the polymerization of MMA and *t*BA initiated by diphenylmethyl anion in toluene and in THF.^{149,150} The crown ether addition substantially increased the monomer conversion and initiator efficiency and improved the MWD of the resulting PMMA. Although no kinetic studies on this system were performed, it is assumed that the crown ether peripherally solvates the counterion, limiting the possibility of backbiting termination.

Addition of cryptand 222 in the polymerization of MMA with Na⁺ counterion in THF increases the propagation rate constants by orders of magnitude, indicating the presence of ligand-separated ion pairs and free anions.¹¹⁵

Quantum-chemical calculations showed that a variety of structures can be formed by various σ -ligands, including dimers and triple ions.¹⁷⁵

3.19.2.2.2 Lewis acid (µ-type) coordination

Alkali alkoxides have a significant effect on the polymerization of alkyl (meth)acrylates.^{162–165} Lochmann and Müller¹⁶⁴ found that the addition of lithium *t*-butoxide strongly affects the rates of propagation and backbiting termination in the oligomerization of MMA and $tBA^{176,177}$ in THF at +20 °C (**Figures** 9 and 10). For MMA, the rate constant of propagation is decreased by one order of magnitude but the termination rate constant is decreased by two orders. Thus, the enolate-alkoxide adduct has a 10 times lower tendency to undergo termination than the uncomplexed ion pair.



Scheme 8 Aggregation and peripheral chelation of PMMA-Li in the anionic polymerization of MMA in THF.



Scheme 9 Pyridine adduct as initiator for MMA polymerization in THF.



Figure 9 First-order time-conversion plots of the anionic polymerization of *t*BA initiated by *tert*-butyl α -lithioisobutyrate in THF at +20 °C.¹⁷⁷ Reprinted with permission from Wiley-VCH.

In the presence of tBuOLi, cyclization of the tetramer and higher oligomers is so slow that hardly any cyclic β -ketoesters are detected. The addition of tBuOLi in MMA polymerization leads to a higher limiting conversion and thereby enhances the livingness of the active centers facilitating the preparation of block copolymers.^{163,178}

However, although *tert*-butoxide enhances the livingness of polymerization, the MWD of the resulting polymers becomes broader,¹⁷⁷ unless the alkoxide is added in large (10:1) excess.^{179–181} This is explained by the existence of various mixed tetrameric (or higher) aggregates in 3:1, 2:2, and 1:3 ratios of the enolate chain-end and *t*-butoxide, which are in slow equilibrium with each other (Scheme 10). In the 3:1 adduct, the degree of aggregation is even higher than in the noncomplexed dimer. Only in the presence of a large excess of alkoxide the equilibrium is shifted to the side of the 1:3 adduct with only one kind of chain-end.

Until the late 1980s, the controlled polymerization of alkyl acrylates had not been achieved. Incomplete polymerization and very broad MWD (see Figures 6 and 11(a)) were reported. It was assumed that this might be due to both backbiting termination and a transfer reaction between the anion and a hydrogen in α -position to an in-chain ester group. In 1987, Teyssié and his co-workers^{147,182} reported for the first time the



Figure 10 Dependence of the rate constants of propagation, k_i (a), and cyclization, k_{ci} (b), on the chain length (*i*) of the living oligomers in the absence and presence of *t*BuOLi in THF at 20 °C. [MIBLi]₀:[*t*BuOLi]₀ = 1:2:3.¹⁶⁴ Reprinted with permission from Wiley-VCH.



Scheme 10 Equilibria in the polymerization of (meth)acrylates in the presence of tBuOLi in THF.

living anionic polymerization of *t*BA in THF in the presence of an excess of lithium chloride (LiCl), leading to polymers with narrow MWD (**Figure 11(b**)). It was assumed that the beneficial effect of LiCl is due to complexation with chain-ends which suppress backbiting termination.

Kinetic experiments of Müller and co-workers, however, showed that LiCl affects the rate of propagation, but not the amount of termination.^{131,176,177} The observed rate constant of propagation passes a slight maximum and then decreases with increasing LiCl/ $[P^*]$ ratio (Figure 12). Simultaneously, a strong decrease in the polydispersity index was observed with increasing concentration of LiCl. These observations were explained by the formation of 1:1 and 2:1 adducts of differing activity

(Scheme 11). Quantum-chemical calculations confirmed that the 1:1 complex is more stable by 4 kJ mol^{-1} than the noncomplexed dimer.¹⁸³ Whereas the equilibrium between noncomplexed dimer and unimer is slow, it is faster between the dimer and the LiCl-complexed unimer. The inefficiency of LiCl to control termination is demonstrated by the fact that one cannot control the polymerization on *n*-butyl acrylate (*n*BA) with this ligand. However, aluminum alkyls and σ , μ -ligands can lead to a living polymerization (see below).

Various Lewis acids can be used to modulate the dynamic associative equilibrium of enolate ion pairs in alkyl (meth) acrylate polymerization. Baskaran and Sivaram¹¹¹ examined the effect of LiClO₄ using DPHLi initiator at -78 °C in THF



Figure 11 SEC traces of P*t*BA synthesized in the absence (a; PDI = 3.6) and in the presence of excess LiCl (b; PDI = 1.2) in THF using mono-functional α -methylstyryllithium as initiator.¹⁴⁷ Reprinted with permission from the American Chemical Society.



Figure 12 Effect of LiCl on the observed rate constant of polymerization in the anionic polymerization of MMA in THF at –65 °C initiated with MIBLi.¹³¹ Reprinted with permission from Wiley-VCH.

and obtained PMMA with narrow MWD. It was found that the presence of 5 mol of LiClO₄ per mol of DPHLi improved the polydispersity index of PMMA from 1.18 to 1.07. This clearly shows that LiClO₄ perturbs the dynamics of the classical ion pair equilibrium, similar to LiCl. The bi-logarithmic plot of k_{app} versus $[P^*]$ resulted in linearity with a slope of 0.5, similar to the plot in the absence of LiClO₄. However, the obtained rates are lower. The fractional reaction order indicates that the propagating ion pairs exist in equilibrium with associated species in the presence of LiClO₄. The observed lower rate constant, $\bar{k}_{p,obs}$, in the presence of LiClO₄ was attributed to the formation of less reactive mixed aggregates.

The influence of LiClO₄ is also seen in the polymerization of *t*BA in THF at -78 °C. The obtained PtBA in the absence of LiClO₄ had a broad MWD ($M_w/M_n = 2.1$) with low initiator efficiency (0.56) compared to the one obtained in the presence of LiClO₄ ($M_w/M_n = 1.06$) (Figure 13).

3.19.2.2.3 σ-μ-Type coordination

Additives that contain alkoxy and alkoxide functionalities for efficient coordination with propagating enolate ion pairs have been developed by Wang *et al.*¹⁶⁸ as a new class of ligands for the controlled polymerization of alkyl (meth)acrylates in both polar and nonpolar solvents. Alkoxyalkoxides combine advantages of alkoxides (μ -type ligands) and Lewis bases (σ -type ligands) in one molecule. These additives allow a fast and controlled anionic polymerization of methacrylates and even primary acrylates. Since these ligands were mostly used in nonpolar solvents, they are reported in Section 3.19.2.4.2 further below.

Baskaran¹³³ reported the use of dilithium triethylene glycoxide as σ -µ-type ligand to achieve control over the living anionic polymerization of MMA using DPHLi as initiator at 0 °C in THF, resulting in quantitative conversion, relatively narrow MWD and high $(1.29 \le M_w/M_n \le 1.37),$ initiator efficiency $(0.81 \le f \le 1)$. The enhanced living character brought by polydentate dilithium alkoxide ligand was attributed to the formation of sterically hindered mixed aggregates whose equilibrium dynamics between complexed ion pairs and uncomplexed ion pairs is fast enough to produce narrow MWD PMMA at 0 °C. 133,170 The stability of enolate ion pair with $\sigma\text{-}\mu\text{-}type$ ligands is very high as has been demonstrated through a repeated monomer resumption experiment in the presence of bislithium salt of triethyleneglycol in THF at -20 °C (Figure 14).¹³³ The number-average molecular weight of the PMMA increased linearly within more than 1 h, confirming the stability of the complexed enolate ion pairs. The complex structure of the chain-end, involving tetrameric and hexameric aggregates with coordination of the ether oxygens with lithium, was also confirmed by quantum-chemical calculations.¹⁸⁴

3.19.2.3 Metal-Free Anionic Polymerization

3.19.2.3.1 Group transfer polymerization

In 1983, Webster and co-workers¹⁸⁵ at DuPont demonstrated for the first time that a silyl ketene acetal (silyl ester enolate, **Scheme 12(a)**) acts as an initiator for the controlled polymerization of alkyl (meth)acrylates at room temperature. The presence of a small amount of nucleophilic or Lewis acid catalyst is necessary, leading to poly(alkyl methacrylates) with narrow MWD. The process was called GTP on the basis of the proposed mechanism which involves the transfer of the trimethylsilyl group coordinated with a nucleophilic catalyst from the initiator or propagating chain-end to the carbonyl oxygen of the incoming monomer (b). It was proposed that the intramolecular transfer takes place via an eight-member transition state during propagation.

Various nucleophilic anions and Lewis acids have been used as catalysts.¹⁸⁵⁻¹⁹⁶ Lewis acids are believed to activate monomers by coordination with carbonyl oxygen of acrylates, as indicated by the large amount of Lewis acid necessary (10% based on monomer) for the polymerization. Associative and dissociative mechanisms have been proposed depending on



Scheme 11 Equilibria in the polymerization of (meth)acrylates in the presence of LiCl and quantum-chemical (density functional theory) calculations of MIBLi model active center in THF.¹⁸³ Reprinted with permission from the American Chemical Society.



Figure 13 Influence of LiClO₄ on the synthesis of PtBA in THF (1) in the presence of LiClO₄, $M_{n,SEC} = 78\,980$, $M_w/M_n = 1.06$, [LiClO₄]/[DPHLi] = 20, and (2) in the absence of LiClO₄, $M_{n,SEC} = 63\,170$, $M_w/M_n = 2.10$.¹¹¹ Reprinted with permission from the American Chemical Society.



Figure 14 Repeated monomer resumption experiment of MMA polymerization in the presence of bislithium salt of triethyleneglycol using DPHLi as initiators in THF at –20 °C. Time interval between each monomer dose is 20 min.¹³³ Reprinted with permission from Wiley-VCH.

the type of catalyst used for GTP. Nucleophile-assisted GTP involves an enolate anion as intermediate during the propagation. In some cases the nucleophilic catalyst also accounts for an associative mechanism. Taking the presence of enolate anions as active centers into account is important in understanding the propagation of nucleophile-assisted GTP. Brittain and Dicker¹⁹⁷ demonstrated that the side reaction present in the GTP is similar to backbiting, present in the classical anionic polymerization of MMA. They reported a side reaction of terminal silyl ketene acetal onto the antepenultimate carbonyl group leading to displacement of silylmethoxide and formation of the typical cyclic β -ketoester in GTP.

Brittain and Dicker¹⁹⁸ compared the relative rates of propagation and termination for anionic and GTP processes and showed that GTP has a lower propensity to termination versus propagation as compared to classical anionic polymerization. Thus, the extent of termination is very low in GTP, probably due to the large counterions of the catalysts (e.g., *tris*(dimethylamino)sulfonium, TAS⁺) and due to the small amount of catalyst (1 mol.% to initiator) used, leading to a low concentration of chain-ends. Schubert *et al.*¹⁸⁸ found that the polydispersity of PMMA obtained in nucleophile-catalyzed GTP increases with increasing concentration of catalyst (**Figure 15**). The termination reaction in GTP becomes insignificant when catalyst concentration was kept low, but it dominates with increasing concentration of catalyst.

There has been a long discussion on the mechanism of GTP in the literature, which seems to depend on the type of catalyst used for the polymerization.^{187,191,198–205} Double-labeling experiments of Webster and Sogah supported a direct transfer of the pentacoordinated siliconate from a chain-end to the incoming monomer's carbonyl group indicating 'associative' mechanism.²⁰⁶ Kinetic experiments enabled Mai and Müller^{199,202,207} to propose a modified two-stage associative mechanism in which the monomer adds to the α -carbon of pentacoordinated siliconate chain-end and subsequently silyl group migration takes place to the carbonyl oxygen of the monomer.

Quirk^{208,209} proposed a 'dissociative' mechanism where the pentacoordinated siliconate dissociates into an ester enolate anion and the corresponding trimethylsilyl-nucleophile compound. A fast exchange of activity between dormant silyl ketene



Scheme 12 GTP of MMA with a nucleophilic catalyst.



Figure 15 Dependence of polydispersity index, $D(M_w/M_n)$, on the initial catalyst concentration, $C_{c,0}$, in the polymerization of MMA using 1-methoxy-1-trimethylsiloxy-2-methyl-1-propane (MTS) as initiator and TPS.HF₂ as catalyst in THF at 23 °C.¹⁸⁸ Reprinted with permission from Wiley-VCH.

acetal and active enolate chain-ends is required to have a control of molecular weight and narrow MWD. Alternately, if dissociation is irreversible, the free enolate anion can only exchange activity in a direct reaction between an active enolate and a dormant silyl ketene acetal (degenerative transfer; **Scheme 13**).²⁰⁸



 $\label{eq:scheme13} \begin{array}{l} \mbox{Intermolecular activity exchange of an enolate anion with a silyl ketene acetal.} \\ \end{array}$

More importantly, it was found that the reaction order with respect to the catalyst concentration for the GTP of MMA obtained by different research groups varied depending on the nature of catalyst and its concentration.^{187,191,199,202,207} Comparing the experimental data and the calculations of Müller and Litvinenko led to the conclusion that the mechanism of GTP strongly depends on the nature of the nucleophilic catalyst.^{132,143–146,204} Catalysts that bind very strongly to silicon, like bifluoride, seem to undergo an irreversible dissociative (enolate) mechanism, whereas less 'silicophilic' catalysts, like oxyanions, may add via both pathways.

The active centers of GTP of MMA undergo chain transfer reaction with various carbon acids $(18 < pK_a < 25)$,^{200,210} which indicates their higher reactivity analogous to ester enolate active centers $(pK_a \sim 30-31)^{211}$ in the classical anionic polymerization.

More detailed discussions are given in Chapter **3.22** on GTP in this volume²² and also in a number of reviews.^{199,212-216}

3.19.2.3.2 Tetraalkylammonium counterions

Reetz and co-workers^{217–219} first used metal-free carbon, nitrogen, or sulfur nucleophiles as initiators for the controlled anionic polymerization of *n*BA. It was thought that replacing the metal counterion in the polymerization would reduce the problem associated with aggregation and improve the control over the polymerization. Tetrabutylammonium salts of malonate derivatives provided poly(*n*-butyl acrylate) (*Pn*BA) of relatively narrow MWD at room temperature (Scheme 14). Many metal-free initiators for the polymerization of alkyl (meth)acrylates using a variety of anions and cations have been reported (Scheme 15).^{208,220–224}

Baskaran *et al.*²²⁵ studied the effect of nonmetal counterions on the anionic polymerization of MMA. They performed anionic polymerization of MMA in the presence of tetrabutylammonium and tetramethyldiethylguanidinium counterions



Scheme 14 Metal-free anionic polymerization of *n*BA with tetrabutylammonium counterions in THF at 25 °C.



Scheme 15 Various metal-free carbanions used for alkyl (meth)acrylate polymerization.

using 1,1-diphenylhexyl anion as initiator at -40 °C. The polymerization is very fast and the conversion is quantitative within 2 min; however, the obtained polymers had broad/bimodal distribution with low initiator efficiency. Residual initiator color was seen depending on the initiator/monomer concentration indicating a slow initiation process. Bordwell and Fried²¹¹ have also reported a long induction period in the polymerization of MMA initiated with nonmetal-containing initiators. The incomplete initiation was interpreted by considering both an ion-pairing and an initiation equilibrium between the metal-free initiator and monomer (Scheme 16).²²⁵

The apparent equilibrium constant, K_i , for the initiation of alkyl (meth)acrylate monomer follows eqn [17].

$$K_{\rm i} \approx K_{\pm} = \frac{K_{\rm d1}}{K_{\rm d2}} \times K_{-}$$
 [17]

where K_{d1} and K_{d2} are the dissociation constants of the metal-free initiator and metal-free enolate ion pair, respectively, and K_{\pm} and K_{-} are the equilibrium constants for initiation of ion pairs and the free anions, respectively.

The tendency for ion pair dissociation strongly depends on the nature of anion and cation. Thus, K_i should strongly depend on the ion pair dissociation constants of metal-free initiator and the enolate ion pair. The tetrabutylammonium cation is quite large, leading to a larger interionic distance,



Scheme 16 Equilibrium addition of initiator to MMA and their ion-pairing effect.²²⁵

 $a \sim 5-6$ Å, than that of the alkali cation ($a \sim 1.5$ Å). The dissociation constant is exponentially proportional to the interionic distance (log $K_d \sim a$). Thus, K_i for tetrabutylammonium or guanidinium counterions appears to be very low as one expects a higher dissociation constant, K_{d2} for bulky nonmetal enolate (as it is seen for the other system). The presence of residual initiator confirms that the apparent equilibrium constant of initiation is indeed lower compared to propagation. This leads to an incomplete initiation.

3.19.2.3.3 Phosphorous-containing counterions

Zagala and Hogen-Esch²²⁶ introduced tetraphenylphosphonium (TPP⁺) counterion to the anionic polymerization of MMA at ambient temperature in THF and produced PMMA in quantitative yield with narrow MWD. Unlike other metal-free counterions, the polymerization in the presence of TPP⁺ counterion produced narrow MWDs (**Figure 16(a)**). Unexpectedly, the reaction solution during the polymerization was characterized by an orange-red color. A detailed kinetic study of the polymerization of MMA using trityl TPP⁺ showed that the polymerization is very fast (half-lives at room temperature in the seconds range) (**Figure 16(b**)); however, the rate constants are two orders of magnitude lower than expected for such a large counterion.²²⁷

It was concluded that the active centers exist in equilibrium with a dormant species. NMR and UV investigations on the model compound of the growing PMMA chain-end, that is, methyl tetraphenylphosphonium isobutyrate, revealed the existence of a phosphor ylide as dormant species (Scheme 17).²²⁸ This system is different compared to tetrabutylammonium counterion as the phenyl group in the counterion undergoes a nucleophilic attack by the enolate ion and forms an ylide intermediate. The ylide exists in equilibrium with enolate ion pairs. According to the kinetic and spectroscopic data the fraction of active enolate chain-ends is only 1%. The bis(triphenylphosphoranylidene)ammonium (PNP⁺) cation shows a lower tendency for ylide formation and leads to higher rates, 229 whereas the (1-naphthyl)triphenylphosphonium (NTPP⁺) cation has a strong tendency for ylide formation and propagates extremely slowly.230



Figure 16 (a) SEC eluograms at different times during the polymerization of MMA using PPh₄ counterion in THF. $[M]_0 = 0.2 \text{ mol } |^{-1}$, $[I]_0 = 10^{-2} \text{ mol } |^{-1}$. (b) First-order time-conversion plots at -20, 0, and +20 °C for the anionic polymerization of MMA in THF using PPh₄ as counterion. $[M]_0 = 0.2 \text{ mol } |^{-1}$, $[I]_0 = 5.2 \times 10^{-3} \text{ mol } |^{-1}.^{227}$ Reprinted with permission from the American Chemical Society.



Scheme 17 Dynamic equilibrium between ylide, enolate ion pair, and enolate anion.

A phosphorous-containing cation that cannot form an ylide, the tetrakis[*tris*(dimethylamino)phosphoranylidenamino]phosphonium (P_5^+) counterion, showed fast polymerization with half-lives in the 0.1 s range, and the rate constants are in the expected order of magnitude due to the absence of dormant ylide formation.²³¹ Figure 17 shows how



Figure 17 Arrhenius plot for the polymerization of MMA in THF with various counterions: (----) Li⁺; (-----) Na⁺, K⁺, Cs⁺; (•) Ph₃C⁻TPP⁺; (**n**) Ph₃C⁻PNP⁺; and (\triangle) DPH⁻P₅⁺.^{229,231} Reprinted with permission from Wiley-VCH.

these large counterions fit into the Arrhenius plot obtained with various metallic counterions, the cryptated sodium ion and the free anion. Quantum-chemical calculations have confirmed the ylide structure of various phosphorus-containing counterions.²³²

3.19.2.4 Polymerization in Nonpolar Solvents

In nonpolar solvents the anionic polymerization of alkyl (meth)acrylates is complicated by the slow dynamics of the equilibria between multiple aggregates of ion pairs leading to very broad MWDs.¹⁰⁸ In addition, it leads to more isotactic polymers, which have much lower glass transition temperatures than syndiotactic ones. Thus, a controlled polymerization has only been possible in the presence of ligands.

The ability of LiClO₄ in moderating the polymerization of MMA in toluene/THF (9:1, v/v) mixed solvent was shown using DPHLi as initiator at different temperatures.¹¹¹ In the absence of LiClO₄, the polymerization process at –78 °C is complex as evident from the formation of gel phase. The soluble portion of PMMA exhibited that the $M_{n,SEC}$ is less than that of $M_{n,cal}$ with broad MWD ($M_w/M_n = 2.8$) (Figure 18(a)). It was later confirmed that the formation of the gel phase is dependent on the initiator concentration.²³³ However, the usefulness of LiClO₄



Figure 18 SEC traces of PMMA synthesized in the presence (b) and in the absence (a) of LiClO₄ in toluene/THF (9:1, v/v) mixed solvent at $-78 \,^{\circ}C.^{111}$ Reprinted with permission from the American Chemical Society.

in improving the reaction, even in solvents of such a low polarity, was shown by the absence of gel phase during the polymerization and the formation of PMMA with narrow MWD ($M_w/M_n = 1.1$) (Figure 18(b)). The presence of Lewis acid ligand alters the dynamics of the equilibria between non-associated, associated, and ligand-complexed ion pairs and controls the polymerization process.^{131,176,177}

3.19.2.4.1 μ-Type coordination

Hatada and co-workers^{156,234–238} first employed various aluminum alkyls, in particular triethylaluminum, Et₃Al, as additive and *t*-BuLi as initiator in the polymerization of MMA in toluene at –78 °C. They obtained syndiotactic polymers with controlled molecular weight and rather narrow MWD. The complexation of the aluminum compound with the initiator as well as the propagating center is essential to have a proper control of the polymerization. Ballard and his co-workers¹⁵⁷ demonstrated the living nature of MMA polymerization at ambient temperature in the presence of bulky diaryloxyalkylaluminum. NMR and quantum-chemical investigations^{239–241} on the model active center (i.e., ethyl α -lithioisobutyrate, EIBLi) in the presence of MMA and trialkylaluminum confirmed the coordination of the aluminum to the ester oxygen in the dimer of the lithium enolate. The mechanism is complicated by the fact that Et₃Al also forms complexes with the carbonyl groups of the monomer and the polymer. In addition, other carbonyl groups can coordinate with free coordination sites of the lithium atoms (Scheme 18). This leads to a physical gel at higher conversion and a downward kink in the time-conversion plot.²³⁰

Schlaad et al.^{158,242} used several Lewis bases to attach to the free coordination sites of the lithium ion, thus suppressing the network formation during polymerization. Linear first-order time-conversion plots with higher rates and polymers with much narrower MWD were obtained in the presence of excess methyl pivalate and methyl benzoate. A further improvement was the use of tetraalkylammonium halides as additives, forming a complex with trialkylaluminum, for example, $NBu_4^+[Al_2Et_6Br].$ They observed linear first-order time-conversion plots using EIBLi as initiator in the presence of high concentration of $NBu_4^+[Al_2Et_6Br]$. The rate of the polymerization is two orders of magnitude higher as compared to the EIBLi/AlEt₃ initiating system in toluene/methyl pivalate (3:1 v/v) mixed solvent.^{159,243} At low concentrations of NBu₄⁺[AlEt₆Br], the MWD of PMMA is bimodal at low monomer conversion and becomes narrow for higher monomer conversion. Moreover, the first-order time-conversion plots at lower concentration of NBu₄⁺[AlEt₆Br] show an upward curvature indicative of a gradual increase in k_{app} at lower monomer conversion and become linear at higher monomer conversion (Figure 19).²³⁰ Similarly, cesium halides can be used as coligand.²⁴⁴ This system combines the advantages of a nonpolar solvent (toluene), convenient temperatures (-20 °C) with easily controllable rates (minutes to hours), and very narrow MWD (PDI < 1.1).



Scheme 18 Structures of intra- and intermolecular coordination leading to a coordinative network of living polymer chains in the presence of Et₃AI.²⁴¹



Figure 19 First-order time-conversion plots of MMA polymerization at -20 °C with EIBLi/NBu₄⁺[Al₂Et₆Br]⁻ in toluene at different concentrations of NBu₄⁺[Al₂Et₆Br]⁻. [EIBLi]₀ = 0.44 × 10⁻³ mol I⁻¹; [NBu₄Br]/ [AlEt₃] = 0.5/1.1 (\blacktriangle), 1.2/2.5 (•), 6.9/15.0 (•) mol I⁻¹; and [MMA]₀ = 0.23 mol I⁻¹.²³⁰ Reprinted with kind permission from the American Chemical Society.

The rather complex kinetics of the process were attributed to an equilibrium between the trialkylaluminum–enolate complex (or its dimer) (Scheme 19(a)), a trialkylaluminum– halide–enolate 'ate' complex with tetrabutylammonium counterion (Scheme 19(b)), and a tetraalkylammonium trialkylaluminum enolate (Scheme 19(c)).^{241,243}

This system is also useful for the controlled polymerization of *n*BA below -65 °C, in particular when using cesium fluoride/triethylaluminum as ligand.^{244,245} Primary acrylates had eluded a controlled anionic polymerization so far, except for the use of lithium alkoxyalkoxides as σ , μ -ligands (see below).

Ihara *et al.*^{246,247} reported the use of triisobutylaluminum in combination with potassium *tert*-butoxide for the living anionic polymerization of *t*BA and MMA in toluene at 0 °C.

The triethylaluminum system was further modified by Kitayama's group who revived the Ballard system of bulky diphenoxyalkylaluminum ligands and found that these systems lead to a very high control of stereoregularity.^{248–250} A further improvement was obtained by Hamada *et al.* at Kuraray company by adding multidentate σ -ligands, like DME, to these systems, allowing for the living polymerization of MMA and even *n*BA at 0 °C.^{251–254} At present this system seems to be the most useful one to polymerize *n*-alkyl acrylates in a controlled way. Kuraray is now marketing a PMMA-*block*-PnBA-*block*-PMMA thermoplastic elastomer, 'KURARITY[®]', based on this process.

3.19.2.4.2 σ-μ-Type coordination

Polydentate lithium alkoxyalkoxides and aminoalkoxides as well as dilithium alkoxyalkoxides have been used as powerful additives in the alkyl (meth)acrylate polymerization in nonpolar medium.^{133,151,168,170,171,255} In the presence of these ligands, living polymerization of even primary acrylates proceeded in a controlled manner in THF, in toluene, and in toluene-THF (9:1 v/v) mixed solvent at $-78 \, ^{\circ}\text{C}$.²⁵⁶ The rate of MMA polymerization in the presence of lithium 2-methoxyethoxide (LiOEM) in toluene is extremely high ($k_p > 10^4 1 \, \text{mol}^{-1} \, \text{s}^{-1}$).¹⁷⁰ The polymerization proceeds with half-lives in the subsecond range without termination at 0 °C (Figure 20).

The MWDs of the PMMAs are quite narrow with quantitative monomer conversion which is remarkable considering the relatively high temperature used for the polymerization $(M_w/M_n = 1.1 \text{ at } -40 \text{ }^{\circ}\text{C} \le T \le 0 \text{ }^{\circ}\text{C})$ (Figure 21). The high rates of polymerization in the presence of σ -µ-type coordinated ligand in such a low polar medium, toluene or toluene-THF (9:1 v/v), are similar to the polymerization performed in pure THF with cryptated counterions. These rates are higher than those obtained with lithium counterion in toluene without additive by three orders of magnitude, which suggests that there may be 'ligand-separated' ion pairs participating in the polymerization.

The polymerization of *n*BA is also living at -20 °C in the presence of LiOEM in toluene. The polymerization is so fast (half-lives in the range of a few milliseconds) that it can only be controlled in a flow-tube reactor.¹⁷⁰

The polymerization of MMA involving alkoxyalkoxides has been commercialized by Arkema (former Elf-Atochem) to synthesize polystyrene-*block*-polybutadiene-*block*-PMMA (Nanostrength[®]) where the PMMA block is synthesized in a flow-tube reactor.²⁵⁷

3.19.2.5 Coordinative Anionic Initiating Systems

3.19.2.5.1 Aluminum porphyrins

Kuroki and his co-workers²⁵⁸ found that methylporphyrinatoaluminum (TPP)AlMe initiates the living polymerization of alkyl (meth)acrylates upon irradiation by visible light (Scheme 20). The polymerization was simply performed by exposing the reaction mixture containing MMA and (TPP)AlMe (100:1 ratio) to visible light and terminating the reaction after 12 h by adding methanol. PMMA was obtained in quantitative conversion and with narrow MWD ($1.06 < M_w/M_n < 1.2$).

The effect of light is observed not only in the initiation step but also in the propagation steps. NMR studies confirmed that the polymerization proceeds via a concerted mechanism, where the MMA coordinates with the aluminum atom leading to







Figure 20 First-order time-conversion plot for the anionic polymerization of MMA ($[M]_0 = 0.2 \text{ mol } I^{-1}$) initiated by DPHLi ($[I]_0 = 10^{-3} \text{ mol } I^{-1}$) in toluene at 0 °C in the presence of different amounts of LiOEM.¹⁷⁰ Reprinted with permission from the American Chemical Society.



Figure 21 SEC of PMMA synthesized in the presence of LiOEM additive. Reaction time is given in milliseconds. Experimental conditions: T = -20 °C; $[I]_0 = 10^{-3} \text{ mol I}^{-1}$; $[M]_0 = 0.2 \text{ mol I}^{-1}$, $[LiOEM]/[I]_0 = 5$ in a 95/5 toluene/THF solution.¹⁷⁰ Reprinted with permission from the American Chemical Society.

conjugate addition of the methyl group of the initiator to monomer to form an aluminum porphyrin enolate (Scheme 20). The aluminum porphyrin enolate once again coordinates with MMA and propagation occurs through a repeated Michael addition process. Visible light accelerates this initiation and propagation to yield quantitative conversion.

Lewis acids such as methylaluminum diphenolates and trialkyl- and triarylaluminum compounds also accelerate the polymerization of methacrylic esters via aluminum porphyrin enolate (Figure 22). The acceleration effects of trialkylaluminum in the polymerization of *tert*-butyl methacrylate (*t*BMA) and MMA were attributed to monomer activation and suppression of aluminum porphyrin degradation presumably through steric repulsion between the bulky porphyrin ligands and the Lewis acid.^{259–263} More details can be found in reviews by Aida²⁶⁴ and Sugimoto and Inoue.²⁶⁵

3.19.2.5.2 Metallocenes

Metallocenes with various rare earth central atoms, such as $((C_5Me_5)_2SmH)_2$ or the complexes derived from $(C_5Me_5)_2Yb$



Scheme 20 Aluminum porphyrin-initiated MMA polymerization.



Figure 22 Rate acceleration in the presence of trimethylaluminum for the polymerization of *t*BMA (a) and MMA (b) initiated using (TPP)AIMe.²⁵⁸ Reprinted with permission from the American Chemical Society.

(THF)₂₁ show high catalytic activity in the polymerization of MMA in toluene between 40 and -78 °C, leading to syndiotactic PMMA with narrow MWD.²⁶⁶⁻²⁶⁸ The living nature of the chain-ends at room temperature was demonstrated by monomer resumption experiments. The living MMA dimer was crystallized and X-ray diffraction showed that the samarium central atom is coordinated with the enolate oxygen of the chain-end and to the carbonyl group of the penultimate monomer unit. The proposed mechanism assumes that the lanthanide complex coordinates with the carbonyl group of MMA and transfers hydride or an alkyl group to the α-carbon forming an intermediate that coordinates with the incoming monomer and propagates (Scheme 21). Later, it was shown that a living polymerization of acrylates can also be obtained.²⁶⁹ More details can be found in a review by Yasuda.²⁷⁰ Zirconocenes have also been used as initiators for the polymerization of (meth)acrylates.^{271,272} A review was published by Chen.273

3.19.3 Anionic Polymerization of Other Acrylic Monomers

3.19.3.1 N, N-Dialkylacrylamides

Polymers of mono- and dialkylacrylamides are gaining increasing interest due to their thermoresponsive properties in aqueous solution.^{274,275} However, the anionic polymerization of N,N-dimethylacrylamide (DMAAm) and

N,*N*-diethylacrylamide (DEAAm) in polar and nonpolar solvents using alkyllithium initiators is complicated due to the presence of slow aggregation dynamics of the propagating amido enolate ion pairs similar to ester enolate ion pairs in alkyl (meth) acrylate polymerization. Attempts were made to use different initiators in combination with coordinating ligands to control the polymerization, and only minimum control on molecular weight, MWD, and the stereostructure of the polymers was obtained.^{276–280}

Major advances were reported by Nakahama et al. for the anionic polymerization of DMAAm and DEAAm by the use of organolithium and organopotassium initiators in the presence of Lewis acids (Et₂Zn, Et₃B, and Et₃Al) in THF.^{279,281-283} A great influence of the systems consisting of a particular type of initiator/additive/solvent on the tacticity and the solubility of the resulting polymer was clearly demonstrated. The authors suggested that the coordination of the amidoenolate with the Lewis acid leads to a change of the stereostructure of the final polymer along with the retardation of the polymerization. Highly isotactic PDEAAm was obtained by using LiCl with organolithium initiator whereas highly syndiotactic and atactic polymers were obtained in the presence of Et₂Zn or Et₃B. Polymers rich in syndiotactic triads are not soluble in water, whereas other microstructures lead to hydrophilic polymers.²⁸² Ishizone et al. reported the successful synthesis of PtBA-b-PDEAAm in THF at -78 °C. For that purpose, tBA was first initiated by diphenylmethylcesium in the presence of Me₂Zn, and DEAAm was then initiated by the PtBA-Cs macroinitiator leading to a well-defined block copolymer $(M_{\rm w}/M_{\rm p} = 1.17).^{68}$

André *et al.*²⁸⁴ performed kinetic studies on the polymerization of DEAAm in THF in the presence of triethylaluminum at –78 °C. The kinetics of this process is very complex. It involves two equilibria: activation of monomer and deactivation of chain-ends by Et₃Al. In addition, Et₃Al interacts with the monomer amide groups and with THF. All these effects are in a delicate balance that depends on the ratio of the concentrations of Et₃Al, monomer, and chain-ends. However, the initiator or blocking efficiencies of these systems remained low (f < 0.70). Quantum-chemical calculations on up to trimeric models confirm the various equilibria involved.²⁸⁵ Et₃Al-coordinated, solvated unimers are the most stable species in the presence of Et₃Al, whereas unimers and dimers coexist in the absence of ligand.

Only one example was reported recently by Kitayama and Katsukawa²⁸⁶ for the polymerization of DMAAm in toluene. Living character was observed using a system based on *t*-BuLi/*bis*(2,6-di-*tert*-butylphenoxy)ethylaluminum in toluene at 0 °C. Well-defined block copolymers PDMAAm-*block*-PMMA



Scheme 21 Polymerization of MMA using samarium complex as initiator.

could be obtained in good yield but no kinetic studies were performed.

Due to their acidic proton, the direct anionic polymerization of *N*-monoalkylacrylamides such as *N*-isopropylacrylamide (NIPAAm) is not possible. By using *N*-methoxymethyl-substituted NIPAAm, Ishizone and Ito²⁸⁷ synthesized well-defined polymers using organopotassium initiator in the presence of Et_2Zn , but no living character was described. Tabuchi *et al.*²⁵⁰ used *N*-trimethylsilyl-substituted NIPAAm to obtain highly isotactic polymers, but no MWDs were shown due to the poor solubility of the resulting polymers in common solvents. However, these promising methods have opened new synthetic strategies to polymerize *N*-monosubstituted acrylamides with the advantages of anionic polymerization.

It is important to note that *N*,*N*-dialkyl methacrylamides such as *N*,*N*-dimethylmethacrylamide do not undergo anionic polymerization under various reaction conditions. This strange behavior is attributed to an insufficient stabilization of the propagating amidoenolate. However, some strained cyclic-substituted monomers such as *N*-methacryloyl-2-methylaziridine and *N*-methacryloylazetidine undergo anionic polymerization and produce controlled molecular weight polymers with narrow MWD in the presence of LiCl or Et₂Zn in THF.²⁸⁸ It appears that the polymerizability is dependent on the nature of substitution at the nitrogen. **Table 2** shows a list of linear alkyl- and cyclic alkyl-substituted alkyl

 Table 2
 Polymerizability of some *N*,*N*-dialkyl methacrylamides via anionic polymerization



methacrylamides and their anionic polymerizability. It is believed that the nonplanar conformation of the strained ring at the nitrogen in the monomer plays an important role in anionic propagation of these alkylacrylamides. The substitution effect at the amide nitrogen and its influence on the aggregation dynamics of propagating ion pair have not been thoroughly studied in these systems.

3.19.3.2 (Meth)acrylonitrile

The polarization of π -electrons in (meth)acrylonitrile is substantially high due to the strong negative inductive effect of the cyano group. Thus, (meth)acrylonitrile can be initiated by weak bases or nucleophiles, like alkoxides.²⁸⁹⁻²⁹² The polymerization of acrylonitrile (AN) requires to be performed in a highly polar solvent such as dimethylformamide (DMF), DMAC, or DMSO in order to keep the growing polyacrylonitrile (PAN) soluble in the polymerization medium.^{289,293} The synthesis of highmolecular-weight PAN is very essential for carbon-fiber production. However, the solubility of high-molecular-weight PAN is limited in its monomer and the polymerization reaction needs to be conducted in aprotic polar medium where PAN is soluble. The limited solubility of PAN in its monomer restricts the effective use of free radical-initiated suspension or emulsion processes. Moreover, the interaction of electron-deficient propagating free radicals of PAN with basic solvents also limits the molecular weight of the polymer in classical radical polymerization. Thus, the anionic polymerization of AN is thought to be a method of choice for high-molecular-weight PAN synthesis. However, the complexities associated with side reactions in anionic initiation and propagation of AN (see below) prevented so far the realization of synthesizing high-molecular-weight polymers via anionic polymerization. 289,294

Alkali metal containing initiators such as nBuLi, alkoxides, and malonates as well as trivalent phosphorus compounds have been used for (meth)acrylonitrile polymerization (Scheme 22). Polymerization of AN using metal alkyls in hydrocarbon solvents proceeded with severe side reactions such as proton, hydride transfer, and nitrile addition. As the polymerization is conducted in polar solvent such as DMF, highly reactive initiators, such as nBuLi, react with solvent and the resulting adduct, dimethylamino-n-butyl-lithium methoxide, acts as an initiator for the polymerization of AN. Aldler and co-workers²⁹⁵ observed that the reaction order for the polymerization of AN using the nBuLi-DMF adduct as initiator is dependent on the concentration of the initiator at low temperature. This indicated that some portion of the initiator remains in cross-association with the propagating anions during the polymerization. Moreover, the presence of various transfer reactions restricts the controlled polymerization of AN and generally produces a partial conversion with a low initiator efficiency. 296-299

Other initiators that have been used for AN polymerization include trivalent phosphorous compounds; dialkylaminotitanium, allyl molybdenum, and tungsten compounds; and metal-free ammonium salts of malonates and carbazolides.^{220,293,295,300–303} All of these initiators produce PAN less efficiently with varying degrees of molecular weight and MWD control. The side reactions can be classified as given in

(i)
$$R^{\Theta}Mt^{\oplus}$$
 + $n CH_2 = CH \xrightarrow{I} DMF, RT or -30 °C R + (CH_2 - CH) + CH_2 - CH^{\Theta}Mt^{\oplus} \xrightarrow{I} CH_2 - CH^{\Theta}Mt^{\oplus}$

 $R = (C_2H_5OOC)_2CH^-, (CH_3)_2N-CH(nBu)O^-, RO^-$

(ii)
$$R_3P + {}^{n}CH_2 = CH \xrightarrow{P} R_3P + CH_2 - CH \xrightarrow{P} CH_2 - CH$$

 $R = (C_2H_5)_3P, (C_2H_5O)_3P$



(a) Hydride transfer

$$R + \begin{pmatrix} CH_2 - CH_2 - CH_2 - CH_2 & H_2 \\ I \\ CN & I \\ CN & CN & CN \end{pmatrix} \xrightarrow{R_{tr}} R + \begin{pmatrix} CH_2 - CH_2 - CH_2 & H_2 - CH_2 \\ I \\ CN & H_2 & H_2 \\ CN & H_2 & H_2 \\ Hydride transfer & H_2 & H_2 & H_2 \\ H$$

(b) Solvent addition



(c) Cyclization



Scheme 23 Side reactions involved in anionic polymerization of AN.

Scheme 23. The propagating anion can undergo termination via transfer to monomer and react with solvent or monomer via protonation. Depending on the type of solvent used, solvent molecules can react with the propagating anions. Another form of side reaction is chain transfer via inter- and intramolecular cyclization to produce yellow coloration.

The side reactions such as chain transfer and transformation of the propagating carbanion to an inactive imino anion can be reduced through the use of trivalent phosphorous compounds as initiators, for example, trialkyl phosphites or phosphines. These compounds are mild bases and do not participate in proton abstraction reaction; they initiate AN through a zwitterion mechanism. The addition of phosphites or phosphines to the monomer generates a zwitterion, which acts as a propagating active center in the polymerization (Scheme 22). However, the association of the phosphonium cation with the propagating anion reduces the rate of propagation selectively in the initial stages of the polymerization, resulting in a broad MWD of PAN.²⁹³ Tetraalkylammonium halide can be added to the zwitterion-mediated polymerization of AN to change the chain-end association and to convert the counterion into

ammonium in the polymerization.³⁰⁴ Among the various trivalent phosphorus initiators, triethylphosphite initiates AN in DMF producing high-molecular-weight PAN useful for spinning fibers without appreciable control in molecular weight and MWD.²⁹³

3.19.3.3 Vinyl Ketones and Acrolein

Methyl vinyl ketone (MVK) and acrolein are reactive polar vinyl monomers that undergo anionic polymerization with severe side reactions. Although anionic polymerization of these monomers has advantages, they have never been polymerized in a controlled manner through ionic initiators, the reason being the high reactivity of ketone or aldehyde pendant groups that undergo side reactions with the initiator, propagating center, and inter/intramolecular cyclization leading to an uncontrolled polymerization with low conversion and broad MWD.

Only few attempts have been made to polymerize MVK through anionic polymerization.^{305,306} The polymer produced exhibited a large amount of hydroxyl group as a result of

(1) Poly(methyl vinyl ketone) intramolecular cyclization



(2) Polyacrolein intramolecular cyclization



Scheme 24 Intramolecular cyclization reactions in the anionic polymerization of (1) MVK and (2) acrolein.

base-catalyzed inter- and intramolecular allyl condensation to form cyclic ketone with hydroxyl functional group (Scheme 24). Nevertheless, the synthesis of stereoregular poly(vinyl ketone) has been reported using LiAlH₄ or Zn(*i*-C₄H₉)₂ as initiator.³⁰⁷

The polymerization of acrolein using radical and cationic initiators generally produces cross-linked and insoluble polymers with low conversion.³⁰⁸⁻³¹⁰ The pendant aldehyde group is highly sensitive to nucleophilic attack, though acrolein can be polymerized using anionic initiators to produce soluble polymers under appropriate conditions.^{308,310,311} The complexity of the polymerization arises with the nucleophilic attack of either anionic initiators or the propagating enolate chain-ends at the carbonyl groups of monomer or the polymer chain. Moreover, the reactive proton in the monomer is susceptible to transfer during the polymerization that limits the formation of high-molecular-weight polyacrolein.

The highly reactive acrolein monomer can undergo polymerization via an attack of the vinyl group (1,2- or 1,4-addition) or the aldehyde group (3,4-addition) (Scheme 25).^{308,311} The mechanism is complex and the mode of monomer addition appears to depend on the stabilization of the propagating anions and their aggregation dynamics. The participation of enolate anions in the propagation leads to 1,4-addition. The conformation of all these modes of addition has been observed through NMR analysis of the oligomers obtained in anionic polymerization of acrolein using t-BuLi as initiator in THF at low temperature.^{312,313} New methods using ligands to modulate the reactivity of anions in the polymerization of these reactive monomers have not been attempted so far.

3.19.4 Anionic Polymerization of Other Polar Vinvl **Monomers**

3.19.4.1 Polymerization of Vinylpyridines

2-Vinylpyridine (2VP) and 4-vinylpyridine (4VP) belong to a class of polar vinyl monomers that are important in many applications due to the ability of their polymers to form complexes of the electron-rich pyridine ring and to form polyelectrolytes through protonation or quaternization with alkyl or aryl halides. In early 1961, Natta et al.³¹⁴ reported the synthesis of stereospecific poly(2-vinylpyridine) (P2VP) using phenylmagnesium halides and dialkylmagnesium in toluene. The obtained P2VPs were isotactic in nature and insoluble in acetone. The stereospecificity was lost when dialkyl amides and alkyllithiums were used as initiators. These ionic initiators produce noncrystallizable amorphous polymers. Natta et al. attributed the stereospecificity in the reaction to the coordination ability of 2VP with counter cations during the propagation. Alkali metals have lower ability to form coordination with the monomer compared to magnesium.³¹⁴ The reactivity of metal alkyls is too high for vinylpyridines, complicating the anionic polymerization.

3.19.4.1.1 Complexities in anionic polymerization of vinylpyridines

Complications arise from a strong electron-accepting character of vinylpyridines that leads to the formation of complexes with anions during initiation and propagation. Due to their high electron affinity, vinylpyridines can undergo secondary reactions with propagating anions during initiation and propagation. Earlier reports suggested that an electron transfer





1.4-addition

Scheme 25 Different forms of monomer addition in the anionic polymerization of acrolein.



Scheme 26 Side reactions (a and b) and cross-association (c) in anionic polymerization of 2VP.

to 2VP during initiation with reactive carbanions could generate a dimeric anion and a nitranion through the participation of pyridine ring in the polymerization.^{315,316} The presence of side reactions in the anionic polymerization of vinylpyridine has been reported in both polar and nonpolar solvents (Scheme 26).^{317–320} A major side reaction associated with vinylpyridines is the attack of anions to the pyridine ring of either monomer or polymer (Scheme 26(a) and (b)).³¹⁹ Cross-association of the initiator with the propagating poly (vinylpyridine) anion is a problem (Scheme 26(c)) when less reactive anions are used as initiators in hydrocarbon solvents.^{317,318}

The extent of these side reactions in the polymerization depends on the reactivity of the initiator, temperature, and solvent. The addition of the propagating carbanion onto the pyridine ring was reported in a sequential block copolymerization of 2VP with polydienyl and polystyryllithium chain-ends in nonpolar and polar solvents.³¹⁹ A large fraction of branched polymer was obtained in benzene, and gel formation was noticed in THF. The delocalization of electron density in the pyridine ring stabilizes the propagating anions (Scheme 27) helping to reduce side reactions in the polymerization. Association of the initiator with the propagating anions is known in the case of magnesium counterion in toluene.^{321,322}

The problem in the case of 4VP is to find a suitable solvent for the polymerization as the solvents that are generally used for anionic polymerization such as benzene, toluene, THF, and even the monomer are nonsolvents for high-molecular-weight poly(4-vinylpyridine) (P4VP).

3.19.4.1.2 Controlled homo and block copolymerization

The polymerization of 2VP was successfully carried out without any side reactions in polar solvents using disodium

 α -methylstyrene tetramer dianion.³²³ Sterically hindered carbanions with electron-delocalizing substitution can suppress side reactions during initiation and enable one to prepare well-defined poly(vinylpyridine)s. Isotactic poly(vinylpyridine)s can be prepared using magnesium-containing initiators in nonpolar solvents.³¹⁸

Fisher and Szwarc³²³ and Shimomura and co-workers³²⁴ found that the rate constant of propagation of 2VP in the presence of sodium as counterion in THF increases with decreasing concentration of living anions, $[P^*]$ (Figure 23), similar to the polymerization of styrene in THF. The dependence of $k_{p,app}$ was found to increase linearly with the reciprocal square root of the living chain-end concentration, $[P^*]^{-1/2}$, which indicates the presence of an equilibrium of ion pairs and free anions. The obtained rate constant for free ions, k -, is comparable to that of styrene polymerization. On the other hand, the propagation rate constant of the ion pairs is much larger $(k_{+} = 2100 \,\mathrm{l}\,\mathrm{mol}^{-1}\,\mathrm{s}^{-1})$ when compared with styrene polymerization ($k_{\pm} = 80 \, \text{lmol}^{-1} \, \text{s}^{-1}$). This behavior was attributed to a loose intramolecular association of the sodium counterion with the lone electron pairs of nitrogen atoms of the adjacent rings (Scheme 28). The polymerization of 2VP using DPHLi as initiator in THF proceeds in a controlled manner at low temperature.

Hubert *et al.*³²⁵ showed that the polymerization of 2VP proceeds without termination and transfer reactions using DPHLi as initiator in a nonpolar solvent such as toluene at 20 °C (Figure 24). Although the stabilization of the propagating anion should decrease its reactivity, here again, a high propagation rate constant ($k_p = 640 \, l \, mol^{-1} \, s^{-1}$) was observed when compared to styrene polymerization under similar condition. This was attributed to a high reactivity of the monomer toward nucleophilic addition. Unlike styrene







Figure 23 Plots of $k_{p,obs}$ vs. $1/[P^*]^{1/2}$ for sodium P2VP anions in THF (\circ , \Box) at 25 °C; (Δ) at 0 °C; (x) at -20 °C; and (\bullet) at -60 °C.³⁰⁸ Reprinted with permission from the American Chemical Society.



Scheme 28 Solvation states of P2VP chain-ends in polar and nonpolar solvents.



Figure 24 First-order time-conversion plot of anionic polymerization of 2VP using DPHLi at 20 °C in toluene at different initiator concentrations. [I]₀/(mol Γ^{-1}) = 11 (*), 5.9 (**■**), 1.6 (**□**), 1.0 (•), and 0.35 ($^{\bigcirc}$).³²⁵ Reprinted with permission from Wiley-VCH.

polymerization in nonpolar solvents, the reaction order with respect to initiator was close to unity indicating absence of aggregated species in the polymerization. The support for the presence of only one type of propagating species also came from conductivity measurements of the polymerization solution in THF which showed smaller values compared to the living polystyryllithium solution.^{326,327} The kinetics of the polymerization of 2VP and the spectroscopic studies of model compounds of propagating centers suggest that the counterion is intramolecularly complexed with the nitrogen of the adjacent or penultimate rings of pyridine units that act as solvated ion pairs (Scheme 28(b)).^{322,326,328} Thus, the kinetics of 2VP is controlled by intramolecularly solvated ion pair with free anions in THF.

The stabilization of chain-ends is critical in forming block copolymers from vinylpyridines. This is mainly because of the side reactions involving the –N=C– unit of the aromatic ring

with the propagating polymeric anions leading to branching. In general such secondary reactions can be controlled by using bulky stabilized anions for initiation such as DPHLi and conducting the polymerization in a polar solvent, like THF, at low temperature. To avoid broadening of the MWD of the resulting poly(vinylpyridine)s, it is important to control the rate of polymerization by conducting the polymerization at low temperature; otherwise, one has to mix monomer and initiator faster than the half-life of the polymerization. The polymerization of vinylpyridines at higher temperature leads to uncontrolled molecular weight and broad MWD. However, it has been shown that the controlled polymerization can be achieved at higher temperatures (0 °C) in THF mixed with strongly interacting polar cosolvents such as pyridine, DMF, and hexamethylphosphortriamide (HMPT).³²⁹ These polar solvent mixtures stabilize the monomer and the propagating species through coordination and enhance the solubility of poly(vinylpyridine)s, especially P4VP.³³⁰

The high solubility of P2VP and the side-reaction-free nature of the polymerization using appropriate initiators in THF allow one to prepare successful block copolymers with other monomers at -78 °C. Di- and multiblock copolymers of 2VP with styrene, MMA, ethylene oxide, and n-hexyl isocyanate have been prepared. 331-335 The poor solubility of P4VP restricts controlled homo and block copolymerization of 4VP in pure THF though low-molecular-weight polymers have been successfully synthesized at -78 °C. Creutz and co-workers³³⁶ reported the homo and block copolymerization of 4VP at 0 °C in pyridine mixed with THF (10% v/v). They developed a new solvent composition to characterize the homo and the copolymers of 4VP by SEC. The use of DMF, trimethylamine, and pyridine in 8:1:1 volume composition avoids adsorption of polymer on the SEC column.336 Block copolymerization with tBMA using living P4VP lithium or potassium proceeds in a controlled manner in THF with pyridine- and HMPT-containing solvents at -78 and 0 °C, respectively, resulting in P4VP-block-PtBMA with narrow MWD.329 However, the reverse addition of monomer, that is, block copolymerization of 4VP, with living chains of PtBMA anions produces diblock copolymer with contamination of some unreactive homo-PtBMA in pyridine-containing solvent at 0 °C.330,336 This is due to the lower nucleophilicity of polymethacrylate chain-ends. Block copolymers produced at a low temperature in THF/DMF mixed solvent produced broad MWD $(M_w/M_n = 1.5)$, indicating the presence of side reactions.³²⁹ These reports revealed that the residual unreactive PtBMA anions are reactive for further growth with tBMA monomer. A high reactivity of *t*BMA with respect to the 4VP chain-ends was attributed to be the reason for this behavior at $0 \circ C.^{336}$

Another approach for the stabilization of propagating poly (vinylpyridine) anions is through the interaction with LiCl ligand.³³⁷ Quirk and Corona-Galvan³³⁷ have demonstrated the synthesis of well-defined polyisoprene-*block*-P2VP diblock copolymer using LiCl as ligand with propagating polyisopropenyllithium anions (PILi) in benzene at 8 °C. The side reaction associated with the pyridine ring was completely suppressed in the presence of LiCl ([LiCl]/[PILi] = 5–15) in benzene. Thus the stabilization of living chain-ends of vinyl-pyridines using coordination with polar organic solvents and inorganic ligand in nonpolar solvents is essential for successful block copolymerization.

3.19.4.2 Polymerization of Cyanostyrenes

Cyano-substituted styrenes are among the most highly reactive monomers, which are difficult to polymerize in a controlled manner using anionic initiators. The high reactivity of cyanostyrenes is attributed to the strong electron-withdrawing ability of the cyano group on the aromatic ring, which delocalizes the π -electron of the vinyl bond. More importantly, highmolecular-weight polymers are not soluble in THF at low temperatures. The effect of cyano groups on the stabilization of propagating anions depends on the position of cyano-substitution which, in some cases, renders the species unstable and unreactive. The problem associated with the controlled anionic polymerization of various substituted cvanostyrenes in THF at -78 °C can be attributed to (1) intramolecular attack of propagating anions on the cyano group in the case of ortho-cyanostyrene and (2) formation of stable resonance-stabilized propagating anion coordination with lithium counterion and cyano group in the case of meta-cyanostyrene. However, this side reaction and resonance stabilization, which render unstable and nonreactive the propagating species, do not occur in the anionic polymerization of 4-cyanostyrene (4CNS) (Scheme 29).

The anionic polymerization of 4CNS was achieved using specially built reactors under high vacuum condition. It is difficult to avoid rapid auto-polymerization after purification of 4CNS. In order to overcome the solubility problem, Driva *et al.*³³⁸ used *N*,*N*-dimethylacetamide (DMAc), a good solvent for P4CNS, as a cosolvent in THF and obtained controlled polymers using DPHLi as initiator. However, Ishizone *et al.*^{27,339–341} showed that the anionic polymerization of 4CNS in THF at -78 °C is feasible. Although high-





3.19.5 Conclusions

The mechanisms of anionic polymerization of nonpolar and polar monomers are now well understood and an increasing number of monomers are available to be used in a living/ controlled fashion, for example, primary acrylates, the polymerization of which had eluded control for more than 30 years. A number of important applications exist in science and nanotechnology: block copolymers with poly(meth)acrylate and poly(vinylpyridine) blocks have been used extensively, taking advantage of the self-assembly of these polymers for structuring bulk materials and thin films²⁷⁴ and to form micelles and vesicles in solution.^{342,343} These self-organized nanostructures can be used to generate a large number of multicompartment nanoparticles, which will be reviewed in Chapter 3.20 of this volume.³⁴⁴ The first commercial applications are emerging, though not for the mass market. examples PS-block-PB-block-PMMA being (Nanostrength[®]) and PMMA-block-PnBA-block-PMMA (KURARITY®). The lack of large-scale products may be partially due to the necessity of intensive purification of all reagents and low temperatures in some cases. Also, the number of accessible monomers is limited. Anyway, the possibility to construct complicated polymer structures in a well-defined way has inspired theoreticians and experimental physicists for more than 50 years now.

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3.20 Industrial Catalysts for Alkene Polymerization

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3.20.1	Catalysts for Polyolefin Production	657
3.20.1.1	Introduction	657
3.20.1.2	Mechanism of Metal-Catalyzed Polymerization	658
3.20.1.3	Processes to Produce Polyolefins	659
3.20.1.4	Polyolefin Product Market Overview	661
3.20.2	Historical Development of Commercially Practiced Alkene Polymerization Catalysts	661
3.20.2.1	Standard of Indiana Catalyst	661
3.20.2.2	Phillips Chromox Catalyst	661
3.20.2.3	Titanium Ziegler–Natta Catalysts for Polyethylene	661
3.20.2.4	Titanium Ziegler–Natta Catalysts for Polypropylene	662
3.20.2.5	Vanadium Catalysts for Making EPDM Rubber	662
3.20.2.6	Organochrome Catalysts	663
3.20.2.7	Metallocene Catalysts: Harbingers of the Future	663
3.20.2.8	MAO: The Kaminsky Activator and Single-Site Catalysis	663
3.20.2.9	Metallocene Catalysts: The Significance of Substitution	664
3.20.2.10	'Noncoordinating' Anions: Alternative, Discrete Activators	664
3.20.2.11	The CpSiNR Ligand for Constrained Geometry Catalysts	664
3.20.2.12	Commercialization of Metallocene Catalysts	665
3.20.2.13	Other Single-Site Catalysts	666
3.20.3	Global Polyolefin Catalyst and Product Markets	667
3.20.3.1	Polyolefin Market Overview	667
3.20.3.2	Polypropylene Applications	667
3.20.3.3	Polyethylene Applications by Catalyst	668
3.20.3.3.1	Chrome catalyst applications	668
3.20.3.3.2	Ziegler-Natta catalyst applications	669
3.20.3.3.3	Metallocene/single-site catalyst applications	669
3.20.3.3.4	EPR and EPDM applications	669
3.20.3.4	Catalyst Demand by Product Type	670
3.20.3.4.1	Catalyst demand for PP	670
3.20.3.4.2	Catalyst demand for HDPE	670
3.20.3.4.3	Catalyst demand for LLDPE	670
3.20.4	Conclusion	671
References		671

3.20.1 Catalysts for Polyolefin Production

3.20.1.1 Introduction

The polymerization of alkenes, or olefins, has created one of the most important classes of materials for modern society: polyolefins. With their low cost, efficient manufacture, chemical inertness, and ability to make thermoplastic or thermoset materials with a wide range of properties, polyolefins have become the predominant polymers in use today. Since the middle of the twentieth century, transition metal catalysts have been central to the discovery and development of polyolefins. For the purposes of this discussion, polyolefins will be defined as polymers of ethylene, propylene, and higher linear α -olefins. The development of the commercial catalysts used to form polyolefins will be addressed, while styrenics and diene-based materials will not be covered.

The first commercial polyolefin arrived with Imperial Chemical Industries's (ICI) production of free-radicalpolymerized, low-density polyethylene (LDPE) in the 1930s. The process was carried out in supercritical ethylene at extreme pressures and produced polymer chains with a hyperbranched structure due to free radical rearrangements. The plastic flowed very easily as a result of the long-chain branching, had modest strength properties, and due to the branching was significantly less dense than the theoretical maximum for polyethylene (PE), thus the 'low density' label. It is the material against which later polyolefins would be judged.

In the 1950s, almost two decades after the launch of LDPE, transition metal catalysts proved capable of producing unbranched linear low density polyethylene (LLDPE) and linear 'high-density' polyethylene (HDPE), both of which had significantly different properties from LDPE. Remarkably, the discovery occurred nearly simultaneously in three different research groups using three different catalyst systems. First was Standard of Indiana's reduced molybdate on alumina catalyst in 1951,¹ followed by Phillips with chromium oxide on silica ('chromox') catalysts,² and Ziegler's titanium chloride/ alkylaluminum halide systems³ in 1953 (only the latter two were widely commercialized). At about the same time, crystal-line polypropylene (PP) was produced in the Phillips labs

using a chromium catalyst as well as in the Natta and Ziegler labs using the titanium halide catalysts.^{1,2,7} The linear PE and highly crystalline PP are both higher melting and tougher than their LDPE predecessor and gave rise to entirely new markets which are now larger globally than any other polymer. All these transition metal-catalyzed polymerization systems were characterized by low alkene pressures (hundreds of psi vs. tens of thousands for high-pressure LDPE), broadened molecular weight distributions (MWDs), the absence or strong reduction of the long-chain branches (LCBs) characteristic of high-pressure PE, and the ability to incorporate other 1-alkenes to produce copolymers.

3.20.1.2 Mechanism of Metal-Catalyzed Polymerization

While the detailed mechanism of chain propagation may vary from system to system, most if not all are now believed to proceed by the Cossee–Arlman⁴ mechanism in which an olefin monomer undergoes a concerted insertion into a metal– polymer chain bond via a 4-center transition state (Figure 1). Several fundamental steps describe the process. Initiation occurs when a metal center is transformed so that it is bonded to a group via a metal–carbon sigma bond. Propagation occurs when olefins insert into this metal–carbon bond, extending the chain. Spontaneous termination of the polymer chain occurs when a hydrogen on the β -carbon of the chain migrates to the

Initiation/activation - A metal-carbon bond capable of inserting an olefin is created at the (usually cationic) metal center

M-X $\xrightarrow{alkylating agents, activators}$ M^+ X = e.g., halide, alkoxide, etc. R = e.g., methyl, hydride, ethyl, etc.

Propagation/chain growth - Olefins insert into the metal-carbon bond (Cossee - Arlman transition state shown)



Here R = methyl R' = H (ethylene), butyl (hexene), etc.

Spontaneous termination/Beta-hydride elimination - creates unsaturated chain end



Chain transfer to hydrogen - creates saturated chain end



Chain transfer to aluminum - creates saturated chain end after hydrolysis



P = polymer chain

Chain transfer to monomer - creates unsaturated chain end



Figure 1 Mechanistic steps common to chain-growth olefin polymerizations.

metal creating a metal hydride. The metal hydride can reinitiate polymer growth by inserting an olefin to form a new metalcarbon sigma bond. The polymer chain thus produced has an unsaturated end group. Polymer chain transfer can also occur to hydrogen, aluminum alkyls, or even monomers, ending chain growth and reinitiating the sequence to new polymer chain growth. Deactivation occurs by reaction with poisons or by thermal decomposition of the catalyst center.

From the attention generated by Ziegler and Natta's 1963 Nobel Prize and the understanding based on the 1964 Cossee-Arlman mechanism, the subsequent several decades saw generations of refinements to the Ziegler-Natta system; the advent of vanadium catalysts, some 'single sited', for the production of ethylene propylene copolymers (EPMs) and ethylene propylene diene copolymers (EPDMs), which are both widely used as rubbers; the discovery of organochromium catalysts for HDPE; and the introduction of slurry loop and gas-phase heterogeneous process technology. In the early 1980s, the field was again revolutionized by Kaminsky's discovery of the methylalumoxane (MAO) activator that led to single-site behavior and phenomenal activities for metallocene catalysts. Others, particularly Exxon, Fina, and Hoechst, soon showed that systematic variation of the metallocene structure leads to exquisite control of polymer structures and, consequently, the polyolefin properties. While MAO has an undetermined polymeric structure, discrete 'noncoordinating' anions (NCAs) of known structure stabilize metallocene cations and, therefore, produce equally active catalysts.^{10,17,18} An additional advantage of the NCAs is the elimination of the need for the high aluminum to transition metal ratios required by MAO. Bercaw's linked cyclopentadienylamide ligands were shown by Dow (constrained geometry catalysts) and Exxon to give high activity when bound to titanium (see below). While these two catalyst systems, metallocene and constrained geometry, long seemed unique in giving defined, single-site PE, numerous nonmetallocene catalyst systems have been developed in the 1990s, some of which have become commercially viable in PE, EP, and PP applications. The uniting feature of these metal catalyzed systems is the hypothesis that a metal-carbon bond is formed in which olefins can repeatedly insert, creating polymers by a chain-growth mechanism.

3.20.1.3 Processes to Produce Polyolefins

There are two classes of polymerization processes: (1) heterogeneous processes in which the polymer grows as a solid particle below its melting point and is suspended in a liquid or gaseous diluent that contains polymerizable monomers, and (2) homogeneous processes in which the polymer grows as a molten or dissolved material in a homogeneous liquid or supercritical medium containing polymerizable monomers. Heterogeneous processes require a solid catalyst, often created by supporting the catalyst on a template such as amorphous silica particles so that the polymer grows as a well-defined granule with a shape determined by the template. Heterogeneous processes, also called 'particle form' processes, must be operated below the softening point of the polymer product so that the growing granules do not stick together, forming a solid mass that forces a process shutdown. Advantages of these processes are ease of separation of the polymer product from diluents and monomers leading to lower energy costs and lower capital costs due to the lower pressures associated with low-temperature operations. Because supported catalysts tend to have lower activities than catalysts in solution, the reactors are usually very large and have long residence times of an hour or more. Heterogeneous processes can be classified into slurry processes and gas-phase processes. The commercially significant slurry processes are slurry loops and stirred-tank reactors. Gas-phase processes are either fluidized-bed or stirred-bed reactors. Of these, the fluidized bed gas-phase processes can be scaled to the largest size, with a single reactor capable of producing 600 kt of polymer per year (Figures 2 and 3).

Homogeneous processes consist of stirred-tank solution reactors and supercritical stirred autoclave and tubular reactors. Homogeneous processes must be run above the crystallization points of the polymer products which often require high temperatures and pressures, which in turn translate to the need for thicker steel walls on the reactors. This increases cost and limits the size of the reactors. Stirred-tank reactors are usually run in series and can have large production capacities. An advantage of homogeneous processes is higher catalyst activities and shorter residence times, which facilitates making changes between polymer grades with minimal 'off spec' material. Homogeneous processes are also easier to model and predict from lab-scale experiments. Supercritical PE requires extremely high pressures, for example, 40 000 psi, and so results in high capital cost equipment (Figures 4 and 5).

While polyolefins are sold based on the performance of the polymer products, the product's properties are determined by the catalyst type and process conditions used to make them. The final properties may in turn determine which processes can be used for commercial production. For example, highly amorphous polymers such as ethylene propylene rubber (EPR) or very low-density PE (VLDPE) generally must be made in homogeneous processes because the soft materials would



Figure 2 Gas-phase heterogeneous polymerization process.



Figure 3 Slurry-phase heterogeneous polymerization process.



Tubes are several in. dia. and 500–1200 m long Make 40–200 Kta (Kilotons per annum)

Figure 4 High-pressure homogeneous polymerization process.





Autoclaves can be 1 ft dia. and 8–10 ft long Make 20–100 Kta, <1 min residence time



Stirred tanks can be large Make 70–400 Kta, 5–10 min residence time

Figure 5 Solution homogeneous polymerization process.


Figure 6 Plastics market share by volume. Source: CMAI global.

agglomerate into a solid mass in the particle form (heterogeneous) gas-phase or slurry polymerization processes.

3.20.1.4 Polyolefin Product Market Overview

The global market for thermoplastic resins have reached over 175 million metric tons annually. Polyolefins now comprise more than half of this total because of their excellent performance at low cost (Figure 6). Their applications are growing faster than Gross Domestic Product (GDP) rates as these materials enable new applications and displace costlier, more resource-intensive materials such as engineering plastics, metal, paper, and wood in existing applications. A more detailed account of the properties of various classes of polyolefins will be given later in the chapter.

3.20.2 Historical Development of Commercially Practiced Alkene Polymerization Catalysts

3.20.2.1 Standard of Indiana Catalyst

The first 'low-pressure' PE catalyst invented,¹ the Standard of Indiana catalyst system, saw relatively little commercial practice. Their 1951 patent discloses reduced molybdenum oxide or cobalt molybdate on alumina for ethylene polymerization, preferably in aromatic solvents. Later work concerning the use of promoters was also disclosed.¹ At least one plant was built to use the catalyst, but the process was not competitive with those that followed it.

3.20.2.2 Phillips Chromox Catalyst

Impregnation of chromium oxide into porous, amorphous silica-alumina followed by calcination in dry air at 400–800 °C produces a precatalyst that presumably is reduced by ethylene during an induction period to form an active polymerization catalyst (Figure 7).² Other supports such as silica, alumina, and titanium-modified silicas can be used and

together with physical factors such as calcination temperature will control polymer properties such as molecular weight. The precatalyst can be reduced by CO to an active state. The percent of metal sites active for polymerization, their oxidation state, and their structure are the subject of debate. These so-called 'chromox' (also CrO_x) catalysts are highly active and have been licensed extensively by Phillips for use in a slurry loop process. While most commonly used to make HDPE, they can incorporate α -olefins to make LLDPE. The MWDs of the polymers are very broad with polydispersity index (PDI) greater than 10 compared to a PDI = 2 for polymer produced by a single-site catalyst. The catalysts are very sensitive to air, moisture, and polar impurities.

3.20.2.3 Titanium Ziegler–Natta Catalysts for Polyethylene

For their work in the discovery of a new class of highly active catalysts for polymerization of ethylene, propylene, and dienes, Karl Ziegler and Guilio Natta shared the 1963 Nobel Prize in Chemistry. Today, these catalysts together with the Phillips catalyst are responsible for the majority of the world's PE production. Loosely defined, 'Ziegler-Natta catalysts' are polyolefin catalysts derived from transition metal halides and main group metal alkyls.^{1,5–8} In modern usage, this generally means titanium (and sometimes vanadium) chlorides with aluminum alkyls and/or alkylchlorides. Numerous large research and commercialization efforts have progressed titanium-based systems through five or six generations, particularly for isospecific propylene polymerization. Most early systems used titanium halides with aluminum metal or aluminum alkylhalides to produce some form of crystalline TiCl₃, usually the α form, often with Al within the chloride layer lattice. The Ti centers could be in +3, +4, and even +2 oxidation states. Aluminum alkyl cocatalyst was required for activity. In the next generation, large increases in activity were achieved by dispersing the titanium chloride centers over a solid MgCl₂ layer lattice, and this is now standard commercial practice.

Silica or other porous supports may be used to introduce these catalysts into heterogeneous processes. As with most heterogeneous systems (e.g., organochrome and chromox catalysts), there are multiple active sites, which may only be a fraction of the total metal centers. The exact structure and number of active sites are usually a topic of debate due to the problem of extremely active catalysts: they must be used in extremely low concentration and usually cannot be detected directly at 'real world' conditions. Multiple sites lead to PE and PP chains with varying structures from chain to chain, though the typical molecular weight polydispersity indices of 3.5–6 for Ziegler–Natta catalysts are still much narrower than that for the chromox PE catalysts. Some PE producers, for example, Dow and Nova, use these catalysts in solution processes, but most of the PE volume and essentially all PP volume comes from



Figure 7 Formation of a chromium oxide catalyst.

supported catalysts due to their use in the heterogeneous gas-phase PE processes extensively licensed by Univation (originally Union Carbide) and Ineos (originally British Petroleum), the slurry PP processes licensed by Lyondell-Basell (formerly Montell) and Ineos (formerly BP-Amoco), and the slurry PE processes licensed by Mitsui and others. These catalysts are substantially less sensitive to air and moisture than chromium-based systems. Polymer molecular weight can be reduced by the addition of H_2 , and α -olefin comonomers (predominantly butene and hexene) are copolymerized with ethylene enabling a very wide range of densities and molecular weights.

3.20.2.4 Titanium Ziegler-Natta Catalysts for Polypropylene

Natta's finding, that high-molecular-weight (HMW), highly crystalline PP could be produced by titanium catalysts has led to the development of arguably the highest performance industrial catalysts known. Propylene is polymerized with high regio- and stereospecificities (Figure 8) leading to highly regular chains that form helices in crystalline domains with melting points over 165 °C. The configuration in which the stereocenters with the methyl side branches are all of the same *meso* configuration is termed isotactic and results in high melting point and reasonably fast crystallization kinetics.

The first generation of catalysts utilized Stauffer Chemical Company 'AA-TiCl₃' produced from aluminum reduced TiCl₄. Because the catalyst activities and isotacticities of the polymers were not high, the polymer had to be washed to remove atactic, amorphous polymer and catalyst residues (deashing). While in PE production silica has been the primary support used to disperse catalyst and create a template for the growth of polymer granules, magnesium chloride was found to be the best support for PP catalysts. The morphology of the catalyst particles is controlled by catalyst synthesis conditions aided by the use of 'internal donors' such as benzoate esters, phthalate esters, certain diethers, and, more recently, succinates (Lyondell-Basell). The thus formed spherical particles are activated with aluminum alkyl cocatalysts and treated with 'external donors,' typically silvlethers such as tetraethoxysilane or dimethoxydicyclopentylsilane, to enhance iso selectivity, increase activity, and otherwise modify the catalyst performance. Productivities can be on the order of 100 000 g PP g⁻¹ catalyst with stereo errors less than 1% so that no extraction of atactic polymer or catalyst residue is required. It is quite remarkable that more than 1000 insertions of PP can occur per second with fewer than 1% errors in selecting the very indistinct enantio face of the propylene monomer. Because the growing polymer particles templated by the MgCl₂ support are inherently porous, they can be conveyed into a gas-phase reactor under ethylene/propylene

atmosphere to produce EPR, creating a low-cost blend of isotactic PP (iPP) and EP known as impact copolymer (ICP). The ICP copolymers have wide use in the automotive industry to make light parts that retain their structural integrity over a high-temperature range due to the iPP and can absorb impacts without breaking due to the EPR.

3.20.2.5 Vanadium Catalysts for Making EPDM Rubber

Natta and Ziegler found early on that vanadium halides could be treated with aluminum alkyls to form catalysts competent for alkene polymerizations. A variety of simple precursors in various oxidation states, for example, VCl₃, VCl₄, and VOCl₃. can be treated with aluminum alkyl halides to produce active catalysts. Unlike the titanium and chromium systems, the vanadium catalysts can be single sited with narrow MWDs and more importantly narrow composition distributions. Also unlike the other systems, vanadium incorporates α -olefins at rates somewhat slower but comparable to ethylene. For this reason, vanadium catalysts are used commercially to make EPMs and EPDMs that can have at least 50 mol.% ethylene with the balance being predominantly other olefins and much smaller amounts of diolefins (Figure 9).

The distribution of the monomers is nearly random, with the product of observed reactivity ratios for the α -olefin and ethylene encompassing a small range of about one. At molecular weights of higher than 30 000 Da, these copolymers are elastomers and can be vulcanized by known methods such as peroxide curing to form crosslinked rubbers. Cyclic dienes such as 5-ethylidene-2-norbornene (ENB) and dicyclopenatdiene (DCPD) are incorporated into the polymers at low levels to allow for later sulfur or resin induced crosslinking to form an alternate EPDM rubber. The double bond in the strained five-membered ring is quite reactive and readily inserts into the growing polymer chain, leaving the unstrained, sterically crowded, and less-reactive double bond available for postreactor vulcanization. On the other hand, 5-vinyl-2-norbornene (VNB) is used in very low levels because both the strained double bond and the pendant vinyl group are incorporated into the growing polymer chains, creating in-reactor crosslinks, which can lead to precipitous increases in molecular weight and gelling. An attribute of these elastomers compared to



Figure 9 Cyclic dienes.



Figure 8 Polypropylene tacticity

natural rubber is that EPM and EPDM rubbers are environmentally stable because they have saturated backbones. Because the materials begin to flow at room temperature, they would agglomerate in typical gas-phase and slurry heterogeneous processes leading to mass fouling of the impellers and the walls. Solution polymerization with refrigeration to remove the heat of polymerization is the most widely used method of manufacture, though a novel method of manufacture using carbon black as a partitioning agent has been practiced in a gas-phase reactor. Catalyst activities are low enough to require deashing of the polymer to remove both the vanadium and the attendant aluminum compounds. The need for refrigeration as well as de-ashing and recovery of the polymer from solution adds significant cost to the products. ExxonMobil has taken advantage of the single-sited nature of these catalysts to run them under living conditions in a tubular reactor with a plug flow regime since 1983. The reactor has zones of different monomer concentrations such that one polymer chain is produced per vanadium center and the polymer chains have tapered block copolymer structures. EPR and EPDM have found uses in automotive industry under the hood applications, weather seals, roofing membranes, electrical insulation, and oil viscosity modifiers. Commercial producers of EPDM rubber and their associated brand names are ExxonMobil (Vistalon[™]), Dow (Nordel[™]), Mitsui (Tafmer[™]), DSM (Keltan[™]), Lanxess, and Jilin petrochemicals.

3.20.2.6 Organochrome Catalysts

Like the Phillips 'chromox' catalysts, the organochromium catalysts introduced by Union Carbide in the 1970s required an oxide support. Both disilyl chromates, $(R_3SiO)_2CrO_2$, Figure 10, and chromocenes, $(C_5H_5)_2Cr$, Figure 11, are believed to bond to an oxo functionality on the support, ultimately leading to Cr^{2+} species. How these form the active species and its nature remain unproven. These catalysts have been licensed extensively in gas-phase processes, but only for HDPE production because of negligible comonomer incorporation ability. MWDs are broad, and hydrogen lowers molecular weight by chain transfer. These systems are very sensitive to impurities as with the Phillips catalyst.

3.20.2.7 Metallocene Catalysts: Harbingers of the Future

While some commercial solution catalysts (e.g., vanadium halide/alkyl aluminum EPDM systems) exhibited single-site behavior (e.g., PDI=2) earlier, metallocenes ushered in well-understood, finely tunable single-site polymerization capability on a far broader scale. Metallocenes are molecular transition metal compounds containing the flat cyclopentadienyl ring bound 'side-on' to the metal center. Shortly after their discovery in the 1950s, it was known that metallocenes could polymerize or oligomerize olefins in the presence of aluminum alkyl cocatalysts. By the 1970s, it had been found that small amounts of water increased the system's activity.^{3,9,10} Around this time, Ballard at ICI showed that unactivated, neutral group 3 metallocenes could polymerize olefins to HMW with narrow MWDs.^{11,12} Despite these many works demonstrating most of the major characteristics of the current state of the art polymerization catalysts, the critical breakthrough came in the activator.

3.20.2.8 MAO: The Kaminsky Activator and Single-Site Catalysis

In 1976, Kaminsky, Sinn, and co-workers discovered that water-treated trimethylaluminum (TMA) activates metallocenes orders of magnitude better than previous systems.^{3,9,10,13} This finding has revolutionized the field of ethylene and α -olefin polymerization, laying the foundation upon which all further advances were built. The key activator, known as methylalumoxane (MAO), is generally formed by reacting less than one water with one AlMe₃ to create polymeric structures $(MeAlO)_n(AlMe_3)_m$ thought to contain chains, rings, three-dimensional cage structures, and unreacted TMA. Typically formed in toluene, the original MAO has a tendency to form gels. Versions incorporating, for example, isobutyl groups modified methylalumoxane (MMAO) have differing properties such as hydrocarbon solubility and less gelation. The optimal activator will vary from system to system. Despite the 'multisited' structure of MAO, many MAO-activated metallocenes give polymers with narrow MWDs (PDI = 2.0) and narrow comonomer distributions, behavior characteristic of only a single active structure. The contrast with multisited Ziegler and chrome systems led to use of the term 'single-site catalysts' to describe these systems (Figure 12).





Highly active olefin polymerization catalysts Single-site behavior (MWD = 2.0)

Figure 12 Formation of a zinconocene/MAO catalyst.

3.20.2.9 Metallocene Catalysts: The Significance of Substitution

The parent metallocenes used by Kaminsky *et al.* are rarely used commercially, so it is fair to say that the breakthrough was not completed until the recognition that subtle variations in the metallocene molecular structure dramatically change the catalyst performance and polymer characteristics. Welborn and Ewen of ExxonMobil led in this discovery, leading to base patent coverage in the field (**Figure 13**).^{14a} Patents and articles on metallocene derivatives now number into the thousands. Ewen as well as Brintzinger and Kaminsky, Spaleck *et al.* at Hoechst^{14b,14c} Waymouth,^{15,16} and many others advanced the mechanistic insights into these systems by studying tacticity control in PP.

3.20.2.10 'Noncoordinating' Anions: Alternative, Discrete Activators

Elucidation of the nature of the active species in MAO/metallocene catalyst systems was the subject of intensive research efforts with contributions coming from many laboratories. While it would be artificial to attribute credit to any one group for solving the mystery, it was the discoveries by Jordan¹⁷ and by Turner and Hlatky of ExxonMobil¹⁸ that most clearly established the current view. They demonstrated that metallocene cations possessing stable non coordinating anions (NCAs) such as tetraarylborates were extremely active for olefin polymerization and single sited in nature. This strongly implied that MAO functions by abstracting an anionic ligand from a neutral metallocene to form a metallocenium cation and an MAO anion. Indeed Marks¹⁹ showed that a neutral aryl borate could abstract a methyl group to form a metallocenium–anion pair with high activity. Because of the known structure of these activators *vis-a-vis* MAO, these are often referred to as 'discrete activators.' These activators are commercially viable, often yielding greater activity than MAO with the cost advantage that large molar excesses are not needed as with MAO. Conversely, such systems are often very sensitive to impurities, whereas excess MAO acts as an impurity scavenger (Figure 14).

3.20.2.11 The CpSiNR Ligand for Constrained Geometry Catalysts

Biscyclopentadienyl (bis-Cp) metal complexes were not the only single-site catalysts for olefin polymerization. Monocyclopentadienyl complexes often showed activity, but generally were not competitive catalysts except when linked to a bulky amido group. Thus, Bercaw's CpSiNR ligand was placed on titanium by workers at Dow²⁰ and Exxon²¹ and found to produce very active catalysts with attractive features (Figure 15). Both companies filed patents in the US and







Figure 15 The bridged Cp amido ligand system.

World offices within days of each other, resulting in interferences and court actions over catalyst, activator, and polymer, which were finally settled after more than a decade. Dow proceeded with commercialization of the system dubbing them constrained geometry catalysts (CGC) because of the bridge between the cyclopentadienyl and amide ligands.

3.20.2.12 Commercialization of Metallocene Catalysts

In commercial practice mono and bis-Cp catalysts show sensitivity to oxygen, water, and polar functionality more comparable to chrome catalysts. Depending on catalyst molecular structure, the molecular weight capability and comonomer incorporation level vary over a tremendous range beyond the capabilities of other commercial catalysts. Comonomer incorporation is usually more facile and more evenly distributed throughout the chain than in the older 'conventional' systems in addition to less chain to chain molecular weight and comonomer variation. Bis-Cp catalysts are very sensitive to chain termination by H2, while mono Cp amide (constrained geometry) catalysts are more like titanium Ziegler systems in this regard. The systems are supported on silica when used in slurry- or gas-phase processes, and both MAO and NCA activations are practiced. Although the major components of these catalysts - metal complex, MAO, and discrete activators - are inherently more expensive than conventional catalyst raw materials, volume manufacture and high activity have reduced costs to acceptable levels when combined with premiums commanded by the polymer products.

Though not well known, the commercial use of metallocenes for polymerization began in 1985 with Uniroyal's sale of Trilene[™] low-molecular-weight (LMW) PE products. Exxon began production of metallocene VLDPE in a high temperature and pressure unit in 1991 under the Exact™ trade name using a proprietary metallocene catalyst such as those covered by the famous '800' patent^{14a} that was central to several legal contests over rights to produce metallocene polymers. These polymers are characterized by very narrow MWDs and comonomer distributions, which lead to high strength and uniformity. In 1993, Dow introduced constrained geometry catalyst produced polymers using a solution process to make VLDPE and LLDPE. These polymers generally emphasized easier processability relative to the bismetallocenes. Then in 1994, Exxon launched commercial metallocene products from the low-pressure, low-temperature, very large-scale Unipol[™] gas-phase process. Metallocene PP was introduced by Exxon and Hoechst in the following year, and medium-density metallocene PE produced in slurry loop reactors was sold by Exxon in 1996. With the DuPont/Dow solution process to produce EPDM polymers, all major processes and PE/PP polymer types were being produced by single-site catalysts.

'Constrained Geometry Catalyst.'

While many commercialization announcements had been made up to 2000, relatively few producers beyond those mentioned above had initiated full commercial production. However, strong demand, production of specialty products such as cyclic copolymers, the sale of single-site catalyst licenses, the announcement of new nonmetallocene single-site catalysts, and the expiration of early patents have finally brought these new technologies into their own by 2011 after more than two decades of commercial development. While the early technologies of high-pressure chrome catalysts and Ziegler–Natta catalysts for PE and for PP command the large majority of commercial production, the single-site polymer volumes have become substantial and are growing much faster. In metallocene PE, the lead producers are ExxonMobil, Dow, and Mitsui, but now significant producers also include Borealis, ChevronPhillips, Total, and Braskem. Metallocene PP has lower activity, lower tacticity (and melting point), and higher cost than Ziegler–Natta's and so has not yet grown to large volumes. The main practitioners have been ExxonMobil, Lyondell-Basell Inc., and Novolen. The EPDM market is much smaller and higher value than the PE markets. Metallocene EPDM, which does not require deashing like the conventional vanadium systems, has grown to a significant percentage of the market with Dow, Mitsui, and ExxonMobil being the main producers.

3.20.2.13 Other Single-Site Catalysts

This section seeks to highlight the single-site catalyst systems that have attracted significant industrial interest and which were not described in the earlier sections that focused on metallocene and constrained geometry catalysts. For more comprehensive coverage of single-site olefin polymerization catalysts, the reader is referred to several excellent reviews written over the last decade on this broader topic.²² We use the term 'single-site catalyst', as it is commonly used, to denote all catalyst systems that use a single, well-defined, metal–ligand complex as a catalyst precursor. It is important to recognize, however, that 'single-site' is somewhat misleading because the polymers produced by these systems sometimes have broad or multimodal molecular weight and/or compositional distributions that indicate the presence of multiple catalytically active species.

Cyclopentadienyl-containing group 4 complexes dominated the field of single-site catalysis for many years due to their unique high activity and good properties. Beginning in the mid-1990s, however, the picture began to change as new classes of noncyclopentadienyl complexes were explored that led to the discovery of new, highly active catalyst systems. Remarkably, some of these postmetallocene catalysts featured late transition metal centers. Three of these which have attracted a large degree of commercial interest are shown in Figure 16. Family 1 are Ni- and Pd-based diimine 'Versipol^{TM'} catalysts from the labs of Brookhart (University of North Carolina) and DuPont Central Research.²³ The activated Ni derivatives are highly active ethylene polymerization catalysts, with activities comparable to those of metallocenes. The Pd catalysts, while of much lower activity, can form highly branched PE via a chain-walking mechanism. Additionally, they tolerate and incorporate some polar olefins. Family 2 are pyridyl bis(imine)-based Fe and Co catalysts discovered



Figure 16 Selected late transition metal postmetallocene catalysts of industrial interest.

independently by Brookhart and Bennet (DuPont)²⁴ and Gibson.²⁵ Early reports indicated that the activated complexes catalyzed ethylene polymerization to form highly linear PE. The Fe catalysts were exceptionally active. Subsequent studies on the ligand framework has allowed for this system to be used for ethylene oligomerization to produce a Schulz–Flory distribution of highly linear α -olefins. The salicylaldiminato complexes of Ni (Structure 3) were reported by Grubbs and co-workers.²⁶ Upon loss of the dative donor ligand from the Ni center, these complexes formed neutral olefin polymerization catalysts that demonstrated a good degree of tolerance to common oxygen-containing functional groups. Another desirable feature of these catalysts is that they are capable of incorporating substituted norbornenes and α, ω -dienes.

Early transition metal complexes featuring heteroatom donor ligands have also yielded several catalyst families of interest to the polyolefins industry (Figure 17). In 1996, Scollard and McConville reported that the Ti diamides with bulky 2,6-disubstuted aryl groups (Structure 4), when activated with MAO, formed highly active catalysts for the homopolymerization of 1-hexene.²⁷ Remarkably, activation of the dimethyl derivatives (X = Me) with $B(C_6F_5)_3$ afforded a living system at ambient temperature. Subsequently, Schrock (of MIT) and ExxonMobil developed a series of group 4 diamide complexes containing a dative donor in the ligand framework (Structure 5).²⁸ Both ether and amine donors have been explored. Univation Technologies has filed numerous patent applications related to their ProdigyTM Bimodal Catalyst technology that describe using these diamide catalysts in combination with metallocenes in a mixed catalyst system to produce bimodal PE in a single reactor.²⁹

Fujita and co-workers at Mitsui have been very active in the discovery and development of polyolefin catalysts supported by heteroatom donor ligands.³⁰ They have discovered several different extremely active catalyst families based on group 4 metals bound to a pair of monoanionic bidentate ligands. Included are the bis(pyrrolideimine) (Structure 6) and the bis(phenoxyimine) (Structure 7) complexes, the latter of which are known as FI catalysts. The FI catalysts have been extensively developed and studied, both by researchers at Mitsui and in academic labs. These studies have shown these catalysts to be capable of forming a broad range of polyolefin products that include linear high-density PE, syndiotactic PP, isotactic PP, and multimodal PE. Stephan's titanium bis-phosphinimide systems disclosed with Nova show performance comparable to the constrained geometry catalysts of Dow and ExxonMobil,³¹ but much higher patent activity on related cyclopentadienyl-containing systems (Structure 8) suggests these are behind Nova's new PE products from their solution process. More recently, these catalyst systems have been licensed to DSM for making EPDM reportedly with higher diene incorporation capability.

In their alliance with Dow, Symyx discovered two classes of Hf and Zr catalysts capable of making crystalline PP at high temperatures that appear to have seen commercial practice. These are the complexes of pyridyl amides³² (Structure 9) and bis(biphenylphenolate)ethers (bppe) (Structure 10).³³ More recently, Dow has reported that combination of a pyridyl amide complex with a Mitsui FI catalyst and an excess of aluminum or zinc alkyls allows for the production of olefin block copolymers (OBCs) through a 'chain shuttling'



Figure 17 Selected group 4 metal postmetallocene catalysts of industrial interest.

mechanism, which they have commercialized under the InfuseTM OBC brand.³⁴ Given the current state of the technology, it seems very likely that advances in conventional, metallocene and nonmetallocene catalyst systems will continue to drive commercial polyolyolefin product and process performance to new levels for decades to come.

3.20.3 Global Polyolefin Catalyst and Product Markets

3.20.3.1 Polyolefin Market Overview

Global polyolefin demand grew over 5% per year between 1990 and 2010 to a volume of 120 000 000 metric tons. The high-pressure free-radical-polymerized LDPE grew just 1.25% per year. On the other hand, LLDPE, HDPE, and PP grew at 7.6%, 5.3%, and 6.8%, respectively (Figure 18).

3.20.3.2 Polypropylene Applications

Most PP is produced with titanium-based Ziegler–Natta catalysts. The key features of PP include toughness and heat resistance. Toughness is driven by molecular weight, and heat resistance is maximized by uniformity of propylene insertion in the growing chain. In addition to propylene homopolymers, markets also value random copolymers of ethylene and heterophasic or impact copolymers which include rubber domains for impact absorption. Thermoplastic olefins (TPOs) are a class of even higher-impact PP characterized by higher rubber or plastomers content, incorporated in additional sequential reactors or by extrusion compounding (Figure 19).

The largest application for homopolymer PP is fibers and raffia (woven fabrics for bags, etc.) One of the fiber applications for PP has been carpet; however, that preference is somewhat regionally dependent and is also influenced by fashion trends. On the other hand, nonwoven technologies such as melt-blown and spun-bond PP consume large quantities into medical and hygiene applications such as hospital gowns, hygiene products, and diapers and incontinence products. These nonwovens are also used in filtration products for air, water, and other uses. Generally, nonwoven technologies prefer narrow MWD and relatively LMW for easy drawing of the fibers to maximize strength. Metallocene catalysts have grown in these nonwoven markets where narrow MWD and LMW can be accomplished without peroxide chain scission. Rapid



Figure 18 Global polyolefin demand, thousand metric tons. Source: CMAI global.



Figure 19 Classes and applications of polypropylene. Source: Phillip Townsend Associates.

crystallization can also be important for processing, giving advantage to minimal chain defects.

The other two large applications for PP homopolymer are film and injection molding. Oriented PP film is highly utilized in packaging, building on it is stiffness, clarity, and gloss. It is a key component in pouches. Injection-molded articles include appliances where the polymer is frequently talc filled for enhanced stiffness and heat resistance. Advantages include corrosion resistance.

Impact or heterophasic copolymers have supplanted more costly engineering thermoplastics in many applications. Products are optimized relative to the amount of EPR incorporated as well as processing characteristics. Increasing rubber content compromises stiffness due to reduced iPP 'scaffolding'. Nevertheless, the rubber mitigates the low-temperature brittleness of homopolymer, allowing low-temperature applications from packaging to automotive bumpers. Heterophasic copolymers are typically produced with Ziegler–Natta catalysts, particularly high-crystallinity versions. Applications range from automotive bumpers and body panels to rigid packaging applications for redi-serve microwaveable containers and 'plastic jars'. Impact copolymers provide housing in small appliances and outdoor furniture (Figure 20).

Randomly incorporated ethylene introduces 'defects' along the backbone. These defects disrupt crystallization, reducing the modulus, melting point, and heat of fusion. The incorporation of random ethylene also reduces haze. Butene has also been used as a comonomer in PP. With the development of metallocene catalysts, even higher α -olefins such as hexene could be incorporated. While these alternative copolymers are now technically feasible, they have not seen commercial growth. The higher α -olefin copolymers promise improved toughness, potentially extending the low-temperature performance.

3.20.3.3 Polyethylene Applications by Catalyst

Because high-pressure, free-radical-initiated PE does not involve a catalyst, it is not considered here. As mentioned previously, there are three catalyst families prominent in PE polymerization: chrome, Ziegler–Natta, and metallocene/single-site.

3.20.3.3.1 Chrome catalyst applications

Chrome catalysts generally produce broad MWD products that are attractive for applications such as blow-molding and thermoforming. These converting technologies produce 'hollow' parts for packaging and other 'durable' end-uses such as automotive fuel tanks. HDPE is commonly chosen for these applications, taking advantage of higher stiffness and heat resistance (Figure 21).

While chrome catalysts intrinsically produce broad MWD products, Ziegler–Natta catalysts are utilized for these applications via the use of series reactors. The feeds to the two reactors are adjusted to produce LMW polymer in the first reactor and HMW polymer in the second. This balances toughness (HMW) and processability (LMW). Bimodal MWD products are especially common in film where the combination of toughness and higher density has enabled extensive downgauging of film for light-weight duty such as lawn-and-leaf bags or can liners for offices.



Figure 20 Applications and markets of polypropylene impact copolymers. Source: Phillip Townsend Associates.



Figure 21 HDPE end-uses and converting technology. Source: Phillip Townsend Associates.

3.20.3.3.2 Ziegler–Natta catalyst applications

Ziegler–Natta catalysts are even more common in LLDPE applications where narrow MWD is the norm for film in packaging and other applications. Densities in the range of $0.920 \,\mathrm{g\,cc^{-1}}$ exhibit an attractive balance of stiffness and toughness as measured by tear strength or puncture and impact resistance. Reducing density (reflecting lower crystallinity) also suppresses melting point, making LLDPE a popular choice for heat sealing layers in film (Figure 22).

The density in LLDPE is suppressed via incorporation of a comonomer, typically butene, hexene, or octene. (Note that polar comonomers, while attractive, are poisonous to most olefin polymerization catalysts.) The longer comonomer (hexene or octene) is more effective in linking crystals within the polymer, enhancing toughness. Ziegler–Natta catalysts are applied in essentially all polyolefin processes, from solution to gas-phase, single reactor or series.

3.20.3.3.3 Metallocene/single-site catalyst applications

Two key differences between metallocene/single-site and Ziegler–Natta catalysts are uniformity of comonomer incorporation and molecular weight. While narrowing MWD exacerbates the challenges of processability (higher head pressure and lower melt strength), the improvement in other properties compensates. The improved toughness enables the use of higher-density (stiffer) grades, a combination which allows downgauging or light-weighting. The elimination of higher-density molecules (lower comonomer) reduces haze, improving the optical properties for packaging films. The elimination of LMW/high-comonomer molecules reduces tackiness, lowering the required anti-block additives that negatively impact optics.

The uniformity of MWD and comonomer incorporation associated with metallocene/single-site catalysts enabled major reduction in density/melting point while retaining free-flowing pellets for converting. Due to diminished stickiness and extractables, metallocene catalyzed products were introduced with melting points as low as 70 °C. This reduction allows significantly faster sealing in film packaging applications, allowing overall faster packaging.

Later metallocene/single-site catalysts were developed, which drove the production of LCBs. These LCBs increased entanglement in the molten polymer, resulting in more stable blown film processing. They also reduced extrusion pressures and allowed higher throughput.

3.20.3.3.4 EPR and EPDM applications

Synthetic rubber (EPR) was produced as early as 1961 using broad MWD multisited vanadium catalysts. The resulting polymers performed well in wire and cable applications where their toughness and easy extrusion brought resilience to electrical applications. By the 1970s, EPR was finding use in O-rings and brake applications. Dienes (EPDM) were incorporated to enhance crosslinking and further improve processability.

The 1980s brought refinements to the vanadium catalysts, generating single-site versions yielding very narrow MWD. New applications included thermoplastic vulcanizates and oil modification. As with PE, these narrow distribution catalysts were adapted for use in sequential reaction, yielding bimodal or multimodal polymers. The new polymers moved into automotive body sealing and weather stripping, oil modification, and



Figure 22 LLDPE markets and converting technology. Source: Phillip Townsend Associates.

polymer modifiers, where their pelletized delivery facilitated compounding operations. The broad MWD also drove use in calendared applications and belts. These catalyst systems also enabled incorporation of dienes based on norbornene, which supported new cure or crosslinking systems.

EPR/EPDM found use in gaskets, belts, membranes (such as roofing), and cushioning (such as motor mounts in cars). They foamed well and were frequently used for impact absorption, from shoes to pneumatic parts. Their durability grew demand in conveyor belts, They were incorporated into automotive exterior parts, bringing low-temperature toughness from mud flaps to bumpers. Stable profile extrusion and durability encouraged use in tubing.

By the turn of the century, metallocene catalysts were developed for EPR and EPDM. The catalyst efficiency eliminated the need for deashing, and the products were frequently pelletized for easy handling. As mentioned earlier, metallocenes extended LLDPE to significantly lower-density products, called plastomers, which combined the toughness of LLDPE with the low-sealing temperatures of LDPE and ionomers. So too in EPR/EPDM, the metallocene catalysts allowed broader reactor operating conditions and incorporated higher α -olefins, suggesting new levels of toughness. Additionally, metallocene catalysts supported pelletization of elastomer products for ease of use in compounding and other polymer modification markets.

3.20.3.4 Catalyst Demand by Product Type

If we classify polyolefin catalysts by the type of polymer produced, we find that HDPE commands the largest volume. It is produced with both chrome catalysts for applications requiring properties engendered by very broad MWDs (e.g., blow-molding and film) and with Ziegler–Natta catalysts. The latter make both high-density products with narrow MWDs (e.g., rotational molding) in a single reactor and, through the series slurry reactors, high-density products with broad, bimodal MWDs useful for the same applications as chrome catalysts. As discussed previously, the type of product to be sold will determine which processes may be used for its production (Figure 23).



Global demand for PO catalysts in 2007 is estimated to be 8,696 tons

3.20.3.4.1 Catalyst demand for PP

PP catalyst supply is essentially all titanium Ziegler–Natta catalysts typically manufactured as magnesium chloride supported solids which are activated at the manufacturing plant with aluminum alkyls and 'external donors.' Prepolymerization in a small prereactor is common. The largest licensor of PP process technology is Lyondell-Basell Inc. with Spheripol slurry loop and related processes, and there is more diversity of process technologies than with LLDPE. While process licensors are the largest suppliers of catalyst, there are a significant number of third-party Ziegler–Natta PP catalyst suppliers who neither license process technology nor produce PP (Figure 24).

3.20.3.4.2 Catalyst demand for HDPE

Catalysts for producing HDPE include both chromium and titanium systems and, to a lesser extent, metallocenes. The largest licensors of process technology are Phillips slurry loop using chromox catalysts and Univation (Unipol[™]) gas phase using titanium, chromox, and organochrome catalysts. There is significant volume in series slurry reactors, most notably Mitsui stirred-tank technology, using titanium catalysts to make bimodal HDPE. The chromox catalysts for slurry processes are largely supplied by Grace-Davison and Ineos as reduced chromium on silica that is calcined on-site by the polymer producer and then introduced into the reactor. Organochrome as well as chromox catalysts are supplied by Univation for licensees of their gas-phase process. Most titanium catalysts are supplied by the process licensor or made on the manufacturing site under license, but more third-party supply has entered the market in recent years (Figure 25).

3.20.3.4.3 Catalyst demand for LLDPE

The LLDPE process licensing field is less fragmented than PP or HDPE with the gas-phase processes of Univation (Unipol[™]) and Ineos (Innovene[™]) comprising the majority of production through licensed manufacturing capacity using titanium and metallocene catalysts. The solution processes of Dow (Dowlex[™]) and Nova (Sclair[™]) account for the majority of the remaining capacity also using titanium and metallocene



Global PP catalyst demand by process technology

Figure 24 Polyproplene catalyst demand (percent). Source: Chemical Market Resources, Inc.

Figure 23 Polyolefin catalyst demand (tons, percent). Source: Chemical Market Resources, Inc.

Global HDPE catalyst demand by process technology



Figure 25 HDPE catalyst demand (percent). Source: Chemical Market Resources, Inc.

catalysts. As with HDPE, most catalyst is supplied by the licensor or made on-site by the licensee, but third-party supply has been increasing (Figure 26).

3.20.4 Conclusion

It is nearing a century since the discovery of high-pressure LDPE. Because of their versatile properties and very low cost of production relative to competing polymers, metals, and natural materials, polyolefins will enjoy continued robust growth for the foreseeable future. The versatility of and therefore markets for polyolefins were increased dramatically in the 1950s with the introduction of transition metal polymerization catalysts. Succeeding waves of catalyst innovations have ensued, enabling growth, and there is every reason to expect that trend to continue many years into the future.



Global LLDPE catalyst demand by process technology

Figure 26 LLDPE catalyst demand (percent). Source: Chemical Market Resources, Inc.

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Biographical Sketches



Alan Vaughan was born in North Carolina, and grew up in Kansas City, Missouri. He attended Vanderbilt University and was introduced to Organometallic Chemistry through the labs and course work of Prof. Chuck Lukehart. Vaughan received his PhD degree in inorganic chemistry from the University of Chicago in 1990 in the Group of Greg Hillhouse. His dissertation work concentrated on metal-mediated reactions of nitrous oxide. He then spent a year as an NIH Fellow studying osmium-catalyzed asymmetric dihydroxylations of olefins with Barry Sharpless at MIT, followed by 2 years in the group of Dick Schrock searching for new olefin metathesis catalysts.

In 1993 Vaughan joined Exxon Chemical's olefin polymerization catalysis group in Baytown, Texas where he was fortunate to play a role in the commercialization of metallocene catalysts that are used in world-scale reactors to make over 2 billion pounds of premium polyethylene a year. His assignments have included research and catalyst business roles in the Univation Joint Venture and managing the Organometallic Catalysis and High Throughput Polymer Tools Group in ExxonMobil Chemical Research. Presently, he manages contract negotiations for heterogeneous catalysts for the refineries and chemical plants.



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John R. Hagadorn attended the University of Oregon as an undergraduate student. There, he had his first exposure to research in the lab of Kenneth Doxsee, where he worked on unusual synthetic routes to metal sulfides. He received a BS degree in chemistry in 1993. Then he headed to Berkeley to begin graduate studies in chemistry under the guidance of John Arnold. After earning his PhD degree for research related to transition metal amidinates, he went to the University of Minnesota as a NIH Postdoctoral Fellow to work with Bill Tolman and Larry Que on biomimetic iron complexes. In 2000, he joined the faculty at the University of Colorado and then moved to the Houston area in 2006 to join the Catalyst Group within Global Research at ExxonMobil Chemical Co. Since then, he has enjoyed working on a broad range of projects related to catalysis and polyolefins.

3.21 Metallocene Alkene Polymerization Catalysts

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3.21.1	Introduction	673
3.21.2	Definition of a Metallocene Polymerization Catalyst	674
3.21.3	General Mechanism	675
3.21.3.1	Activation and Cocatalysts	676
3.21.3.2	Propagation Steps	678
3.21.3.3	Termination Events	680
3.21.4	Ethylene Polymerization	681
3.21.4.1	Types and General Properties of PE	681
3.21.4.2	PE s Produced by Different Catalysts	682
3.21.4.3	Factors Affecting Catalyst Activity and Molecular Weight	683
3.21.5	1-Alkene Polymerization	685
3.21.5.1	Stereoselectivity	685
3.21.5.2	Aselective	685
3.21.5.3	Isoselective	685
3.21.5.4	Syndioselective	685
3.21.5.5	Hemiisoselective	685
3.21.5.6	Stereoblock	686
3.21.6	Diene Polymerization	687
3.21.6.1	Conjugated Dienes	687
3.21.6.2	Nonconjugated Dienes	687
3.21.7	Copolymerization	687
3.21.7.1	Ethylene/Propylene	687
3.21.7.2	Ethylene/Higher 1-Alkenes	689
3.21.8	Conclusions	690
3.21.9	Outlook	693
References		694

3.21.1 Introduction

The complexity of a polymerization reaction can be subdivided into monomer complexity and catalyst/initiator complexity. Arguably, the simplest organic monomer is ethylene and its elaboration results in increasingly intricate monomers such as 1-alkenes, disubstituted alkenes, and dienes, followed by the endless gamut of monomers bearing heteroatoms such as monofunctionalized alkenes, heterocycles, difunctionalized monomers, and so forth. Similarly, catalysts or initiators can be rather simple, as found with classic cationic, anionic, and radical initiators. Decades of research have identified increasingly complex polymerization pathways, including those that employ inorganic catalysts, coordination compounds as catalysts, organometallic catalysts, and enzymatic catalysts.

The focus of this chapter is the polymerization of relatively simple alkenes with metallocene catalysts. As **Figure 1** illustrates, this particular intersection of basic alkenes with relatively complex catalysts lies in a region where the catalyst significantly multiplies the value of an inexpensive alkene – resulting in intricate and highly engineered polymers. Thus, it is easy to understand the great interest with which chemists – especially industrial chemists – have developed metallocene-based catalysts, which are a subset of the broader classification termed 'single-site catalysts'. Their importance derives from their capacity to convert abundantly available monomers into polymers with valuable properties.

The first preparation of 'polymethylene' - a polyethylene analog - was conducted via diazomethane decomposition, although the process was suitable for laboratory scale only.¹ To achieve the industrial-scale synthesis of polyethylene (PE), Imperial Chemical Industries (ICI) employed the radical polymerization of ethylene, a high-pressure (100 MP) and high-temperature (200-300 °C) process, leading to low-density polyethylene (LDPE).² Hogan and Banks³ at Phillips Petroleum and also Karl Ziegler⁴ polymerized ethylene using activated transition metal catalysts, allowing the production of high-density polyethylene (HDPE) with considerably lower pressures and temperatures. While the LDPE polymer was largely amorphous, HDPE was a highly linear and crystalline polymer.⁵ Giulio Natta⁶ developed the stereoselective polymerization of propylene to isotactic polypropylene using the newly developed catalysts of Ziegler. Both Phillips and Ziegler-Natta (ZN) catalysts are heterogeneous systems.^{5a,5b,7} The Phillips catalysts are based on SiO₂-supported chromium; they produce PE with a high degree of olefinic end groups.⁸ Unlike Phillips catalysts, ZN catalysts employ multiactive catalyst centers and produce polymers with a broad molecular weight distribution (MWD).^{5a,9}



Figure 1 Complex metallocene catalysts have the capacity to convert simple monomers, such as ethylene and 1-alkenes, into complex, functional polymers.

The next generation of catalyst systems was based on soluble metallocene/methylaluminoxane (MAO). The single-site nature of these catalysts could produce polyolefins of narrow MWD with very high activity and new polymer architectures.^{5a,10} The processes that preceded metallocene technology produced a mixture of polymeric products that were nonuniform in structure and properties; this was problematic for the end-use materials. However, the homogeneity of the metallocene system and product uniformity allowed for a more precise polymer design to meet the exact needs of a given application. Among all catalysts used for ZN polymerization of olefins, arguably the most scientifically important and commercially promising is the group 4 metallocene system together with MAO cocatalyst, with respect to the following criteria:

- Activity
- Selectivity (largely stereoselectivity)
- Simplicity (avoiding the complexity of heterogeneous catalysts)
- Versatility, according to the following three viewpoints:
 - 1. Variable catalyst structure (transition metal and ligand effects)
 - Novel polyolefin materials obtained via controlling microstructure of monomer enchainment into the macromolecular chains and controlling molecular weight and MWD of the polymer
 - 3. The ability to tailor the stereoregularity (tacticity) of the polymer chains.
- Adaptation of catalyst systems to existing pilot and industrial plant production using solution, slurry, or gas phase processes
- Scientific benefits
 - 1. Understanding of catalyst structure
 - 2. Polymerization mechanism
 - 3. Catalyst-polymer structure relationship.

The consequences of this single-site control is the synthetic ability to form a number of isotactic, syndiotactic, or other

kinds of polymers having interesting properties and a wide range of molecular weight control, from dimers to oligomers to ultrahigh high-molecular-weight polymers.^{5a,10c,11}

3.21.2 Definition of a Metallocene Polymerization Catalyst

The general term metallocene derives from the more specific term ferrocene, the name ascribed to a 'sandwich' compound of dicyclopentadienyl iron (Cp_2Fe) introduced by Geoffrey Wilkinson, R. B. Woodward, and E. O. Fischer. In ferrocene itself, the iron atom is sandwiched between parallel, planar cyclopentadienyl ligands (Figure 2(a)).¹² Figure 2(b) depicts the general structure of a group IV bent metallocene, which by itself, or upon ligand elaboration can be the transition metal component of an olefin polymerization system.

To better understand the polymerization process and to be able to rationally design better catalyst systems, single-site homogeneous catalyst systems were developed as models of the heterogeneous systems employed commercially. Of particular interest were metallocene-type catalysts, which had been discovered to be slightly active for polymerizations in the early work of Natta *et al.*¹³ Until the accidental discovery of MAO by Sinn, Kaminsky and coworkers¹⁴ in 1980, however, the activity of metallocene catalysts was far too low to be useful. Activation of a metallocene precursor such as $(\eta^5-C_5H_5)_2ZrCl_2$ with MAO was found to yield extremely active polymerization catalysts, and the number of metallocene-type catalysts reported in the literature has since exploded.^{10c}

These compounds can be employed as single, binuclear, or even multinuclear complexes of mainly zirconium, titanium, and hafnium for olefin polymerization. Among them, zirconium compounds are the most common and generally the most active catalysts. Particularly at higher temperature, zirconium catalysts are more stable and more active than titanium and hafnium.^{5,10c,15} They are generally soluble in hydrocarbons and ideally exhibit only one type of active center. Their chemical structure is readily modified by introducing variously substituted cyclopentadienyl ligands, resulting in an estimated 10000 or more metallocene-type structures that have been prepared. Thus, by controlling the structure of the catalyst used, it is possible to control (and sometimes predict) the resulting molecular weight and its distribution, comonomer content, and tacticity of the final product - all factors that impact the thermo-mechanical properties of the obtained polymer.^{10,11}

The activity of metallocene catalysts can be 10 000 times greater than that of classical, heterogeneous ZN systems. The activity of a zirconocene catalyst activated with MAO may reach



Figure 2 (a) The 'sandwich' compound ferrocene. (b) General structure of a group IV bent metallocene compound (M = Ti, Zr, or Hf; X = alkyl or halogen).

up to 40 000 kg PE/(g Zr h). The complexes that contain halogen atoms in the precursor form are typically more active than the corresponding complexes with alkyl (usually methyl) groups. Some are so active that each active zirconium atom produces about 46 000 PE chains per hour of polymerization. In this case, the average insertion time for each ethylene molecule into the growing polymer chain is about 3×10^{-5} s, a turnover frequency which rivals that of an enzyme. Certain homogeneous zirconocene catalysts are believed to become 100% activated for the polymerization of olefins. PE obtained using the metallocene/MAO catalyst typically has a narrow MWD (M_w/M_n) of between 1 and 2 (usually closer to 2), with a trace of vinyl end-groups (0.11–0.18 per 1000 carbon atoms). Thus, metallocene/MAO systems are generally well-behaved single-site olefin polymerization catalysts.^{5a,5b,8c,16,17}

Obviously, not all cyclopentadienyl transition metal complexes are active for olefin polymerization. Most metallocenes of transition metals of group IV (Ti, Zr, or Hf) and a few examples of group III metals (Sc, Y, and La) can become active catalysts.^{5a,5b,8c,15a,18} The most active catalysts are often those with indenyl ligands containing a methyl or ethyl substituent in the 2 position. These substitutions of the indenyl ring dramatically discourage β -hydrogen transfer to monomer and result in polymer chains of higher molecular weight.^{5a,10c,19} The molecular weight of the polyolefin may be lowered by increasing the polymerization temperature, increasing MAO concentration, decreasing polymerization pressure (concentration) of monomer, or by the addition of molecular hydrogen.²⁰ Metallocene catalysts can be divided into three different structural categories:

- 1. Unbridged metallocenes Common metallocenes with freely rotating cyclopentadienyl ligands with or without substitution (Figure 3(a)).
- ansa-metallocenes (ansa is the Latin term for a curved handle attached at both ends, commonly found on ornamental vases) – A metallocene containing a single bridge (Figures 3(b) and 3(c)) or a double bridge (Figure 3(d)),^{10g,21} usually containing carbon or silicon.
- Constrained geometry catalysts (CGCs) Technically not metallocenes, but mono-cyclopentadienyl complexes with a connected amide substituent (Figure 3(e)).

Metallocene catalysts may be employed as homogeneous catalysts or as supported, heterogeneous systems using suitable immobilized media. Heterogeneous catalysts have certain advantages such as improved morphology of the obtained polymer and reduced fouling of the polymerization reactor. While homogeneous and heterogeneous metallocene catalyst systems of group IV of transition metals are capable of producing HDPE, the CGCs are uniquely able to produce linear low-density polyethylene (LLDPE, a copolymer of ethylene and an α -olefin) with a truly random distribution of comonomer. CGCs can even produce analogs of LDPE, which is typically produced by high-pressure and high-temperature technology via a radical polymerization mechanism or by late transition metal homogeneous catalyst systems.²² Preparation methods for metallocene catalysts have been reviewed.^{10f,15a,18b,23}

3.21.3 General Mechanism

At least two mechanistic steps are commonly accepted for all coordination polymerizations:

- Complexation (adsorption, π-complex formation) of monomer to the transition metal via an available vacant coordination site
- Migratory insertion of the complexed monomer into a metal-carbon bond already present in the catalyst system, leading to polymer chain growth.

An active catalyst site requires a metal-carbon bond that may have existed in the pre-catalyst, may have been formed upon initial activation by cocatalyst (via ligand exchange), or may exist because of a previous migratory insertion event. In most cases, the starting precursor of the catalyst is a metallocene dichloride (dichlorides are usually the most active precursors for coordination polymerization) complex, which obtains a vacant site as a consequence of reaction with cocatalyst (see Section 3.21.3.1 below). In the case of metallocene activation by MAO, the produced active center is a strongly Lewis acidic cationic metal complex stabilized by a bulky MAO anion; the transition metal bears a vacant coordination site ready for complexation of the olefinic monomer (Figure 4(a)).^{10c,11e,24} In this respect, a weak interaction of the ion implies a greater catalyst activity. A stronger interaction of the anion generally causes decreased molecular weight, decreased stereoselectivity, and a decreased melting point of the obtained polymer (with α -olefins, when tacticity is an issue). Therefore, the presence of a bulky ligand and/or a bridge ligating the cyclopentadienyl rings can repel the MAO anion away from the active center, increasing both activity and stereoselectivity. Although the complexation and migratory insertion of ethylene is comparatively simple, such steps for an α -olefin (1-alkene) can have different regiochemical and stereochemical results. The energetic barriers are generally different for each possibility and



Figure 3 Exemplary structures of metallocene catalysts for olefin polymerization: (a) unbridged metallocene; (b, c) *ansa*-metallocenes with a single bridge; (d) *ansa*-metallocene with a double bridge and; (e) a constrained geometry catalyst (CGC, technically not a metallocene).



Figure 4 (a) Activation reaction of a metallocene complex by methylaluminoxane (-AI(Me)O-). M = transition metal atom and \Box = vacant coordination site. (b) A general mechanism for metallocene-mediated olefin polymerization.

thus the outcome may be affected by polymerization conditions such as temperature and monomer concentration, as well as steric effects associated with the ancillary ligand surrounding the active metal catalyst.^{5a,5b,10c,10h,10i,24f,25} Figure 4(b) presents a general mechanism for metallocene-mediated olefin polymerization.²⁶

3.21.3.1 Activation and Cocatalysts

So far, the most widely used and versatile cocatalyst for metallocene-mediated polymerization is MAO. Undoubtedly, the success of metallocene catalysts is tied to the discovery of MAO, which is formed by the partial hydrolysis of trimethylaluminum (TMA). Cocatalysts should play different roles during polymerization. In particular, MAO performs at least five important functions:

 It activates the metal catalyst via ligand exchange reactions, typically replacing chloro ligands with methyl ligands (Figure 4(a)). Thus, it acts as an alkylation agent for the generation of transition metal–alkyl bonds. Generally, the ligand exchange reaction is fast with metallocene dichlorides, a common starting complex (or pre-catalyst) used for polymerizations.

- 2. It functions as a counter anion with the cationic transition metal catalyst. It acts as a Lewis acid for abstracting a halide or alkyl anion from the metal, generating the electrophilic, transition metal cation. As a counter anion, it serves to stabilize the active cation.
- Where appropriate, it can act as a scavenger for the removal of impurities such as water and other contaminants containing heteroatoms.
- 4. It can function as a chain-transfer agent.
- It serves as a reactivating agent for otherwise inactive metallocene species.

MAO is industrially prepared by careful and controlled partial hydrolysis of TMA with water in a highly exothermic reaction (**Figure 5**). It is possible to use inorganic compounds containing some water (hydrates) such as $Al_2(SO_4)_3 \cdot 14-18H_2O$, $MgCl_2 \cdot 6H_2O$, and $CuSO_4 \cdot 5H_2O$, at the laboratory scale. Two additional methods for obtaining MAO from TMA (or alkyl-aluminoxanes from other trialkyl aluminum compounds) include the use of partially humid monomer or the intentional addition of partially humid nitrogen.²⁷

In spite of its great performance and the large number of scientific studies aimed at MAO, its structure is not clearly understood. It can be considered as a mixture of linear and

$$nH_2O + (n+1) \xrightarrow[H_3C]{I} \xrightarrow{CH_3} H_3C \xrightarrow{CH_3} H_3C \xrightarrow{CH_3} H_3C \xrightarrow{CH_3} H_3C \xrightarrow{L} H_$$





Figure 6 (a) Linear and (b) cyclic structures of MAO.^{5a,5b,12} (c) Two-dimensional ladder and (d) three-dimensional cage structures of MAO oligomers.^{12f} And a proposed (e) three-dimensional host-guest structure for MAO, wherein the guest is the active cationic catalyst.^{12f}

cyclic oligomers that are probably in a dynamic equilibrium. MAO generally contains at least one oxo bridge between two or more aluminum centers, which can be part of a larger unit with the formula Al₄O₃Me₆. MAO also contains mixtures of linear species such as Me₂AlO-[Al(Me)O]_x-AlMe₂ and cyclic species such as $-[Al(Me)O]_x$ for which x = 2-20. Oligometric MAO has a molecular weight of 1200-1600 and is usually soluble in aromatic hydrocarbons, such as toluene. Oligomeric chains of MAO are usually depicted as (a) linear or (b) cyclic compounds as in Figure 6. Two-dimensional ladder (Figure 6(c)) or three-dimensional cage (Figure 6(d)) structures are also likely; these are generated because of coordination of oxophilic aluminum with oxygen atoms of nearby oligomer chains. A three-dimensional host-guest cage structure has also been postulated, as shown in Figure 6(e).^{5a,5b,12f,28,29} Although the structures of MAO are varied and complex, for simplicity it is common to just consider MAO as its monomeric repeat unit, Al (Me)O.

The interaction of a metallocene dichloride with MAO results in several important equilibria. As a result of methyl anion/chloride ligand exchange, the monomethyl chloride species, Cp₂Zr(Me)Cl, forms first. Excess MAO can lead to the dimethyl species, Cp₂ZrMe₂. Finally, MAO functions as a strong Lewis acid and removes the chloride ligand from Cp₂Zr(Me)Cl or a methyl anion from Cp₂ZrMe₂, resulting in the presumed cationic species Cp₂Zr⁺Me, which includes the necessary metal–carbon bond and vacant coordination site with a loosely bound MAO-derived counter anion (Figure 7).^{25b,25c,30}

It is generally assumed that some of the aluminum centers in [Al(Me)O] have a high tendency to abstract a methyl anion from Cp₂ZrMe₂.³¹ Therefore, it is clear that the concentration of the active cation in the final reaction of **Figure 7** will be higher if the Al/Zr quotient is increased. From the above equilibria, the need to use a large excess of MAO with respect to group IV metallocene in order to obtain a highly active alkene polymerization catalyst is understandable. Unfortunately, homogeneous metallocene catalysts require a large excess of MAO (often greater than 1000:1 for Al:transition metal) to reach the maximum catalytic activity, which to some extent diminishes the economic viability of metallocene/MAO polymerizations in a commercial setting. Methods to overcome this problem include:

- 1. The use of cationic metallocene compounds that do not need any cocatalyst for polymerization.^{15a}
- The immobilization of catalysts and/or cocatalysts onto inorganic compounds such as Al₂O₃, SiO₂, MgCl₂, or polymeric materials – methods which may receive deserved attention in industrial and academic research.^{22b,27d,29a,32}

With discoveries of boron-based cocatalysts such as triphenylboron, ammonium tetraphenylborate salts, and finally pentafluorophenyl derivatives of borate $[B(C_6H_5)_4]^-$, olefin polymerization catalysis was developed without a reliance on alkylaluminum species. Although the activity with nonfluorinated boron-based cocatalysts was invariably low, the fluorinated analogs exhibited olefin polymerization behavior similar to that of metallocene/MAO catalyst systems. The boron and borate compounds are typically used in a 1:1 molar ratio with transition metal (stoichiometric or near stoichiometric). Because these activators do not alkylate the transition metal, the metallocene precatalyst employed must already bear alkyl groups. Thus, zirconocene dimethyl species combine with boron or borate activators to generate active cationic polymerization catalysts. Figure 8 shows typical activation reactions with borate (a, b) and boron (c) activators.

Perfluorinated triphenyl boron and perfluorinated tetraphenylborate species have stoichiometric advantages compared to MAO, but they have specific drawbacks including higher cost



(a)
$$\operatorname{Cp}_{2}\operatorname{ZrMe}_{2}$$
 + $[\operatorname{PhNHMe}_{2}]^{\bigoplus} [\operatorname{B}(\operatorname{C}_{6}\operatorname{F}_{5})_{4}]^{\bigcirc}$ \longrightarrow $[\operatorname{Cp}_{2}\operatorname{ZrMe}]^{\bigoplus} [\operatorname{B}(\operatorname{C}_{6}\operatorname{F}_{5})_{4}]^{\bigcirc}$ + PhNMe_{2} + MeH_{2}
(b) $\operatorname{Cp}_{2}\operatorname{ZrMe}_{2}$ + $[\operatorname{Ph}_{3}\operatorname{C}]^{\bigoplus} [\operatorname{B}(\operatorname{C}_{6}\operatorname{F}_{5})_{4}]^{\bigcirc}$ \longrightarrow $[\operatorname{Cp}_{2}\operatorname{ZrMe}]^{\bigoplus} [\operatorname{B}(\operatorname{C}_{6}\operatorname{F}_{5})_{4}]^{\bigcirc}$ + $\operatorname{Ph}_{3}\operatorname{CMe}_{2}$
(c) $\operatorname{Cp}_{2}\operatorname{ZrMe}_{2}$ + $\operatorname{B}(\operatorname{C}_{6}\operatorname{F}_{5})_{3}$ \longrightarrow $[\operatorname{Cp}_{2}\operatorname{ZrMe}]^{\bigoplus} [\operatorname{MeB}(\operatorname{C}_{6}\operatorname{F}_{5})_{3}]^{\bigcirc}$

Figure 8 Metallocene activation via (a, b) fluorinated borate and (c) fluorinated boron activators.

and the possibility of fluorine incorporation into the resulting polymer.²⁸ However, employment of perfluorinated tetraphenylborate as the counter anion generally imparts high ethylene and α -olefin polymerization activity, which at least is very important from a scientific viewpoint. Moreover, strong Lewis acids such as B(C₆F₅)₃ are able to abstract a methyl anion from dimethyl metallocenes and result in a poorly coordinated counter anion (see **Figure 8(c)**). In the case of activating *rac*-(C₉H₆CH₂CH₂C₉H₆)ZrMe₂, utilization of either the boron or borate activation modes results in comparable olefin polymerization behavior with respect to activity and polymer characteristics such as molecular weight and MWD.³³

MAO may be used as a homogeneous solution in a solvent such as toluene, as a solid chemical dissolvable in polymerization media, as a supported compound, termed SMAO, immobilized on relatively inert solid media such as SiO₂, Al₂O₃, or MgCl₂, or finally, as a mixture of solution MAO with SMAO. Generally, the heterogenization of a metallocene catalyst for polymerization occurs via one of three different methods:^{32a}

- 1. Supporting the metallocene catalyst itself
- 2. Supporting the cocatalyst, MAO, or boron-based activator
- Covalent anchoring of the metallocene catalyst to a suitable support using a coupling agent.

In the case of homogeneous polymerization, a high Al/M quotient of at least 1000 is often required to obtain highly active catalysts. In this case, the large mass quantity of cocatalyst can adversely affect the resultant polymer morphology and fouling of the polymerization reactor walls can be serious. By supporting the MAO (the SMAO approach), the Al/M quotient needed to reach high activity is sharply decreased to less than 100 and polymer morphology is improved while reactor fouling becomes less likely – but catalyst activity may decrease somewhat. Also, the use of heterogeneous systems generally improves the chances of a stable rate/time polymerization profile.^{22b,27d,29a,32}

The activation of a metallocene catalyst for polymerization results in an unsaturated cationic species containing a metalcarbon bond with an adjacent, vacant coordination site capable of coordinating an olefin monomer. The activation can be achieved by several different reagents, including MAO, fluorinated boron, and fluorinated borate species. The activated polymerization catalyst is a cationic transition metal species (typically titanium, zirconium, or hafnium) with an accompanying counter anion that derived from the cocatalyst activator. In the case of borate activators, the catalyst requires existing metal–alkyl bonds (instead of chlorides) and the reaction often benefits from trialkylaluminum scavengers to remove impurities such as traces of water or other Lewis basic species. In contrast, MAO or supported alkylaluminoxane prepared by reaction of AlR₃ with MgCl₂ may be used with a metallocene catalyst bearing chloride ligands. The MAO or SMAO behaves as an impurity scavenger, an alkylating agent, and a cation generation agent, making these activators more common for industrial applications. Thus, alkylaluminoxanes, such as MAO or R₃Al–MgCl₂, can fulfill all of the five roles defined above for a cocatalyst activator.³⁴

MAO activates metallocene catalysts via a Lewis acidic site within its structure. It has been suggested that there is only one Lewis acidic site in each oligomer of [Al(O)Me]_n.²⁸ The cocatalyst/metal quotient has an important effect on the polymerization behavior of the metallocene catalyst especially activity. Generally, increasing the quotient increases the activity of the catalyst; however, at very high quotients the cocatalyst activity begins to decrease. The distance between the cationic metal and the anionic counterion can certainly affect the catalytic behavior of metallocene catalyst. Sterically hindered metallocenes and CGCs effectively push the anion away from the cationic active center and thus have lower barriers to cation/anion separation, which is viewed as necessary to reveal an open coordination site for monomer complexation. Thus, polymerization activity can be very high, even with bulker olefins. Copolymerizations of higher a-olefins with ethylene are generally feasible. For a certain sterically expanded CGC activated with MAO, it has been reported that propylene is polymerized with a greater activity than ethylene.³⁵

3.21.3.2 Propagation Steps

The metallocene catalyst polymerization active center is generally characterized as a coordinatively unsaturated cationic center of a transition metal with which an anion derived from a cocatalyst (e.g., MAO) is loosely associated; additionally there is a metal-carbon bond present and this alkyl group is the growing polymer chain (see **Figure** 7).³⁶ The propagation steps that constitute chain growth generally consist of three consecutive and repeating events:³⁴

- Complexation of the monomer to the vacant coordination site of the metal
- 2. Migratory insertion of the complexed monomer into the metal-carbon bond
- Regeneration of an active center, which contains a new vacant coordination site.

Thus, the propagation steps are consecutive and rapid insertions of coordinated monomer into the growing polymer chain. Both the position of the coordinated monomer and the location of the regenerated vacant site can significantly impact the catalyst polymerization stereoselectivity, an issue that will be discussed in Section 3.21.5. While there is just one possibility for ethylene coordination and insertion, there are four possible modes for 1-alkene (α -olefin) coordination and insertion. Selection among these modes determines the



Figure 9 Four different coordination modes for a 1-alkene monomer.^{10c,24f}

microstructure and configuration of the resulting polymer, and therefore, greatly impacts the properties obtained.^{10c,24f,37} **Figure 9** depicts the four possible complexation modes possible for a 1-alkene monomer immediately before migratory insertion. Generally, metallocene polymerization catalysts employ a 'primary' or 1,2 insertion mode and thus modes (c) and (d) are highly preferred. 'Secondary' 2,1 insertion modes (a) and (b) are generally uncommon with metallocenes. The basis of this selectivity is probably steric since a primary insertion keeps the olefin substituent away from the congested metal center.³⁸ The regularity of the complexation and insertion modes represented by (c) and (d) at the active center determines the configuration of the formed polymer stereocenters and thus, the tacticity.^{36d,39}

Once the vacant coordination site is occupied by a complexed monomer, the next productive step is the migratory insertion of the monomer into the metal–carbon bond. Two limiting insertion mechanisms are conceivable:^{37,39}

- 1. A chain migratory insertion mechanism
- 2. A chain stationary insertion mechanism.

After the chain migratory insertion mechanism, the newly formed polymer chain occupies the position that previously was the vacant coordination site, where the monomer coordinated. After a chain stationary insertion mechanism, it is predicted that the newly formed polymer chain occupies its original position. Although a distinction between these two mechanisms may not be important for ethylene polymerization, it is crucial to understanding the polymerization of 1-alkenes, where stereochemistry is highly relevant.

The chain migratory insertion mechanism is universally accepted and the original mechanistic description originated with Cossee and Arlman⁴⁰ for heterogeneous ZN catalyst polymerizations. Figure 10 shows the Cossee–Arlman mechanism

wherein a 2+2 cycloaddition necessarily results in migration of the growing polymer chain to the coordination site that was previously vacant. Note that a separate equilibrium does allow for an 'apparent' chain stationary insertion mechanism, but the elementary reaction step for monomer insertion always involves chain migration.

There is an additional interaction that can affect metallocene catalyst polymerization. The 'agostic' (from Greek, meaning to hold to one's self) interaction is a metal-hydrogen interaction between the electrophilic metal center and the bonding electrons of a C-H bond, usually on the growing polymer chain.⁴¹ An α -agostic interaction (involving the C–H bond of an α -carbon) limits rotational degrees of freedom and can stabilize the transition state for monomer insertion by increasing the effective electron count at the metal and reorienting orbital lobes for increased overlap.⁴² The α -agostic interaction is probably only feasible for primary alkyl groups (e.g., M-CH2-CH (Me)-polymer) and unlikely for sterically encumbered secondary alkyl groups (e.g., M-CH(Me)-CH2-polymer). Since 1-alkene polymerizations with metallocenes proceed via a primary insertion mechanism, the α -agostic interaction is generally possible in the transition state for propagation.⁴³ Additionally, β -agostic and γ -agostic interactions have been proposed and these are illustrated in Figure 11.44

If an unlikely secondary insertion of a 1-alkene does occur, leaving $-CH_{2}$ - at the β -carbon, a ground state β -agostic interaction may be formed because this satiates the electrophilicity of the metal with the electron density of a sterically accessible C-H bond.⁴⁵ This interaction blocks the open coordination site and thereby slows subsequent monomer coordination and insertion. A ground state γ -agostic interaction is believed to result following the insertion of monomer into a metal–carbon bond with α -agostic assistance. The insertion event converts the α -hydrogen into a γ -hydrogen. The γ -agostic interaction is



Figure 10 The Cossee–Arlman mechanism for 1-alkene polymerization requires a chain migratory insertion step. 5b M = transition metal atom and \Box = vacant coordination site.



Figure 11 The metal-hydrogen agostic interaction can occur with the α -, β -, or γ -hydrogen of a pendant alkyl chain.



Figure 12 Chain migratory mechanism for olefin polymerization with metallocene catalysts.

usually fleeting and is generally free to rearrange to a ground state β -agostic interaction prior to the transition state α -agostic structure.

Figure 12 summarizes the propagation events for olefin polymerization. Monomer coordinates to a vacant site on the cationic metallocene catalyst. Primary monomer insertion is assisted by an α -agostic interaction during a four-membered cyclic transition state, resulting in a ground state γ -agostic interaction. This can rearrange to a β -agostic interaction but must forego this interaction to create an open coordination site for subsequent monomer coordination.

3.21.3.3 Termination Events

There are five major chain termination events for metallocene-catalyzed olefin polymerization (M = the transition metal and ancillary ligands):

- 1. β -hydrogen elimination M-CH₂-CH(CH₃)-Polymer \rightarrow M-H + CH₂=C(CH₃)-Polymer
- 2. β-hydrogen transfer to monomer (chain transfer to monomer)

 $M-CH_2-CH(CH_3)-Polymer + CH_2=CH(CH_3) \rightarrow M-CH_2-CH(CH_3)-H + CH_2=C(CH_3)-Polymer$

- 3. β -alkyl abstraction M-CH₂-CH(CH₃)-Polymer \rightarrow M-CH₃ + CH₂=CH-Polymer
- Chain transfer to an organometallic compound M-CH₂-CH(CH₃)-Polymer + (CH₃)₂Al(CH₃) → M-CH₃ + (CH₃)₂Al-CH₂-CH(CH₃)-Polymer
- 5. Reaction with hydrogen as a chain transfer agent $M-CH_2-CH(CH_3)-Polymer + H-H \rightarrow M-H + H-CH_2-CH$ (CH₃)-Polymer.

In the absence of MAO, β-hydrogen elimination and β -hydrogen transfer to monomer (chain transfer to monomer) are common chain transfer reactions that lead to polymers with an olefinic end group. Such polymer chains are more susceptible to sunlight and oxidizing agents, adversely affecting their useful lifetime. Under certain conditions, the long chain olefins can function as macromonomers, coordinate and insert, and lead to long-chain branching. When the monomer is ethylene, materials related to LDPE can result. This can be considered a copolymerization process when the macromonomers are effectively reincorporated.⁴⁷ β-alkyl abstraction is relatively rare and generally is observed only when the alkyl group is methyl.⁴⁸ β -alkyl abstractions can also occur when the β -carbon is part of a strained ring, although this does not usually constitute a chain termination event. An example is found in the polymerization of methylene cyclobutane.49

Kinetic studies of olefin polymerization with metallocene catalysts reveal that β -hydrogen elimination and β -hydrogen transfer to monomer are the predominant chain transfer reactions. However, for some substituted *ansa*-metallocene catalysts, β -hydrogen transfer to monomer dominates or may be the exclusive mode.⁵⁰ Most computational studies confirm that the energetic barrier for β -hydrogen transfer to monomer is considerably less than that for β -hydrogen elimination alone.⁵¹

Generally, the quotient of aluminum/transition metal is high in the polymerization medium (e.g., MAO with a 1000:1 ratio of Al:Zr) and chain transfer to aluminum is therefore feasible.⁵² Polymer chains bound to aluminum have been observed⁵³ and can often be functionalized. Exhaustive aqueous quenching must be achieved to replace aluminum with hydrogen and remove inorganics from the polymer since they can contribute to polymer instability and increased ash content. Therefore, chain transfer to aluminum is often not a desirable termination event in commercial polyolefin production.⁵³

The use of molecular hydrogen to regulate molecular weight is a common method in the field of coordination polymerization and has been used since the early generations of ZN catalysts.^{20,54} Hydrogen is inexpensive, simple to employ, and does not introduce impurities into the obtained polymers. Also, chain transfer to hydrogen results in a saturated polymer end group. Therefore, using molecular hydrogen for regulating and reducing polymer molecular weight is a reasonable and effective method.^{5a,5b,10c,55} Moreover, chain transfer to hydrogen results in a metal–hydrogen bond, which is ready for additional olefin insertion. Added molecular hydrogen ensures that all or most metals remain catalytically active.⁵⁶ A net increase in propylene polymerization activity has been reported in the presence of hydrogen using a metallocene catalyst.⁵⁷

The metallocene-mediated chain propagation mechanism involves primary insertion of the α -olefin (1,2-insertion) during the polymerization.⁵⁸ Some misinsertions (secondary, 2,1-insertion) can occur⁵⁹ and these result in pendant secondary alkyl groups into which propylene insertion is comparatively sluggish.⁶⁰ In fact, the 2,1-misinsertion regioerrors highly inhibit the polymerization activity.⁶¹ Chain transfer to molecular hydrogen readily converts secondary alkyl species (e.g., Zr–CHR–CH₂–polymer) to metal hydrides (Zr–H) and consequently reactivates those dormant sites.

3.21.4 Ethylene Polymerization

Ethylene, the simplest olefin monomer, can be polymerized using free radical initiation^{5a,50} or coordination polymerization. The polymerization can be performed via solution, bulk, slurry, and gas phase methods.^{5a,10h,31a} PE is the most commonly used synthetic polymer worldwide. The industrial production and scientific research of PE still continues to expand. This continued growth and reasonable profitability exists because of the variety of applications for which PE is suited. Specific attributes include high chemical resistance, a large range of mechanical properties, low specific gravity, low production cost, and facile processability.^{10h,50}

3.21.4.1 Types and General Properties of PE

'Polyethylene' actually represents several different polymers having similar chemical structure, but different properties, which arise from subtle differences in molecular architecture. **Figure 13** shows the generalized structures of several PE types.⁶² Linear PE is its ideal and simplest form. The polymer is produced via coordination catalysis and has a high level of crystallinity and a high melting point (135 °C). The linear polymers have high symmetry and pack well in the solid



Figure 13 Generalized structures of several polyethylene types.

state, leading to a relatively high-density material and its commonly used name 'high-density polyethylene' (HDPE).

Branched PE is made in two general forms. LDPE is a class of PE containing long and short irregular branches and it is prepared via a free radical process. The other class is LLDPE and is a copolymer of ethylene with another 1-alkene, generally C4 to C8, and most often 1-butene, 1-hexene, 1-octene, or 4-methyl-1-pentene. This polymer contains only short branches and single-site catalysts render a polymer with a very regular distribution of these short chains (termed mLLDPE for 'metallocene' - somewhat of a misnomer because CGCs are usually employed), while classical heterogeneous catalysts generally provide an irregular distribution. Because of the branches, LDPE and LLDPE do not have compact structures and therefore are of lower density with certain processing advantages.^{10h,50} Additionally, there are branched PE s with very low density PE (VLDPE) and ultra-low density PE (ULDPE).

Table 1 summarizes the general properties observed with varying grades of PE, including ultrahigh molecular weight polyethylene (UHMWPE), which lacks branching. UHMWPE has a molecular weight over 5 million Daltons and forms a unique fiber which is one of the strongest materials known for a given weight.^{32a,63}

3.21.4.2 PE s Produced by Different Catalysts

The two main methods used for polymerization of ethylene afford rather different polymeric structures. The polymer produced using free radical polymerization (LDPE) is highly branched (both short and long branches without any regularity) with low crystallinity. In contrast, coordination polymerization using classical ZN,65 Phillips,66 metallocene and post-metallocene⁶⁷ catalysts produce polymers which are naturally linear. However, PE with short and regular branches (and even long-chain branches in certain cases) can be produced with these catalyst systems under certain conditions.⁶⁸ Both HDPE and LLDPE, both of which have an essentially uniform structure, are produced exclusively with coordination catalysts. PEs from single-site metallocene catalysts are generally the most uniform in structure. Figure 14 compares the MWDs obtained from different catalyst systems.^{14,66a,69} In general, ZN catalysts produce PE with a MWD of 5-20, while metallocene catalysts produce PE with a MWD of 1-2, numbers that indicate the presence of a single operative catalytic site. PE produced by the Phillips catalyst has a MWD broader than that from ZN



Figure 14 Comparison of molecular weight distributions of linear polyethylenes obtained using the Phillips, Ziegler, and metallocene catalyst systems.

systems.^{66a} **Table 2** correlates types of PE s with typical catalysts used for their preparation.

Metallocene catalysts are used in both heterogeneous and homogeneous form for polymerization of ethylene in both industrial and academic settings.^{10e,70} Highly active MAO-activated metallocenes were first reported for the polymerization of ethylene.^{14,69} Refined versions of these original catalyst systems are able to polymerize ethylene with high activity to high-molecular-weight polymer with polymerization temperatures of 50-80 °C.71 Catalyst activity generally decreases in the following order: Zr>Hf>Ti.⁷¹ In fact, certain single-site catalysts exhibit activities 10 000 times greater than that of classical, heterogeneous ZN catalysts. Disadvantages include the high quotient of MAO/catalyst needed to reach high activity, the low bulk density of the PE obtained, the irregular shape of the polymer granules (poor morphology), and fouling of the polymerization reactors.⁷² To address these issues, the following approaches were pursued: use of substituted cyclopentadienyl ligands; use of a bridge connecting the metallocene ligands (ansa-metallocenes); use of CGCs (CGCs with pendant amide ligands); and use of supported metallocene catalysts, to name a few.^{10e,73}

Homopolymerization of ethylene can result in PE with long-chain branches when certain group IV CGCs are employed.⁷⁴ These catalysts, which are technically monocyclopentadienyl-amido half-sandwich compounds, can

 Table 1
 Some general properties of polyethylenes^{50d,54a,63,64}

Grade	Density (g cm ^{−3})	Molar mass (g mol ⁻¹)	Crystallinity (%)	Т _т (°С)
HDPE LDPE LLDPE VLDPE ULDPE UHMWPE	$\begin{array}{c} 0.940 - 0.965\\ 0.915 - 0.930\\ 0.90 - 0.94\\ 0.89 - 0.91\\ \sim 0.86\\ 0.93\end{array}$	$\begin{array}{c} 10^{3} 10^{7} \\ 8.9 \times 10^{4} \mbox{ to } 4.7 \times 10^{5} \\ 5.0 \times 10^{4} \mbox{ to } 5.0 \times 10^{5} \\ 5.8 \times 10^{4} \mbox{ to } 1.2 \times 10^{5} \\ \mbox{>}10^{6} \end{array}$	55–95 30–55 40–60 25–40 15 ≥ 50	125–145 104–120 120–125 92–123 ≥132

Polyethylene	Structure	Catalysts for preparation
HDPE	Linear structure (linear carbon chain)	ZN, Phillips, metallocene, and FI catalysts
LDPE	Random branching with either short or long branches	Free radical, metallocene, and late transition metal catalysts
LLDPE	Nonuniformly distributed short-branched copolymer	ZN catalyst
mLLDPE	Uniformly distributed short-branched copolymer; branching increase possible	Metallocene catalyst
VLDPE	High comonomer content; short branches; lower density and $T_{\rm m}$	ZN and metallocene catalysts
ULDPE	Very high comonomer content; short branches; very low T_m and crystallinity (soluble at ambient temperature)	Metallocene and late transition metal catalysts
UHMWPE	Linear structure; very high M_n	ZN, metallocene, and FI catalysts

Table 2	Types	of nolvethylene	and catalysts f	or preparation ^{50a,50d,54a,63}

FI catalysts are a class of phenoxy-imine organometallic complexes pioneered by Fujita et al.⁶⁷¹

form polymers with vinyl end groups via β-hydrogen elimination. The large α-olefins behave as macromonomers and can be incorporated as a comonomer into another PE chain. Thus, insertion of the macromonomer into the metal–polymer bond results in PE with long-chain branching obtained from ethylene alone.⁷⁵ Figure 15 shows the mechanism of this polymerization, which usually requires elevated temperatures (>100 °C) for significant macromonomer incorporation to occur. Thus, LLDPE formed from CGC systems can contain branches that are much larger than that afforded by the added comonomer. This is in contrast to LLDPE made by bent metallocene systems, which show almost no proclivity toward macromonomer reincorporation and yield strictly LLDPE with short branches that match the comonomer.⁷⁶

3.21.4.3 Factors Affecting Catalyst Activity and Molecular Weight

There are many factors that influence a catalyst's polymerization behavior and the properties of the obtained polymer, including the identity of the transition metal, the cocatalyst:catalyst ratio, the role of the solvent, the influence of the ligand structure, the effect of the bridge (for *ansa*-metallocenes), the polymerization temperature, the polymerization pressure, and so on.^{5a,5b} Since reports on catalyst performance employ a very large number of different polymerization conditions, it is quite difficult to reach unanimous conclusions about catalyst behavior.

Two important factors can be considered here in order to assess catalyst behavior: catalyst activity and molecular weight of the obtained polymer (Table 3). In comparing catalysts with simple cyclopentadienyl ligands, Cp₂ZrCl₂/MAO produces



Figure 15 Mechanism of forming polyethylene with long-chain branches from ethylene alone using a constrained geometry catalyst (CGC).

HDPE with lower molecular weight than the polymer made from Cp₂TiCl₂/MAO, while the activity of the Zr-based catalyst is higher than the Ti-based one.⁷⁷ Alkyl-substituted Cp ligands usually have a positive influence on the activity of a metallocene catalyst. Substitution of one hydrogen atom on each Cp with an alkyl group such as methyl or ethyl increased the propagation rates of ethylene polymerization and also the molecular weight of the HDPE obtained. Alkyl substituents are slightly electron donating and reduce the Lewis acidity of the Zr cation in the catalyst, which presumably results in a weaker Zr-polymer bond and an increased rate of propagation and, simultaneously, a decrease in the rate of termination reactions. Thus, the inductive electronic effect of an alkyl group is responsible for both increasing the rate of polymerization and increasing molecular weight. Substitutions of higher linear alkyl groups show a greater effect which is not seen when the alkyl group is branched.^{77b} The use of indenyl (Ind) ligands instead of Cp nearly doubles catalyst activity (Table 3, entries 1 and 2). However, fluorenyl (Flu) ligands often do not impart high activity, which could be blamed on the instability of fluorenyl complexes (Table 3, entry 3).^{10j} The molecular weight of the PE obtained increases slightly by changing Cp to Ind to Flu (Table 3, entries 1-3). This behavior is attributed to ligand bulkiness close to the transition metal, which increasingly prevents the β-H elimination termination reaction, leading to higher molecular weight PE.

Bridged *ansa*-metallocene complexes with considerable steric bulk (Table 3, entries 7–9) exhibit very high polymerization activities, which likely rely on cation/anion separation enforced by the ligand. Analogs with a dimethylsilyl bridge generally had lower activity than those catalysts with a two-carbon bridge. It should be noted that the bridged metallocenes require a much higher cocatalyst:catalyst ratio (e.g., a ratio of Al:Zr = 20 000:1) to show comparably high activity. Therefore, nonbridged catalysts are generally more effective at low ratios of Al:Zr.

The open ligand structure of CGCs (see **Figure 3(e)**) and their tolerance of high polymerization temperatures allow the formation of PE with long-chain branches, usually with high activity.^{77b,78} Certain alkylated CGCs, when activated with boron or borate compounds such as $B(C_6H_5)_3$, $B(C_{12}F_9)_3$, and $[Ph_3C][B(C_6F_5)_4]$ yield ultrahigh molecular weight PE – because of high propagation rates and minimal options for chain termination.⁷⁹ If activated with MAO, the catalyst can produce long-chain branched PE and this behavior indicates that the catalyst is unusually active toward α -olefins. This catalyst behavior might be a result of the low degree of steric hindrance at the

 Table 3
 Comparison of activity and polyethylene molecular weight for several metallocene/MAO catalyst systems^{10j}

Entry	Structure	Activity (kg PE (g M⋅h) ⁻¹)	M _w (g mol⁻¹)
1	CI-Zr-CI	1 490	290 000
2	CI-Zr-CI	3 200	470 000
3	CI-Zr-CI	423	1 000 000
4	CI-Zr-CI Ph	4970	270 000
5	CI-Zr-CI	5724	
6	CI-Zr-CI Ph	15 120	580 000
7	CI-Zr-CI	16200	350 000
8	CI-Zr-CI	26 300	610 000
9	CI-Zr-CI	28 500	440 000

metal center of the catalyst in comparison with metallocenes. That is, CGCs bear a κ^1 -amido instead of an η^5 -cyclopentadienyl ligand. Additionally, the nitrogen atom of the amide ligand donates electron density to the metal center and

prevents the reduction of Ti(IV) to Ti(III). Thus, the high activity of the catalyst can be attributed to an enhanced stability of the Ti(IV) catalyst species.⁸⁰ Moreover, a theoretical study of the catalyst systems (η^5 -C₅H₄SiH₂NH)MMe and [(η^5 -C₅H₄SiH₂NH)

3.21.5 1-Alkene Polymerization

The metallocene-mediated polymerization of 1-alkenes has been a major pursuit of many academic and industrial laboratories since the early 1980s. While inexpensive propylene has received most of the attention, other 1-alkenes have been vigorously studied as well, including linear monomers 1-butene, 1-pentene, 1-hexene, 1-octene, 1-decene, and branched monomers 3-methyl-1-butene, 4-methyl-1-pentene, and vinyl cyclohexane.

3.21.5.1 Stereoselectivity

The focus of this section is the polymerization stereocontrol made possible by ligand modification of metallocenes. Thus, propylene will be the monomer of focus since the stereochemistry of polypropylene is the best understood of any polyolefin,^{10c} if not of any synthetic polymer ever studied. The observed correlation between a catalyst's structure/symmetry and a catalyst's stereoselectivity is often referred to as *Ewen's Symmetry Rules*.⁸² Metallocenes have been manipulated to a remarkable degree to direct the enantiomorphic site control mechanism⁸³ for polymerization stereoselectivity.^{84,85}

3.21.5.2 Aselective

The first metallocene systems that showed significant activity toward propylene were Cp₂MCl₂/MAO, with M=Ti or Zr. These systems afforded 'perfectly' atactic polypropylene, which had been essentially elusive with heterogeneous ZN catalysts.⁸⁶ Subsequently, a number of metallocene systems have been found to be aselective, affording poly(1-alkenes) with little or no stereoselectivity. Generally, these metallocenes are of high symmetry, such as $C_{2\nu}$ (e.g., Cp₂ZrCl₂) or C_s with a mirror plane of symmetry equating the two Cp or Cp-derived ligands (e.g., *meso*-(C₉H₆CH₂CH₂C₉H₆)ZrCl₂) (Figure 16).

The aselectivity is explained as follows. During the transition state for olefin insertion, the two α -hydrogens have an almost equal chance (ignoring the usually minimal effect of chain-end control⁸⁷) of occupying the α -agostic position because of the similar repulsive polymer–ligand interactions



Figure 16 Atactic polypropylene is obtained with most $C_{2\nu}$ metallocenes and most C_s metallocenes with the 'horizontal' mirror plane as shown.

experienced. The kind of stereocenter produced (*R* or *S*) is determined by which enantioface (*re* or *si*) of the approaching monomer is employed for coordination and insertion. In turn, the enantioface that is chosen depends on a repulsive interaction between the growing polymer chain and the methyl group of the inserting propylene monomer during the transition state. Since there is little control in the location of the polymer chain, there is little control in whether an *R* or *S* stereocenter results (**Figure 17**). Obviously, this situation changes for the stereoselective catalysts discussed below. Additionally, simple CGCs are fairly aselective. The parent system, Me₂Si(η^5 -C₅Me₄) (η^1 -N-*t*Bu)TiCl₂/MAO (see **Figure 3(e)**), affords polypropylene that is slightly syndiotactic, yet amorphous with [*rrrr*] = 22%.³⁵

3.21.5.3 Isoselective

Early workers in the field recognized the importance of metallocene symmetry in controlling tacticity. The metallocene-mediated polymerization of propylene to form isotactic polypropylene was first conducted in 1984 in the laboratory of Kaminsky,⁸⁶ who employed the racemic form of the C_2 -symmetric ansa-zirconocene rac-($C_9H_{10}CH_2CH_2C_9H_{10}$) ZrCl₂ which was synthesized in the laboratory of Brintzinger. Figure 18 shows the consensus isoselective mechanism for preparing isotactic polypropylene with C₂-symmetric metallocene catalysts. The growing polymer chain is preferentially directed away from the indenyl ligand into a more open quadrant of the metallocene. Because the coordination sites are homotopic, both sites are selective for the same enantioface of coordinating propylene and isotactic polypropylene is obtained. Isoselectivities for metallocene-based systems can be well over 99%, but have not yet matched the stereoselectivity (or polymer melting temperature) of the best classical heterogeneous ZN systems.88,89 C1-symmetric catalysts can also display high isoselectivity. In this case, both sites have the same enantiofacial selectivity, or a site epimerization mechanism operates such that only one of the two coordination sites is employed for coordination and insertion.⁸⁹

3.21.5.4 Syndioselective

Aware of the early successes for obtaining isotactic polypropylene from C_2 -symmetric metallocenes, Ewen, Ravazi and coworkers reasoned that a C_s -symmetric metallocene with mirror image coordination sites (enantiotopic sites) would afford syndiotactic polypropylene. The synthesis and investigation of the appropriate fluorene-based catalyst system, Me₂C(C₅H₄)(C₁₃H₈)ZrCl₂/ MAO demonstrated this point very well,^{34a} constituted the first practical synthesis of syndiotactic polypropylene, and led to the formulation of *Ewen's Symmetry Rules*.⁸² The syndioselective mechanism is shown in **Figure 19**. Note that a regular alternation of coordination sites is required to maximize syndioselectivity. The most syndioselective systems rely on sterically expanded fluorenyl ligands and can be of the metallocene⁹⁰ or CGC³⁵ type.

3.21.5.5 Hemiisoselective

Hemiisotactic polypropylene is another stereoregular polymer that can be produced by single-site catalysts. The direct formation of this material is possible only with a specific class of C_1 -symmetric cyclopentadienyl-fluorenyl metallocenes. With







Figure 19 Mechanism for syndiotactic polypropylene formation.



Figure 20 Mechanism for hemiisotactic polypropylene formation.

this polymer tacticity, every other stereocenter has the same configuration and these are separated by stereocenters having random stereochemistry.⁹¹ Ewen and Razavi⁹² developed the first hemiisoselective metallocene catalyst, Me₂C(3-Me-C₅H₃) (C13H8)ZrCl2/MAO. This metallocene has two different coordination sites; one is highly isoselective and the other is aselective. Reducing the symmetry of the syndioselective catalyst Me₂C(C₅H₄)(C₁₃H₈)ZrCl₂ from C_s to C_1 symmetry by the addition of a small group on the 3-position of the cyclopentadienyl ring is the main key for the production of hemiisotactic polypropylene in these systems. As a result, two different diastereotopic coordination sites will be available; one is aselective and the other is highly isoselective. Therefore, during the polymerization process, the catalyst alternately employs these two sites, making an interesting architecture of polypropylene. The hemiisoselective mechanism is detailed in Figure 20.93

3.21.5.6 Stereoblock

As apparent from the above sections, tacticity control is normally best exerted with bridged (*ansa*) metallocenes. However, Coates and Waymouth⁹⁴ devised a unique approach to dynamic stereocontrol that relied on the fluxional behavior of an unbridged metallocene catalyst. Figure 21 depicts this strategy wherein the catalyst oscillates between pseudo- C_2 symmetry (racemic forms) and pseudo-Cs symmetry (meso form). Theoretically, reaction conditions can be selected such that the interconversion of rotamers occurs on a timescale somewhat faster than the timescale of polymer chain formation. When propylene enchainment occurs from either of the racemic forms, an isotactic sequence of polypropylene is created. When propylene enchainment occurs from the meso form, an atactic sequence of polypropylene is created. If multiple blocks of the appropriate length are created in the same chain (three at a minimum with isotactic-atactic-isotactic), an elastomeric morphology should result. Indeed, reaction conditions can be tuned to produce thermoplastic elastomeric polypropylene. Subsequently, Busico et al.95 analyzed the polymers by ¹³C NMR at the heptad and nonad levels and concluded that the meso form probably contributes little to the mechanism of stereocontrol. Instead, sequences of ... RRRR... and ... SSSS... are formed as the catalyst oscillates between the two pseudo-C2-symmetric racemic forms. When these isotactic sequences are of the appropriate length and spaced apart by



Figure 21 Proposed mechanism for stereoblock isotactic/atactic polypropylene formation.

intervening, atactic phase boundaries, crystallizable and amorphous sequences coexist in the same polymer chain, resulting in the elastomeric behavior.

3.21.6 Diene Polymerization

3.21.6.1 Conjugated Dienes

Metallocene-mediated diene polymerization is significantly less developed than α-olefin polymerization. Generally, metallocene/ MAO catalyst systems exhibit low activity for the polymerization of conjugated dienes, including styrene, 1,3-butadiene, isoprene, and 1-vinylcyclohexene.96 This low activity is demonstrated by rather low incorporation levels (0.1-2.2 mol.%) when 1,3-butadiene is copolymerized with propylene using a series of well-understood C2-symmetric bis-indenyl catalysts activated with MAO.97 1-Vinylcyclohexene has been polymerized by at least two metallocenes with MAO as the cocatalyst: rac-(C₉H₆CH₂CH₂C₉H₆)ZrCl₂ vields isotactic 1.2-poly (1-vinylcyclohexene) and Me₂C(C₅H₄)(C₁₃H₈)ZrCl₂ yields trans-1,4-poly(1-vinylcyclohexene).98 These conjugated monomers are much more active with mono-cyclopentadienyl (non-metallocene) complexes and numerous articles and reviews are available for that class of catalyst.80,99

The greatest advances in the metallocene-mediated polymerization of conjugated dienes have occurred with lanthanide-based metallocenes, including the metals yttrium, lanthanum, neodymium, and samarium.¹⁰⁰ For example, as shown in Figure 22(a), $(C_5Me_5)_2Sm(THF)_2$ can be activated with either MAO containing triisobutylaluminum (MMAO) or with triisobutylaluminum/[Ph₃C][B(C₆F₅)₄] to yield a highly active catalyst for converting 1,3-butadiene to *cis*-1,4-poly (1,3-butadiene) with up to 98.8% *cis*-1,4 enchainment, M_n around 10^5 – 10^6 , and narrow MWDs less than 2.¹⁰¹ Another example (Figure 22(b)) employs a neutral allyl complex of neodymium incorporating the Ewen–Razavi ligand. This catalyst requires no cocatalyst and converts styrene to highly syndiotactic polystyrene ([*rrrr*] ≥ 99%) with M_n between 21 000 and 135 000 and MWDs near 2.¹⁰²

3.21.6.2 Nonconjugated Dienes

The typical group IV metallocenes have been applied to the polymerization of nonconjugated dienes with great success. Reviews of the zirconocene-mediated cyclopolymerization of linear α, ω -dienes thoroughly explain the detailed



Figure 22 Conjugated diene polymerizations with (a) samarocene and (b) neodymocene complexes.

stereochemical issues involved^{84,103} and Figure 23 encapsulates the key mechanistic events. With 1,5-hexadiene, the percentage of *trans* rings in the formed polymer is acutely sensitive to the ligand structure and varies from 19% with $(C_5Me_5)_2ZrCl_2/MAO$ (Figure 23(b)) to 84% with Cp₂ZrCl₂/ MAO (Figure 23(a)).¹⁰³ Cyclopolymerization is dominant when the ring size is 5, 6, or 7 (Figure 23(c)) and simple 1,2 enchainment, followed by cross-linking ensues with dienes that are too short (1,4-pentadiene) or too long (1,8-nonadiene and longer) for efficient cyclization.

3.21.7 Copolymerization

3.21.7.1 Ethylene/Propylene

The first metallocene-mediated ethylene/propylene copolymerizations were reported by Kaminsky in 1983 and employed the Cp₂TiMe₂/MAO catalyst system.¹⁰⁴ Advantages of metallocenes over classical heterogeneous ZN systems for ethylene/ α -olefin copolymerizations include a more random distribution of comonomer, a narrower MWD, and a decreased fraction of oligomers, which tend to compromise tensile strength and other mechanical properties.^{86,105}

Reactivity ratios have been determined for many systems and representative values are summarized in Table 4. Additional values have been compiled previously.¹⁰⁶ The reactivity ratios vary over 2 orders of magnitude as a function of the ligand structure. Decamethyl zirconocene dichloride (Table 4, entry 5) has a very large $r_{\rm e}$ value and a very small $r_{\rm p}$ value, indicating the extreme steric difficulty of inserting propylene versus ethylene. The syndioselective Ewen-Razavi catalyst (Table 4, entry 6) has a remarkably low r_e value of 1.3, a signal of its indifference toward reacting with ethylene or propylene following an ethylene insertion. For most of the metallocenes (Table 4, entries 3–11), the reactivity ratio product $(r_e \cdot r_p)$, which is a measure of the sequence distribution, is closer to unity than those found with classical heterogeneous ZN systems (Table 4, entries 1-2). Thus, the comonomer distribution or homogeneity can be controlled by the choice of catalyst.

In **Table 4**, all r_e values are greater than unity and all r_p values are less than unity. Thus, these reactivity ratios uniformly suggest that ethylene insertion is more facile than propylene insertion. A curious exception to this 'rule' has been reported for ethylene and propylene homopolymerizations. **Table 5** shows a series of such



Figure 23 The metallocene-mediated cyclopolymerization of 1,5-hexadiene can be (a) *trans* selective or (b) *cis* selective, depending on the catalyst structure. (c) The cyclopolymerization of $\alpha_{,\omega}$ -dienes occurs efficiently for 1,5-hexadiene, 1,6-heptadiene, and 1,7-octadiene.

Entry	Catalyst	Temperature (°C)	r _e	r _p	r _e ∙ r _p	References
1 2	TiCl ₃ /AlEt ₂ Cl MgCl ₂ /EB/TiCl ₄ /AlEt ₃		25 13.4	0.10 0.40	2.5 5.4	105 105
3	CI-Zr-CI		48	0.015	0.72	105
4	Me-Zr-Me		31.5	0.005	0.16	107
5	CI-Zr-CI		250	0.002	0.50	105
6	CITZT-CI		1.3	0.20	0.26	105

 Table 4
 Comparison of reactivity ratios for ethylene/propylene copolymerizations between heterogeneous ZN systems (entries 1–2) and several metallocene/MAO catalyst systems (3–11)

(Continued)

Entry	Catalyst	Temperature (°C)	r.	r_	r. , r.	References
Littiy	outuryor	(0)	re	1p	re rp	110101011000
7		130 140 150	2.89 4.33 6.36	0.324 0.377 0.436	0.94 1.65 2.77	106, 108 106, 108 106, 108
8	CI-Zr-CI	40 60 80	8.03 4.09 2.31	0.08 0.19 0.27	0.64 0.78 0.62	109 109 109
9	Ph Sizr-Cl Ph	40 60 70 80	$\begin{array}{c} 6.66 \\ 4.09 \\ 5.04 \pm 0.05 \\ 3.82 \end{array}$	$\begin{array}{c} 0.26 \\ 0.49 \\ 0.35 \pm 0.03 \\ 0.55 \end{array}$	$\begin{array}{c} 1.73 \\ 2.00 \\ 1.76 \pm 0.03 \\ 2.10 \end{array}$	109 109 110 109
10	CITZT-CI	40 60 80	15.8 7.8 12.0	0.15 0.41 0.30	2.37 3.20 3.60	109 109 109
11		70	2.84 ± 0.55	0.34 ± 0.04	0.83 ± 0.24	110

homopolymerizations with five different metallocene/MAO systems, along with the homopolymerization 'activity quotient', which is simply the activity of a propylene polymerization divided by that of an ethylene polymerization.³⁵ The first four metallocenes (Table 5, entries 1-4) have activity quotients akin to those of all other reported systems - less than unity. However, the sterically expanded CGC (Table 5, entry 5) has a quotient much greater than 1, 5.80. A reasonable explanation for this behavior invokes an electronic preference instead of a steric one in the rate-determining step for polymerization. During the transition state for monomer insertion, the consensus transition state¹¹¹ involves buildup of positive charge at the 2-position of the alkene. Thus, α-olefins are electronically preferred in metal-mediated olefin polymerization, but sterics seem to dominate in all other cases and result in faster rates for the smallest olefin, ethylene.

10 ...

3.21.7.2 Ethylene/Higher 1-Alkenes

The commercial production of LLDPE¹¹² relies on copolymerization with α -olefins such as 1-butene, 1-hexene, 1-octene, and, to a smaller degree, 4-methyl-1-pentene. Propylene is not employed for LLDPE because the relatively small and sparse methyl groups of ethylene/propylene copolymers are accommodated in the crystal and are far inferior to butyl and hexyl groups (from 1-hexene and 1-octene, respectively) for the improvement of mechanical properties. Very long α -olefins, such as 1-hexadecene, have been investigated for creating specialized LLDPE that shares properties with commercial LDPE made via free radical polymerization.¹¹³

A very wide variety of catalysts and comonomers has been investigated in metallocene-mediated ethylene/ α -olefin copolymerization. Table 6 catalogs several of these, along with their

Entry	Catalyst	Ethylene	Propylene	Activity quotient (C_3/C_2)
1	CI-Zr-CI	5860	840	0.14
2		4 820	790	0.16
3	CI-Zr-CI	1 400	1 220	0.87
4		62 480	100	0.001
5		460	2 670	5.80

 Table 5
 Ethylene versus propylene homopolymerization activity (in kg polymer (mol M·h·[monomer])⁻¹) for five metallocene/MAO systems³⁵

 $T_{\rm p}$ = 25 °C; 1000 eq. MAO; 1.6 µmol catalyst; 80 psi ethylene; 30 ml toluene or 30 ml propylene.

respective r_e and $r_{\alpha\text{-olefin}}$ reactivity ratio parameters. As is usual for classical heterogeneous ZN polymerization systems (**Table 6**, entries 1 and 2), the r_e values are very large and the $r_{\alpha\text{-olefin}}$ values are very small. These numbers reiterate the poor ability of heterogeneous systems to accommodate and incorporate α -olefins compared to single-site catalysts. The metallocenes in **Table 6** (entries 3–13) characteristically have much smaller r_e values and larger $r_{\alpha\text{-olefin}}$ values, which allow for a more uniform distribution of comonomer. Furthermore, these reactivity ratios respond to the nature of the organometallic ligand and this response typifies the versatile and utilitarian nature of single-site catalysts.

3.21.8 Conclusions

Since the 1980s, the fields of organic chemistry, inorganic chemistry, organometallic chemistry, polymer chemistry, catalysis, and surface chemistry have all contributed substantially to advance the field of metallocene-mediated olefin polymerization. The development of metallocenes and the investigation of their polymerization behavior have consumed a vast amount of time and effort in the past three decades – both academically and industrially. Economically, efforts in this area have probably surpassed the \$5 billion mark and this number continues to grow.

The most commonly studied olefins are naturally the least expensive: ethylene and propylene. Higher α -olefins have been studied mostly as comonomers since the homopolymers are usually not crystalline thermoplastics like PE and isotactic polypropylene. More exotic olefin monomers have been investigated in the academic realm but some, such as cyclic norbornene (see Chapter 3.26), have also received industrial attention.

After the synthesis and employment of thousands of metallocenes, a vast amount of information has been obtained regarding catalyst structure–polymer property relationships. This information has been adroitly dissected by a large number of scientists to compile a rather detailed mechanistic understanding of the metallocene-mediated polymerization mechanism. Metallocenes have made possible detailed studies on initiation, propagation, termination, kinetics, and stereochemical control. These studies have been integrated to make possible many novel polyolefins with highly engineered microstructures to meet a wide variety of applications – most of which would probably amaze the founders of ZN polymerization.

Entry	Catalyst	α-Olefin	Temperature (°C)	r _e	Γ _{α-Olefin}	$r_e \cdot r_{\alpha \text{-olefin}}$	References
1	TiCl ₄ /Et ₂ AICI MgCl ₂ (THF) ₂	1-Hexene 1-Octene	50 50	74.18 125.99	0.0129 ~0	0.96	114
2	TiCl ₄ /THF/MgCl ₂ /AlEt ₃	1-Hexene	70	120	<<1		115
3		1-Hexene	40	21.0	~ 0		116
		4.11	40	5.0	0.051	0.00	110
4	ci-zr-ci	Т-нехеле	40	5.6	0.051	0.29	116
5		1-Hexene 1-Hexene	40 80	$\begin{array}{c} 12.9 \\ 71 \pm 4 \end{array}$	0.027 < 0.01	0.35 <0.71	116 117
6	CI-Zr-CI	1-Hexene 1-Octene 1-Decene 1-Hexadecene	60 60 60 80	$\begin{array}{c} 32\pm10\\ 59\pm10\\ 80\pm15\\ 51\pm7 \end{array}$	$\begin{array}{c} 0.012 \pm 0.006 \\ 0.004 \pm 0.002 \\ 0.016 \pm 0.007 \\ < 0.01 \end{array}$	0.38 0.24 1.28 < 0.51	118 118 118 117
7		1-Hexene 1-Octene 1-Decene 1-Hexene	150 150 150 20	11.8 10.94 10.4 4 ± 1	$\begin{array}{c} 0.52 \\ 0.35 \\ 0.75 \\ 0.4 \pm 0.1 \end{array}$	6.14 3.83 7.8 1.5 ± 0.6	119 119 119 120
8		1-Octene	140	7.90	0.099	0.78	121

Table 6 Com	nparison of reactivity	ratios for ethylene/ α -olefin copo	ymerizations between hetero	geneous ZN systems (entries ⁻	1–2) and several metallocene/MAO	catalyst systems (3–13)
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(Continued)

Entry	Catalyst	a-Olefin	Temperature (°C)	r _e	ľα-olefin	$\Gamma_{\theta} \cdot \Gamma_{\alpha-Olefin}$	References
9	CI ^{SIZI-} CI	1-Octene	40	18.9	0.014	0.27	122
10	CI ^S ZI-CI	1-Octene	40	19.5	0.013	0.25	122
11		1-Octene	40	10.7	0.076	0.81	122
12		1-Octene	40	10.1	0.118	1.20	122
13		1-Decene	40	14.9	0.49	7.3	123

Table 6(Continued)

3.21.9 Outlook

Metallocenes continue to offer insight into the fascinating process that converts low-utility alkene monomers into high-value plastic materials. Albeit at a slower rate, new metallocenes are still constructed and tested today. Although most current work has migrated to the next generation of nonmetallocene or post-metallocene catalysts (see Chapters 3.23 and 3.24), the birth of single-site catalysts for olefin polymerization began with metallocenes. Figure 24 provides a chronological overview of metallocene catalyst genealogy and development since their birth three decades ago.



Figure 24 Genealogy and development, by year, of selected metallocenes employed as single-site olefin polymerization catalysts.

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3.22 Chain Shuttling Catalysis and Olefin Block Copolymers

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3.22.1	Introduction	699
3.22.2	Block Copolymers from Living Polymerization	700
3.22.3	Olefin Block Copolymers from Reversible Chain Transfer	701
3.22.3.1	Chain Transfer to Metal in Olefin Polymerization	701
3.22.3.2	Reversible Chain Transfer in Olefin Polymerization	702
3.22.4	Identifying Reversibility in Chain Transfer	702
3.22.4.1	Approaches to Identify CCTP Characteristics	702
3.22.4.2	Mathematical Simulation of Single Catalyst Batch Reactions	703
3.22.4.3	A High-Throughput Method for the Discovery of Chain Shuttling Catalyst Systems	706
3.22.4.4	Kinetic Studies via Deuterium Labeling	709
3.22.5	CCTP Characteristics in Single Catalyst Systems	709
3.22.5.1	CCTP in Ethylene Polymerization	709
3.22.5.1.1	Actinides, lanthanides, and yttrium catalyst systems	711
3.22.5.1.2	Iron and cobalt systems	712
3.22.5.1.3	Chromium systems	712
3.22.5.1.4	Group IV systems	712
3.22.5.2	CCTP/CCG in α -Olefin and Styrene Polymerization	712
3.22.6	Reactor Choice for OBC Synthesis	714
3.22.7	Diblock OBCs via Sequential Monomer Addition	716
3.22.7.1	Synthesis of Diblock OBCs in a Continuous Process	716
3.22.7.2	Properties of Diblock OBCs from CCTP	718
3.22.7.2.1	Molecular weight, composition distribution, and thermal characteristics	718
3.22.7.2.2	Solid-state morphology	719
3.22.7.2.3	Optical properties	720
3.22.8	Synthesis of OBCs with Dual-Catalyst Systems	721
3.22.8.1	Ethylene-Based Block Copolymers	721
3.22.8.2	Propylene-Based Block Copolymers and Blends	724
3.22.9	Characterization of Olefin Block Copolymers	726
3.22.9.1	Melting Temperature	726
3.22.9.2	Crystallinity and Solid-State Morphology	727
3.22.9.3	Unique Solution Crystallization Behavior	728
3.22.9.4	Performance Characteristics of OBCs	730
3.22.9.5	Comparison of Living, CCTP, and Chain Shuttling Block Polymer Architectures	731
3.22.10	Olefin Block Copolymer Design and Applications	732
3.22.11	Functional Polyolefins from CCTP Systems	734
3.22.12	Conclusion and Outlook	734
References		735

3.22.1 Introduction

Polyolefins are the most ubiquitous synthetic polymers in the world.¹ High-density polyethylene (HDPE), low-density polyethylene (LDPE), and linear LDPE (LLDPE) are found in a myriad of applications in high volume in part because the properties can be varied so widely. Many modifications to the properties of polyethylene (PE) can be effected by changing catalysts (traditional Ziegler–Natta (Z-N),² metallocene,³ and postmetallocene⁴), changing molecular weight, incorporating linear α -olefin (LAO) comonomers, and/or by blending with other polymers.

For instance, HDPE contains little or no comonomer and is made by a low-pressure catalyzed process. It is high melting $(\sim 135 \,^{\circ}\text{C})$, relatively stiff (high modulus), and difficult to

stretch (high tensile strength).⁵ LDPE is typically made without comonomer using a noncatalyzed high-pressure radical process.⁶ The resulting polymer has a lower melting point than HDPE, primarily because the chains are so branched that they disrupt the crystallization. The lower crystallinity results in decreased density, modulus, and tensile strength. However, LLDPE's short-chain branches increase toughness and long-chain branches impart high melt strength, which leads to processing advantages.

LLDPE, like HDPE, is made in a low-pressure catalyzed process⁷ and is a copolymer containing various levels of LAO, primarily propylene, 1-butene, 1-hexene, or 1-octene. Because it comprises a linear backbone with side chains (methyl, ethyl, butyl, or hexyl), lamellar crystallization is increasingly hindered by higher LAO levels, leading to decreased density,



Figure 1 Relationship between melting point and density for random ethylene-LAO copolymers.

modulus, and tensile strength, but improved toughness, similar to LDPE. LLDPE can also contain long-chain branches (depending on the catalyst and reaction conditions) that affect the melt rheology and solid-state properties.

Despite this tremendous versatility, there is still a fundamental limitation for these random copolymers (RCPs): 'melting point and modulus (stiffness) are inextricably coupled to the density' (or % short-chain branching (SCB) from LAO comonomer) as shown in Figure 1. In other words, stiffness and toughness of PEs are inversely correlated. This is because the same method employed to lower modulus (incorporation of comonomer) results in a thinning of the PE crystals, concomitant with a lowering of the melting point, according to a relationship established by Flory.⁸ Because commercial grades of PE are made with coordination catalysts and incorporation of comonomer is dictated by statistical processes, none can violate this relationship.

To illustrate this relationship, consider a random ethylene copolymer of a density $0.856 \,\mathrm{g\,cm^{-3}}$ containing ~19 mol.% 1-octene comonomer. At room temperature, the material is elastic, or capable of recovering its size and shape after deformation. However, the copolymer loses the desirable properties of an elastomer at higher temperatures; for example, the material has a compression set, a measure of a material's ability to recover its size after compression, of 100% at 70 °C (Figure 2).⁹ The ability to make PE with properties that fall outside these limitations would lead to a tremendous expansion of uses for this polymer, for example, replacing flexible polyvinylchloride (f-PVC), which cannot be incinerated or recycled, or more expensive thermoplastic polyurethanes (TPUs) or thermoplastic vulcanizates (TPVs).

3.22.2 Block Copolymers from Living Polymerization

One approach toward expanding the use of polyolefins is to control microstructure, the orientation, and distribution of comonomer along the polymer backbone. In particular, block



Figure 2 Compression set (elastic recovery under compressive deformation) at 70 °C for an E-LAO random copolymer, flexible polyvinylchloride (f-PVC), thermoplastic polyurethanes (TPUs), and thermoplastic vulcanizates (TPVs). Reproduced with permission from Wenzel, T. T.; Arriola, D. J.; Carnahan, E. M.; *et al.* In *Metal Catalysts in Olefin Polymerization. Topics in Organometallic Chemistry*, Guan, Z., Ed.; Springer-Verlag: Berlin, Germany, 2009; Vol. 26.⁹

copolymers (BCPs) constraining much of the α -olefin to certain blocks of the chain while leaving other blocks linear (no short-chain branches) take on many of the best characteristics of HDPE and LLDPE. Such block architectures could potentially break the relationship of stiffness and toughness that constrains RCPs. The melting point can be controlled by the HDPE region ('hard' polymer) whereas the elasticity or modulus can be controlled by the LLDPE portion ('soft' polymer). These independent optimizations are possible because the HDPE regions of different polymer chains can cocrystallize, while the elastomeric LLDPE portions still provide the elastic properties. In a sense, the material acts as a crosslinked rubber, but unlike normal vulcanized rubber, the crosslinks can be reversed by melting. Therefore, such a material can be melted and re-formed many times (or recycled), unlike vulcanized rubber, which, once crosslinked, retains its shape indefinitely. In general, these types of rubbers are referred to as thermoplastic elastomers (TPEs).¹⁰

Perhaps the best-known TPEs are styrenic block copolymers (SBCs). The majority of these materials have triblock architectures composed of a soft center block having a low glass transition temperature (T_g) such as polybutadiene, capped with end blocks of hard, high T_g polystyrene. The incompatibility of the block types drives the materials to phase separate^{11,12} to create a nanoscale morphology that serves to physically crosslink the material, thus providing elastomeric properties. These SBCs are made using living polymerization techniques, in which chains are grown without termination. These processes enable the synthesis of BCPs by sequential monomer addition.¹³

The predominant approach toward the synthesis of olefin-based BCPs has focused on development of living coordination polymerization systems.¹⁴ Unfortunately, one feature that makes coordination polymerization catalysts so efficient for production of RCPs also limits their use for synthesis of conventional BCPs. These catalysts are susceptible to several chain termination and transfer mechanisms and typically produce many chains during polymerization. Therefore, a sequential monomer addition scheme produces a physical polymer blend with a conventional catalyst (Scheme 1).¹⁵ However, by designing systems that suppress these termination processes, advanced catalysts have been used to make BCPs via sequential monomer addition techniques (Scheme 1).¹⁴ These systems have produced many new BCPs with interesting structures.¹⁶ Unfortunately, the fundamental features that enable precision synthesis also make the processes very inefficient and thus of limited commercial appeal. Conventional catalysts produce hundreds to thousands of chains per metal center, but these living systems produce only one. For these materials to be competitive with other large-volume TPEs, more efficient protocols for BCP synthesis must be developed.

3.22.3 Olefin Block Copolymers from Reversible Chain Transfer

In efforts to provide advantaged materials at higher efficiency than capable in living polymerizations, researchers at The Dow Chemical Company pioneered two alternatives to the 'one-catalyst per polymer chain' approach for synthesis of olefin block copolymers (OBCs) using these reversible chain-transfer processes. One method follows a sequential addition strategy for formation of OBCs with a single catalyst system, in which changing reactor conditions or monomer composition results in formation of distinct blocks (Scheme 2).^{17,18} Another approach for preparation of new OBCs involves a process referred to as 'chain shuttling' where a chain shuttling agent (CSA) is used to pass a growing polymer chain between two different catalysts in a single reactor (Scheme 2).¹⁹ When the two catalysts are selected such that one makes an HDPE and the other makes an elastomeric ethylene-LAO copolymer, chain shuttling enables the catalytic production of statistical multiblock OBCs composed of alternating hard and soft blocks.

For this review, CCTP is a distinguished from chain shuttling in that the former is reversible exchange of polymer chains between like catalysts, whereas the latter is reversible exchange of polymer chains between two or more different kinds of catalysts. Both of these approaches give greatly improved efficiency over living polymerization systems, as they are capable of producing multiple chains per catalyst molecule.

3.22.3.1 Chain Transfer to Metal in Olefin Polymerization

It is well established in olefin polymerization that growing chains can be transferred from a catalyst to an added main group metal in exchange for an alkyl group.² This process, known as chain transfer to metal, is most often irreversible, leading to termination of the growing chain and initiation of a new polymer chain. Irreversible transfer of polymer chains to metal-based chain transfer agents (CTAs) by heterogeneous



Scheme 1 Synthesis of a physical blend and a block copolymer using conventional coordination polymerization and living olefin polymerization catalyst systems. From Hustad, P. D. *Science* **2009**, *325*, 704.¹⁵ Reprinted with permission from AAAS.



Scheme 2 CCTP and chain shuttling processes for synthesis of OBCs. Reproduced with permission from Hustad, P. D. Science 2009, 325, 704.¹⁵ Reprinted with permission from AAAS.

titanium-based Z-N catalysts is known in the literature as far back as 1959^{20} and has been reviewed in detail by Resconi *et al.*²¹ The proposed mechanism of alkyl exchange involves alkyl-bridged heterobimetallic dimer intermediates.

3.22.3.2 Reversible Chain Transfer in Olefin Polymerization

In some special cases, transfer of polymer chains between catalyst and transfer agent metals is reversible. Rather than acting as a final repository for 'dead' polymer chains, the metal reagent serves as a reservoir of 'live' chains that are intermittently reattached to catalyst centers for further growth. Such reversible chain transfer has been called variously catalyzed chain growth (CCG)²² or coordinative chain transfer polymerization (CCTP),²³ and the latter will be used throughout this review. In CCTP, the vast majority of chains lie in a dormant state while attached to the metal. These chains become active only when exchanged with the growing chain from a live catalyst (Scheme 3). With the transition between growing and dormant states, the CCTP process resembles atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer (RAFT), and other 'living' free radical

polymerization processes, which have been used for synthesis of BCPs through sequential monomer addition strategies.²⁴

A necessary precondition for CCTP is reversible chain transfer with a CTA. To achieve efficient CCTP while maintaining optimal polymerization rates, binding with the CTA must not be so strong that the inactive bimetallic dimer is the dominant species, yet there must be sufficient binding to effect alkyl–polymeryl exchange (Scheme 4). Not only is the equilibrium constant important, but the rate constants for complexation and decomplexation should also be as fast as possible (Scheme 5).

3.22.4 Identifying Reversibility in Chain Transfer

3.22.4.1 Approaches to Identify CCTP Characteristics

The most common approach to identification of reversibility in chain transfer has been to conduct polymerizations in the presence of potential transfer agents and observe a reduction in both the molecular weight and molecular weight distribution of the oligomer/polymer. A comprehensive kinetic model to predict the effects of reaction variables on the molecular weight behavior in CCTP systems has been reported.²⁵ This







Scheme 4 Fully reversible binding of the chain transfer agent is required.



Scheme 5 Relationship between alkyl exchange and reversibility $(k_{ct1} \approx k_{ct2})$.

model, which is described in detail below, reveals that single-point experiments are not always sufficient to identify the extent of reversibility in chain transfer. A high-throughput (HTP) screening protocol to identify CCTP characteristics by exploring changes in molecular weight distribution as a function of monomer conversion was also presented in the same report. Of course, the ultimate demonstration of the CCTP capabilities of a polymerization system is the synthesis of BCPs through either sequential addition or chain shuttling polymerization.

3.22.4.2 Mathematical Simulation of Single Catalyst Batch Reactions

Given the large number of potential catalyst/CSA systems, the discovery of a suitable combination of catalysts and CSA is a daunting task. Dow researchers accordingly developed an HTP approach to identify CCTP characteristics in single catalyst/CSA pairs.¹⁹ In order to predict the effects of reversibility on chain transfer, a kinetic model was developed to guide the search for suitable catalyst systems. While some effects of reversible chain

transfer on polymer microstructure were inferred, these simulations revealed the complexity of the system and validated the need for the model. This semibatch mathematical model revealed the conversion dependence of the molecular weight distribution, thus providing a powerful clue as to the reversibility of the chain transfer reaction and facilitating the HTP screening protocol.

The approach to polymer chain-growth modeling is based on population balances for the various polymer species participating in and resulting from chain growth and transfer.²⁶ The kinetics scheme is described in **Scheme 6** below in mathematical fashion and is a precursor to the derivation of population balances. Monomer units are represented as M, and growing polymer chains are represented by the symbol P_{nn} where n is the number of repeat units attached to the active catalyst. Dormant polymer is represented by A_n where n is the number of repeat units attached to the CTA. 'Dead' polymer chains, which arise from chain termination events such as hydrogenolysis and β -hydride eliminations, are represented by D_{nn} where n is the number of repeat units in the free polymer chain.

The simplest scenario to simulate is a homopolymerization during which the monomer concentration is held constant. A constant reaction volume is assumed in order to simplify the system of equations. Conversion of monomer to polymer, $X_{\rm f}$, defined as the mass ratio of polymer to free monomer, is used as an independent variable. Use of this variable simplifies the model by combining several variables, such as catalyst load, turnover frequency, and degradation rate, into a single value. Also, by using conversion instead of time as an independent variable, the model only requires three dimensionless kinetics parameters.

Three kinetics parameters in particular give estimates of the relative rates of chain transfer and shuttling to propagation: (1) the chain transfer constant for sites bearing the original alkyl moiety (virgin CTA sites), C_a^0 , where $C_a^0 = k_{CT}/k_p$, (2) the reversible chain transfer constant, $C_{a'}$ where $C_a = k_{RT}/k_p$, and (3) the molar ratio of shuttling agent sites to catalyst (A_{eq}). A more rigorous treatment for a CSA with multiple alkyl substituents would require more chain transfer constants (ancillary substituents may be alkyl or polymeryl), but this description was deemed sufficient for initial investigations. The only other kinetic parameter required is the intrinsic molecular weight (M_n^0), which is used to indirectly account for background chain transfer. Differential and algebraic equations for the moments of the molecular weight distribution (M_w/M_n) have

Propagation (<i>n</i> =0, 1,2,)	P _n	+	Μ	k _p ──►	P _{<i>n</i>+}	1		Rate = $k_p[M][P_n]$
Background chain transfer (n=1, 2, 3,)			P _n	k _β ►	P ₀	+	D _n	Rate = $k_{\beta}[P_n]$
Chain Transfer to Virgin CTA (n=1, 2, 3,)	Р _{<i>n</i>}	+	A ₀	k _{CT} ►	A _n	+	P ₀	$Rate = k_{CT}[P_n][A_0]$
Reversible chain transfer (n, m = 1, 2, 3,)	P _n	+	A _m	k _{RT} ►	A _n	+	P _m	Rate = $k_{RT}[P_n][A_m]$





Scheme 7 Workflow of the kinetic model, with inputs and outputs. Adapted with permission from Hustad P. D.; Kuhlman, R. L.; Carnahan, E. M.; *et al. Macromolecules* **2008**, *41*, 4081.²⁵ Copyright 2008 American Chemical Society.

been derived from population balances on the above kinetics scheme and are described in detail elsewhere.²³ Separate moments for bulk, growing, and dormant polymer chains were defined, and ratios of these moments were used to express properties such as molecular weights, with F_{wm} as the repeat unit formula weight of the monomer (e.g., 28 g mol^{-1} for ethylene). The workflow of the model, with inputs and outputs, is depicted in Scheme 7.

A series of simulations were performed to investigate the effects of reaction parameters on polymer M_n and M_w/M_n . These values depend on several variables, and fortunately many of them are measurable or determined experimentally. These known inputs include M_{nv}^0 which is determined by catalyst selection (and H₂ concentration); M_{eqr} the molar ratios of monomer to precatalyst, and A_{eqr} , the molar ratio of CTA to precatalyst, which are determined by the experimental design; and X_{fr} which is directly related to the experimentally measured polymer yield. The only dependent variables are the chain transfer and shuttling constants, C_a^0 and C_a . For all the simulations described here, the intrinsic molecular weight and monomer/

catalyst ratio were fixed such that $M_n^0 = 1000 \text{ kg mol}^{-1}$ and $M_{eq} = 1000000$, while the other inputs were varied to determine their influence on M_n and M_w .

A number of interesting and nonobvious insights into molecular weight distributions can be gained from these simulations. For example, Figure 3 demonstrates the effect of X_f on $M_{\rm w}/M_{\rm n}$ as a function of $C_{\rm a}^0$ for irreversible chain transfer where $C_a = 0$. One can consider the horizontal axis in this plot as reaction time. Early in the reaction (i.e., low $X_{\rm f}$), the $M_{\rm w}/M_{\rm n}$ quickly rises above 2.0 due to the fast initial chain transfer, which generates a number of dead chains on the CTA with $M_{\rm p}$ much lower than $M_{\rm p}^0$. As the reaction proceeds, the concentration of virgin CTA is depleted and normal chain transfer and termination events begin to dominate. The dead chains residing on the CTA eventually become outnumbered by eliminated chains that are 'fully grown'. Therefore, the M_n approaches M_n^0 and the M_w/M_n approaches 2.0 at higher X_f . The magnitude of the increase in M_w/M_n and the location of the maximum is a function of C_a^0 , with higher values producing higher and earlier maximum M_w/M_n 's. The M_w/M_n is greater than 2.0 at all



Figure 3 Simulated M_w/M_n vs. conversion as a function of chain transfer constant for irreversible chain transfer, where $C_a = 0$. Adapted with permission from Hustad, P. D.; Kuhlman, R. L.; Carnahan, E. M.; *et al. Macromolecules* **2008**, *41*, 4081.²⁵ Copyright 2008 American Chemical Society.



Figure 4 Simulated M_w/M_n vs. conversion as a function of chain shuttling constant for reversible chain transfer, with $C_a^0 = C_a$. Adapted with permission from Hustad, P. D.; Kuhlman, R. L.; Carnahan, E. M.; *et al. Macromolecules* **2008**, *41*, 4081.²⁵ Copyright 2008 American Chemical Society.

conversions examined in the simulation for this scenario. Thus, the expected polymer from any olefin polymerization in a batch reaction with irreversible chain transfer to metal must have $M_w/M_n \ge 2$. This effect is a result of the batch nature of the reaction, in which the concentration of virgin CTA decreases to near zero as conversion increases.

As an opposite extreme, cases of fully reversible chain transfer ($C_a^0 = C_a$) were simulated. The effect of conversion on M_w/M_n is plotted in **Figure** 4 as a function of C_a with $A_{eq} = 50$. Early in the reaction, or low X_f , the M_w/M_n quickly plunges below 2.0, followed by a steady convergence back to 2.0 at higher X_f . Faster reversible chain transfer produces a lower minimum M_w/M_n and also moves this minimum to lower conversion. One interesting trend is that the M_w/M_n is less than 2.0 at all simulated conversions for reversible chain transfer with $C_a^0 = C_a$, regardless of the absolute value of C_a . This observation sharply contrasts the case of irreversible chain transfer, which has $M_w/M_n \ge 2$ at all conversions.

Investigation of the effect of fully reversible chain transfer on the M_n is also informative. **Figure 5** depicts the relationship of M_n versus X_f as a function of C_a . As may be expected, higher chain transfer constants give lower M_n 's at low conversions. In all cases, M_n increases monotonically toward M_n^0 at higher conversions. Under the model conditions used for this simulation, C_a has very little influence on M_n for $X_f > 2$. As one might expect, plots of M_n versus X_f generally follow this pattern of monotonic increase toward M_n^0 . One consequence of high C_a is the linear increase in M_n at lower conversion. When $C_a \ge 50$, the M_n increases nearly linearly up to $X_f \sim 0.5$ with a γ -intercept near zero (see insert in **Figure 5**). At lower values of C_a , the near



Figure 5 Simulated M_n vs. conversion by chain shuttling constant for reversible chain transfer, where $C_a^0 = C_a$. Adapted with permission from Hustad, P. D.; Kuhlman, R. L.; Carnahan, E. M.; *et al. Macromolecules* **2008**, *41*, 4081.²⁵ Copyright 2008 American Chemical Society.



Figure 6 Simulated M_n and M_w/M_n vs. conversion for polymerization with reversible chain transfer when $C_a^0 = C_a = 50$ and $A_{eq} = 200$. Reproduced with permission from Hustad, P. D.; Kuhlman, R. L.; Carnahan, E. M.; *et al. Macromolecules* **2008**, *41*, 4081.²⁵ Copyright 2008 American Chemical Society.

linearity extends to much higher conversions, but the apparent intercepts from linear fits of M_n for $X_f < 0.4$ increase steadily with decreasing C_a . The positive intercept reflects the competition of chain growth versus chain transfer. These trends suggest that this intercept may be a better measure of shuttling rate than the goodness-of-fit for the line. At higher C_a , the initial chain transfer occurs very early in the reaction when M_n is very low. As C_a approaches zero, the ratio of propagation to transfer increases and the chains grow to higher M_n 's before chain transfer or shuttling), M_n versus conversion is perfectly linear, with a slope of zero and apparent intercept of M_n^0 .

The plot in **Figure 6** depicts the response of both M_n and M_w/M_n as a function of conversion for a realistic case of fast reversible chain shuttling, with $C_a^0 = C_a = 50$ and $A_{eq} = 200$. In the fast reversible chain transfer regime, these reactions have some kinetic resemblance to controlled or living free radical processes. Although many chains are growing simultaneously, only a small fraction of them are alive at any given moment, while most of the chains lie dormant on the CTA. This behavior is also importantly not limited to the low molecular weights normally associated with 'CCG' reactions but can extend to very high-molecular-weight polymers if the value of M_n^0 is sufficiently high.

Each of the cases simulated above consider reactions for which the rate constants for the initial transfer from the virgin CTA and subsequent polymeryl transfer are at most equal, with $C_a^0 \ge C_a$. The magnitude of the difference in k_{CT} and k_{RT} is most likely a function of the nature of the transferable group and the growing polymer chain. If the initiating group is not a good model of the growing polymer chain, initiation is likely to be slower than propagation. On the other hand, 'living' behavior can often be realized by selecting an initiating species that closely resembles the polymer chain.

One interesting observation is revealed in an estimation of the relative rates of propagation (R_P) to reversible transfer (R_{RT}) in these systems. Since the rates are both functions of catalyst

concentration, this important ratio can be estimated for the above case using M_{eq} , A_{eq} , and C_a with the following equation:

$$R_{\rm p}/R_{\rm RT} = \frac{k_{\rm p}[{\rm M}][{\rm P}]}{k_{\rm RT}[{\rm P}][{\rm A}]} = \frac{k_{\rm p}[{\rm M}]}{k_{\rm RT}[{\rm A}]} = \frac{[{\rm M}]}{C_{\rm a}[{\rm A}]}$$

In the above case, with $M_{eq} = 1\,000\,000$, $A_{eq} = 200$, and $C_a = 50$, the rate of propagation is 100 times faster than the rate of reversible chain transfer. Nevertheless, the simulation above clearly shows characteristics normally associated with CCTP, with a linear increase in M_n and M_w/M_n near 1.1.

The situation becomes more complex for semireversible chain transfer, where k_{CT} and k_{RT} are both positive, but $k_{CT} > k_{RT}$. As demonstrated in **Figure** 7, M_w/M_n can be greater than, less than, or equal to 2, depending on the conversion and the magnitudes of the chain transfer constants. The M_n of the polymer is simply a function of C_a^0 ; the value of C_a has no effect on M_n up to $C_a = C_a^0$. However, M_w is dramatically affected by lower values of C_a . If $C_a^0 >> C_a > 0$, then the initial increase in M_w/M_n is dramatic, and M_w/M_n does not dip below 2 until high conversion. However, as C_a approaches C_a^0 , the initial increase in M_w/M_n is negligible, and M_w/M_n drops below 2 at low conversion. In any case, if $C_a > 0$, then M_w/M_n asymptotically approaches 2 from the low side.

3.22.4.3 A High-Throughput Method for the Discovery of Chain Shuttling Catalyst Systems

Original reports of chain shuttling from Dow focused on the dual-catalyst approach to produce statistical multiblock OBCs composed of alternating hard and soft blocks. This scheme requires a chain shuttling polymerization using a catalyst that does not incorporate LAO, a 'poor incorporator', and a catalyst that does, a 'good incorporator'. The kinetic model simulations (Section 3.22.4.2) reveal straightforward methods of determining reversibility in chain transfer. In the cases simulated above, reversible chain transfer is indicated by a reduction in M_n in connection with narrowing of the distribution, such that $M_w/M_n < 2$. These criteria provide a test for finding suitable



Figure 7 M_w/M_n vs. conversion for semireversible chain transfer in simulations with $C_a^0 = 50$. Reproduced with permission from Hustad, P. D.; Kuhlman, R. L.; Carnahan, E. M.; *et al. Macromolecules* **2008**, *41*, 4081.²⁵ Copyright 2008 American Chemical Society.

combinations of catalyst and CSA for use in our two-catalyst system.

Given the multitude of olefin polymerization catalysts, identification of a pair of catalysts with significantly different monomer selectivities that are also capable of chain shuttling was a daunting task. Furthermore, the chosen system should preferably operate at a high solution reaction temperature ($T \ge 120$ °C) to prevent undesired polymer precipitation. An HTP method was adopted to expedite this discovery process. The technique outlined in **Figure 8** employs a parallel screen of the effects of metal alkyl reagents on the molecular weight and molecular weight distributions of PE produced by catalyst/CSA combinations.

To begin the selection process, representative examples were first selected from a broad variety of catalyst structure types known to have high polymerization rates. Ethylene polymerizations were then carried out with these catalysts in combination with a number of potential CSAs using HTP screening techniques.²⁷ Using an array of robotically manipulated individual polymerization reactors combined with rapid polymer characterization methods, more than 1600 individual

polymerization reactions were conducted and evaluated over a three-week period, a feat that would have taken several months using conventional techniques.

Catalyst efficiency, estimated by polymer yield, eliminated several of the potential CSAs due to their inhibition of polymerization. For those combinations that produced a sufficient amount of polymer for characterization, the molecular weights and molecular weight distributions of the PE samples were then compared to control polymers prepared with no added CSA. A reduction in the M_n in combination with a narrowing of the M_w/M_n indicated a 'hit' for chain shuttling behavior.

Another criterion for catalyst selection is relative comonomer incorporation. A proposed material design is one in which the soft segment (SS) is amorphous and the hard segment (HS) contains as little comonomer as possible. To achieve this combination, the chain shuttling catalysts must have very different reactivity ratios. Olefin polymerization catalysts systems typically experience higher reactivity toward ethylene (Monomer 1) than LAOs (Monomer 2), resulting in $r_1 \gg 1 \gg r_2$.²⁸ As a demonstration, consider a hypothetical example where the catalysts have the following reactivity ratios: a good



Figure 8 High-throughput screening protocol for the chain shuttling screen. From Arriola, D. J.; Carnahan, E. M.; Hustad, P. D.; *et al. Science* **2006**, *312*, 714–719.¹⁹ Reprinted with permission from AAAS.



Figure 9 Polymer composition as a function of reactor composition for hypothetical good and poor incorporators.

incorporator (makes SS) with $R_1 = 5$ and $r_2 = 0.1$, and a poor incorporator (makes HS) with $R_1 = 200$ and $r_2 = 0.02$.

The copolymer composition produced by these two catalysts can be estimated using the Mayo–Lewis equation²⁹ and these values of r_1 and r_2 . Figure 9 depicts the hypothetical comonomer content in the polymer (F_2) as a function of the mole fraction of comonomer in the reactor (f_2). The good incorporator produces a material with higher F_2 as f_2 increases. In contrast, the composition from the poor incorporator is relatively flat across a broad range and increases only at very high values of f_2 . The F_2 required to render the copolymer amorphous is comonomer. In this modeled system, the good incorporator produces that composition at $f_2 = 0.57$; at this condition, the poor incorporator incorporator incorporator incorporator incorporator incorporator incorporator produces that composition at $f_2 = 0.57$; at this condition, the poor incorporator incorporator incorporator incorporator ($F_2 = 0.01$).

To identify catalysts with this type of difference in comonomer reactivity, copolymerizations of ethylene and 1-octene at relatively high f_2 were performed. Several different families of catalysts were evaluated under these conditions. The resulting copolymer compositions revealed information about the relative comonomer reactivities; a rigorous definition of the reactivity ratios was not necessary. This screening protocol allowed rapid classification of catalysts into the good or poor incorporator categories.

As shown in Section 3.22.4.2, the molecular weight distribution of a polymer produced with a chain shuttling catalyst/ CSA system is highly dependent on reaction conditions. The extent of reversibility with the catalyst/CSA pairs was therefore further explored through a series of polymerizations over a range of monomer conversions (i.e., yield). A representative example from this secondary screening process is described below for precatalyst 1 (Figure 10). Several members from this well-studied bis(phenoxyimine)-based catalyst family³⁰ were identified as 'poor incorporators' in the primary screen. A series of ethylene-octene copolymerizations using 1 were performed across a range of polymer yields using diethylzinc (DEZ) as CSA (Table 1). The effects of polymer yield on the molecular weight characteristics are depicted in Figure 10.



Figure 10 Molecular weight distribution, M_w/M_n , of polyethylene prepared with 1 using DEZ as CSA as a function of polymer yield. Reproduced with permission from Hustad, P. D.; Kuhlman, R. L.; Carnahan, E. M.; *et al. Macromolecules* **2008**, *41*, 4081.²⁵ Copyright 2008 American Chemical Society.

Table T	Eurylene polymenzation with T in presence of L								
Run	CSA	Time (s)	Yield (g)	M ^{,b} (kg mol⁻ ¹)	M_w/M_n^b				
1	DEZ	16	0.059	6.48	1.38				
2	DEZ	36	0.085	9.59	1.29				
3	DEZ	58	0.117	13.2	1.26				
4	DEZ	92	0.142	17.4	1.23				
5	DEZ	146	0.192	23.7	1.23				
6	DEZ	227	0.275	32.2	1.27				

1 1 1 1 1 A 1 (DET)

^aGeneral polymerization conditions: ethylene pressure = 100 psi, $T = 120 \,^{\circ}\text{C}$. ^bDetermined using GPC relative to polystyrene standards and converted to polyethylene equivalents.

Adapted with permission from Hustad, P. D.; Kuhlman, R. L.; Carnahan, E. M.; et al. Macromolecules **2008**, *41*, 4081.²⁵

Polymerization with 1 without CSA shows no trend in molecular weight response to conversion, and allows estimation of $M_n^0 \sim 260 \text{ kg mol}^{-1}$. In the presence of 29 equiv. DEZ (10 µmol), conversion has a pronounced effect on molecular weight, with a linear increase in M_n to 32 kg mol^{-1} and $M_w/M_n < 1.4$ for each sample. In this case, the M_n is well below M_n^0 even at the highest yield examined, thus the M_w/M_n remains relatively narrow. This plot of experimental data looks remarkably similar to the simulation depicted in Figure 6 for fast reversible chain transfer.

Similar studies were performed with pyridylamide catalysts³¹ such as 4,³² which show that they undergo fast polymeryl chain exchange with DEZ, much like catalyst 1. This particular class of catalyst readily incorporates LAO in general. Dual-catalyst experiments were then designed to probe the possibility of making linear BCPs using chain shuttling polymerization with catalysts 2 and 4. Figure 11 shows an overlay of gel permeation chromatography (GPC) traces obtained from runs comprising only 2/MMAO, only 4/ MMAO, and a combination of 2 and 4 with MMAO. As expected, the GPC trace for the dual-catalyst run roughly comprises those of the single component traces. The GPC trace is dramatically different when a CSA is added in the mixed catalyst system in that a simple composite GPC is not obtained (**Figure 12**). Inclusion of either triethylaluminum (TEA) or DEZ in the run produces a single peak in the GPC, reflecting low M_n and narrow M_w/M_n (see **Table 2**). The octene incorporation data for runs with 8 µmol of CSA indicate an intermediate incorporation level between those found for polymers made by 2 and 4 individually. These data indicate that both catalysts are active and undergoing rapid chain shuttling to produce statistical multiblock OBCs.

3.22.4.4 Kinetic Studies via Deuterium Labeling

²H labeling experiments were used to provide some insight into CCTP processes in ethylene–1-octene copolymerizations using precatalyst 4.³³ Effects of CCTP, including decreases in M_n and M_w/M_n , were observed prior to complete conversion of alkyls to polymeryls on the CSA. These effects were quantified by quenching with D₂O, providing a ²H label at the chain ends. The results indicate that polymeryl-for-polymeryl exchange is kinetically competitive with alkyl-for-polymeryl exchange (Scheme 8), at least in the system studied. Also, ²H labels were located attached to a linear endgroup, consistent with earlier indications that chain transfer is much faster after ethylene insertion than after LAO insertion.

3.22.5 CCTP Characteristics in Single Catalyst Systems

3.22.5.1 CCTP in Ethylene Polymerization

As discussed previously, an effective approach to identifying reversibility in chain transfer is to conduct polymerizations in the presence of potential transfer agents and observe a reduction in both the molecular weight and molecular weight distribution of the oligomer/polymer. Catalyst systems reported to demonstrate this behavior have been reviewed in detail by Kempe,²³ and the following sections review a nonlimiting list of these catalyst systems organized



Figure 11 GPC traces for 2, 4, and combination of the two catalysts without CSA.



Figure 12 GPC traces for 2/4 system with DEZ or TEA as CSA.

Run	Catalyst	CSA	CSA (μmol)	Yield (g)	M ^{_b} (kg moΓ ⁻¹)	M_w/M_n^b	$C_8^{\ c}$
1	4	na ^d	0.8	0.136	262	1.76	6.5
2	2	na ^d	0.8	0.164	14.8	1.63	2.0
3	2 + 4	na ^d	0.8	0.203	32.9	13.6	4.3
4	2 + 4	DEZ	8	0.128	15.2	1.33	5.1
5	2 + 4	DEZ	80	0.093	1.49	1.08	15
6	2 + 4	TEA	8	0.211	15.9	1.98	4.3
7	2 + 4	TEA	80	0.250	3.08	1.84	13

 Table 2
 Ethylene polymerization with 2 and 4 in presence of DEZ and TEA CSA's^a

^aGeneral polymerization conditions: ethylene pressure = 200 psi, T = 130 °C, 1.1 equiv. Cocat to total catalyst. ^bDetermined using GPC relative to polystyrene standards.

^c1-Octene content in the polymer determined by infrared (IR) spectroscopy.

^dna = not applicable, MMAO was added as a scavenger.



Scheme 8 Competitive alkyl vs. polymeryl exchange observed in polymerizations with precatalyst 4.

by metal center. Most systems have been limited to production of very low-molecular-weight PEs, with $M_n < 4000 \,\mathrm{g}\,\mathrm{mol}^{-1}$, due to precipitation at the low reactor

temperatures required for activity of the employed catalyst systems, thereby limiting their use for the synthesis of BCPs.

3.22.5.1.1 Actinides, lanthanides, and yttrium catalyst systems

Actinide, lanthanide, and yttrium-based catalyst systems showing characteristics of reversible chain transfer in ethylene polymerization are summarized in **Table 3**. Samsel and Eisenberg claimed to observe the characteristics in ethylene polymerization with several metallocenes of actinides, such as the bis(pentamethylcyclopentadienyl) thorium complex 5 in combination with aluminum alkyl reagents.³⁴ These systems catalyze the production of aluminum alkyl chain growth products at lower temperatures than those required by the uncatalyzed Ziegler process. The systems were limited to production of low-molecular-weight PE oligomers. Mortreux and co-workers^{35–37} present evidence of chain growth on magnesium catalyzed by lanthanocene-based catalysts 6 and 7 (Scheme 9). The system produces magnesium alkyls containing between 4 and 200 carbons with very narrow molecular weight distributions consistent with fast reversible transfer. Since the catalyst system operates at 80 °C, synthesis of high-molecular-weight PEs in a controlled fashion is not possible. At M_n 's above ~2,000 g mol⁻¹, the molecular weight distributions broaden significantly as a result of precipitation of the magnesium compound.

Kempe reports CCTP in ethylene polymerization using the yttrium-based catalyst system 8/borate combined with a variety of aluminum alkyls.³⁸ Although many aluminum alkyls show

|--|



Scheme 9 Synthesis of magnesium alkyl chain growth products with a samarium catalyst system.



Figure 13 Influence of polymer precipitation on the molecular weight distribution of polyethylene synthesized by the **8**/borate/TIBAO catalyst system. Adapted with permission from Kretschmer, W. P.; Meetsma, A.; Hessen, B.; *et al. Chem. Eur. J.* **2006**, *12*, 8969.³⁸

CCTP characteristics, partially hydrolyzed aluminum alkyls, such as tetraisobutylalumoxane (TIBAO), are preferred due to their beneficial effect on catalyst activity. This system is also stable at reaction temperatures as high as 100 °C, allowing production of slightly higher-molecular-weight polymers with narrow polydispersities. However, even at this temperature, the system can only produce PEs with M_n 's of ~3600 g mol⁻¹ before significant broadening of the molecular weight distribution is observed (Figure 13).

3.22.5.1.2 Iron and cobalt systems

Iron and cobalt-based CCTP systems are summarized in Table 4. Britovsek et al.³⁹ report a CCG on zinc using the bis(imino)pyridyl iron complex 9 in combination with methylaluminoxane (MAO) (Scheme 10). Addition of an increasing amount of Et₂Zn to the catalyst system results in production of a lower-molecular-weight PE, ultimately with a very narrow molecular weight distribution $(M_w/M_n = 1.1)$. The effect of DEZ on the distribution is shown in Figure 14. In addition to synthesis of zinc chain growth products, a nickel-catalyzed displacement is also used in presence of ethylene to produce a Poisson distribution of LAOs (Scheme 10). A thorough evaluation with several other metal alkyl systems is also reported. Of the wide range of compounds studied, only certain zinc reagents and GaMe3 show CCTP characteristics.²² A later study confirms CCTP using Et₂Zn with bis(imino)pyridyl iron precatalysts 9-10, while bis(imino)pyridyl cobalt complexes 11 and 12 exhibit lower degrees of reversibility.⁴⁰

3.22.5.1.3 Chromium systems

Chromium-based catalyst systems reported to exhibit CCTP characteristics are also summarized in **Table** 4. Phenoxyimine-based chromium complexes 13 and 14 showed characteristics of CCTP in combination with $ZnEt_2$, albeit with lower degrees of reversibility than iron complexes 9 and 10.²² Bazan and co-workers demonstrate chain growth on aluminum using chromium complex 15 activated by either MAO or B(C₆F₅)₃.^{41,42} Gabbai has observed similar results with the pentamethylcyclopentadienyl-pentafluorophenyl chromium systems 16 and 17.^{43–45} These catalyst systems give very low-molecular-weight oligomers in the presence of aluminum

alkyls, and in some cases form oligomer mixtures characterized by Poisson and Schulz–Flory distributions.

3.22.5.1.4 Group IV systems

Group IV-based catalyst systems reported to exhibit CCTP characteristics are summarized in Table 5. In addition to the actinides described previously, Samsel^{46,47} also discloses CCTP in ethylene polymerization with several hafnium metallocenes in combination with aluminum alkyl reagents. Researchers at Dow demonstrate CCTP characteristics in bis (phenoxyimine)-based precatalysts 1-3 and the pyridyl-amido hafnium precatalyst 4 in combination with ZnEt2.^{19,23} These catalyst systems were discovered using an HTP screening protocol; the method and additional experimental data are described in detail in Section 3.22.4. The catalysts can synthesize highmolecular-weight semicrystalline ethylene-based polymers with high polymerization efficiencies at temperatures greater than 120 °C, thereby circumventing the precipitation problems that prevent CCTP to higher molecular weights in other systems.

Gibson identified CCTP characteristics in using Et₂Zn with bis(phenoxyimine)-based complexes **18** and **19**, while the metallocene **20** exhibited lower degrees of reversibility.²² Gibson has observed CCTP characteristics in ethylene polymerization with bis(phosphanylphenoxide) complexes **21** and **22** in combination with ZnEt₂ at room temperature.⁴⁸ These catalyst systems give near monodisperse PEs with M_n of ~300 g mol⁻¹ at very high efficiencies (10–30 kg mmol h⁻¹ bar⁻¹).

Bhriain *et al.*⁴⁹ claim that CCTP occurs in ethylenenorbornene copolymerizations using metallocene **23** in combination with zinc or aluminum alkyls. The reversibility is indicated by a reduction in M_n and a modest narrowing of the distribution $(1.6 \le M_w/M_n < 2.0)$. Sita has demonstrated reversible chain transfer in ethylene polymerization using the hafnium amidinate precatalyst **24** with DEZ, producing monodisperse PEs with M_n 's up to 665 g mol⁻¹.⁵⁰

3.22.5.2 CCTP/CCG in α-Olefin and Styrene Polymerization

Although the number of catalyst systems showing characteristics of CCTP in ethylene polymerization is limited, even fewer examples exist of CCTP in polymerization of higher olefins such as



 Table 4
 Iron-, cobalt-, and chromium-based catalyst systems for CCTP of ethylene

propylene. Sita has demonstrated reversible chain transfer using the hafnium amidinate precatalyst 24/borate with DEZ in polymerization of propylene⁵¹ and ethylene, α-olefins, and α,ω-nonconjugated dienes.⁵⁰ Due to the living nature of the polymerization⁵² and amorphous character of the resulting atactic polymer, this catalyst system enables synthesis of highmolecular-weight polypropylenes (PPs) with low values of $M_w/M_{n'}$ achieving M_n 's in excess of 100 000 g mol⁻¹ with $M_w/M_n < 1.2$ (Scheme 11). The amorphous nature of the PP is key to the production of high-molecular-weight materials at the low reaction temperature employed (0 °C), as the polymer remains in solution and does not precipitate during chain growth. As shown in Figure 15, low values of M_w/M_n are maintained across a wide range of molecular weights with this system.

Sita has also reported synergistic effects between aluminum and zinc alkyls with the hafnium amidinate precatalyst 24/ borate system in polymerization of α -olefins (Scheme 12).⁵³ In this ternary system, fast polymeryl exchange occurs between Hf and Zn, and Zn and Al, respectively. The Zn species is the primary CTA, but the Al species serves as the primary dormant



Scheme 10 Chain growth on zinc catalyzed by iron complex 9/MAO and nickel-catalyzed displacement of the resulting zinc alkyls.



Figure 14 GPC traces of the polyethylene synthesized by iron complex **9**/MAO with varying amounts of DEZ. Adapted with permission from Britovsek, G. J. P.; Cohen, S. A.; Gibson, V. C.; *et al. Angew. Chem., Int. Ed.* **2002**, *41*, 489.³⁹

species, or surrogate, due to fast transfer between Zn and Al. This mechanism allows the Zn species to be used catalytically and can be used to produce atactic poly(α -olefins) with low values of M_w/M_n .

Carpentier has shown CCTP character in coordination polymerization of styrene using *ansa*-chloroneodymocene precursor **25** in combination with dialkylmagnesium reagents Mg(*n*-Bu)₂ and Mg(allyl)₂ (Scheme 13). The catalyst system has moderate activity at 60 °C (1–8 kg PS (mol_{Nd} · h)⁻¹) and gives soluble oligostyrenes, with $M_n < 6500 \text{ g mol}^{-1}$ and $M_w/M_n = 1.2-1.5$ in most cases.⁵⁴ In addition, the oligostyrenes have a very high degree of syndiotacticity and are selectively end-capped by butyl or allyl groups derived from the magnesium reagent.

3.22.6 Reactor Choice for OBC Synthesis

Polymer syntheses can be carried out in batch, semibatch, or continuous processes. In batch and semibatch processes, the reactor is charged with a batch of reagents and then the polymerization process is carried out. When the desired polymer is formed, it is removed and the next batch of feed is introduced. A semibatch process is a variant of a batch process in which one or more reactants are added in batch mode while another reagent is fed continuously. BCP syntheses with living polymerizations are typically carried out in batch or semibatch processes. In the simplest case, one monomer is added and polymerization is carried out to complete conversion, then the process is repeated with a second monomer.

Although batch processes are the workhorse in research laboratory environments, continuous (and semicontinuous) reactors predominate for commercial PE production. In a continuous polymerization reactor, all monomers and reagents are constantly fed into the reactor, and the polymer is isolated from the effluent. Flows are adjusted to achieve the desired steady-state conditions as measured by online analytical instruments and polymer analysis.

Researchers at Dow have found that chain shuttling polymerizations are most effectively conducted in continuous reactors.¹⁹ One advantage of this configuration is that the kinetics of chain shuttling benefit from the entire lifetime of the shuttling agent in the reactor. At the high temperatures required for solution-phase synthesis of HDPEs, polymerization catalysts typically activate and terminate (i.e., live and die) relatively quickly, whereas the main group shuttling agents generally experience little or no termination. Therefore, in a batch or semibatch configuration, shuttling can only occur during the (relatively brief) coincident lifetimes of the polymerization catalysts.

Steady-state conditions in a continuous process, on the other hand, constantly provide fresh catalyst throughout the lifetime of the CSA in the reactor. Therefore, in effect, the whole lifetime of the shuttling agent is used, not just the portion that overlaps with the catalysts' lifetimes. The full use of CSA lifetime manifests in shorter average block lengths in the polymer.

A second, more subtle difference is that shuttling occurs more efficiently in a continuous process. Typical CSAs begin as simple metal alkyl species such as Et_2Zn . The initial chain transfer event with Et_2Zn involves exchange of an ethyl moiety for a polymer chain, which initiates growth of a new polymer chain but does not produce any polymer blockiness. Statistically, this event predominates over chain shuttling early in the course of the reaction. Only later in the reaction is the concentration of zinc-polymeryl species sufficient to enable true chain shuttling. In a continuous process, the reactor is populated with a steady-state concentration of these



 Table 5
 Group IV-based catalyst systems for CCTP of ethyene

zinc-polymeryl species. Because the volume of the reactor is large compared with the volume of the continuous feed, the ratio of zinc-polymeryl species to fresh Et₂Zn is very high. Thus, polymeryl interchange predominates over ethyl-for-polymeryl exchange.

An additional complication of using two-chain shuttling catalysts in a batch process is that different onset and decay kinetics of different catalysts could generate polymers with interchain inhomogeneities; no multiblock polymers can be produced when one catalyst type is dead, for example. Thus, a



 $\label{eq:scheme11} \begin{array}{c} \text{Scheme 11} & \text{CCTP of propylene using catalyst system 24/borate and} \\ \text{ZnEt}_2. \end{array}$



Figure 15 GPC traces for atactic PPs made with catalyst **24**/borate. Adapted with permission from Zhang, W.; Wei, J.; Sita, L. R. *Macromolecules* **2008**, 41, 7829–7833.⁵⁰



Scheme 12 Ternary living coordinative chain transfer polymerization using a Hf/Al/Zn catalyst system. Reprinted with permission from Zhang, W.; Wei, J.; Sita, L.R. *Angew. Chem., Int. Ed.* **2010**, *49*, 1786.⁵³

continuous reactor configuration is expected to generate OBC's with a higher fraction of block polymer and more homogeneous composition in this type of polymerization.

Operating an efficient chain shuttling system in a continuous process also affects the molecular weight distribution of the resulting copolymer. Extremely narrow molecular weight distributions can be achieved with fast chain shuttling between two different catalysts in a batch process. However, the same chemistry in a continuous process ideally results in a SchulzFlory molecular weight distribution simply because there is a distribution of residence times in a continuously fed reactor.⁵⁵ This feature is often beneficial, because copolymers with broader distributions of molecular weights are typically easier to process.

Choice of reactor can also have an influence on polymer composition. In batch copolymerizations, simultaneous polymerization of two or more monomers is often complicated by the different reactivities of the two monomers. This preferential monomer consumption can create a composition drift during chain growth and therefore a tapered copolymer composition. In contrast, a continuous stirred-tank reactor (CSTR) is controlled at steady state, thereby ensuring a homogeneous copolymer composition.

3.22.7 Diblock OBCs via Sequential Monomer Addition

BCP synthesis by sequential monomer addition is preferred under conditions that maintain the 'living-like' nature of the polymerization throughout chain growth. Most of the CCTP systems described in Section 3.22.5.1 lose these properties before desirable high-molecular-weight polymers can be achieved because they must be operated at polymerization temperatures below PE's crystallization point. Consequently, the PEs precipitate from solution as they reach a certain chain length, typically at $M_n < 4000 \text{ g mol}^{-1}$. This restriction unfortunately severely limits their use for formation of ethylene-based BCPs via sequential monomer addition.

In contrast, catalysts that can operate in high-temperature processes (>100 °C) can overcome the M_n limitations and form OBCs through sequential monomer addition. Only catalyst systems 1–4 have demonstrated CCTP in ethylene polymerization at reactor temperatures in excess of 100 °C. The solubility of atactic PPs (aPPs) and other poly(α -olefin)s allows CCTP at lower temperatures with these monomers, as described for catalyst system 24.^{51,53} However, this catalyst system has not yet been used to synthesize BCPs using CCTP. To date, only catalyst system 4 has been used to make OBCs using single catalyst CCTP and sequential monomer addition.^{17,18}

3.22.7.1 Synthesis of Diblock OBCs in a Continuous Process

The advantages provided by continuous reactor operation prompted researchers at Dow to explore diblock synthesis using two CSTRs connected in series.¹⁷ Accordingly, the reaction scheme depicted in **Scheme 14** provides a highly flexible process for production of a wide range of diblock OBC compositions. The block composition can be varied by changing the production rate in either reactor. The comonomer content of either block can also be independently tailored by varying the feed compositions because the process operates in two independent reactors. This CCTP scheme also produces multiple chains per catalyst, an advantage over stoichiometric living polymerization systems, but is necessarily stoichiometric in CSA. The reaction produces approximately one chain per CSA alkyl functionality, so the overall molecular weight can be controlled by adjusting the CSA feed rate.

This technology was first demonstrated through synthesis of a copolymer with blocks of both HDPE (density ~ 0.94 g cm⁻³, 0.5 mol.% 1-octene) and very low-density PE (VLDPE,



 $M_{\rm n}$ up to 6500 g mol⁻¹ $M_{\rm w}/M_{\rm n} \sim 1.2-1.5$

Scheme 13 Synthesis of syndiotactic oligostyrenes using catalyst system 25/MgR₂.



Scheme 14 Synthesis of HDPE-*block*-VLDPE diblock copolymers in a series of continuous reactors using catalyst system **4** in combination with ZnEt₂. Reproduced with permission from Hustad, P. D.; Kuhlman, R. L.; Arriola, D. J.; *et al. Macromolecules*, **2007**, *40*, 7061–7064.¹⁷ Copyright 2007 American Chemical Society.

density ~ 0.88 g cm⁻³, 10.8 mol.% 1-octene).¹⁷ Relevant product characterization details are given in **Table 6**. The pyridylamide precatalyst 4^{30} was chosen for these studies due to its high comonomer reactivity, high $M_{n'}^0$ and demonstrated CCTP ability.

The two reactor feeds were controlled to give copolymers with the desired ethylene–octene compositions, and a physical blend was produced for comparison prior to making a diblock OBC. For diblock synthesis, DEZ was added to the first reactor

Table 6 Product and process details for production of a diblock OBC using CCTP in a series of continuous read	ctors
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Sample	Density (g cm ⁻³)	f _{LLDPE} (wt.%)	Δ_{CB}^{a}	M_n^b (g mol ⁻¹)	M _w /M _n ^b	Chains per Zn ^c	Chains per Hf ^c
Blend 1	0.899	0.31	10	25 900	4.42	-	190
Diblock 1	0.899	0.31	10	44 500	1.67	2.5	380
Blend 2	0.876	0.66	40	31 100	3.70	-	570
Diblock 2	0.877	0.52	36	47 000	2.07	2.5	460
Diblock 3	0.875	0.51	34	67 500	2.04	2.8	300

^aDetermined by ¹³C NMR.

^bMeasured by GPC relative to polystyrene standards and converted to polyethylene equivalents.

^cChains per Zn is calculated by using the zinc feed and polymer production rates and the number-average molecular weight of the resulting copolymer corrected for comonomer content. Similarly, chains per Hf is estimated by using the total catalyst metal feed.

Adapted with permission from Hustad, P. D.; Kuhlman, R. L.; Arriola, D. J.; *et al. Macromolecules*, **2007**, *40*, 7061–7064¹⁷ Copyright 2007 American Chemical Society and Hustad, P. D.; Marchand, G. R.; Garcia-Meitin, E. I.; *et al. Macromolecules* **2009**, *42*, 3788.¹⁸ Copyright 2009 American Chemical Society. to achieve the desired melt index ($I_2 = 20 \text{ dg min}^{-1}$, equivalent to an $M_n \sim 15-20 \text{ kg mol}^{-1}$). This material was fed to the second reactor and production was continued under different conditions. The material collected after the second reactor has a lower melt index ($I_2 = 3.9 \text{ dg min}^{-1}$), indicating a higher molecular weight, consistent with the chain extension reaction from the CCTP process.

A second Dow report describes the synthesis of materials with a larger compositional difference in the two blocks, defined as the difference in the molar 1-octene content of the blocks, or Δ_{C8} (Table 6).¹⁸ These samples were designed with high Δ_{C8} to provide materials that self-assemble in the melt and crystallize to form ordered morphologies. Compositions necessary to achieve melt order were predicted using self-consistent field theory (SCFT).^{56,57} For a typical molecular weight and 50/50 composition, OBCs with Δ_{C8} in excess of 20 mol.% are predicted to produce ordered morphologies. The reactor composition was adjusted in the two reactors to give an LLDPE copolymer with ~5 mol.% 1-octene in the first reactor, and the concentration of 1-octene was increased in the second reactor to give Δ_{C8} values in excess of 30 mol.%.

3.22.7.2 Properties of Diblock OBCs from CCTP

A number of methods provide data consistent with the diblock nature of these new OBCs, including molecular weight, thermal, and solution solubility behavior. Details of the characterization of Diblock 1 are described below. Additional details of the unique morphology of high Δ_{C8} Diblocks 2 and 3 are discussed in more detail in the following section.

3.22.7.2.1 Molecular weight, composition distribution, and thermal characteristics

The GPC traces in **Figure 16** reveal a broad molecular weight distribution, $M_w/M_n = 4.42$, for the dual reactor Blend 1. On the other hand, Diblock 1 displays an overall M_w/M_n of 1.67. Diblocks 2 and 3 also have much more narrow distributions than their comparative Blend 2. The narrowing of the

distribution indicates that the polymerization has CCTP characteristics. The theoretical molecular weight distribution from an ideal 'living' polymerization in a series of two CSTR reactors is given by the following equation, where f_1 and f_2 are the mass fractions of polymer comprising the two blocks:¹⁷

$$M_{\rm w}/M_{\rm n} = 2(1 - f_1 f_2)$$

The theoretical lower limit of the molecular weight distribution for Diblock 1 is 1.57. The observed M_w/M_n of 1.67 indicates that the sample contains a very large fraction of polymer chains with the anticipated diblock architecture. The estimated number of chains per zinc and hafnium are also indicative of a high level of CCTP. The M_n of Diblocks 1 and 2 correspond to just over two chains per zinc, but 380 and 455 chains per hafnium, respectively. Diblock 1 also provides a highly unusual example of a polyolefin produced in a continuous process with a molecular weight distribution less than that expected for a polymer prepared with a single-site catalyst (in absence of chain shuttling, $M_w/M_n = 2$).

The comonomer composition distributions of these two materials are also indicative of the block architecture of the OBC. A comparison of solution solubility characteristics as revealed by temperature rising elution fractionation (TREF) is shown in Figure 17. The physical blend displays a peak at 96 °C with a soluble fraction of 56 wt.%, consistent with a physical blend of HDPE and VLDPE. The trace from the diblock OBC reveals a peak at a slightly lower temperature, 93 °C, with no evidence of a shoulder at higher temperature that would indicate uncoupled HDPE. In contrast to the blend, the majority of this sample, 84 wt.%, elutes at this high temperature, while only 13 wt.% of the sample is soluble at room temperature. Since crystallization is an equilibrium process, even samples of HDPE have a small fraction, typically 5-10 wt.%, remaining in solution under the employed TREF conditions. This TREF behavior can only result from OBC architecture with a very homogeneous block structure.

The melting behavior of the two resins also reveals structural differences. The physical blend has a peak melting



Figure 16 Comparison of GPC traces of the Blend 1 and Diblock 1.



Figure 17 Comparison of solution solubility by analytical TREF of the blend and diblock OBC.

temperature (T_m) of 126 °C with a heat of fusion of 104 J g⁻¹, consistent with the high-density fraction of the sample. The diblock sample has similar crystallinity, with heat of fusion of 104 J g⁻¹, reflecting the similar compositions of the two samples. However, the diblock sample displays a lower peak melting temperature, with $T_m = 122$ °C. This depression of peak melting temperature is also consistent with OBC architecture.

3.22.7.2.2 Solid-state morphology

The solid-state morphologies of the high Δ_{C8} Diblocks 2 and 3 are very unusual for polyolefins. Morphologies were examined on simple compression molded films using transmission electron microscopy (TEM), and representative images are shown in **Figure 18**. The samples are stained with ruthenium tetraoxide (RuO₄), which preferentially stains the amorphous ultra low-density PE (ULDPE) phase, to provide contrast for the TEM. The low Δ_{C8} sample, Diblock 1, exhibits uniformly dispersed lamellar crystals, as expected when crystallization proceeds from a homogeneous melt. The Blend 2 sample exhibits macrophase separated morphology typical of an immiscible blend of LLDPE and ULDPE.

In contrast, the high Δ_{C8} OBC samples, Diblocks 2 and 3, exhibit morphologies consistent with self-assembled BCPs having ordered semicrystalline domains, implying confined crystallization from self-assembled melts. As shown in **Figure 18**, these materials exhibit average domain spacings (D_{sp}) of ~140 and 160 nm, respectively. Spacings of this magnitude are typical of BCPs with M_n 's that are 1 order of magnitude higher; in fact, BCPs with M_n 's similar to Diblocks 2 and 3 typically have spacings in the 30–50 nm range.

The domain spacings in these simple unannealed compression molded films are remarkable considering the relatively low M_n 's of the OBCs. One key difference in these diblocks and comparative materials is the broad polydispersity of block lengths imparted by the continuous process. As mentioned previously, living BCP syntheses typically give materials with very narrow molecular weight distributions. Block length polydispersity has been shown to increase domain size,⁵⁸ but the magnitude of this effect in Diblocks 2 and 3 is much larger than predicted.

The unexpectedly large domain sizes of Diblocks 2 and 3 prompted a reexamination of the theories pertaining to the effects of polydispersity, composition, and molecular weight on domain sizes. Contributions from each of these factors are



Figure 18 TEM images of sections taken from compression molded films of diblock and blend samples.



Figure 19 Domain size as a function of M_n for ethylene-*co*-octene OBCs (\blacktriangle), comparative monodisperse EPE triblocks⁵⁹ (\Box), predictions for ethylene-*co*-octene (- -) and EPE (·····) compositions at 80 °C using monodisperse SCFT, and predictions from polydisperse SCFT (X) and SST (—) for ethylene–octene compositions. Adapted with permission from Hustad, P. D.; Marchand, G. R.; Garcia-Meitin, E. I.; *et al. Macromolecules* **2009**, *42*, 3788.¹⁸ Copyright 2009 American Chemical Society.

represented in Figure 19, which plots observed and predicted domain spacings, D_{sp} , as a function of M_n . A comparative set of microphase separated BCPs with ethylene crystallinity and $f_{LLDPE} \approx 0.5^{59}$ and predictions from conventional SCFT and strong segregation theory (SST) are also included for comparison. At similar $M_{n'}$, the hydrogenated butadiene–isoprene–butadiene triblocks (EPE) domain spacings are 2.5–3.6 times smaller than the polydisperse OBCs. Although these theories predict substantial increases in D_{sp} from polydispersity, both predict substantially smaller domain spacings than measured

for Diblocks 2 and 3. An extension of SST was developed to explain these large domain spacings, and the detailed derivation can be found in Reference 18. The new theory demonstrates that many molecules have a weak preference for segregation to the interface versus the center of a domain. One result of this domain swelling is that minor perturbations can produce highly swollen but relatively stable domains.

3.22.7.2.3 Optical properties

The ordered morphologies and unusually large domain spacings impart interesting optical properties to these high Δ_{C8} OBC samples. Films of Diblock 1 and Blend 2 have no unusual optical properties, but Diblocks 2 and 3 appear blue when viewed under ambient light against a black background and yellow when viewed in transmission in front of a white light source. Reflectivities in the ultraviolet and visible (UV-vis) regions of the compression molded films were measured using a spectrophotometer equipped with an integrating sphere detector and are shown in Figure 20.

The color effects are created by scattering as a consequence of the morphology, which approximates a 1D Bragg stack composed of alternating layers of materials with contrast in refractive index, *n*. For a two-component A-B multilayer stack, the first-order wavelength of peak reflectivity at normal incidence, λ_{PR} , is a function of the optical thickness of each layer according to the following equation:

$$\lambda_{\rm PR} = 2(n_{\rm A}d_{\rm A} + n_{\rm B}d_{\rm B})$$

where n_A and n_B are the refractive indices of the two components and d_A and d_B are the respective thicknesses. The refractive index of PE varies with crystallinity, which is easily controlled by comonomer content. In these OBCs, the compositions of the LLDPE and ULDPE blocks correspond to *n* values of 1.510 and 1.473, respectively. Utilizing these values of *n* and the estimated domain sizes from TEM, the predicted first-order wavelength of peak reflectivities can be calculated using the above equation. The calculated reflectance peaks, at 406 and



Figure 20 Reflectance spectroscopy of films of Diblock 1 (■), Diblock 2 (●), Diblock 3 (♦), and Blend 2 (▼). Adapted with permission from Hustad, P. D.; Marchand, G. R.; Garcia-Meitin, E. I.; *et al. Macromolecules* 2009, *42*, 3788.¹⁸ Copyright 2009 American Chemical Society.

486 nm for Diblocks 2 and 3, respectively, are in reasonable agreement with the measured values (369 and 428 nm).

Although periodic structures of BCPs have been used to fabricate photonic materials,^{60–62} it has been a tremendous challenge to form ordered BCP morphologies with domain spacings large enough to interact with visible light.²¹ Since nfor most polymer systems is near 1.5, polymer systems require domain spacings $(D_{sp}'s)$ of ~130 nm to achieve reflectance of visible light. These large periodicities have only been achieved with conventional monodisperse BCPs of very high molecular weight, typically in excess of 500 000 g mol⁻¹.^{60,61} Even with $M_{\rm n}$'s about 1 order of magnitude lower, these high $\Delta_{\rm C8}$, polydisperse OBCs exhibit morphological characteristics and photonic behavior similar to high-molecular-weight, monodisperse BCPs. The capability to fabricate self-assembled structures with tailored domain spacings this large with solvent-free processes has significant implications on scalability and applicability of this technology.

3.22.8 Synthesis of OBCs with Dual-Catalyst Systems

As stated above, reversible chain transfer between two different catalysts, also known as 'chain shuttling', is a useful strategy for the catalytic synthesis of BCPs. BCPs can be envisioned from dual-catalyst chain shuttling processes through both homopolymerization and copolymerization systems. In either case, catalysts must be selected that give polymers with chemically or physically distinguished blocks from a common reaction environment. Although this requirement is quite limiting for radical or ionic polymerization processes, it is relatively easily met with coordination catalysts. In copolymerizations, catalysts with different monomer reactivity ratios can be selected to give blocks differing in chemical composition. Single monomer scenarios could also be designed to give BCPs if catalysts with different stereo- or regioselectivities were employed. For example, a chain shuttling system wherein the two catalysts form isotactic PP (iPP) and aPP would lead to a multiblock copolymer composed of semicrystalline isotactic and amorphous atactic segments.

While CCTP character has been demonstrated in several single catalyst systems, examples of the use of main-group metals to exchange polymer chains between two different catalysts in a common reaction environment are much less common. Dual-catalyst systems claimed to demonstrate some level of reversible chain transfer (see **Table 7**) are summarized below for both ethylene- and propylene-based systems. Characterization data demonstrating that the primary product is BCP are described in greater detail in Section 3.22.9.

3.22.8.1 Ethylene-Based Block Copolymers

Researchers at Dow reported successful production of ethylene-based OBCs using a dual-catalyst chain shuttling system in a continuous solution polymerization reactor. A series of ethylene–octene copolymers of similar melt index were

 Table 7
 Dual-catalyst systems claimed for the synthesis of ethylene-based block copolymers

Precatalyst A	Hard Polymer	Precatalyst B	Soft polymer	Transfer metal	Referenc
R^{2} R^{2} R^{2} R^{1} R^{1} R^{1} R^{2} R^{2} R^{2} R^{2}	HDPE	Me Me	ULDPE	ZnEt ₂	19
2 , $R^1 = iPr$, $R^2 = tBu$ 3 , $R^1 = 2$ -methylcyclohexyl, $R^2 = tBu$		4			
	LLDPE	Me Me	ULDPE	ZnEt ₂	65
26 , M = Zr, R = 2,6-di- <i>i</i> PrPh 27 , M = Hf, R = 2,6-di- <i>i</i> PrPh 28 , M = Hf, R = n-octyl		4			
	HDPE	Ni Br	Hyperbranched PE	ZnEt ₂	66

Sample	Cat. package	[Zn]/[C ₂ H ₄] ^a (× 10 ³)	Density (g cm ⁻³)	M _w ^b (kg mol ^{- 1})	M_w/M_n^b	Chains/Zn ^c	Chains/(Hf + Zr) ^c
1 (Soft PE)	4 + DEZ	1.87	0.862	110	1.97	2.7	230
2 (Hard PE)	3 + DEZ	2.07	0.938	65.0	1.95	4.6	2200
3 (Blend)	3 + 4	-	0.890	137	13.8	-	3600
4 (Low ĆSA)	3+4+DEZ	0.56	0.883	129	3.22	12	820
5 (Mid CSA)	3+4+DEZ	1.40	0.883	119	2.23	3.6	630
6 (High CSÁ)	3 + 4 +DEZ	2.39	0.879	105	1.97	1.9	260

 Table 8
 Process details for production of olefin block copolymers using precatalysts 3 and 4 in presence of DEZ

^aThe [Zn]/[C₂H₄] ratio is defined as the molar ratio of chain shuttling agent to ethylene in the reactor.

^bDetermined by GPC relative to polystyrene standards.

^c Chains/Zn was calculated using the zinc feed and polymer production rates and the number-average molecular weight of the resulting copolymer corrected for comonomer content. Similarly, chains/(Hf+Zr) was estimated using the total catalyst metal feed.

produced with a composition of \sim 30% (by weight) hard and 70% soft blocks (Samples 1–6, **Table 8**). The level of DEZ was systematically varied to study the effects of CSA ratio on polymer microstructure.

Individual catalyst experiments confirmed the difference in reactivity ratios for the catalyst pair, as precatalysts **3** and **4** gave copolymers with density (ρ) of 0.860 and 0.936 g cm⁻³, respectively (Samples 1 and 2). These two baseline polymerizations provided an estimate of the catalyst ratio necessary to achieve the desired composition for the dual-catalyst products; an overall density of ~0.88 g cm⁻³ was targeted to give the desired copolymer composed of 30% high-density material. (The reciprocal density relationship $\rho = 1/(f_1/\rho_1 + f_2/\rho_2)$ was used to estimate the resulting overall density of the desired polymer blend.) A series of products, Samples 3–6, were produced at four different levels of blockiness including a blend sample prepared in absence of DEZ. The blockiness, or average block length and number of blocks per chain, was adjusted by varying the ratio of concentrations of DEZ to ethylene ([Zn]/[C₂H₄]).

The copolymer prepared without DEZ, Sample 3, is clearly shown to be bimodal by GPC, with $M_w/M_n = 13.8$ (Figure 21).

The GPC trace was deconvoluted into components of $M_{\rm w} \sim 240\,000$ and $\sim 9600\,{\rm g\,mol^{-1}}$, reflecting the differing propensities for hydrogen-induced termination of the two catalysts. The molecular weight distribution narrows as DEZ is added, as expected for an efficient chain shuttling polymerization; $M_{\rm w}/M_{\rm n}$ = 1.97 at the highest DEZ level examined (Sample 6). This narrow molecular weight distribution is normally associated with a single-catalytic species and is indicative of the multiblock nature of the copolymer, since several shuttling events are required to generate such a homogeneous molecular weight distribution.

This molecular weight response clearly indicates that chain-shuttled ethylene–octene BCPs, rather than blends, are formed upon introduction of DEZ. The M_n can also be used in conjunction with the DEZ feed and polymerization rate to calculate the number of chains produced per Zn molecule. The low DEZ level of Sample 4 results in the production of ~12 chains per Zn. However, the reaction is practically stoichiometric at higher DEZ (no H_2), with production of Sample 6 resulting in 1.9 chains per Zn (or ~1 chain per Zn–alkyl moiety). This example indicates that nearly every polymer chain exited the



Figure 21 GPC traces for **3**/4 system with and without DEZ as CSA. From Arriola, D. J.; Carnahan, E. M.; Hustad, P. D.; *et al. Science* **2006**, *312*, 714–719.¹⁹ Reprinted with permission from AAAS.

reactor bound to the CSA, with very little chain termination, demonstrating the efficiency of the chain shuttling reaction.

Despite the potentially stoichiometric nature of the reaction with the CSA, a similar calculation of the number of chains per catalyst molecule reveals that the polymerization is highly catalytic in the hafnium and zirconium species. The chain shuttling methodology is capable of generating unlimited OBC chains per catalyst (e.g., \sim 260 chains per total catalyst in Sample 6).

The chain shuttling process offers a high level of control over the resulting OBC microstructure. The average number of blocks per chain can be adjusted by modifying the ratio of CSA to monomer; higher values of $[Zn]/[C_2H_4]$ result in shorter block lengths. The hard/soft composition (i.e., density) can be easily varied by adjusting the ratio of the two catalysts in the reactor feed. This feature is demonstrated in Samples 7–12, in which the amount of HS was varied from 18 to 82 wt.% by adjusting the ratio of precatalysts 4 to 3 (Table 9). The overall molecular weight can be controlled through a combination of $[Zn]/[C_2H_4]$ ratio, hydrogen feed, and/or the reactor temperature.

In addition to facile control over several aspects of the resultant polymer architecture, the chain shuttling process also provides control over the difference in SCB between the two polymer types, labeled Δ_{CS} for ethylene–octene OBCs, via catalyst selection. The plot in Figure 9 illustrates this difference

for a hypothetical dual-catalyst chain shuttling system. The mole fraction of comonomer in the reactor can be manipulated to control Δ_{C8} , but the SCB level of the HS remains relatively constant for the catalyst pair depicted in the diagram. Because the two catalysts operate simultaneously in the reactor, the segment compositions are coupled; that is, selection of a SCB level for one catalyst determines the SCB level of the other. This difference in SCB (Δ_{C8}) arises from the difference in ethylene/LAO selectivity of the two catalysts. For the catalyst pair described previously, at reactor conditions for which 4 produces a ULDPE with density = 0.857 g cc⁻¹ (~18 mol.% octene), precatalyst 3 produces an HDPE with density = 0.939 g cc⁻¹ (~1 mol.% octene).

Density limits for PE are ~0.853 to 0.960 g cc⁻¹, so the component blocks of this polymer are near the extremes. However, there are some applications that may benefit from smaller Δ_{C8} . For example, some applications require lower processing temperatures and therefore cannot tolerate polymers with high $T_{\rm m}$. Other applications require hydrocarbon solubility, which is significantly reduced in polymers with highly crystalline blocks. Thus, alternative catalysts with varying LAO selectivities can enable new polymers to address such applications.

Accordingly, a series of imine-amide catalysts⁶³ (26–28) with ethylene selectivity ranging from very high to intermediate were investigated (Table 10). Importantly, these catalysts also

 Table 9
 Production of OBCs with varying hard/soft ratio using 3/4/DEZ

Sample	Density (g cm ⁻³)	HS content ^a (wt.%)	Precat. ratio ^b ([4]/[3])	[Zn]/[C ₂ H ₄] ^c (× 10 ³)	M _w ^d (kg mol⁻ ¹)	M_w/M_n^d
7	0.865	18	3.5	2.40	112	1.97
8	0.880	27	2.3	1.61	124	2.06
9	0.893	40	1.0	1.41	110	2.11
10	0.902	57	0.61	1.38	108	1.95
11	0.910	67	0.49	1.46	99.8	1.90
12	0.920	82	0.18	1.11	102	1.93

^aHard segment (HS) content is estimated by ¹³C NMR spectroscopy.

^b[4]/[3] is the molar ratio of precatalyst 4 to 3 in the reactor feed.

^c[Zn]/[C₂H₄] is defined as the molar ratio of chain shuttling agent to ethylene in the reactor.

^dDetermined by GPC relative to polystyrene standards.

DLL									
Sample	HS cat.	SS cat.	Precat. ratio ^a ([Cat]/[4])	Zn ^b (ppm)	Density (g cm ⁻³)	Est. HS density ^c (g cm ⁻³)	Est. SS content (wt.%)	M _w ^d (kg mol⁻ ¹)	M _w /M _n ^d
13	3	4	2.7	256	0.877	0.939	73	118	1.95
14	-	4	-	242	0.857	-	100	139	1.90
15	26	-	0.0	186	0.932	0.932	0	70	2.29
16	26	4	1.9	0	0.883	0.932	63	81	5.71
17	26	4	0.8	219	0.880	0.932	68	119	2.11
18	27	4	3.0	201	0.869	0.898	69	127	2.13
19	28	4	15.7	221	0.867	0.891	69	129	2.06

 Table 10
 Process details for production of olefin block copolymers using HS precatalysts 3, 26, 27, and 28 with SS precatalyst 4 in presence of DEZ

^aThe molar ratio of the hard catalyst to soft catalyst **4** in the reactor feed.

^bZn (ppm) is the residual zinc content in the polymer as measured by XRF spectroscopy.

^cThe reciprocal density relationship $\rho = 1/(f_{HS}/\rho_{HS} + f_{SS}/\rho_{SS})$ was used to estimate the resulting overall density of the desired polymer blend, assuming $\rho_{SS} = 0.857 \text{ g cc}^{-1}$. ^dDetermined by GPC relative to polystyrene standards. show characteristics of fast chain shuttling with DEZ.⁶⁴ These catalysts were evaluated in a similar continuous reactor protocol to synthesize OBCs with varying Δ_{C8} , holding several variables constant in order to isolate the effects of varying the 'hard' catalyst, selected from catalysts 3, 26, 27, and 28. The SS catalyst (4) and the chain shuttling agent (DEZ) were held constant in all experiments. The [octene]/[ethylene] ratio was also fixed to give a constant SS composition equivalent to a copolymer with density = 0.857 g cc^{-1} . Furthermore, the flow of 4 was held constant while the flow of the hard catalyst was adjusted to achieve the target ethylene concentration. As a result, each of the resultant polymers contains about 60-70% soft block. The CSA concentration, [DEZ], was also held essentially constant, although this does not ensure the same average block length, because the different polymers' block architectures are governed by different shuttling kinetics. Finally, the melt index of each of the OBCs was adjusted to $I_2 = 1$ $(M_{\rm w} \sim 120 \, \rm kg \, mol^{-1})$ by adjusting hydrogen flow. Samples 14 and 15 describe control runs for OBC preparation using 4 and 26 as the soft and hard catalysts, respectively. Sample 16 was prepared in the absence of CSA (only H₂ for molecular weight control) to generate a blend for comparison to the OBC made in Run 5. Samples 17-19 were prepared with precatalysts 26-28 in combination with 4 using DEZ as the CSA.

The basic polymer characteristics are tabulated in **Table 10**. All of the new polymers, Samples 13, 17, 18, and 19, have characteristics indicative of a blocky architecture. Despite the use of two catalysts, M_w/M_n is about 2 for all of these examples. As previously described, this narrow molecular weight distribution is a result of the shuttling process, in which polymer chains are exchanged among multiple active catalyst sites prior to termination, leading to an averaging effect for chain termination. The comparative blend, Sample 16 (with H₂ for molecular weight distribution $(M_w/M_n = 5.71)$). The broader molecular weight distribution for this control experiment confirms the blend in the absence of shuttling agent, and supports the assertion that DEZ shuttling leads to blocky architecture.

Xiao and co-workers⁶⁵ have claimed the synthesis of BCPs from only ethylene by partnering metallocene 29 with α -diimine nickel catalyst 30 (Scheme 15). In presence of



Scheme 15 Polyethylene architectures afforded by catalyst systems **29**/MAO and **30**/MAO.

ethylene, the 29/MAO catalyst system forms HDPE while 30/ MAO gives a highly branched architecture through a 'chain walking' mechanism. Addition of DEZ to the polymerization gave materials with intermediate branching levels and fairly narrow PDIs.

3.22.8.2 Propylene-Based Block Copolymers and Blends

Catalyst systems reported for synthesis of blocky propylenebased materials are summarized in **Table 11**. Chien and co-workers reported propylene polymerizations with a dual-catalyst system comprising either of two isospecific metallocenes **29** and **32** with an aspecific metallocene **31**.⁶⁶ They reported that the combinations gave PP alloys composed of iPP, aPP, and a small fraction (7–10%) claimed by ¹³C NMR to have a stereoblock structure. Chien later reported on product made from mixtures of isospecific and syndiospecific PP precatalysts **29** and **33**.⁶⁷ As in the above examples, the resulting polymer was largely a blend of isotactic and syndiotactic PP (sPP) with a small stereoblock fraction. The mechanism for formation of the stereoblock fraction was proposed to involve the exchange of propagating chains between the two different catalyst sites.

Przybyla and Fink⁶⁸ reported that a 1:1 combination of the isospecific precatalyst 32 with syndiospecific precatalyst 34 on MAO-impregnated silica using either triisobutylaluminum (TiBA) or TEA gave a polymer with decreased ¹³C NMR pentad ratios ([mmmm]/[mmmr] and [rrrr]/[rrrm]) claimed to be indicative of a block structure. This is of interest because the previous report by Song *et al.*⁶⁹ stated that a similar supported system showed no evidence of chain exchange. However, it should be noted that other stereoerror ratios, unrelated to block junctions, changed as well, suggesting other factors can affect the stereoselectivity. This was especially apparent when the catalysts were supported on a different type of silica. Here, the [mmmm]/[mmmr] and [rrrr]/[rrrm] ratios increased beyond those expected for the polymer blend, providing further support for the notion that factors other than block formation can change the apparent ratios of those errors.

Lieber and Brintzinger⁷⁰ reported a detailed study using mixtures of precatalysts with different stereospecificities. Isospecific precatalyst 35 undergoes facile chain transfer to trimethylaluminum (TMA), as revealed by an increase in isopropyl end groups and a sharp reduction in molecular weight in the presence of TMA (there was no exchange with TiBA). Aspecific precatalyst 31 was affected similarly by TMA (again, no effect with TiBA). The dual-precatalyst system 35/31 at high [MAO] produced an ether-soluble atactic fraction and an insoluble isotactic fraction as expected for these catalysts. However, the polymer samples also contained as much as 27% of a third fraction that was soluble in hexane. A blend of polymer obtained from individual polymerizations using 35 and 31 contained no such hexane-soluble fraction (subsequent to ether extraction). The [mmmm] content of this fraction was about half that of the insoluble isotactic fraction, consistent with a 50/50 blend or BCP. The latter was proposed based on the unique solubility. The authors proposed that efficient polymer chain exchange between active catalyst sites and the aluminum centers of the cocatalyst were required for formation of stereoblock copolymer.

Precatalyst A	Poly. A	Precatalyst B	Poly. B	Transfer metal	Reference
CI-Zr-CI	iPP		aPP	MAO	67
	iPP	31 $CI-Zr-CI$ 31 31	aPP	MAO	67
32 CI-Zr-CI 29	iPP	Ph. Ph ZrCl ₂	sPP	MAO	68
ZrCl ₂	iPP	ZrCl ₂ 34	sPP	MAO-silica with TiBA or TEA	69
Si ZrCl ₂	iPP		aPP	ТМА	71
CMe ₃ Si ZrCl ₂ 36 CMe ₃	iPP	Ph. Ph ZrCl ₂ 33	aPP	TMA	73
Me Me // Hf N ,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	iPP	Me Me Hf N (S)-37	iPP	ТМА	74

Table 11	Dual-catalyst systems claimed for the synthesis of propylene-based block copolymers and blends

The authors conducted a similar investigation of precatalysts **36** and **31** using TiBA and trityl tetrakis(pentafluorophenyl)borate as the cocatalyst. They concluded that this material contained no fraction that could be characterized as blocky. It was therefore proposed that reversible chain transfer occurred only with MAO or TMA and not with TiBA. This stands in contrast to the work of Chien *et al.*⁶⁶ and Przybyla and Fink⁶⁸ (*vida supra*), who claim reversible chain transfer with TiBA in similar catalyst systems. Lieber and Brintzinger also investigated a mixture of isospecific **36** and syndiospecific **33** in attempts to prepare iPP/sPP BCPs. Extraction of such similar polymers was acknowledged to be difficult and even preparative TREF⁷¹ was only partially successful.

Tynys *et al.*⁷² reported possible polymer chain exchange with PP produced with a combination of **36** and **33** with TMA. The number of stereoerrors increased in the binary system at higher TMA levels. As discussed in the case of Przybyla and Fink (*vida supra*), pentad analysis is less compelling evidence for reversible chain transfer. In addition, the GPC data showed bimodal peaks, indicating very limited reversible transfer.

Busico, Stevens, and co-workers⁷³ reported the first conclusive ¹³C NMR evidence for PP chain shuttling between enantiomeric catalysts derived from the pyridylamide precatalyst (*R*)-37. The main evidence for chain shuttling between enantiomers was the presence of $m_x(rr)m_y$ stereoerrors in iPPs made with *rac*-37 (Figure 22(a)). In contrast, these stereoerrors were absent in iPPs made with the enantiopure catalyst (Figure 22(b)). According to the authors, "this is the first ¹³C NMR evidence of chain shuttling for polyolefins in general. For PP in particular, in previously claimed cases the microstructural analysis of the polymer was inconclusive, and fractionation results revealed that the samples were largely physical blends, with at most a minor fraction of stereoblock chains."⁷³



Figure 22 Direct ¹³C NMR evidence of polypropylene chain shuttling at enantiomorphous catalyst sites using precatalyst **37**. Adapted with permission from Alfano, F.; Boone, H. W.; Busico, V.; *et al. Macromolecules* **2007**, *40*, 7736–7738.⁷³ Copyright 2007 American Chemical Society.

The microstructure was analyzed using a quantitative statistical analysis with a simple enantiomorphic-sites stochastic model in Coleman–Fox form.⁷⁴ The model fits the data to two adjustable parameters, the probability σ of inserting propylene with the favored enantioface and the probability P_{inv} of inverting the configuration of the propagating center. In the case of the racemic precatalyst, the probability of chain shuttling is $2P_{inv}$. With *rac*-**37**, P_{inv} increased with decreasing [propylene] and increasing [TMA], both of which increase the relative ratio of rates of chain shuttling to propagation. Importantly, the iPP made with (*R*)-**37** showed no evidence of stereoblock character (Figure 22), validating chain shuttling as the mechanism responsible for the microstructure afforded by (*R*)-**37**.

This study also demonstrated that the nature of the solvent can have an effect on the chain shuttling kinetics. Under constant conditions, a change in solvent from toluene to the more polar 1,2-difluorobenzene gave PPs with more narrow molecular weight distributions. In addition, P_{inv} was higher by a factor of 6–9 in samples made in 1,2-difluorobenzene. These data indicate that choice of solvent is an important consideration in design of new chain shuttling systems.

3.22.9 Characterization of Olefin Block Copolymers

For typical random polyolefins, the molecular structure can be determined by measuring a few key properties, such as composition, molecular weight, and molecular weight distribution. These same features can be measured for OBCs, but isolated measurements are not sufficient to characterize a block structure. A combination of techniques must be used to confirm that a material is an OBC. The following section describes several characterization techniques that provide evidence of the block structure of OBCs and provides illustrative examples.

3.22.9.1 Melting Temperature

One of the most striking properties of OBCs is the decoupling of melting temperature ($T_{\rm m}$) and density. Figure 23 shows the typical relationship between density and melting point for random ethylene–LAO copolymers; as more comonomer is added, density and $T_{\rm m}$ decrease according to this relationship. OBCs made with chain shuttling using the catalyst system 3/4/DEZ have melting points up to ~60 °C higher than that expected for a statistically RCP prepared at equivalent density. The circled symbols are several OBCs prepared by chain shuttling catalysis.¹⁹ While a typical RCP with density of 0.88 g cm⁻³ would melt at ~60 °C, Samples 4–6 made by chain shuttling do not melt until almost 120 °C.

The principle melting features are determined by the octene content in the hard block, as incorporated by the 'hard' catalyst, and can thus be varied. This relationship is demonstrated with Samples 13 and 17–19 made using precatalysts **3**, **26**, **27**, and **28** (Figure 24). In these copolymers, the composition of the soft block is constant, but the octene content in the hard block is varied according to the copolymerization characteristics of the 'hard' catalysts. Precatalysts **3** and **26** both incorporate very little octene and give OBCs,



Figure 23 OBCs made with preatalysts **3** and **4** have melting points much higher than the corresponding random copolymers at equivalent density. From Arriola, D. J.; Carnahan, E. M.; Hustad, P. D.; *et al. Science* **2006**, *312*, 714–719.¹⁹ Reprinted with permission from AAAS.



Figure 24 Differential scanning calorimeter (DSC) traces for OBCs made using two catalysts and a chain shuttling agent. The polymers have nominally the same soft segment composition but varying hard segment compositions.

Samples 13 and 17, with $T_{\rm m}$ = 118 °C. Precatalysts 27 and 28 are better incorporators of comonomer and thus give OBCs with lower peak $T_{\rm m}$'s, 111 and 91 °C, respectively, in Samples 18 and 19.

3.22.9.2 Crystallinity and Solid-State Morphology

Melting point alone cannot be used to uniquely identify an OBC, as blends of high- and low-density polyolefins also exhibit an elevated melting point at equivalent density. For example, Sample 3 in Figure 23 (small circle) is a 70/30 physical blend of 0.86 and $0.94 \,\mathrm{g\,cm^{-3}}$ ethylene-octene copolymers, and the melting point is similar to the OBCs. Physical blends of polymers of such disparate densities are not phase-continuous, however, and segregate into large (> 1 μ m) domains of the high- and low-density polymers.



Figure 25 Several samples of ethylene–octene copolymers having similar comonomer content, crystallinity, and melt index. Sample three is a physical blend of high- and low-density copolymers. Samples 4–6 are OBCs prepared with several different levels of chain shuttling agent. From Arriola, D. J.; Carnahan, E. M.; Hustad, P. D.; *et al. Science* **2006**, *312*, 714–719.¹⁹ Reprinted with permission from AAAS.

Figure 25 reveals differences in appearance of pressed plaques of Samples 3–6. Note that Sample 3, the physical blend, is opaque, while the OBC samples have differing degrees of clarity. These differences can be explained by examining the distribution of crystallinity in the sample.



Figure 26 Polarized optical micrographs of several polymers from top left to lower right: a random ethylene–octene copolymer; high-density polyethylene; Samples 3–6.

Figure 26 reveals optical micrographs of the above samples through plane-polarized light, as well as reference samples including an RCP of equivalent density and HDPE. RCPs in this density range exhibit only fringe micelle crystallinity.⁷⁵ HDPE shows the traditional patterns of spherulitic crystallinity filling the image. Remarkably, OBCs also show spherulites at a density range where none should be evident for an RCP. Moreover, the relative size and distribution of these spherulites can be influenced by the amount of CSA employed to produce the polymer. At higher [CSA]/[C₂H₄] ratios, shuttling is fast with respect to propagation, and shorter ethylene blocks are produced which result in smaller spherulites. Conversely, longer ethylene runs at lower [CSA]/[C₂H₄] ratios result in a fewer number of larger spherulites. All samples (with the exception of the HDPE) have approximately the same density and crystallinity.

Compared to their statistical RCP counterparts, OBCs exhibit a unique crystalline morphology with 'space-filling spherulitic' structure and a better-organized crystalline morphology while maintaining a lower glass transition temperature.^{76,77} Based on these observations, Wang *et al.*⁷⁶ have developed a new classification for the observed crystalline morphologies (**Figure 27**). Detailed X-ray studies have identified the crystal structures to be mostly orthorhombic in nature.⁷⁸

3.22.9.3 Unique Solution Crystallization Behavior

OBCs show very different solution crystallization behavior than statically RCPs.⁷⁹ **Figure 28** shows the analytical TREF profile comparing an OBC to a commercially available RCP (AFFINITY[™] VP8770 from The Dow Chemical Company) and a polymer blend with components that are representative of the HS and SS within the OBC. **Table 12** summarizes the analytical characteristics of these polymers and as shown, these polymers have similar crystallinity and within a similar molecular weight range. **Figure 28** shows that for this particular OBC, which was made using precatalysts 3 and 4 with DEZ as CSA, 90 wt.% of the polymer eluted at a peak temperature of 80 °C. The nearly complete elution of this OBC, despite being $0.878 \,\mathrm{g\,cc^{-1}}$ (19 wt.% crystallinity) is unique when compared with the blend and RCP that have peak elution percentages of 35 and 75 wt.%, respectively. For the 0.889 g cc⁻¹ blend, the 35 wt.% of the ATREF peak is consistent with the targeted amount of high crystallinity polymer made. The fraction eluting below 30 °C is referred to as the noncrystalline or 'purge' fraction and contains the soft, low crystallinity polymer made. The 55 °C elution temperature and 75 wt.% peak area for the RCP $(0.887 \,\mathrm{g}\,\mathrm{cc}^{-1})$. For the OBC, the area of the eluted peak was significantly higher than the targeted amount of HSs in the overall polymer (29 wt.% HSs for this particular OBC). This indicates that the HSs dominate the elution behavior of the OBC and are present in the backbone of the chains (supporting the contention that the soft, lower crystallinity segments are connected to the hard, higher crystallinity segments, which provides an indication of its blocky nature).

To support this hypothesis, the OBC sample can be fractionated by a TREF experiment. Preparative TREF fractionation of the OBC, followed by evaluation of the comonomer content by ¹³C NMR, reveals the data shown in Figure 29. For traditional RCPs produced with the same comonomer type, a distinct relationship between the elution temperature and comonomer content is observed, indicating that regardless of the catalyst nature, the fractions from these RCPs have a statistically random distribution of comonomer. Historically, Wild⁸⁰ has demonstrated that the peak elution temperature directly relates to the degree of SCB in a copolymer. Thus, according to this behavior, each molecule present in a polymer blend will dissolve and elute according to its comonomer content. The results are expected to follow a calibration line in which TREF behavior can be predicted, which is labeled 'Random copolymer line' in Figure 29.

The triangles reveal the comonomer content of the TREF fractions from an OBC. At any given temperature, the polymer eluting has much more comonomer than would be expected



Figure 27 Classification schemes of blocky and statistical EO copolymers. Reproduced with permission from Wang, H. P.; Khariwala, D. U.; Cheung, W.; et al. Macromolecules 2007, 40, 2852.⁷⁶ Copyright 2007 American Chemical Society.



Figure 28 Analytical TREF profiles of a random copolymer, an OBC, and a blend of HDPE with ultra low-density polyethylene (ULDPE) of similar overall densities. Reproduced with permission from Li Pi Shan, C.; Hazlitt, L. *Macromol. Symp.* **2007**, *257*, 80.⁷⁹

for a polymer fraction that has a random distribution of SCB. The only explanation is that the comonomer is blocked, as was expected from the chain shuttling mechanism. The extent of deviation from statistical RCPs can be quantified since the amount of comonomer can be predicted from a given elution temperature for a statistically RCP, the 'blockiness' of an OBC can be defined on the basis of Flory's equilibrium crystallization theory.⁸¹

The solution properties of OBCs can also be tuned by varying the composition of the blocks through catalyst selection. As demonstrated in the melting characteristics of Samples 17–19 described above, selection of 'hard' catalysts of differing octene incorporation rates allows the solubility to be tuned. TREF curves for these samples are shown in **Figure 30**. These new polymers show a range of elution temperatures corresponding to the octene content of the HSs. Polymers made with more ethylene-selective HS catalysts have higher TREF elution temperatures. This ability to tune solubility properties is important in many potential OBC applications requiring solubility.

 Table 12
 Analytical characteristics of the materials compared in Figure 28, including a random copolymer, an OBC, and a blend of HDPE with ultra low-density polyethylene (ULDPE) of similar overall densities

Example	Density (g cc ⁻¹)	M _w (kg mol ^{−1})	M _w /M _n	Crystallinity (wt.%)	Т _т (°С)	Т _с (°С)	ATREF Peak T (℃)	Peak (wt.%)
RCP	0.887	98.0	2.2	25.6	83.2	65.1	55	75
Blend OBC	0.890 0.879	137 105	14 2.0	30.8 18.8	125 120	111 101	82 96	35 90



Figure 29 Comonomer content vs. TREF elution temperature for an OBC and a blend of two random copolymers. Reproduced with permission from Li Pi Shan, C.; Hazlitt, L. *Macromol. Symp.* 2007, *257*, 80.⁷⁹



Figure 30 Temperature rising elution fractionation (TREF) data for OBCs made using two catalysts and a chain shuttling agent, illustrating that crystallization behavior can be controlled by the comonomer content of the hard blocks. The polymers have nominally the same soft segment composition, but varying hard segment compositions.

3.22.9.4 Performance Characteristics of OBCs

OBCs made by chain shuttling between catalysts incorporating large and small amounts of comonomer, respectively, can produce polymer microstructures which block the comonomer, thus exhibiting crystallization behavior that is distinct from that of RCPs of equivalent crystallinity. These novel microstructures extend the traditional regime of flexibility and heat resistance for olefin-based TPEs. Figure 31 compares the dynamic storage modulus versus temperature for two random olefin elastomers and an OBC with similar crystallinity.

Compared to the ethylene-octene RCP and propyleneethylene RCP, the OBC shows a plateau modulus that extends beyond 100 °C until the melting point of the high crystalline hard blocks is reached. The moduli of the RCPs decrease quickly after 50 °C, which signifies that the softening or melting point has been reached. Based on the architecture of the elastomer, the OBC also exhibits a low T_g that is characteristic of ethylene–LAO elastomers containing high comonomer levels. This is contrasted with the propylene–ethylene RCP, which exhibits a higher T_g that arises from its propylene crystallinity.

As a consequence of their unique crystalline network morphology, OBC's display improved elastomeric properties compared to equivalent RCPs. The engineering stress-strain



Figure 31 Plot of storage modulus vs. temperature for statistically random ethylene–octene and propylene–ethylene copolymers compared to an ethylene–octene OBC. Reproduced with permission from Wenzel, T. T.; Arriola, D. J.; Carnahan, E. M.; *et al.* In *Metal Catalysts in Olefin Polymerization. Topics in Organometallic Chemistry*; Guan, Z., Ed.; Springer-Verlag: Berlin, Germany, 2009; Vol. 26.⁹



Figure 32 Engineering stress–strain curves comparing an OBC and a random copolymer. Reproduced with permission from Karande, S. V.; Cheung, Y. W.; Diehl, C. F.; Levinson, M. J. In 64th Annual Technical Conference, Society of Plastics Engineers, 2006.⁸⁴

curves in **Figure 32** show the higher extensibility and improved strain hardening of the OBC.^{82,83} The hysteresis curves in **Figure 33** also show that the elastic recovery of the OBC is also better than the RCP.

The use temperature of a polyolefin elastomer is determined by the range between the T_{g} and the T_{m} . These new OBCs have increased the use temperature range of olefin-based elastomers by > 40 °C, enabling the introduction of these polymers to many new markets and applications where a polyolefin solution was previously unavailable. The extension of the temperature plateau and network structure that is developed from the OBC's crystallinity translates to better high-temperature elastomeric properties for the OBCs. For example, the 70 °C compression set of an OBC is much lower than that of a comparable ethylene–LAO RCP and is closer to that of f-PVC, TPU, or TPV materials.⁸⁴ Figure 34 compares the compressive recovery at 70 °C of an OBC and other TPEs. OBCs exhibit excellent compression set where RCPs (of similar density) have none. Compared to other materials, OBCs have similar recovery to other nonpolyolefin materials.

3.22.9.5 Comparison of Living, CCTP, and Chain Shuttling Block Polymer Architectures

Several differences in the BCP microstructure and architectures distinguish OBCs prepared using chain shuttling and continuous CCTP from BCPs afforded by living polymerization systems. Figure 35 depicts some typical polymer chains to illustrate these differences. BCPs from living polymerization systems have very narrow molecular weight distributions, with M_w/M_n approaching 1.0 for both the overall chains and blocks within chains. The number of blocks per chain is clearly defined by the process conditions. As discussed previously, precise block junctions are difficult to obtain in ethylene– α -olefin copolymers due to reactivity differences, and these materials normally have tapered compositions from the differences in reactivity if two monomers are polymerized simultaneously in batch polymerizations.

Multiblock OBCs from chain shuttling polymerization have very different architectures. The overall chains and blocks within chains have distributions of molecular weights, with M_w/M_n approaching 2.0. The statistical shuttling process produces chains with a distribution in the number of blocks per chain. The block junctions are precise since each block is grown on a different catalyst, and the compositions are homogeneous since the OBCs are produced at steady state in a continuous reactor.

Diblock OBCs from continuous CCTP are different from either of the previous two families of copolymers. The continuous process produces blocks lengths with M_w/M_n approaching 2.0. However, the CCTP process in a series of reactors results in a narrower overall distribution, with M_w/M_n approaching 1.5 in the case of a symmetric diblock.



Figure 33 Engineering stress–strain loading and unloading cycle for an OBC (a) and a comparable RCP copolymer (b). Reproduced with permission from Karande, S. V.; Cheung, Y. W.; Diehl, C. F.; Levinson, M. J. In 64th Annual Technical Conference, Society of Plastics Engineers, 2006.⁸⁴



Figure 34 Compression set at 70 °C for an OBC and other materials. Reproduced with permission from Wenzel, T. T.; Arriola, D. J.; Carnahan, E. M.; *et al.* In *Metal Catalysts in Olefin Polymerization. Topics in Organometallic Chemistry*, Guan, Z., Ed.; Springer-Verlag: Berlin, Germany, 2009; Vol. 26.⁹

The number of blocks per chain is determined by the number of reactors connected in series. Finally, the dual-reactor scheme ensures precise block junctions with homogeneous segment compositions.

These differences in block architecture of the multiblock and diblock OBCs are apparent in a comparison of the solubility characteristics. **Figure 36** shows analytical TREF traces for a physical blend, multiblock OBC, and diblock OBC with similar composition. Both OBCs have lower purge fractions and elute at lower temperatures than the high-density fraction of the blend. However, the multiblock OBC elutes at a lower temperature and over a broader temperature range than the diblock OBC.

3.22.10 Olefin Block Copolymer Design and Applications

While properties of conventional RCPs are controlled by a few simple parameters (e.g., crystallinity and molecular weight), OBCs from CCTP and chain shuttling catalyst systems have opened up new dimensions for polymer designers to control the properties of the neat polymer and formulated products. The balance of properties can now be controlled independently by tailoring the ratio of individual crystallinity of each block and the ratio of hard and soft blocks (which controls the overall composition and crystallinity), the overall molecular weight, and the molecular weight of


Figure 35 Comparison of ethylene–α-olefin block copolymer architectures from living polymerization, chain shuttling, and continuous CCTP. Adapted with permission from Wenzel, T. T.; Arriola, D. J.; Carnahan, E. M.; *et al.* In *Metal Catalysts in Olefin Polymerization. Topics in Organometallic Chemistry*; Guan, Z., Ed.; Springer-Verlag: Berlin, Germany, 2009; Vol. 26.⁹



Figure 36 Comparison of solution solubility by analytical TREF of a blend, diblock, and multiblock OBC with similar overall density (~0.90 g cm⁻³). Adapted with permission from Wenzel, T. T.; Arriola, D. J.; Carnahan, E. M.; *et al.* In *Metal Catalysts in Olefin Polymerization. Topics in Organometallic Chemistry*, Guan, Z., Ed.; Springer-Verlag: Berlin, Germany, 2009; Vol. 26.⁹

the blocks (or average number of blocks per chain) (Figure 37). In all, there are many industrial applications that require a balance of properties such as heat resistance,

flexibility, abrasion resistance, and elastic properties. The differentiated property balance from RCPs allows OBCs to bridge many performance gaps between polyolefins and



Figure 37 New dimensions to define the structure of OBCs.

nonpolyolefin materials, allowing use in many previously inaccessible applications.

Compared to traditional polyolefin RCPs, unique material properties such as flexibility, heat and abrasion resistance along with elastic properties such as low compression set and permanent set can be combined. In addition, the incorporation of fast crystallizing hard blocks promotes quicker solidification as the viscosity increases upon cooling for rapid part setup in injection molding and extrusion applications.

Dow developers and partners having first access to these materials have explored the use of OBCs for various industrial applications such as elastic films, fibers, soft touch materials, extruded profiles, injection molded articles, and so on. For example, polyolefin oil-filled systems used to make compounds for soft touch handles, grips, and gaskets benefit from increased elastic performance and temperature resistance.^{85,86} Other examples include adhesives that utilize OBCs with low hard block contents to obtain the soft adhesive character but at the same time offer the cohesive strength and heat resistance required for demanding pressure sensitive adhesives.^{87,88}

For additional cohesive strength and elasticity, OBCs with higher levels of hard block are useful for nonwoven elastic fibers and temperature-resistant materials such as retortable cap liners for food packaging. The ability to control the microstructure in combination with understanding of material science compatibility allows for expanded use of polyolefins in the replacement of other conventional materials and polymers such as glass, metal, PVC, EVA, and SBCs.

OBCs possessing two segments that are not typically miscible with each other offer new opportunities for compatibilization and improved miscibility. Improved polymer miscibility with HDPE/PP has been demonstrated by improvements in adhesion.^{89,90} However, for ethylene–octene copolymer and OBC blends, the critical comonomer content difference has been observed to be lower than that of two random EO copolymers.⁹¹ SEBS/OBC blends, similar to SEBS/polyolefin blends, remain immiscible but can be used to improve processability and high temperature compression set.⁹² Overall, OBCs offer new material property combinations for blend compatibilization, property-balance improvement, and/or improved processability, but each system needs to be designed appropriately.

3.22.11 Functional Polyolefins from CCTP Systems

In contrast to conventional coordination polymerization, CCTP and chain shuttling processes can be run such that practically every polymer chain is end-capped with a reactive metal–carbon bond. Various researchers have used this as a chemical handle to add polar functionality to the polyolefin. A prerequisite for these transformations is a reactive metal group at every chain end. This can be accomplished with reversible or irreversible chain transfer systems. The difference in these two, as discussed previously, is that reversible chain transfer will produce end-functional PEs with narrow molecular weight distributions.

The reactive metal–polymeryl bond has been used to form various chain end functional polyolefins, including hydroxyls, ^{46,93–95} azides, ⁹⁶ amines, ⁹⁶ and iodo-functional materials (Scheme 16). ⁹⁶ A number of PEs bearing initiators for free-radical polymerizations^{94,96,97} and macromonomers^{94,96} have been reported in recent years. These building blocks have been used to synthesize a variety of functional polyolefin block and graft copolymers. These materials show promise for improved compatibility and adhesion to polar materials.

3.22.12 Conclusion and Outlook

The production of OBCs has been an aspiration of academic researchers and polymer manufacturers alike. Tremendous progress toward this end has been achieved in recent years with the discovery of several designer catalysts capable of living olefin polymerization. However, the stoichiometric nature of the living process coupled with related process limitations of low polymerization temperatures and slow batch processes have precluded these approaches from widespread application.

The chain shuttling and CCTP systems described above overcome these challenges, providing means for production of new polyolefins that display advantaged combinations of physical properties. Chain shuttling polymerization offers a remarkable variety of OBC compositions whose properties are almost infinitely tunable. Similarly, the dual-reactor CCTP scheme offers high flexibility in product design. The split can easily be varied by changing the production rate in either reactor, while the comonomer content of either block can be tailored by varying the feed compositions or even introducing another catalyst into one reactor (as long as the new catalyst also does CCTP).

The properties of these new OBCs break the long-held modulus-density relationship, thereby allowing the creation of elastomers with higher use temperatures. The technology has been developed to such a degree that The Dow Chemical Company has introduced a new family of materials under the trade name INFUSE[™] Olefin Block Copolymers. While this technology introduces a solution to a long-standing challenge, it also poses several new questions. Future efforts will likely



Scheme 16 Synthesis of functional polyethylene using CCTP.

lead to further elucidation of the kinetic and mechanistic intricacies of chain shuttling reactions, discoveries of catalysts with improved performance, and application of this technology to other polymer systems.

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Biographical Sketches



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Roger L. Kuhlman graduated from Grinnell College (Iowa) in 1991 with BA degrees in chemistry and German. He then studied late transition metal polyhydride complexes under the guidance of Professor Kenneth Caulton at Indiana University, receiving his PhD in 1995. After postdoctoral studies investigating reactions in supercritical fluids with Professor Joe Kolis at Clemson University, he joined Union Carbide Corporation in 1997. He has continued his research at Union Carbide and The Dow Chemical Company for the last 14 years, pursuing varied interests including homogeneous and heterogeneous catalyst discovery, gas-phase polyethylene process continuity, polymer grafting, high-throughput experimentation, mechanistic studies, polyolefin BCPs, polymer solution rheology, cellulosic polymers, and polymer dispersions.



Colin Li Pi Shan received his BSc (1996) and MSc (1998) degrees in engineering chemistry from Queen's University (Kingston, Ontario) and his PhD in chemical engineering (2002) from the University of Waterloo under the supervision of Professors Joao Soares and Alexander Penlidis. He is currently a product development scientist for The Dow Chemical Company, Elastomers R&D. He is a subject matter expert for polyolefin microstructure analysis to support catalyst discovery, material science, and product development. His interests include developing structure–property relationships of olefinic elastomers and BCPs in applications such as adhesives, impact modifiers, and EPDM-related technologies.

3.23 Living Transition Metal-Catalyzed Alkene Polymerization: Polyolefin Synthesis and New Polymer Architectures

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2 22 1	Introduction	740			
0.20.1	Introduction	740			
3.23.2	Living Orenni Polymerization Delv(1 hevene)	741			
3.23.2.1	Poly(1-nexene)				
3.23.2.2	Polypropylene	741			
3.23.2.3	Polyetnytene Delvalating from Conjugated Dianas, Cuelia Olating, and Delay Manamara	741			
3.23.2.4	Polyolenns from Conjugated Dienes, Cyclic Olenns, and Polar Monomers	742			
3.23.2.5	Criteria for Living Polymerization	742			
3.23.3	Early Metal Dietin Polymerization Catalysts	743			
3.23.3.1	Vanadium Acetylacetonoate Catalysts	743			
3.23.3.2	Metallocene and Unbridged Half-Metallocene Catalysts	743			
3.23.3.3	Catalysts Bearing Monocyclopentadienyl-amido Ligands	/45			
3.23.3.3.1	1-Hexene polymerization	745			
3.23.3.3.2	Propylene polymerization	746			
3.23.3.3.3	Copolymerization of ethylene/norbornene and propylene/norbornene	746			
3.23.3.4	Monocyclopentadienylzirconium Amidinate Catalysts	747			
3.23.3.4.1	1-Hexene polymerization	747			
3.23.3.4.2	Propylene polymerization	749			
3.23.3.4.3	Polymerization of 1,5-hexadiene	750			
3.23.3.5	Catalysts Bearing Diamido Ligands	750			
3.23.3.6	Catalysts Bearing Diamido Ligands with Neutral Donors	751			
3.23.3.7	Amine-Phenolate Titanium and Zirconium Catalysts	751			
3.23.3.7.1	Polymerization of α -olefins	751			
3.23.3.7.2	Propylene polymerization	752			
3.23.3.8	Titanium Catalysts Bearing Tridentate Aminodiol Ligands	753			
3.23.3.9	Titanium Catalysts for Styrene Homo- and Copolymerization	753			
3.23.3.10	Bis(phenoxyimine)titanium Catalysts	754			
3.23.3.10.1	Propylene polymerization	754			
3.23.3.10.2	Ethylene polymerization	755			
3.23.3.10.3	Polymerization of cyclopentene, norbornene, and 1,5-hexadiene	756			
3.23.3.11	Bis(phenoxyketimine)titanium Catalysts	757			
3.23.3.12	Bis(pyrrolide-imine)titanium Catalysts	759			
3.23.3.13	Bis (indolide-imine) titanium Catalysts	759			
3.23.3.14	Bis (enaminoketonato) titanium Catalysts	759			
3.23.3.15	Bis(phosphanylphenoxide)titanium Catalysts	761			
3.23.3.16	Catalysts Supported by sp^2 and sp^3 Carbon Donors	761			
3.23.3.17	Aminopyridinatozirconium Catalysts	762			
3.23.3.18	Tris(pyrazolyl)borate Catalysts	762			
3.23.3.19	Bis(dimethylamidopyridine)zirconium Catalysts	762			
3.23.4	Non-group 4 Early Metal Polymerization Catalysts	763			
3.23.5	Rare-Earth Metal Catalysts	764			
3.23.6	Late Metal Olefin Polymerization Catalysts	764			
3.23.6.1	Nickel and Palladium α -Diimine Catalysts	764			
323611	Polymerization of α -olefins	764			
323612	Pronylene polymerization	767			
323613	Ethylene polymerization	768			
3 2 3 6 1 4	Other monomers	700			
3 23 6 2	Nickel α -Keto- β -diimine Catalysts	770			
3 23 6 3	Other Nickel Catalysts	770			
3 23 6 4	Other Palladium Catalysts	77/			
3 23 6 5	Monoevelonentadienvl Cobalt Catalysts	774			
3 23 7	Aution and Summary	774			
Deferences	outtook and outfiniary	775			
nelelellües		//5			

3.23.1 Introduction

One of the ultimate challenges in polymer chemistry is the development of new synthetic methods for the polymerization of a wide range of monomers with well-defined stereochemistry¹ while controlling molecular weight and molecular weight distribution.^{2–4} Over the last half century, a primary goal of synthetic polymer chemistry has been the development of chain-growth polymerization methods that enable consecutive enchainment of monomer units without termination. Known as living polymerizations,⁵ these systems allow precise molecular weight control as well as the synthesis of a wide array of polymer architectures.⁶ Additionally, living polymerization methods allow the synthesis of end-functionalized polymers in addition to the creation of virtually limitless types of new materials from a basic set of monomers.

Today, polyolefins are by far the largest volume class and most important commercial synthetic polymers.⁷ Since the initial discoveries of Ziegler⁸ and Natta,⁹ remarkable advances have been reported concerning the control of comonomer incorporation as well as dramatic improvements in activity. Homogeneous olefin polymerization catalysts now exist that are unparalleled in all of polymer chemistry concerning the detailed control of macromolecular stereochemistry.¹⁰ However, olefin polymerization catalysts have traditionally been inferior to their other chain-growth counterparts in one respect. While extraordinary advances in living/controlled polymerization have been discovered using anionic,¹¹ cationic,^{12,13} and radical-based polymerization,¹⁴⁻¹⁸ until very recently there existed a comparative lack of living olefin polymerization systems. The main reason for this is that alkene polymerization catalysts often undergo irreversible chain transfer to metal alkyls and β -elimination reactions that result in chain termination and the initiation of new polymer chains by the catalyst (Scheme 1). However, systems are now available that have acceptable rates of propagation with negligible rates of termination that allow the truly living polymerization of alkenes, which facilitates block copolymer synthesis.

Perhaps the most important application of living olefin polymerization is the production of block copolymers, which is typically achieved via sequential monomer addition. Physical blends or random copolymers often give rise to materials whose properties are intermediate between those of the respective homopolymers. Block copolymers, on the other hand, often furnish materials whose mechanical properties are superior to the sum of their parts. This unique behavior is often due to microphase separation of the different segments of the block copolymer into discrete domains that give rise to otherwise unattainable morphologies.¹⁹⁻²¹ One of the most highly sought goals in the field of olefin polymerization is the synthesis of block copolymers containing isotactic polypropylene (iPP) domains that are envisioned to possess material properties of great industrial importance. For example, diblock copolymers containing iPP segments may serve as compatibilizers in blends containing iPP homopolymers.²² One of the most actively pursued block copolymer structures are those with 'hard' or semicrystalline end blocks (e.g., polyethylene (PE), iPP, and syndiotactic polypropylene (sPP)) and amorphous midblocks (e.g., atactic polypropylene (aPP) and poly (ethylene-co-propylene) (poly(E-co-P))); triblock copolymers of this type have been shown to behave as thermoplastic elastomers.^{23–30}

This review is a comprehensive account of living alkene polymerization systems, with special attention paid to systems developed in the past couple of years focusing on the polymer types and architectures as in our previous reviews.^{2–4} This



Scheme 1 Mechanism of propagation and chain transfer in transition-metal catalyzed olefin polymerization.

review will primarily focus on living polymerization of terminal alkenes with some coverage of nonconjugated dienes and cyclic olefins.

3.23.2 Living Olefin Polymerization

3.23.2.1 Poly(1-hexene)

One of the most commonly employed monomers for detailed studies of living olefin polymerization is 1-hexene due to the fact that it is an easily handled liquid, and molecular weight determination of its polymers is accomplished at or slightly above room temperature employing low-boiling gel permeation chromatography (GPC) eluents (Figure 1). However, due to their poor mechanical properties, poly(1-hexene) (PH) and homopolymers derived from higher α -olefins (with the exception of poly(4-methyl-1-pentene)) are of little commercial significance for applications requiring rigid materials. One application of amorphous poly(α -olefin)s is as impact strength modifiers when blended with polypropylenes (PPs).⁷

3.23.2.2 Polypropylene

While PH is an amorphous material regardless of the level of tacticity, PP can range from amorphous to semicrystalline due to the variability in the level of tacticity. The bulk properties of the polymer are intimately related to its tacticity, with *a*PP (**Figure 2**) being an amorphous material with limited industrial uses (e.g., adhesives, sealants, and caulks) and *s*PP and *i*PP being semicrystalline materials with relatively high T_m values of ~150 and ~165 °C, respectively. The slow crystallization rates limit the commercial impact of *s*PP. On the other hand,



Figure 2 Polypropylene microstructures.

numerous catalysts, both heterogeneous and homogeneous, are capable of isospecific propylene polymerization. When combined with *i*PP's highly desirable mechanical properties (durability, chemical resistance, and stiffness), it is obvious why the vast majority of industrially produced PPs are of the isotactic variety.³¹

3.23.2.3 Polyethylene

In addition to *i*PP, PE represents another commercially important material. The annual production of PE worldwide is in excess of £80 billion.³² Considering the simplicity of ethylene, the range of different polymer architectures derived from it is truly impressive (**Figure 3**). The properties of PEs vary greatly depending on the polymer's microstructure (i.e., branched or linear) from high-density plastics with relatively high melting points (linear PE: $T_m \sim 135$ °C) to low-density, branched material with T_m as low as 105 °C. The mechanism by which





Figure 3 Polyethylene morphologies.

ethylene is polymerized will ultimately determine the microstructure and therefore the properties of the resultant PE. While most early transition metal olefin polymerization catalysts furnish linear PE, late metal catalysts based on nickel or palladium typically give rise to branched structures.²²

3.23.2.4 Polyolefins from Conjugated Dienes, Cyclic Olefins, and Polar Monomers

Beyond simple a-olefins, the polymers obtained from both nonconjugated dienes and cyclic olefins provided materials with desirable properties. Nonconjugated dienes are versatile monomers in that they can furnish polymers with a variety of microstructures depending on the mechanism by which they are polymerized. For example, 1,5-hexadiene can be cyclopolymerized to furnish a polymer with methylene-1,3-cyclopentane (MCP) units (Figure 4). Depending on the selectivity of the ring-closing reaction, cis- or trans-rings may be formed. Polymers containing mostly cis-rings exhibit higher T_m values than those with mostly trans-rings (e.g., for poly(methylene-1,3-cyclopentane) (PMCP) having > 90% cis-ring content the $T_{\rm m}$ is 189 °C whereas the $T_{\rm m}$ of those containing 82% *trans*-rings is 102 °C).^{33,34} Polymerization of 1,5-hexadiene can also lead to vinyl-tetramethylene (VTM) units, which may serve as a synthetic handle by which polymer functionalization can be achieved.35

Similarly, homopolymers of cyclic olefins (e.g., polycyclopentene and polynorbornene (PNB), **Figure 5**) are characterized by extremely high melting points and low solubility in most organic solvents. Taken together, these properties of cyclic olefin homopolymers make them difficult to process and therefore commercially insignificant. However, upon incorporation into copolymers with α -olefins, materials with desirable properties can be obtained. The copolymers typically exhibit high chemical resistance, good optical properties, and facile processability.³⁶ In addition to simple hydrocarbon systems, copolymers of polar monomers with olefins are attractive due to enhanced physical properties such as biocompatibility and ease of processing.³⁷

3.23.2.5 Criteria for Living Polymerization

The homopolymerization of the aforementioned alkenes will be discussed in order of early metal- to late metal-catalyzed polymerizations with special emphasis paid to block copolymers and new polymer architectures. Note that in this review, we refer to living species for alkene polymerization as catalysts, not initiators, to emphasize the fundamental catalytic event of monomer enchainment, not polymer chain formation. There are seven generally accepted criteria for a living polymerization: (1) polymerization proceeds to complete monomer conversion, and chain growth continues upon further monomer addition; (2) number-average molecular weight (M_n) of the polymer increases linearly as a function of conversion; (3) the number of active centers remains constant for the duration of the polymerization; (4) molecular weight can be precisely controlled through stoichiometry; (5) polymers display narrow molecular weight distributions, described quantitatively by the ratio of the weight average molecular weight to the number average molecular weight $(M_w/M_p \sim 1)$; (6) block copolymers can be prepared by sequential monomer addition; and (7) end-functionalized polymers can be synthesized.³⁸ Few polymerization systems, whether ionic, radical, or metal mediated, that are claimed to proceed by a living mechanism have been shown to meet all of these criteria. This review will therefore include all systems that claim living alkene



Poly(methylene-1,3-cyclopentane) PMCP

Figure 4 Polymers derived from 1,5-hexadiene polymerization.





ne Poly(ethylene-*co*-norbornene) Poly(E-*co*-NB)



Poly(methylene-1,3-cyclopentane-co-3-vinyltetramethylene) Poly(MCP-co-3-VTM)



Poly(ethylene-co-cyclopentene) Poly(E-co-CP)

polymerization, provided a number of the key criteria have been met. It should be added that failure to meet the academic criteria for living polymerization does not mean that such systems might not be highly useful from a technical standpoint. As a result, we believe it is better to be inclusive rather than exclusive, and let the reader decide whether the capabilities of the catalyst systems described herein might be of use in their planned application.

3.23.3 Early Metal Olefin Polymerization Catalysts

3.23.3.1 Vanadium Acetylacetonoate Catalysts

In the 1960s, Zambelli *et al.*³⁹ discovered that activation of VCl₄ with Et₂AlCl at -78 °C in the presence of propylene furnished syndio-enriched PP. Linear growth of molecular weight over time for a period of 25 h was observed.³⁹ In a subsequent report, the PPs produced by VCl₄/Et₂AlCl were shown to possess very narrow molecular weight distributions $(M_w/M_n = 1.4-1.9)$.⁴⁰

The first example of a truly living alkene polymerization catalyst was reported by Doi et al.41,42 in 1979. Activation of V (acac)₃ (1, Figure 6) with Et₂AlCl in the presence of propylene at temperatures ≤-65 °C furnished syndio-enriched PP ([r] = 0.81) exhibiting narrow molecular weight distributions $(M_{\rm w}/M_{\rm n} = 1.07 - 1.18)$ and $M_{\rm n}$ as high as $100\,000\,{\rm g\,mol}^{-1}$. A linear increase in M_n over the course of 15 h was additionally observed. Initially, only about 4% of vanadium centers were shown to be active; however, addition of anisole to the polymerization led to a threefold increase in the number of active vanadium centers.43 Utilizing the living nature of 1/Et₂AlCl, Doi and coworkers⁴⁴ were able to synthesize block copolymers of propylene and ethylene. Specifically, an sPP-block-poly(E-co-P)-block-sPP triblock copolymer was synthesized via sequential monomer addition and it exhibited a narrow molecular weight distribution $(M_w/M_n = 1.24)$ with $M_{\rm p} = 94\,000\,{\rm g\,mol^{-1}}$ and a propylene content of 70 mol.%.

By replacing the acetylacetonoate ligands of **1** with 2-methyl-1,3-butanedionato ligands (**2**, Figure 6), Doi and coworkers⁴⁵ found that nearly all of the vanadium centers were active for polymerization with essentially the same degree of syndioselectivity as **1**/Et₂AlCl. In addition, the living character of propylene polymerization by **2**/Et₂AlCl was maintained up to -40 °C (M_w/M_n as low as 1.4).^{46,47} Copolymerization of propylene and ethylene by **2**/Et₂AlCl was also shown to be living.⁴⁸

An important application of living olefin polymerization is in the synthesis of end-functionalized polymers, which is typically achieved by reaction of the living chain end with an



Figure 6 Vanadium catalysts for living olefin polymerization.

electrophile. The vanadium-based living olefin polymerization catalysts discovered by Doi and coworkers^{49–53} proved to be particularly amenable to this application. The structures of end-functionalized sPPs prepared in this manner are summarized in Scheme 2.

Furthermore, one of the most challenging goals in polymer synthesis is the incorporation of polar monomers due to the limited ability of many catalysts to tolerate polar functionalities. In 1983, Doi et al.49 reported the use of 1/Et2AlCl (Figure 6) for the synthesis of a series of PP-block-poly(tetrahydrofuran) (THF) AB-type diblock copolymers by quenching a living propylene polymerization with iodine and using the iodide-terminated PP to initiate cationic polymerization of THF. Catalyst 1/Et₂AlCl has also been used to synthesize (PMMA = poly(methyl methacrylate)).⁵⁴ PP-block-PMMA At -78 °C, 1/Et₂AlCl was used to polymerize propylene to which methyl methacrylate (MMA) was then added. The MMA polymerization, which was proposed to proceed via a radical mechanism, was conducted at 25 °C to form the diblock copolymer.

In addition to exhibiting living behavior for propylene polymerization, vanadium acetylacetonoate complexes (Figure 6) have also been shown to be living for 1,5-hexadiene polymerization as well as for 1,5-hexadiene/propylene copolymerization.⁵⁵ At -78 °C, 1/Et₂AlCl polymerized 1,5-hexadiene to produce a low molecular weight polymer ($M_n = 6600 \text{ g mol}^{-1}$, $M_w/M_n = 1.4$) that contained a mixture of MCP and VTM units in a 54:46 ratio. The distribution of these two units varied in 1,5-hexadiene–propylene random copolymers as a function of 1,5-hexadiene incorporation.

3.23.3.2 Metallocene and Unbridged Half-Metallocene Catalysts

Since the discovery of their catalytic activity, group 4 metallocene complexes have found extensive use as olefin polymerization catalysts.¹ Due to their high propensity toward termination via chain transfer (e.g., β-H elimination/transfer and transfer to alkylaluminum species) there have been few examples of living olefin polymerization using metallocene-based catalysts. However, several groups have shown that by employing well-defined boron-based activators⁵⁶ at low reaction temperatures these termination pathways can be suppressed. For example, Fukui et al.57 reported the living polymerization of 1-hexene with rac-(Et) Ind_2ZrMe_2 (3, Figure 7) activated with $B(C_6F_5)_3$ at -78 °C in which $Al(nOct)_3$ was used as a scavenging agent to furnish isotactic PHs with narrow molecular weight distributions $(M_w/M_n = 1.22 - 1.29)$. While the molecular weights were relatively low $(M_n \le 5400 \,\mathrm{g \, mol^{-1}})$, the M_n was shown to increase linearly with reaction time. In 2009, Kotzabasakis et al.58 reported the polymerization of higher α -olefins with a C_s-symmetric metallocene catalyst (4, Figure 7). Upon activation with [B(C₆F₅)₄][Me₂NHPh] at 0 °C, 4 produced polymers of higher α -olefins (1-hexene, 1-octene, 1-decene, 1-tetradecene, and 1-hexadecene) with narrow molecular weight distributions $(M_w/M_n < 1.5)$.

Upon evaluation of an unbridged half-metallocene complex bearing a phenoxide donor, Nomura and Fudo⁵⁹ demonstrated that 5 (Figure 7) was also capable of polymerizing 1-hexene in a living fashion. When activated with $[Ph_3C][B(C_6F_5)_4]$ in the



Scheme 2 End-functionalized polypropylene from vanadium-based catalysts.



Figure 7 Metallocene-based catalyst precursors for living polymerization.

presence of Al(*i*Bu)₃ at $-30 \degree$ C, 5 furnished PHs with narrow polydispersities ($M_w/M_n = 1.27-1.64$) and high molecular weight (M_n up to $1.865000 \text{ g mol}^{-1}$). The M_n was shown to increase linearly with turn-over number (TON).

In addition to 1-hexene, living metallocene catalysts have been reported for propylene polymerization. Sassmannshausen *et al.*⁶⁰ reported that 6 (Figure 7) activated with $B(C_6F_5)_3$ at -20 °C produces atactic, high-molecularweight PP that exhibits elastomeric properties with $M_{\rm w}$ = 1 103 000 g mol⁻¹ and $M_{\rm w}/M_{\rm n}$ = 1.4. From analysis of the GPC trace for this sample, it was estimated that 48% of the polymer was composed of PP with a narrow molecular weight distribution ($M_{\rm w}/M_{\rm n}$ = 1.10). The polymerization also showed a linear increase in molecular weight with time.

Utilizing zirconocene catalysts, Fukui and coworkers⁵⁷ have reported that 7 (Figure 7) activated with $B(C_6F_5)_3$ at -78 °C in the presence of $Al(nOct)_3$ produces PP with $M_w/M_n \le 1.15$ ($M_n = 9400-27300 \text{ g mol}^{-1}$). The polymerization shows a

linear increase in M_n with time and it was later reported that quenching the polymerization with CO resulted in aldehyde-functionalized polymer chains.^{61,62} Additionally, the hafnium analog (8, Figure 7) was shown to be living at –50 °C. Fukui and Murata⁶³ were also able to show that iso-enriched PP ([*mm*] = 0.42) could be formed from a mixed catalyst system 7/B(C₆F₅)₃/9 at –50 °C. Over 26 h, the polymerization exhibits a linear increase in M_n with time and M_n up to 17 600 g mol⁻¹ ($M_w/M_n = 1-1.41$).

In 1991, Turner and Hlatky⁶⁴ reported on the synthesis of diblock copolymers of ethylene and propylene using a hafnocene catalyst. Activation of Cp₂HfMe₂ (8, Figure 7) with [PhNMe₂H][B(C₆F₅)₄] in the presence of propylene furnishes *a*PP. At 0 °C, the rate of termination via β -H transfer was slow enough to allow for the synthesis of *a*PP-*block*-PE via sequential monomer addition. Both orders of monomer addition (ethylene followed by propylene and propylene followed by ethylene) were successful in furnishing a polymeric product that contained a majority (50–60%) of diblock material isolated by hexanes extraction.

In a subsequent report by Fukui and coworkers, the synthesis of *a*PP-*block*-poly(E-*co*-P) diblock copolymers using 7, 8, and Cp₂⁺HfMe₂ activated with B(C₆F₅)₃ and employing Al(*n*Oct)₃ as a scavenger was achieved through sequential monomer addition at low temperatures ($T_{rxn} = -78$ °C for 8 and Cp₂⁺HfMe₂; $T_{rxn} = -50$ °C for 8).⁶² The resultant polymers exhibited narrow molecular weight distributions ($M_w/M_n = 1.07 - 1.30$) and $M_n = 71000 - 155000 \text{ g mol}^{-1}$ with propylene contents between 65 and 75 mol.%.

Starzewski and coworkers⁶⁵ have reported a metallocene with the existence of donor and acceptor groups in the sand-wich structure (10, Figure 7) that generates elastomeric PP in a syndioselective fashion ([rr] = 0.52) upon activation with

methylaluminoxane (MAO) at -8 to -6 °C. While the polydispersity indexes (PDIs) are somewhat broad ($M_w/M_n = 1.5-1.6$, M_n up to 531000 g mol⁻¹), the M_n was shown to increase linearly with time over 1 h. The system was also claimed to be living for ethylene and propylene copolymerization.

In addition to 1-hexene and propylene, metallocene catalysts have been identified for the living polymerization of ethylene. Employing Cp₂^{*}ZrCl₂/MAO (**11**, **Figure 7**), di Lena and Chen⁶⁶ polymerized ethylene in a quasi-living fashion at 60 °C. Over the course of 20 min, polymer molecular weight increased ($M_n = 1300-4400 \text{ g mol}^{-1}$) while molecular weight distributions remained relatively narrow ($M_w/M_n = 1.4-1.7$). The quasi-living behavior of **11** compared to the nonliving behavior exhibited by 7/MAO for ethylene polymerization is attributed to the increased steric bulk around the active site, which suppresses β-H elimination and transfer reactions.

Finally, while investigating cyclic olefin polymerization, Tritto and coworkers^{67,68} have shown that *rac*-Et(Ind₂)ZrCl₂/ MAO (12), 90% *rac*/10% *meso*-Et(4,7-Me₂Ind)₂ZrCl₂ (13), and *rac*-H₂C(3-tBuInd)₂ZrCl₂/MAO (14) exhibit quasi-living behavior for ethylene–norbornene (NB) copolymerization (Figure 8).

3.23.3.3 Catalysts Bearing Monocyclopentadienyl-amido Ligands

3.23.3.3.1 1-Hexene polymerization

In spite of the large number of metallocene-based polymerization catalysts, there remain relatively few examples of living systems. Titanium complexes bearing a linked monocyclopentadienyl-amido ligand, such as 15 (Figure 9), have been shown to polymerize 1-hexene in a living



Figure 8 Zirconocene precatalysts for living ethylene/norbornene copolymerization.



Figure 9 Monocyclopentadienyl-amido catalyst precursors for living polymerization.

fashion when activated with $B(C_6F_5)_3$ in the presence of $Al(nOct)_3$ at $-50 \,^{\circ}C.^{69}$ The PH formed was syndio-enriched ([n] = 0.49) with M_n up to 26 000 g mol⁻¹ and $M_w/M_n = 1.07 - 1.12$. A linear relationship between M_n and polymer yield was also demonstrated. In a subsequent report, $15/(B(C_6F_5)_3/Al(nOct)_3)$ was also shown to polymerize 1-octene and 1-butene in a living fashion.⁷⁰

3.23.3.3.2 Propylene polymerization

In addition to living 1-hexene polymerization, **15** (Figure 9) upon activation with $B(C_6F_5)_3$ in the presence of $Al(nOct)_3$ can also produce syndio-enriched PP ($[rr] \sim 0.49$) at -50 °C in a living fashion.⁶⁹ Subsequent studies showed that when activated with 'dried' MAO (dMAO) (free of trimethylaluminum), **15** could polymerize propylene at 0 °C producing PP with a higher degree of syndiotacticity ($[rr] \sim 0.63$) and with a relatively narrow molecular weight distribution ($M_w/M_n = 1.22$, $M_n = 157\ 000\ \text{gmol}^{-1}$).⁷¹ Nishii *et al.*⁷² also demonstrated significant solvent effects on the tacticity of the resulting PP. For example, polymerization of propylene with **15**/dMAO in heptane at 0 °C results in polymer with higher tacticity than when the reaction is carried out in toluene ($[rr] = 0.73\ \text{vs.}\ 0.60$) or chlorobenzene ([rr] = 0.42).

Utilizing these solvent effects, Nishii et al.73 cleverly prepared stereoblock copolymers of propylene containing sPP and aPP segments (Scheme 3) by initial polymerization in heptane followed by addition of more propylene and chlorobenzene. The resultant sPP-block-aPP had $M_{\rm p} = 94700 \,\mathrm{g \, mol^{-1}}$ with a narrow PDI ($M_w/M_n = 1.27$). Cai et al.⁷⁴ have also described similar effects of the tacticity of PP generated from 15/dried modified methylaluminoxane (MMAO) (dMMAO) under varying propylene pressures. At low pressure (0.2 atm) aPP is furnished, but at higher pressure (1 atm) syndiotactic PP is sPP-block-aPP copolymer generated. An and an sPP-block-aPP-block-sPP copolymer were synthesized by varying propylene pressure over the course of the polymerization.

Cai *et al.*⁷⁵ also examined structural variants of **15** (**16** and **17**, **Figure 9**) by introducing *tert*-butyl substituents into the fluorenyl ligand framework. When activated with dMMAO at 0 °C, **16** produced *s*PP ([*rr*]~0.83). While the molecular weight distribution was somewhat broad (M_w/M_n = 1.68, M_n = 202 000 g mol⁻¹), a two-stage sequential polymerization of 0.63 g propylene revealed a near doubling of molecular weight than was obtained from a single-stage polymerization. Catalyst **17**/dMMAO furnished polymer with even higher tacticity ([*rr*]~0.93) and lower molecular weight distribution (M_w/M_n = 1.45). After further expanding the sterics about the fluorenyl, **18**/dMMAO was utilized in the production of polypropylene with decreased syndioselectivity ([*rr*]~0.45)

compared to the polymer obtained from 17/dMMAO.⁷⁶ While molecular weights $(M_n = 44\,000 - 150\,000\,\mathrm{g\,mol^{-1}})$ increased with polymer yield, molecular weight distributions were broadened ($M_w/M_n = 2.91-4.61$). Although some characteristics of a living polymerization were exhibited, a two-stage sequential polymerization resulted in polypropylene that was nearly identical to that obtained from the single-stage polymerization. Further increasing the steric bulk of the fluorenyl ligand from 17 to 18 resulted in a loss of both living character and syndioselectivity for the polymerization of propylene. Employing an indenyl-based ligand, 19/dMAO at 0 °C affords iso-enriched PP ([mm] = 0.40) with quasi-living behavior.⁷⁷ Later, Dare et al.⁷⁸ reported that a similar complex 20/MAO furnished PP at 0 °C that was syndio-enriched ([rr] = 0.56) and exhibited a somewhat narrow PDI $(M_w/M_p = 1.37)$ $M_{\rm n} = 108\,000\,{\rm g\,mol^{-1}}$).

3.23.3.3.3 Copolymerization of ethylene/norbornene and propylene/norbornene

In addition to linear α -olefins, Shiono and coworkers reported that 15/MAO (Figure 9) catalyzed the living copolymerization of ethylene and NB. For example, at 0 °C 15/MAO can furnish poly(E-*co*-NB) with 53 mol.% NB and $M_n = 78000 \text{ g mol}^{-1}$ with $M_w/M_n = 1.16$.⁷⁹ Furthermore, a linear increase in M_n with reaction time was observed for this system. When activated with MAO at 40 °C, a similar compound, 20 (Figure 9), also provided ethylene–NB copolymers with fairly narrow PDIs $(M_w/M_n = 1.21-1.27)$.⁸⁰

Hasan *et al.*⁸¹ also reported the living copolymerization of propylene and NB with 15/dMAO (Figure 9) to produce copolymers with very high T_g values (249 °C) and narrow molecular weight distributions ($M_w/M_n = 1.16$). In a later report, the copolymerization of higher α -olefins (1-hexene, 1-octene, and 1-decene) with NB by 15/MAO was reported; however, molecular weight distributions were somewhat broadened ($M_w/M_n = 1.36-1.72$).⁸²

Activation of **17** (Figure 9) with dMMAO containing 0.4 mol.% triisobutylaluminum (TIBA) in the presence of NB catalyzed living polymerization at 20 °C.⁸³ The molecular weight distributions obtained were narrow ($M_w/M_n = 1.07-1.08$). Additionally, a two-stage reaction was shown to increase the molecular weight of the second step by double that of the first step when each was carried to quantitative conversion.

In 2006, Cai *et al.*⁸⁴ were able to show that 17/MAO could also copolymerize propylene and NB in a living fashion to form random and block copolymers. For example, three *s*PP-*block*-poly(P-*co*-NB) diblock copolymers were synthesized through sequential monomer addition that had similar molecular weights ($M_n \sim 20000 \text{ g mol}^{-1}$, $M_w/M_n = 1.21-1.32$).



Scheme 3 Synthesis of sPP-block-aPP using solvent polarity to control tacticity.



Scheme 4 Catalytic synthesis of block copolymers from norbornene and propylene using 17/dMMAO-TIBA.

Cai *et al.*⁸³ were able to show that 17/dMMAO containing 1.8 mol.% TIBA could furnish PNB-*block*-poly(P-*co*-NB)-*block*-PP triblock copolymers in a catalytic fashion. The successive addition of NB and propylene before complete consumption of NB gives PNB-*block*-poly(P-*co*-NB)-*block*-PP terminated with a Ti–PP bond, which can be exchanged with TIBA. Repeated addition of NB and propylene gives a catalytic synthesis of the triblock copolymers in this system (Scheme 4).

3.23.3.4 Monocyclopentadienylzirconium Amidinate Catalysts

3.23.3.4.1 1-Hexene polymerization

In 2000, Jayaratne and Sita⁸⁵ reported monocyclopentadienyl acetamidinate zirconium dimethyl compounds that exhibited

living polymerization behavior at temperatures between -10 and 0 °C. At 0 °C, **21a**/[PhNMe₂H][B(C₆F₅)₄] (**Figure 10**) formed atactic PH (*a*PH) with a narrow polydispersity (M_w/M_n = 1.10) and lack of olefinic resonances in ¹³C and ¹H NMR spectra. The C₁-symmetric complex, **21b**, when activated in an identical manner at -10 °C furnished highly isotactic PH ([*mmm*] > 0.95) with a narrow molecular weight distribution (M_w/M_n = 1.03–1.13). The molecular weight was shown to increase linearly with conversion. This was the first report of a Ziegler–Natta polymerization catalyst that was both living and highly isospecific for α -olefin polymerization. Covalently attaching **21b** to a cross-linked polystyrene (PS) support was also shown to furnish a living and isoselective 1-hexene polymerization catalyst (**22**, **Figure 10**).⁸⁶ The hafnium congener of **21b** (**23a**, **Figure 10**) and its diisobutyl



Figure 10 Monocyclopentadienyl amidinate and iminopyrrolyl complexes.



Scheme 5 Degenerative group transfer polymerization employing **21b**.

analogue (23b) were also shown to be living and isospecific 1-hexene polymerization catalysts albeit with a rate \sim 60 times slower than 21b.⁸⁷

As discussed above, 21b/[PhNMe₂H][B(C₆F₅)₄] polymerizes 1-hexene in a living manner to produce highly isotactic PH. However, when a substoichiometric amount of the borate is used (e.g., $[PhNMe_2H][B(C_6F_5)_4]$: [21b] = 0.5), the resulting polymer is considerably less isotactic with an [mm] content of approximately 45-50% resulting from degenerativetransfer (DT) polymerization (Scheme 5), which will be discussed in detail in the following section. This system has been employed to make a diblock poly(α -olefin) sample.⁸⁸ Initially, **21b** was activated with 0.5 equivalent of [PhNMe₂H][B(C_6F_5)₄] and used to polymerize 1-hexene resulting in the formation of an aPH block. After 2 h, 1-octene was added along with an additional 0.5 equivalent of the borate leading to the growth of an isotactic poly(1-octene) block. GPC analysis revealed clean formation of the aPH-block-i-poly(1-octene) diblock copolymer with $M_{\rm n} = 12400 \,{\rm g \, mol^{-1}}$ and $M_{\rm w}/M_{\rm n} = 1.04$.

Upon replacing the Cp^{*} moiety with the less sterically demanding Cp ligand, Keaton *et al.*⁸⁹ were able to greatly increase the 1-hexene polymerization activity for this class of catalysts. When activated with [PhNMe₂H][B(C₆F₅)₄] at -10 °C, compounds **24a–24c** (Figure 10) furnished *a*PHs with narrow molecular weight distributions ($M_w/M_n = 1.03-1.10$); however, a decrease in enantiofacial selectivity was also observed. The more open environment of the active site did impart the ability to polymerize the more challenging vinylcyclohexane (VCH).

Upon activation with [PhNMe₂H][B(C₆F₅)₄] at -10 °C, **24a** and **24b** furnished highly isotactic poly(VCH)s ([*mmmm*] = 0.95) with narrow polydispersities ($M_w/M_n = 1.04-1.10$). The authors postulate that the high degree of isoselectivity displayed is likely the result of chain-end control. Exploiting the living nature of **24c**/[Ph₃C][B(C₆F₅)₄] for 1-hexene and VCH polymerization, a triblock copolymer of isotactic poly (VCH)-*block-a*PH-*block*-isotactic-poly(VCH) was prepared via sequential monomer addition.⁸⁹ The triblock copolymer exhibited a narrow polydispersity ($M_w/M_n = 1.08$) and $M_n = 24400 \text{ g mol}^{-1}$ with a VCH content of 33 mol.%.

In 2004, the effect of further structural elaboration of the amidinate ligand framework on polymerization behavior was reported.⁹⁰ Specifically, altering the identity of the distal R³ substituent (Figure 10) led to dramatic effects on both the living character and stereospecificity of 1-hexene polymerization. At -10 °C, polymerization of 1-hexene by 25a or 25b $(R^3 = Ph \text{ or } H)/[PhNMe_2H][B(C_6F_5)_4]$ furnished polymer with a significantly lower degree of isotacticity than the PH produced by 21b/[PhNMe₂H][B(C₆F₅)₄], and in the case of 25b, the polymerization is no longer living. Furthermore, 25c $(R^3 = tBu)/[PhNMe_2H][B(C_6F_5)_4]$ was found to be completely inactive for polymerization. The loss in stereocontrol of 25a was attributed to a 'buttressing effect' by which the tBu and Et groups were 'pushed' forward toward the active site leading to a lack of steric discrimination at the metal center for olefin coordination. The decrease in stereoselectivity of 25b was attributed to a low barrier to metal-centered epimerization relative to 21b. Interested in further varying the amidinate portion of the precatalyst, Yasumoto *et al.*⁹¹ recently reported the synthesis and 1-hexene polymerization behavior of Cp^{*} hafnium dimethyl complexes bearing an iminopyrrolyl ligand. At 0 °C or below, compounds 26a–26c/[Ph₃C][B(C₆F₅)₄] (Figure 10) polymerized 1-hexene to furnish polymers with narrow molecular weight distributions ($M_w/M_n = 1.07-1.12$) and $M_n = 9000-36\,100\,\mathrm{g\,mol^{-1}}$. The PHs were all significantly iso-enriched with the highest level of isotacticity ([*mmmn*] = 0.90) being obtained from 26b at –20 °C. The polymerization of 1-hexene with 26a exhibited a linear dependence of M_n versus time at –20 and 0 °C.

3.23.3.4.2 Propylene polymerization

In addition to living 1-hexene polymerization, Harney et al.²⁷ have shown that **21b** activated with [PhNMe₂H][B(C_6F_5)₄] in a stoichiometric ratio furnished highly isotactic PP ([mmmm] = 0.71) in a living fashion $(M_w/M_n \le 1.20)$. Interestingly, activation with 0.5 equivalent of $[PhNMe_2H][B(C_6F_5)_4]$ resulted in the production of *a*PP where the M_n was also shown to increase linearly with time $(M_w/M_n \sim 1.05)$. A DT polymerization that proceeds through a rapid and reversible methyl group transfer between the cationic (active) and neutral (dormant) zirconium centers was considered as the mechanism for this living system (Scheme 5).⁸⁸ Additionally, the methyl-polymeryl dormant species can undergo epimerization that is faster than propagation. Thus, through a combination of methyl group transfer and epimerization at dormant sites, each occurring faster than propagation, stereocontrol is greatly diminished leading to an atactic microstructure. However, upon addition of a second 0.5 equivalent of [PhNMe₂H][B(C₆F₅)₄], all Zr species become active for polymerization, thereby 'turning off' DT and initiating isospecific polymerization, which can advantageously be used for the production of block copolymers. Later, Harney et al.92 synthesized stereogradient PP by initial polymerization under DT polymerization conditions followed by slow introduction of $[PhNMe_2H][B(C_6F_5)_4]$ to 100% activation.

The living degenerative transfer system that was employed by Harney *et al.*²⁷ to make block copolymers from 1-hexene and 1-octene was also applied to propylene polymerization. Formation of a PP diblock copolymer with **21b**/[PhNMe₂H] $[B(C_6F_5)_4]$ was accomplished by initial activation with 0.5 equivalent of [PhNMe₂H][B(C₆F₅)₄] furnishing an *a*PP

segment followed by complete activation with another 0.5 equivalent of $[PhNMe_2H][B(C_6F_5)_4]$ to furnish the aPP-block-iPP. It was found that related complex 29 could effectively reinvoke DT by irreversibly transferring a methyl group to the active polymerization species. In addition to synthesizing an aPP-block-iPP diblock copolymer, an aPP-block-iPP-block-aPP triblock and an aPP-block-iPP-block-aPP-block-iPP tetrablock sample were formed (Scheme 6). The polymers had very similar molecular $(M_{\rm n} = 164\ 200 - 172\ 400\ {\rm g}\ {\rm mol}^{-1}, M_{\rm w}/M_{\rm n} = 1.19).$ weights Testing of the tensile properties of the block copolymers showed good elastomeric behavior. For example, the triblock copolymer displayed an elongation to break of 1530%, the highest of the three samples.

Zhang and Sita⁹³ also prepared bimetallic analogues of **21b** to investigate further the effects of DT polymerization (**27a–27c**, **Figure 10**). Upon activation with 2 equivalents of [PhNMe₂H][B(C₆F₅)₄] at –10 °C, compounds **27a–27c** were all found to be living and isoselective for propylene polymerization (M_n up to 50 000 g mol⁻¹, M_w/M_n = 1.1–1.2), with the degree of stereoselectivity decreasing as the two metal centers are brought closer together. Activation under substoichiometric conditions, the frequency of [*mr*] stereoerrors in the PP decreases as the two metal centers are brought closer together resulting from an increased barrier to metal-centered epimerization of the dormant site. A linear increase in M_n with time was observed for **27a** under substoichiometric activation conditions to further illustrate the living behavior of the system.

Zhang and Sita⁹⁴ have also reported a modified amidinate hafnium catalyst (**28**, **Figure 10**) that furnished *a*PP of high molecular weight ($M_n = 137000 \text{ g mol}^{-1}$, $M_w/M_n = 1.12$) upon activation with 1 equivalent of [PhNMe₂H][B(C₆F₅)₄] at –10 °C. M_n of up to 830000 g mol⁻¹ could be obtained with this system; however, significant broadening of the PDI was observed ($M_w/M_n = 2.43$). Furthermore, this system demonstrated the first example of living coordinative chain-transfer polymerization (CCTP)⁹⁵ of propylene with diethyl zinc. It was further used for the living CCTP of ethylene, 1-hexene, 1-octene, and 1,5-hexadiene in addition to living CCTP copolymerization of ethylene with the aforementioned higher α -olefins.⁹⁶



Scheme 6 Synthesis of propylene-based block copolymers using 21b/MAO.

3.23.3.4.3 Polymerization of 1,5-hexadiene

In addition to 1-hexene and propylene, Jayaratne *et al.*⁹⁷ showed that **21a–21c**/[PhNMe₂H][B(C₆F₅)₄] (**Figure 10**) were active for the cyclopolymerization of 1,5-hexadiene at –10 °C. The polymers produced possessed \geq 98% MCP units and exhibited narrow polydispersities ($M_w/M_n = 1.03-1.09$). The selectivity of ring closure was ubiquitously *trans*, the stereoselectivity increased with increasing steric bulk of the amidinate ligand (**21a**: %*trans* = 64; **21c**: % *trans* = 82).

Utilizing the living behavior of **21b**/[PhNMe₂H][B(C₆F₅)₄] (**Figure 10**), Jayaratne *et al.*⁹⁷ were able to prepare diblock and triblock copolymers of 1-hexene and 1,5-hexadiene. At –10 °C, isotactic PH-*block*-PMCP and isotactic-PH-*block*-PMCP-*block*-PH were obtained from **21b**/[PhNMe₂H][B(C₆F₅)₄] through sequential monomer addition. The diblock copolymer possessed M_w/M_n = 1.05 and M_n = 22 800 g mol⁻¹ with T_m = 91 °C. The triblock copolymer had M_w/M_n = 1.10, M_n = 30 900 g mol⁻¹, and T_m = 79 °C. Atomic force microscopy (AFM) revealed that microphase separation of the crystalline PMCP and amorphous PH had occurred.

3.23.3.5 Catalysts Bearing Diamido Ligands

While group 4 metallocene-based olefin polymerization catalysts have dominated the field of homogenous olefin polymerization catalysis since the late 1950s,¹ the development of complexes bearing non-Cp ligands as potential olefin polymerization catalysts has become a rapidly expanding area over the last 15 years.^{98,99} Scollard and McConville¹⁰⁰ reported that titanium complexes bearing diamide ligands, compounds 30a and 30b (Figure 11), polymerized 1-hexene, 1-octene, and 1-decene to high molecular weight $(M_{\rm p} = 121500 -$ 164 200 g mol⁻¹) and narrow PDI ($M_w/M_p = 1.07$) upon activation with B(C₆F₃)₃ at room temperature. Polymerization of 1-hexene by $30b/B(C_6F_5)_3$ exhibited a linear increase of M_n with time. Later, Jeon et al.¹⁰¹ reported the living polymerization of 1-hexene catalyzed by a structurally similar zirconium diamide with an ethylene bridging unit (31). When activated with B(C₆F₅)₃ at -10 °C, 31 (Figure 11) furnished PHs with $M_{\rm n} =$ ca. 30000-175000 g mol⁻¹ and $M_{\rm w}/M_{\rm n} = 1.18-1.27$. It was also shown that the $M_{\rm p}$ increased linearly with increasing monomer loading. Utilizing sequential monomer addition, Jeon et al.¹⁰¹ prepared a block copolymer of 1-hexene and 1-octene. The polymer produced at 0 °C possessed a narrow polydispersity $(M_w/M_p = 1.21)$ and $M_p = 109\,000\,\mathrm{g\,mol^{-1}}$.

In 2002, Hagimoto *et al.*¹⁰² reported that upon activation with dMMAO at 0 °C, McConville's dimethyldiamidotitanium complex (**30a**, Figure 11) was capable of polymerizing propylene in a living manner. The PPs obtained from **30a**/ dMMAO were atactic and displayed narrow molecular weight distributions ($M_w/M_n = ca. 1.16-1.3$). The M_n was shown to increase linearly with polymerization time from 10 to 25 min (M_n up to ca. 30 000 g mol⁻¹). In later reports, Shiono and coworkers¹⁰³⁻¹⁰⁶ discussed the effects of supported MMAOs on the propylene polymerization behavior of **30a**. Three different supports for MMAO were investigated: SiO₂, Al₂O₃, and



Figure 11 Olefin polymerization catalysts catalysts bearing diamido ligands.

MgO. Regardless of the support, polymerization of propylene by **30***a*/supported MMAO at 0 °C exhibited a linear increase of M_n with time.

3.23.3.6 Catalysts Bearing Diamido Ligands with Neutral Donors

Interested in investigating the effects of neutral donors on the diamido olefin polymerization systems, Schrock and coworkers synthesized tridentate diamido group 4 complexes bearing a central oxygen donor. The authors postulated the neutral donor would enhance stability of the corresponding cationic alkyl active species.^{107,108} At 0 °C, **32a**/[PhNMe₂H][B(C₆F₅)₄] (**Figure 11**) furnished *a*PH with $M_n =$ ca. 4000–40 000 g mol⁻¹ and $M_w/M_n = 1.02-1.14$. A linear increase in M_n with momer conversion was observed. Upon activation with [PhNMe₂H][B(C₆F₅)₄], the titanium congener (**32b**) decomposed to unidentifiable species that were not active for 1-hexene polymerization. The analogous hafnium complex (**32c**) furnished PH with broadened molecular weight distribution $(M_w/M_n = 1.19-1.53)$ and anomalous M_n values when activated with [PhNMe₂H][B(C₆F₅)₄].

Mehrkhodavandi et al.¹⁰⁹ developed a second class of catalysts bearing diamidopyridine ligands that were shown to be effective living olefin polymerization catalysts. The diamidopyridine zirconium complexes 33a and 33b (Figure 11) when activated with [Ph3C][B(C6F5)4] produce PHs with narrow polydispersities ($M_w/M_n < 1.08$). The identity of the alkyl group bound to zirconium was shown to greatly affect the polymerization behavior. Upon activation, 33a reacts with 1-hexene to a significant extent by 2,1-insertion into the initial Zr-Me bond to give a 3-heptyl complex that undergoes β -H elimination to yield 2-heptenes. Only a fraction that undergoes 1,2-insertion gives a stable propagating species. No 2,1-insertion into the Zr-iBu bond is observed upon activation of 33b giving rise to a relatively well-behaved polymerization system in which M_n values are 3 times higher than those expected based on the assumption of one polymer chain per metal center (M_n^{theo}). At 0 °C, the diisobutyl hafnium analog (34) was shown to polymerize 1-hexene in a living fashion upon activation with $[Ph_3C][B(C_6F_5)_4]$ to furnish PHs with $M_{\rm w}/M_{\rm n} = 1.02 - 1.05$ and $M_{\rm n} = 10\,000 - 50\,000\,{\rm g\,mol}^{-1}$ that matches $M_n^{\text{theo}, 110, 111}$ The apparent difference in polymerization behavior is attributed to greater stability toward β-H elimination in this system. Upon replacing the mesityl groups with 2,6-C₆H₃Cl₂ within the ligand framework of 34, Schrock and coworkers¹¹² found that the living character of 1-hexene polymerization catalyzed by 35/[Ph₃C][B(C₆F₃)₄] was slightly diminished with evidence of β-H elimination. Despite the fact that β-H elimination was observed, the resultant polymers still displayed narrow polydispersities $(M_w/M_n = 1.01 - 1.05)$ and the M_n values were about 90% of those expected.

The diamidoamine complexes of zirconium and hafnium are a third class of compounds for olefin polymerization introduced by Schrock and coworkers.^{113–115} When activated with [Ph₃C] [B(C₆F₅)₄], **36a** (R¹ = R² = Me, **Figure 11**) was shown to be active for 1-hexene polymerization furnishing PHs that possessed $M_w/M_n = 1.1-2.1$ and $M_n = 19\,200-45\,000 \,\mathrm{g \, mol^{-1}}$ that deviated from the expected values.¹¹³ Later studies showed that **36a** undergoes deactivation via an intramolecular C–H activation of the *ortho*-Me on the mesityl group upon methide abstraction. Replacing the *ortho*-Me with *ortho*-Cl (**36b**) and subsequent activation with [PhNMe₂H][B(C₆F₅)₄] at 0 °C gives rise to a catalyst that is living for 1-hexene polymerization.¹¹⁴ The resultant polymer exhibited narrow polydispersities ($M_w/M_n = 1.01-1.04$) and M_n values that were in good agreement with M_n^{theo} . Utilizing [Ph₃C][B(C₆F₅)₄] or B(C₆F₅)₃ as an activator, the hafnium analogue of **36b** (**36c**) exhibited significant termination via β-H elimination.¹¹⁵

3.23.3.7 Amine-Phenolate Titanium and Zirconium Catalysts

3.23.3.7.1 Polymerization of α -olefins

In 2000, Tshuva *et al.*¹¹⁶ reported the synthesis and subsequent olefin polymerization behavior of a titanium complex bearing an amine bis(phenolate) ligand, which incorporated an additional amino side-arm donor (**37a**, **Figure 12**). When activated with B(C₆F₅)₃ at room temperature, **37a** furnished *a*PHs with narrow molecular distributions ($M_w/M_n = 1.09-1.18$) and the M_n was shown to increase linearly with time. Upon omission of the amino side-arm donor (**38**), only low molecular weight PH ($M_n = ca. 2000 \text{ g mol}^{-1}$) with $M_w/M_n = 1.92-2.43$ was obtained. However, replacing the bulky *t*Bu groups with sterically less demanding chlorides (**37b**) allowed the living polymerization of 4-methyl-1-pentene to furnish atactic poly(4-methyl-1-pentene).¹¹⁷

Tshuva et al.¹¹⁸ also reported in 2000 the synthesis and polymerization behavior of the C₂-symmetric, ethylene-bridged zirconium analog (39a, Figure 12) of 37a. At room temperature, $39a/B(C_6F_5)_3$ furnished highly isotactic PH and poly(1-octene). The PHs exhibited narrow polydispersities $(M_w/M_n = 1.11 - 1.15)$ with $M_n = ca. 4000 - 12000 \text{ g mol}^{-1}$; the M_n was shown to increase linearly with monomer consumption. Reducing the substituent size on the phenoxide moiety (39b) resulted in aPH with a broadened molecular weight distribution $(M_w/M_p = 1.57)$. In a subsequent report, it was shown that replacing the ortho- and para-tert-butyl substituents of 39a with chlorides (39c) resulted in greatly diminished living behavior.¹¹⁹ Importantly, the titanium congener (39d) and the analogous 2,4-dibromophenol-bearing complex (39e) polymerized 1-hexene in a living manner for a period of 40-75 min when activated with $B(C_6F_5)_3$. The PHs exhibited extremely high molecular weights (Mn up to $1\,750\,000\,\mathrm{g\,mol^{-1}},\,M_{\rm w}/M_{\rm n}\,{\leq}\,1.2$) and moderate degrees of isotacticity (39d: [mm] = 0.60, 39e: [mm] = 0.80).

A third class of novel olefin polymerization catalysts featuring [ONOO] group 4 metal complexes bearing a methoxy side-arm donor (40) was introduced by Tshuva et al.¹²⁰ in 2001. At room temperature, 40/B(C₆F₅)₃ (Figure 12) furnished PHs with narrow polydispersities $(M_w/M_n = 1.07 - 1.12)$ and high molecular weights ($M_{\rm n}$ up to 445 000 g mol⁻¹). A linear increase in M_n with increasing reaction time was observed for up to 31 h. The living character of the polymerization was maintained upon heating to 65 °C for 1 h as evidenced by the narrow polydispersity of the resultant polymer $(M_w/M_n = 1.30)$. Kol and coworkers were able to apply this catalyst system to the synthesis of block copolymers of 1-hexene and 1-octene. Using $40/B(C_6F_5)_3$ (Figure 12), a block copolymer of 1-hexene and 1-octene was prepared via sequential monomer addition where each domain had an atactic microstructure. The polymer possessed a narrow molecular weight distribution $(M_w/M_p = 1.2)$ and an $M_p = 11600 \text{ g mol}^{-1}$.



Figure 12 Titanium and zirconium complexes bearing [ONNO], [ONO] and [ONOO] ligands.

Further modification of the catalyst system through introduction of the 2,4-dimethyl- or 2,4-dichlorophenoxide moiety led to a loss of living character.¹²² Additionally, the zirconium and hafnium analogs of 40 were also shown to deviate from living behavior ($M_w/M_n = 1.4-3.0$).¹²³

The effect of the neutral oxygen donor's identity on the polymerization behavior of the [ONOO] titanium complexes has also been investigated. Substituting the methoxy donor of 40 with a tetrahydrofuran (THF) moiety (41a, Figure 12) leads to similar polymerization results; however, replacing the benzyl ligands with methyl ligands (41b) results in a dramatic increase in the duration of the living period for up to 6 days at room temperature upon activation with $B(C_6F_5)_3$. The resultant aPH had an M_n up to 816 000 g mol⁻¹ and $M_w/M_n = 1.04 - 1.12$.¹²¹ The extremely long-lived catalyst generated from 41a (Figure 12) was used to prepare a block copolymer of 1-hexene and 1-octene through sequential monomer addition to furnish PH-*block*-poly(1-octene). The block copolymer had $M_{\rm n} = 34\,000\,{\rm g\,mol^{-1}}$ while maintaining the low $M_{\rm w}/M_{\rm n} = 1.16$.

Further modification of the system through introduction of a furan donor (42, Figure 12) into the ligand framework led to a 10-fold increase in polymerization activity relative to 41a/B (C₆F₅)₃ furnishing PHs of high molecular weight (M_n up to 500 000 g mol⁻¹, $M_w/M_n \le 1.37$).¹²⁴ The increase in activity of 42/B(C₆F₅)₃ resulted in diminished living character of the 1-hexene polymerization exhibiting a linear increase in M_n over the course of only 2 h.

3.23.3.7.2 Propylene polymerization

Busico and coworkers¹²⁵ have investigated the propylene polymerization behavior of Kol's octahedral [ONNO] zirconium complexes 39a and 39b (Figure 12). In contrast to the living 1-hexene polymerization observed for $39a/B(C_6F_5)_3$, the polypropylenes produced by 39a and 39b/[PhNMe₂H][B(C₆F₅)₄]/ Al(iBu)₃ showed evidence of termination via chain transfer to Al and β-H transfer to monomer. Utilizing Kol's diamino bis (phenolate)zirconium catalyst (39a, Figure 12), Busico and coworkers¹²⁶ reported the preparation of a diblock copolymer of iPP and PE under 'quasi-living' conditions in 2003. Using 39a/[PhNMe₂H][B(C₆F₅)₄] with 2,6-di-tert-butylphenol-modified Al(iBu)₃ as scavenger, a diblock copolymer of ethylene and propylene was prepared by sequential monomer addition of ethylene (1.5 min) and propylene (20 min). The resultant copolymer possessed a narrow polydispersity (M_w/M_p) as low as 1.2 when $M_n = 6500 \text{ g mol}^{-1}$). Characterization of the copolymer by ¹³C NMR spectroscopy and differential scanning calorimetry (DSC) was consistent with a block structure. These results represented the first synthesis of an iPP-block-PE copolymer via sequential monomer addition at polymerization durations greater than 1 min.

In a subsequent report, Busico and coworkers¹²⁷ reported that modification of the ligand framework resulted in the controlled polymerization of propylene with this class of catalysts. By installing bulky 1-adamantyl (43a) or cumyl (43b) substituents at the *ortho*-position of the phenol moiety (Figure 12), PPs with narrow molecular weight distributions were obtained $(M_w/M_n = 1.2-1.6)$ under the same activation procedure. For $43a/[PhNMe_2H][B(C_6F_5)_4]/Al(iBu)_{3/4}$ a linear increase of M_n with time is observed over the course of 3 h; however, after 3 h resonances consistent with terminal vinylidene groups were apparent in the ¹³C NMR spectrum. Chain transfer to aluminum was suppressed by the addition of 2,6-di-tert-butylphenol. The PP formed by 43a/[PhNMe₂H][B(C₆F₅)₄]/Al(*i*Bu)₃ was highly isotactic ([mmmm] = 0.985, $T_m = 151 \text{ °C}$). Utilizing sequential monomer addition of ethylene and propylene, $43a/[PhNMe_2H][B(C_6F_5)_3]$ with 2,6-di-tert-butylphenolmodified $Al(iBu)_3$ as a scavenger in the synthesis of a diblock copolymer was achieved. The resultant iPP-block-PE displayed higher molecular weight $(M_n = 22000 \text{ g mol}^{-1}, M_w/M_n = 1.3)$ and $T_{\rm m}$ of the *i*PP block (152 °C) than analogous block copolymer obtained from 39a.127

In 2009, Cipullo et al.¹²⁸ reported the polymerization behavior of 44a and 44b (Figure 12), the hafnium analogs of 43a and 43b, which were both found to be living for the polymerization of ethylene and propylene. Following activation with MAO and 2,6-di-tert-butylphenol in the presence of propylene, 44b produced *iPP* ([*mmm*] = 0.970) with increasing molecular weight $(M_n = 6200 - 13900 \text{ g mol}^{-1})$ over the course of 9 h while maintaining narrow molecular weight distributions $(M_w/M_n = 1.3-1.5)$. In addition to propylene, 44b/MAO/2,6di-tert-butylphenol was found to be living for the polymerization of ethylene over the course of 4 h, a significant improvement relative to 43a. Utilizing this improved living behavior, 44b/MAO/2,6-di-tert-butylphenol was used to prepare a triblock copolymer. The resultant iPP-block-poly (ethylene-co-propylene)-block-iPP possessed narrow polydispersity $(M_w/M_p = 1.2, M_p = 22000 \text{ g mol}^{-1})$ while maintaining a high T_m (143 °C).

3.23.3.8 Titanium Catalysts Bearing Tridentate Aminodiol Ligands

The importance of neutral donors in the ligand framework of living olefin polymerization catalysts was also demonstrated recently by Sundararajan and coworkers.^{129,130} In 2002, the authors reported titanium dichloride complexes of tridentate aminodiol ligands (*rac-* and *meso-*45, **Figure 13**) treated with MAO furnished PHs possessing relatively narrow

polydispersities $(M_w/M_n = 1.07 - 2.9)$ with a range of tacticities depending on the symmetry of the catalyst precursor.¹²⁹ Incorporation of a pendent methoxy donor into the aminodiol ligand framework gave rise to catalysts that were capable of living 1-hexene polymerization.¹³⁰ At temperatures between -10 and 30 °C, both 46a/MAO and 46c/MAO furnished PHs with low polydispersities $(M_w/M_n = 1.06 - 1.11)$ and $M_{\rm n} = 73\,000 - 424\,000\,{\rm g\,mol^{-1}}$. The highest degree of isotacticity ([mmmm] = 0.85) was obtained for polymer produced by 46a at -10 °C. Additionally, a linear dependence of $M_{\rm n}$ on reaction time was observed at -10 °C. The zirconium congeners of 46a and 46c (46b and 46d, Figure 13) have been prepared by Sudhakar¹³¹ and upon activation with MAO gave similar results for 1-hexene polymerization. A linear relationship between M_n and reaction time was observed at 28 °C.

3.23.3.9 Titanium Catalysts for Styrene Homo- and Copolymerization

As opposed to other homopolymers of higher α -olefins, polystyrene has found extensive use as a commodity material. Recently, Okuda and coworkers¹³² have demonstrated the first report of living and isospecific polymerization of styrene with a series of titanium complexes bearing tetradentate [OSSO] bis(phenolate) ligands. When activated with [PhNMe₂H][B(C₆F₅)₄] in the presence of Al(*n*Oct)₃ at 25 °C, 47 (**Figure 14**) produced highly isotactic PS (*i*PS) ([*mm*] > 0.95) with narrow molecular weight distributions ($M_w/M_n = 1.08 - 1.27$) and $M_n = 18300 - 106100 \text{ g mol}^{-1}$. The M_n was shown to increase as a linear function of the conversion.

Zhang and Nomura¹³³ reported on the living copolymerization of ethylene and styrene using a cyclopentadienyl









(ketimide)titanium(IV) complex (48, Figure 14) in 2005. Upon activation with MAO at 25 °C, 48 furnished poly (ethylene-*co*-styrene) with narrow polydispersities ($M_w/M_n = 1.14 - 1.36$) and $M_n = 53\,000 - 173\,000\,\mathrm{g\,mol^{-1}}$. The M_n was shown to increase linearly with time. Interestingly, 48/MAO exhibited nonliving behavior for styrene and ethylene homopolymerizations despite the living behavior observed for the copolymerization of the two monomers.

3.23.3.10 Bis(phenoxyimine)titanium Catalysts

3.23.3.10.1 Propylene polymerization

In 1999, Fujita and coworkers reported on a class of group 4 complexes bearing chelating phenoxyimine ligands, including **49a (Figure 15)**. When activated with MAO, these complexes showed extremely high activity for ethylene polymerization.^{134–136} Interested in the development of catalysts that could produce stereoregular polymers, Coates and coworkers used a pooled combinatorial approach to screen bis(phenoxyimine)titanium complexes for propylene polymerization behavior. Despite the C_2 -symmetry of the catalyst precursor, **49b**/MAO furnished syndiotactic PP ([r] = 0.94) resulting from a chain-end control mechanism.¹³⁷ Later, several studies revealed an unusual 2,1-insertion mechanism.^{138–140} In addition, calculations on the system have supported a ligand

isomerization event that interconverts the $\not\subset$ and \otimes isomers of the active species between consecutive insertions, causing an alternation between *si* and *re* coordination of propylene, which leads to syndiotactic polymer formation.^{141–143}

It was later found that the incorporation of fluorinated N-aryl moieties into the bis(phenoxyimine) ligand framework could provide catalyst precursors for the syndiotactic and living polymerization of propylene. At 0 °C, 50/MAO (Figure 15) produced highly syndiotactic PP ([rrrr] = 0.96), which had a peak melting temperature of 148 °C.¹⁴⁴ The polymerization exhibited a linear increase in M_n with PP yield while polydispersities remained narrow $(M_w/M_n \le 1.11)$ for M_n up to $100\,000\,\mathrm{g\,mol^{-1}}$. It was also shown that 50/MAO could copolymerize ethylene and propylene in a living fashion by cleanly synthesizing a monodisperse PP-block-poly(E-co-P) sample $(M_w/M_p = 1.12, M_p = 145\,100\,\mathrm{g\,mol^{-1}})$. Utilizing the living nature of 50/MAO, an sPP-block-poly(E-co-P) diblock copolymer of high molecular weight $(M_{\rm n} = 145\,100\,{\rm g\,mol^{-1}})$ $M_{\rm w}/M_{\rm p}$ = 1.12) was prepared through sequential monomer addition.144 Several studies on the physical properties of sPP-block-poly(E-co-P) diblock copolymers made using 50/ MAO have been conducted including those involving the morphology,¹⁴⁵ thermodynamic behavior, and self-assembly¹⁴⁶ of the materials. In a subsequent work, the addition of a third block was employed in the formation of an sPP-block-poly



Figure 15 Bis(phenoxyimine)titanium complexes.

(E-co-P)-block-sPP triblock copolymer.²⁸ Transmission electron microscopy (TEM) revealed that the polymer exhibited a microphase-separated morphology with *s*PP cylinders in a poly(E-co-P) matrix. Tensile testing revealed a strain at break of about 550%.

Saito *et al.*¹⁴⁷ independently reported that 51/MAO was also living and syndioselective ([*rr*] = 87%) for propylene polymerization at room temperature, producing polymer with $M_n = 28500-108000 \text{ g mol}^{-1}$ and $M_w/M_n = 1.07-1.14$. Living ethylene/propylene copolymerization and block copolymer formation have also been demonstrated with 51/MAO.¹⁴⁸ Exploiting this living behavior, *sPP-block-poly*(E-*co-P*), PE-*block-sPP*, and PE-*block-*poly(E-*co-P*)-*block-sPP* have been prepared through sequential monomer addition.^{149,150} Furthermore, employing a supported cocatalyst with 51 has also shown characteristics of living behavior. Polypropylene formed using 51/MgCl₂/*i*-Bu_nAl(OCH₂CH(Et)(CH₂)₃CH₃)_{3-n} had narrow PDIs ($M_w/M_n = 1.09-1.17$, $M_n = 53000-132000 \text{ g mol}^{-1}$) and the polymerization exhibited a linear increase in M_n with reaction time.¹⁵¹

Studies on the effect of the fluorination pattern of the N-aryl ring revealed that complexes bearing the 2,4-di-tert-butyl phenoxide moiety require at least one ortho fluorine on the N-aryl ring to exhibit living propylene polymerization behavior.^{152,153} As the amount of fluorination of the N-aryl moiety is decreased from the perfluoro complex 50 to the monofluoro complex 52a (Figure 15), activities and tacticities for propylene polymerization also decreased while the polydispersities remain consistently low $(M_w/M_n \le 1.11, M_n \text{ up to } 28900 \text{ g mol}^{-1})$ upon MAO activation. Installing a trifluoromethyl group at the para-position of the N-aryl moiety (52e, Figure 15) led to an increase in activity of approximately 1.5 times that of 50/ MAO with similar tacticity ([rrrr] = 0.91).¹⁵⁴ Interestingly, complexes related to 52a-52c, where the para-substituent of the phenoxide moiety is H, produced amorphous PP upon MAO activation. These samples gave bimodal GPC traces, each composed of a narrow peak $(M_w/M_n \le 1.10)$ and a broad peak $(M_{\rm w}/M_{\rm n} = 4.19 - 14.9).^{155}$

Modification of the *ortho* substituents on the phenolate ring has yielded a number of new complexes. Of note, a complex bearing an *ortho*-phenolate trimethylsilyl group, **53** (Figure 15), has been shown to produce *s*PP with very high melting temperatures (T_m up to 156 °C) in a living fashion.¹⁵⁶ Changing the aforementioned *ortho* position to a larger triethylsilyl group (**54a**) gave similar results as **53** with lower activity.¹⁵⁷ Decreasing sterics through employment of a methyl (**54b**) or isopropyl (**54c**) group in the *ortho* position resulted in a substantial loss of stereocontrol producing amorphous PP that exhibited fairly narrow polydispersities ($M_w/M_n \sim 1.2$).

Subsequent modifications to both the phenoxide and *N*-aryl moieties, relative to **50**, have also been made. For example, **55** (**Figure 15**) contains a 2,6-F₂C₆H₃ *N*-aryl moiety and iodine substituents on the phenolate ring. When activated with MAO at 25 °C, **55** was reported to produce amorphous PP, which exhibited a narrow molecular weight distribution $(M_w/M_n = 1.17, M_n = 200\ 000\ \text{g}\ \text{mol}^{-1})$.^{158,159} Furthermore, complexes **56a** and **56b** employ 3,5-difluorophenyl *N*-aryl groups and substituents smaller than *tert*-butyl in the *ortho* position of the phenoxide moiety. Both **56a** and **56b**/MAO were shown to furnish amorphous PP ($[rrrr] \le 0.48$) with narrow molecular weight distributions ($M_w/M_n = 1.13-1.16$, M_n

up to $240\,000\,\mathrm{g\,mol^{-1}}$).¹⁶⁰ This finding was surprising in that both complexes lack *ortho*-fluorines on the *N*-aryl moiety.

In a final variation to the bis(phenoxyimine) complexes, two different phenoxyimine ligands were coordinated to one titanium center. Using gel permeation chromatography as a combinatorial screening method, a number of heteroligated phenoxyimine complexes bearing one nonliving (*ortho*-nonfluorinated ligand) and one living ligand (*ortho*-fluorinated ligand) displayed superior activities over their homoligated counterparts.¹⁵³ For example, PP produced with **49b**/MAO (**Figure 15**) exhibited a broad PDI ($M_w/M_n = 1.41$) and a turn-over frequency (TOF) of $42 h^{-1}$ while **50**/MAO exhibited a narrow PDI ($M_w/M_n = 1.06$) and a TOF of $221 h^{-1}$. However, the heteroligated catalyst **57**/MAO (**Figure 16**) produced PP with $M_n = 70 200 \text{ g mol}^{-1}$ and $M_w/M_n = 1.16$ and exhibited a TOF of $760 h^{-1}$. Additionally, syndiotactic polymer ([*rrrr*] = 0.91) was formed with this heteroligated catalyst.

3.23.3.10.2 Ethylene polymerization

Many of the same titanium bis(phenoxyimine) catalysts used for living propylene polymerization have also been reported for the living polymerization of ethylene. In 2001, Saito et al.¹⁶¹ found that activation of 51 with MAO at 25 °C (Figure 15) furnished linear PE with high molecular weight and narrow distribution $(M_n = 412\,000\,\mathrm{g\,mol^{-1}})$ molecular weight $M_w/M_n = 1.13$). Furthermore, polymerizations at 25 and 50 °C exhibited a linear increase in M_n with reaction time. It was later reported that addition of an equimolar amount of functionalized α -olefin, H₂C=CH(CH₂)_n-Y (Y=OAlMe₂, n=4 and $Y = OSiMe_3$, n = 9), to 51/MAO and subsequent living ethylene polymerization furnished hydroxyl-terminated PEs upon acidic workup.¹⁶² This strategy was also successful for the production of hydroxyl-terminated syndiotactic PP from 51/MAO. Furthermore, addition of the aforementioned functionalized α -olefins as a chain-end capping agent furnished telechelic syndiotactic PPs bearing hydroxyl groups at both chain ends upon acidic workup.

While bis(phenoxyimine) titanium complexes can provide highly syndiotactic PP, copolymers that incorporate PE blocks have also been synthesized with these catalysts. Using 51/MAO (Figure 15), a PE-*block*-poly(E-*co*-P) diblock and a PE-*block*-poly(E-*co*-P)-*block*-PE triblock copolymer have been synthesized through sequential monomer addition.¹⁴⁹ A PE-*block*-poly(E-*co*-P) diblock copolymer was also synthesized using 55/MAO (Figure 15).^{158,163} While the molecular weight of the polymer was quite high with $M_n = 2\,000\,000\,\mathrm{g\,mol^{-1}}$, the molecular weight distribution was fairly broad ($M_w/M_n = 1.60$).

Some of the early titanium bis(phenoxyimine) catalysts have also been used for living ethylene polymerization. In 2003, Reinartz *et al.*¹⁶⁴ reported that 49b when activated with MAO at 50 °C polymerized ethylene to produce PE with $M_w/M_n = 1.10$ and $M_n = 44500 \text{ g mol}^{-1}$. In 2004, Ivanchev *et al.*¹⁶⁵ reported a near-linear increase in M_v with time for the polymerization of ethylene with 49a/MAO at 30 °C. In later work on the same system, Furuyama *et al.*¹⁶⁶ found that molecular weight distributions were low at a reaction time of 1 min $(M_w/M_n = 1.12, M_n = 52000 \text{ g mol}^{-1})$ while the PDI broadened significantly at reaction times of just 5 min $(M_w/M_n = 1.61, M_n = 170000 \text{ g mol}^{-1})$. Other related complexes were synthesized and screened for ethylene polymerization. Complexes



Figure 16 Titanium complexes bearing phenoxyimine ligands.

58a and **58b**/MAO (Figure 16) showed a near-linear increase in M_v with times up to about 20 min.¹⁶⁷

To investigate the effect of the substituent at the ortho position of the phenoxide moiety, complexes 54b and 54c and 59a and 59b (Figures 15 and 16) were screened for ethylene polymerization.168 When activated with MAO at 25 °C, each complex produced PE with a narrow molecular weight distribution $(M_w/M_n = 1.05 - 1.16, M_n \text{ up to } 75\,000\,\text{g}\,\text{mol}^{-1});$ however, reaction times were kept to 1 min. While all the catalysts were living, activities were about an order of magnitude less than 51/MAO. Having shown that 51, 54b, and 59a and 59b/MAO were living for ethylene polymerization, Furuyama et al.¹⁶⁸ investigated the ability of these catalysts to produce ethylene/ α -olefin copolymers in a living fashion. Copolymerizations with ethylene and either 1-hexene, 1-octene, or 1-decene were carried out with each catalyst at 25 °C. In all cases, polymers with narrow molecular weight distributions were obtained $(M_w/M_n \le 1.22)$. As the steric bulk of the ortho substituent decreased, increased a-olefin incorporation was observed. A series of PE-block-poly (E-co-1-hexene) samples was produced using 54b/MAO via sequential monomer addition. Molecular weight distributions for the block copolymers were generally low $(M_w/M_n = 1.11 - 1.31)$ for $M_{\rm p}$ up to 121000 g mol⁻¹) and 1-hexene contents of up to 28.9 mol.% were estimated.

The role of *N*-aryl fluorination on ethylene polymerization behavior has also been explored. Each of the catalysts 60a-60c/MAO (Figure 16) has been shown to be well behaved for

ethylene polymerization at 50 °C and **60a**/MAO and **60b**/MAO produced polymer with narrow molecular weight distributions at reaction times between 1 and 5 min ($M_w/M_n \sim 1.05$, $M_n = 13\ 000-64\ 000\ g\ mol^{-1}$).^{149,169} Finally, Mitani *et al.*¹⁷⁰ reported that ZnEt₂ could be used as a chain-transfer agent in the living ethylene polymerization employing **61a**/MAO (**Figure 16**) leading to zinc end-functionalized chains and a titanium species that reinitiates living ethylene polymerization upon the addition of monomer. Despite being living for ethylene polymerization, **61b** was no longer living in the presence of ZnEt₂.

3.23.3.10.3 Polymerization of cyclopentene, norbornene, and 1,5-hexadiene

Bis(phenoxyimine) titanium complexes have also been employed in the living copolymerization of ethylene and cyclic olefins. Utilizing 50/MAO and varying ethylene pressure, a series of poly(E-co-CP)s with different cyclopentene (CP) contents was prepared (Figure 15, Scheme 7).¹⁷¹ When ethylene pressure was low (<1 psig), an almost perfectly alternating copolymer was formed $(M_n = 21\,000\,\text{g mol}^{-1}, M_w/M_n = 1.34)$ $T_g = 10.1$ °C). However, the use of higher ethylene pressures (3 psig) resulted in the formation of a random copolymer containing 36 mol.% CP $(M_{\rm n} = 133\,000\,{\rm g\,mol^{-1}})$ $M_{\rm w}/M_{\rm n}$ = 1.24, $T_{\rm g}$ = -4.5 °C). Microstructural analysis using ¹³C NMR spectroscopy revealed that in both cases, all CP units were isolated and enchained in a 1,2 fashion. Tri- and



Scheme 7 Synthesis of ethylene/cyclopentene block copolymers using 50/MAO

multiblock copolymers were synthesized in which the constituent blocks differed in their CP content.

Copolymers from ethylene and NB have also been made using 50/MAO.¹⁷² With this catalyst, a high molecular weight, low PDI poly(E-co-NB) sample was prepared ($M_n = 238\ 000\ \text{g}\,\text{mol}^{-1}$, $M_w/M_n = 1.05$) containing 62 mol.% ethylene and a T_g of 86.5 °C. In addition, 50/MAO was also used to synthesize a high molecular weight poly (E-co-P)-block-poly(E-co-NB) sample ($M_n = 576\ 000\ \text{g}\,\text{mol}^{-1}$, $M_w/M_n = 1.13$).

In addition to cyclic olefins, Hustad and Coates¹⁷³ found that bis(phenoxyimine) titanium complex 50 (Figure 15) was also capable of living 1,5-hexadiene polymerization and 1,5-hexadiene/propylene copolymerization. Homopolymerization of 1,5-hexadiene with 50/MAO at 0 °C produced a high molecular weight polymer with a narrow PDI $(M_{\rm n} = 268\,000\,{\rm g\,mol}^{-1}, M_{\rm w}/M_{\rm n} = 1.27)$. The polymer showed the presence of two distinct units - the expected MCP units as well as 3-VTM units. As shown in Scheme 8, the MCP units are proposed to arise from 1,2-insertion of 1,5-hexadiene followed by a 1,2-cyclization. However, an initial 2,1-insertion of 1,5-hexadiene followed by a 1,2-cyclization forms a strained cyclobutane species. After a β-alkyl elimination, the 3-VTM unit is generated. Additionally, propylene/1,5-hexadiene copolymers with high molecular weights were also produced $(M_{\rm n} = 119\ 000 - 145\ 000\ {\rm g\ mol}^{-1},\ M_{\rm w}/M_{\rm n} = 1.09 - 1.16).$

Using 50/MAO, Hustad and Coates¹⁷³ reported the living copolymerization of propylene and 1.5-hexadiene to produce random copolymers comprised of units of propylene, MCP, and 3-VTM. Through sequential monomer addition, an sPP-block-poly(P-co-MCP-co-3-VTM) diblock copolymer was synthesized with 50/MAO (Scheme 9). The molecular weight distribution of the block copolymer was low $(M_w/M_p = 1.11)$ $M_{\rm n} = 93\,300\,{\rm g\,mol^{-1}}$) and contained 4.3 mol.% MCP units and 2.7 mol.% 3-VTM units. A poly(E-co-P)-block-poly (MCP-co-3-VTM) was also synthesized ($M_n = 524700 \text{ g mol}^{-1}$, $M_w/M_n = 1.13$). Lastly, 50/MAO has been used to produce a high molecular weight poly(MCP-co-3-VTM)-block-poly (E-co-NB) sample with $M_{\rm n} = 451\,000\,{\rm g\,mol^{-1}}$ and $M_{\rm w}/M_{\rm n} = 1.41.^{172}$

3.23.3.11 Bis(phenoxyketimine)titanium Catalysts

While bis(phenoxyimine) titanium complexes furnish *s*PP, it had been proposed that placing a substituent at the imine carbon of the ligand could prevent the isomerization responsible for the production of *s*PP and lead to the formation of *i*PP.¹⁷⁴ Ketimine complexes **62a–62c** (Figure 17) were synthesized and found to be sparingly active for propylene polymerization, despite the ability to polymerize ethylene in a living fashion upon activation.^{164,174} Complexes bearing smaller *ortho* substituents on the phenolate ring were reasoned



Scheme 8 Polymerization of 1,5-hexadiene with 50/MAO.



Scheme 9 Synthesis of propylene/1,5-hexadiene block copolymers using 50/MAO.



	R ¹	R ²	R ³	R ⁴
64a	CI	Н	Me	Ph
64b	Br	Н	Me	Ph
64c	Ph	Н	Me	Ph
64d	Bn	Н	Me	Ph
64e	-(CH ₂) ₄ -		Н	Ph
64f	Me	Н	CI	Ph
64g	Me	Н	F	Ph
64h	Me	Н	OMe	Ph
64i	Me	Н	Me	Me
64j	Me	Н	Me	<i>i</i> Pr
64k	Me	Н	Me	Су
64I	Me	Н	Me	Cycloheptyl
64m	Me	Н	Me	CF3
64n	Me	Н	Me	2-Naphthyl
64o	Me	Н	Me	1-Naphthyl
64p	Me	Н	Me	4-Methoxyphenyl
64q	Me	Н	Me	Mesityl
64r	Me	Н	Me	C_6F_5

Figure 17 Bis(phenoxyketimine)titanium complexes.

to enable higher propylene activities by providing a sterically less-encumbered active site. With this in mind, complexes 63a-63d (Figure 17) were synthesized and screened for propylene polymerization.¹⁷⁴ Upon activation with MAO at 0 °C, each complex produced PP with a narrow molecular weight distribution $(M_w/M_n = 1.12 - 1.17, M_n = 2700 - 35400 \text{ g mol}^{-1})$, and 63c/MAO was shown to exhibit a linear increase in M_n as a function of yield. The resulting polymers displayed a variety of tacticities, with 63c/MAO furnishing PP with the highest tacticity $([mmmm] = 0.53, T_m = 69 °C)$. As a comparison, the analogous aldimine of 63c (63e) in which $R^3 = H$ furnishes *a*PP with $M_n = 123 \ 100 \ \text{g mol}^{-1}$ and $M_w/M_n = 1.13$. Further exemplifying the living nature of 63c/MAO for partially isospecific propylene polymerization, an iPP-block-poly(E-co-P) sample was produced with this catalyst. After polymerization of propylene to form an *i*PP block of $M_n = 28100 \text{ g mol}^{-1}$ $(M_w/M_n = 1.10)$, ethylene was added to the reaction yielding a diblock copolymer with $M_{\rm n} = 62\,000\,{\rm g\,mol^{-1}}$ and $M_{\rm w}/M_{\rm n} = 1.10.$

To obtain higher isoselectivity, Edson et al.²⁹ systematically varied ortho-, meta-, and para-substituents on the phenoxide moiety in addition to the ketimine substituent in complexes 64a-64r (Figure 17). All the complexes produced PP with a narrow molecular weight distribution $(M_w/M_n = 1.07 - 1.33)$, $M_{\rm n}$ = 3000–364 000 g mol⁻¹) upon activation with MAO except those bearing ancillary methoxy groups in the ligand framework (64h and 64p). The tacticities of the resulting polymers differed, with 64k/MAO producing PP with the highest tacticity $([mmmm] = 0.73, T_m = 116.8 \circ C)$ in addition to exhibiting a linear increase in $M_{\rm p}$ as a function of polymer yield. Exploiting the living nature of the 64k/MAO, block copolymers containing iPP blocks were prepared via sequential monomer addition.²⁹ Specifically, iPP-block-poly(E-co-P)-block-iPP, iPPblock-poly(E-co-P)-block-iPP-block-poly(E-co-P)-block-iPP, and iPP-block-poly(E-co-P)-block-iPP-block-poly(E-co-P)-block-iPP*block*-poly(E-*co*-P)-*block*-*i*PP copolymers were prepared. The polymers had narrow molecular weight distributions $(M_{\rm w}/M_{\rm n} = 1.13 - 1.30)$ high and molecular weights

 $(M_n = 102\ 000 - 235\ 000\ \text{g mol}^{-1})$. Testing of the tensile properties of the block copolymers showed good elastomeric behavior, with the triblock copolymer displaying an elongation at break of 1000%.

In addition to propylene, Reinartz *et al.*¹⁶⁴ reported that **62a–62c** when activated with MAO at 0 and 20 °C (**Figure 17**) all produced PE that exhibited a narrow molecular weight distribution ($M_w/M_n \le 1.08$) and had number average molecular weights ($M_n = 15000-47000 \text{ g mol}^{-1}$) that coincided with M_n^{theo} . A linear increase in M_n with polymer yield for the polymerization catalyzed by **62**c/MAO at 0 °C and for **62b**/MAO at 50 °C was demonstrated. A related complex (**65, Figure 17**), when activated with MAO at 50 °C, produced PE with $M_w/M_n = 1.08 (M_n = 9000 \text{ g mol}^{-1}).$ ¹⁶⁶

3.23.3.12 Bis(pyrrolide-imine)titanium Catalysts

In 2000, Yoshida *et al.*¹⁷⁵ reported the behavior of bis(pyrrolide-imine)titanium complexes for ethylene polymerization; however, living behavior was not observed. As a result, Fujita and coworkers^{176–178} turned their attention to the copolymerization of ethylene and NB. At 25 °C, **66a–66d**/MAO (**Figure 18**) furnished poly(E-*alt*-NB) with narrow molecular weight distributions and high molecular weights ($M_w/M_n = 1.10-1.24$, $M_n = 127\ 000-600\ 000\ g\ mol^{-1}$). A linear increase of M_n with time over the course of 20 min was observed. The copolymers were found to contain 95% perfectly alternating units. The polymer chain-end structures were consistent with chain initiation by insertion of NB into the Ti–Me bond, and a last inserted NB unit after termination by protonolysis. This suggests NB plays a stabilizing role for the active species against termination processes.

Utilizing **66b**/MAO (**Figure 18**), Yoshida *et al.*¹⁷⁸ were able to prepare block copolymers containing poly(E-*co*-NB) and PE segments as well as block copolymers containing poly (E-*co*-NB) segments with varying degrees of NB incorporation. Block copolymers of the type poly(E-*co*-NB)_x-*block*-poly (E-*co*-NB)_y with 7.6 mol.% NB incorporation in the first block and 27 mol.% NB overall were prepared by initiating the polymerization with ethylene containing the desired amount of NB. After the first block had been formed, supplemental NB was added while maintaining the ethylene feed (**Scheme 10**). Additionally, PE-*block*-poly(E-*co*-NB) was prepared through sequential monomer addition. The diblock copolymer exhibited a narrow polydispersity ($M_w/M_n = 1.56$) and $M_n = 414\,000 \,\mathrm{g}\,\mathrm{mol}^{-1}$ with an NB content of 31 mol.%.

3.23.3.13 Bis(indolide-imine)titanium Catalysts

Expanding on imine ligated catalysts, Fujita and coworkers¹⁷⁹⁻¹⁸³ synthesized bis(indolide-imine)titanium complexes and evaluated their potential as ethylene polymerization catalysts. When activated with MAO at room temperature, compounds 67a-67c (Figure 18) furnished PE with narrow molecular weight distributions $(M_w/M_p = 1.11 - 1.23)$ with $M_p = 11000 - ca.90000 \text{ g mol}^{-1}$. At 25 °C, a linear increase of M_n with increasing polymer yield was observed for 67a-67c/MAO. Exhaustive fluorination of the N-aryl moiety (67d) resulted in living behavior at -10 °C $(M_w/M_p = 1.12 - 1.15)$, while polymerization at 25 °C led to a broadened molecular weight distribution $(M_w/M_n = 1.93)$.^{180,181} Using 67c/MAO (Figure 18), Fujita and coworkers^{181,182} were able to prepare PE-block-poly(E-co-P) copolymers containing 8.0 mol.% propylene via sequential monomer addition with $M_{\rm w}/M_{\rm n} = 1.17$ and $M_{\rm n} = 31400 \,{\rm g \, mol^{-1}}$. TEM visualization of the block copolymer revealed microphase separation of the poly(E-co-P) and PE domains, which were evenly dispersed throughout the sample.

3.23.3.14 Bis(enaminoketonato)titanium Catalysts

The synthesis and ethylene polymerization activity of bis (enaminoketonato)titanium complexes were reported by Li and coworkers¹⁸⁴ in 2004. Upon activation with MMAO at 25 °C, 68a and 68b (Figure 19) furnish linear PEs with narrow molecular weight distributions $(M_w/M_p = 1.25 - 1.45)$ and $M_{\rm n} = 51\,000 - 129\,000\,{\rm g\,mol^{-1}}$. At 25 °C, a linear increase in $M_{\rm p}$ with reaction time is observed with 68a/MMAO. Yu and Mecking¹⁸⁵ reported ortho-fluorination on the N-aryl moiety (69a, Figure 19) furnished living and thermally robust ethylene polymerization catalysts upon MAO activation. A linear increase in $M_{\rm p}$ over time was observed at 25, 50, and up to 75 °C. Nonliving behavior observed for 69b/MAO supports the fact that the living behavior of 69a/MAO is not steric in nature, illustrating another example in which ortho-fluorination appears beneficial for living polymerization. Employing 69a/ MAO, a PE-block-aPP was synthesized through sequential monomer addition.¹⁸⁵ Polymerization of ethylene in a living fashion followed by removal of excess monomer in vacuo and subsequent propylene polymerization furnished the diblock copolymer with $M_n = 190000 \text{ g mol}^{-1}$ and $M_w/M_n = 1.12$.

In addition to ethylene homopolymerization, the copolymerization of ethylene and NB by **68a–68d**/MMAO was also shown to possess some characteristics of a living polymerization.¹⁸⁴ The polymers obtained from polymerizations conducted at 25 °C displayed narrow molecular weight



Figure 18 Bis(pyrrolide-imine)titanium and bis(indolide-imine)titanium complexes.



Scheme 10 Sythesis of ethylene/norbornene block copolymers using 66b/MAO.



Figure 19 Bis(enaminoketonato)titanium complexes for living olefin polymerization.

distributions $(M_w/M_n = 1.07 - 1.54)$ with $M_n = ca.$ 150 000– 580 000 g mol⁻¹. The NB content ranged from 35 to 55 mol.%. At 25 ° C, a linear increase in M_n with reaction time was demonstrated for **68a**/MMAO over the course of 20 min. Utilizing the living nature of the **68**/MAO, a PE-*block*-poly(E-*co*-NB) block copolymer was prepared through sequential monomer addition. The diblock copolymer had a narrow polydispersity $(M_w/M_n = 1.38, M_n = 143\ 000\ g mol^{-1})$ and an NB content of 11 mol.%. The copolymerization of ethylene and CP by **68a**/MMAO and **68d**/MMAO was also shown to possess some characteristics of living behavior.¹⁸⁶ At temperatures from –10 to 30 °C, poly(E-*co*-CP) s with narrow molecular weight distributions $(M_w/M_n = 1.23 - 1.82)$ were produced. Additionally, a PE-*block*-poly(E-*co*-CP) was prepared in a manner similar to the PE-*block*-poly(E-*co*-NB). Tang *et al.*¹⁸⁷ discussed the effects of further ligand modifications on the copolymerization behavior of bis (enaminoketonato)titanium catalysts. At 25 °C, **70**/MMAO (**Figure 19**) produced poly(E-*co*-NB) with narrow polydispersities ($M_w/M_n = 1.18-1.31$, $M_n = ca$. 200 000–570 000 g mol⁻¹) and NB content ranging from 45 to 47.8 mol.%. The polymerization displayed a linear increase of M_n with time of t = 5-20 min.

In addition to NB and CP, Pan *et al.*¹⁸⁸ found **68a**, **69a**, **69c**, and **69d** were active for the polymerization of ethylene and dicyclopentadiene upon activation with MAO at 25 °C. Depending on the monomer feed, the resultant polymers contained up to 47.8 mol.% dicyclopentadiene with a nearly alternating structure. Over the course of 20 min, **68a**/MAO (Scheme 11) produced a copolymer with increasing molecular



Scheme 11 Synthesis of ethylene/dicyclopentadiene block copolymers using 68a/MAO.

weights $(M_n = 47\ 000\ \text{g}\ \text{mol}^{-1})$ while maintaining narrow polydispersities ($M_w/M_n = 1.06 - 1.14$). Analysis of the ¹³C NMR spectra revealed a copolymer containing only unreacted CP units, suggesting the copolymerization proceeds through enchainment of the NB portion of the dicyclopentadiene exclusively. Utilizing sequential monomer addition, a PE-block-poly(E-alt-dicyclopentadiene) was produced. Characterization using AFM and TEM revealed а microphase-separated material. Additionally, Li and coworkers were able to produce functionalized diblock copolymers through reaction of the remaining alkene.

3.23.3.15 Bis(phosphanylphenoxide)titanium Catalysts

In 2006, Long *et al.*¹⁸⁹ reported the synthesis of group 4 metal complexes (71a–71f, Figure 20) featuring two bidentate ligands equipped with phenoxide and phosphine donors. At 25 °C, 71a–71f/MAO were found to be active for the polymerization of both ethylene and propylene although polydispersities were broadened ($M_w/M_n > 1.49$). In a subsequent report, He *et al.*¹⁹⁰ synthesized 71g and 71h and found 71g/MAO exhibited a nearly linear increase of M_n over the first 10 min of the ethylene polymerization. Furthermore, the resultant polymers had relatively narrow molecular weight distributions ($M_w/M_n = 1.31-1.33$), indicative of at least quasi-living behavior.

To enhance the living nature of the system, Li and coworkers explored the copolymerization of NB and ethylene. He *et al.*¹⁹⁰ found that the copolymerization of ethylene and NB by **71g**/MAO resulted in polymers with narrow molecular weight distributions ($M_w/M_n < 1.2$) for NB incorporation of more than 10 mol.%. Additionally, the molecular weight was found to increase linearly with polymer yield. Further exemplifying the living nature of the catalyst, a poly(E-*co*-NB)_x-*block*-poly (E-*co*-NB)_y was produced. After formation of the first block containing 25 mol.% NB, supplemental NB was added to the system resulting in a second block containing 44 mol.% NB. The resultant block copolymer exhibited high molecular weight ($M_n = 32\,000\,\mathrm{g\,mol^{-1}}$) and narrow molecular weight distributions ($M_w/M_n = 1.17$).

3.23.3.16 Catalysts Supported by sp² and sp³ Carbon Donors

One of the more recent classes of catalysts to emerge is the C_1 -symmetric pyridylamidohafnium complexes

(72, Figure 20) developed by Dow and Symyx^{191–193} that furnish high molecular weight and highly isoselective poly (α -olefin)s at high reaction temperatures upon activation. Domski *et al.*¹⁹⁴ have shown that the catalyst derived from a C_s -symmetric pyridylamidohafnium complex (73, Figure 20) furnished isotactic PH in a living fashion when activated with B(C₆F₅)₃. The PHs exhibited narrow polydispersities ($M_w/M_n \le 1.20$, M_n up to 152 000 g mol⁻¹) and the M_n was shown to increase linearly with monomer conversion. At 50 °C, the molecular weight distribution of the polymer produced by 73/B(C₆F₅)₃ remains narrow, suggesting that living behavior is maintained at elevated temperatures.

In addition to living 1-hexene polymerization, Domski et al.¹⁹⁴ have shown that 73/B(C₆F₅)₃ furnished isotactic PP ([mmmm] = 0.56) with a narrow molecular weight distribution $(M_{\rm p} = 68\,600\,{\rm g\,mol^{-1}}, M_{\rm w}/M_{\rm p} = 1.05)$ at 20 °C. The mechanism of stereocontrol proceeded by an enantiomorphic site control mechanism, which is quite unusual for a Cs-symmetric catalyst. Detailed mechanistic studies with 72 (Figure 20) by Froese et al.^{192,195} have shown the 1,2-insertion of an olefin into the Hf-CAryl bond generates an sp³-hybridized carbon donor atom that supports the active metal center; it is likely that the isoselectivity observed with $73/B(C_6F_5)_3$ results from a similar activation mechanism. With this in mind, Domski et al.¹⁹⁶ prepared a new pyridylamidohafnium complex (rac-74, Figure 21) supported by an sp³carbon donor that was generated via insertion of a ligand-appended alkene into the neutral pyridylamidohafnium trimethyl precursor generating a mixture of diastereomers (61:39 ratio). Upon activation with $B(C_6F_5)_{3\prime}$, rac-74 furnished isotactic PP ([mmmm] = 0.80) with a narrow molecular weight distribution $(M_w/M_n \le 1.05, M_n \text{ up to } 124\,400\,\text{g mol}^{-1})$ and TOF of 2800 h^{-1} . The M_n was shown to increase linearly with polymer yield over the course of 45 min.

Edson *et al.*¹⁹⁷ were able to further exploit the area of olefin polymerization catalysts supported by sp^3 -carbon donors through the synthesis and subsequent metallation of vinyl-appended phenoxyamine ligands. The resultant complexes of zirconium and hafnium (*rac*-**75a** and *rac*-**75b**, **Figure 21**) bearing six-membered metallacycles were obtained as diastereo-isomeric mixtures resulting from migratory insertion of a benzyl group to the ligand-appended vinyl group on the neutral phenoxyamine metal tribenzyl precursor. Upon activation, *rac*-**75a** and *rac*-**75b** formed highly active polymerization catalysts (TOF>930 h⁻¹) that isoselectively





Figure 20 Bis(phosphanylphenoxide)titanium and pyridylamidohafinum precatalysts.



Figure 21 Hafnium and zirconium precatalysts for living olefin polymerization.

polymerized both 1-hexene and propylene. At 0 °C, *rac*-75b/B (C₆F₅)₃ produced isotactic PH in a living fashion. Molecular weights ($M_n = 70\,000-240\,000\,\text{g mol}^{-1}$) increased linearly as a function of conversion while polydispersities remained narrow ($M_w/M_n = 1.10-1.15$). Living 1-hexene polymerization behavior was not observed for the zirconium analog (*rac*-75a).

Despite its living nature for 1-hexene polymerization, living propylene polymerization behavior was not observed for the hafnium analog (*rac*-75b); however, living isoselective polymerization of propylene was observed for the zirconium analog (*rac*-75a). At 0 °C, *rac*-75a/B(C₆F₅)₃ produced polypropylene with narrow polydispersities ($M_w/M_n = 1.17-1.19$), while molecular weights ($M_n = 60\,000-220\,000\,\mathrm{g\,mol^{-1}}$) were observed to increase linearly with polypropylene yield. Utilizing the living nature of *rac*-75a, a diblock copolymer was synthesized by sequential monomer addition. The resultant *i*PP-*block*-poly(E-*co*-P) had an $M_n = 122\,000\,\mathrm{g\,mol^{-1}}$ and a narrow molecular weight distribution ($M_w/M_n = 1.20$).

3.23.3.17 Aminopyridinatozirconium Catalysts

In 2007, Kretschmer *et al.*¹⁹⁸ described a zirconium catalyst supported by bis(aminopyridinato) ligands (**76**, **Figure 22**) that was living for ethylene polymerization at elevated temperature. Upon activation with $[R_2NMeH][B(C_6F_5)_4]$ ($R = C_{16}H_{33}-C_{18}H_{37}$) in the presence of tetra-(2-phenyl-1-propyl)aluminoxane at 50 °C, **76** furnished linear PE of high molecular weight ($M_n = 1.745000-2.301000 \text{ g mol}^{-1}$) and narrow molecular weight distributions ($M_w/M_n = 1.26-1.30$). No evidence for β -H elimination or chain transfer was evident and continued chain growth was observed even after polymer precipitation.

3.23.3.18 Tris(pyrazolyl)borate Catalysts

In 2008, Jordan and coworkers^{199,200} described tris(pyrazolyl) borate complexes (77, 78, Figure 22) that displayed characteristics of living ethylene polymerization at low temperatures. In the presence of 40 equivalents of ethylene at -78 °C, 77/[Ph₃C] $[B(C_6F_5)_4]$ furnished linear PE with $M_n = 2000 \text{ g mol}^{-1}$ that was in good agreement with M_n^{theo} . No olefinic resonances were observed. Additionally, quenching with Br2 furnished doubleend-capped PE featuring a benzyl group on one polymer chain end and bromine substituent on the opposite polymer chain end. Similar results were obtained with 78/[Ph₃C][B $(C_6F_5)_4$ in the presence of 38 equivalents of ethylene at -78 °C; however, observed molecular weights ($M_n = 2800$ -3800 g mol⁻¹) were approximately 3 times higher than M_n^{theo} . The authors attribute this apparent disparity to incomplete activation of the hafnium complex. Double-end-capped polyethylene bearing benzyl and bromine substituents was also synthesized upon bromine quench of $78/[Ph_3C][B(C_6F_5)_4]$.

3.23.3.19 Bis(dimethylamidopyridine)zirconium Catalysts

In 2009, Annunziata *et al.*²⁰¹ reported a new class of olefin polymerization catalysts bearing dianionic tridentate amidomethylpyridine ligands, which exhibited some characteristics of living polymerization. Upon activation with $Al^{i}Bu_{2}H/MAO$, **79** (Figure 22) produced isotactic PH ([*mmm*] = 0.99) with



Figure 22 Precatalysts for living olefin polymerization.

narrow molecular weight distributions ($M_w/M_n = 1.2$). Furthermore, 79/AlⁱBu₂H/MAO produced polypropylene lacking olefinic end groups with $M_w = 38\,000\,\mathrm{g\,mol^{-1}}$ and $M_w/M_n = 1.4$. Activation of 79 with AlⁱBu₂H and [HNMe₂Ph] [B(C₆F₅)₃] in the presence of ethylene resulted in linear PE with a narrow molecular weight distribution ($M_w/M_n = 1.2$).

3.23.4 Non-group 4 Early Metal Polymerization Catalysts

While complexes of group 4 transition metals dominate the field of living olefin polymerization, there are rare examples of group 3 complexes displaying characteristics of living behavior. In 2005, Ward *et al.*²⁰² reported the synthesis and 1-hexene polymerization behavior of a unique C_3 -symmetric scandium complex bearing a tripodal trisoxazoline ligand. When treated with 2 equivalents of [Ph₃C][B(C₆F₅)₄] at -30 °C in the presence of 1-hexene, **80** (Figure 22) produced isotactic PH ([*mmm*] = 0.90) lacking olefinic end groups with $M_n = 750000 \text{ gmol}^{-1}$ and $M_w/M_n = 1.18$.

In addition to 1-hexene, living ethylene polymerization has been reported for non-group 4 early metal catalysts. In 1985, Jeske *et al.*²⁰³ showed that organolanthanide complexes were promising for living ethylene polymerization. The dimeric bis (Cp^{*}) hydride complexes (**81a–81c**, Figure 23) furnished high molecular weight PEs ($M_n = 96\ 000-648\ 000\ g mol^{-1}$), and molecular weight distributions were for the most part lower than 2.0 (e.g., **81c** exhibited $M_w/M_n = 1.37-1.68$). The living nature of **81a–81c** is further supported by observations that catalytic activity is maintained for up to 2 weeks, M_n increases with time, and the number of polymer chains per metal center is consistently less than 1.

In 2005, Wang and Nomura²⁰⁴ reported that arylimido(aryloxo)vanadium dichloride complex 82 (Figure 23) activated with Et_2AICI exhibited characteristics of living ethylene polymerization. At 0 °C, the PE produced had a narrow molecular weight distribution $(M_w/M_n = 1.42)$ and high molecular weight $(M_n = 2570\ 000\ \text{g mol}^{-1})$. Additionally, the M_n was shown to increase in a linear fashion with increasing TON. In addition to living ethylene polymerization, 82/Et₂AlCl was reported to catalyze the quasi-living copolymerization of ethylene and NB.²⁰⁴ At 0 °C, poly(E-*co*-NB) with 5.1–39.9 mol.% NB content was obtained from 82/Et₂AlCl. The polymers exhibited narrow molecular weight distributions $(M_w/M_n = 1.29-1.73)$ and high molecular weights $(M_n = 327\ 000-2\ 570\ 000\ \text{g mol}^{-1})$.

Upon investigating the ethylene polymerization behavior of dialkyl(benzamidinate)yttrium complexes, Bambirra *et al.*²⁰⁵ reported that at least some characteristics of living behavior were observed. When treated with [PhNMe₂H][B(C₆F₅)₄], **83** (**Figure 23**) furnished PE that displayed narrow molecular weight distributions ($M_w/M_n = 1.1-1.2$) and high molecular weights ($M_w = 430\ 000-1\ 269\ 000\ g\ mol^{-1}$) with about 1.1 polymer chains per metal center being produced.

While studying a series of group 5 catalysts, Mashima et al.²⁰⁶ reported on the synthesis and ethylene polymerization behavior of cyclopentadienyl(η^4 -diene)tantalum complexes. Upon activation with MAO at temperatures of -20 °C or below, compounds 84a, 85a, and 86 (Figure 23) furnished PEs with narrow molecular weight distributions $(M_w/M_n \le 1.4, M_n = 8600 - 42\,900\,\mathrm{g\,mol}^{-1})$. Below $-20\,^{\circ}\mathrm{C}$, ethylene polymerization by 85a/MAO displayed a linear increase of M_n with increasing reaction time. The activity for ethylene polymerization was shown to depend on the substitution pattern of the η^4 -diene ligand, with the highest activity being obtained in the case where 2,3-dimethyl-1,3-butadiene is used (85b) and the lowest when isoprene is employed (85c).²⁰⁷ When activated with MAO, the analogous niobium complexes (87a-87d, Figure 23) were also shown to behave as living ethylene polymerization catalysts up to 20 °C ($M_w/M_p = 1.05$ -1.30, $M_{\rm n} = 5100 - 105400 \,{\rm g \, mol^{-1}}$).²⁰⁸ The dependence of activity on the η^4 -diene ligand employed mirrored that observed for the analogous tantalum compounds.



Figure 23 Non-group 4 early metal olefin polymerization precatalysts.



Figure 24 Early metal and rare earth precatalysts for olefin polymerization.

Finally, MacAdams *et al.*²⁰⁹ investigated chromium complexes bearing 2,4-pentane-*N*,*N*'-bis(aryl)ketiminato ((Ar) $_2$ nacnac) ligands for ethylene polymerization. At room temperature in the presence of ethylene, **88** (Figure 24) formed linear PE with narrow molecular weight distributions ($M_w/M_n = 1.17-1.4$). The M_n was shown to increase linearly with polymer yield. These results represented the first report of living ethylene polymerization with a chromium-based catalyst.

3.23.5 Rare-Earth Metal Catalysts

In addition to early metal catalysts, several living rare-earth metal catalysts have been reported. In 2008, Ravasio *et al.*²¹⁰ described the copolymerization of ethylene with NB catalyzed by rare-earth metal half sandwich complexes **89a–89d** (Figure 24). Upon activation, **89a** and **89b**/[Ph₃C][B(C₆F₅)₄] showed excellent activities for the copolymerization of ethylene and NB. Specifically, **89b**/[Ph₃C][B(C₆F₅)₄] furnished poly (E-*co*-NB) with 29–42 mol.% NB. Over 3 min, a linear increase in molecular weight ($M_n = 100\,000-250\,000\,\text{gmol}^{-1}$) was observed while a narrow molecular weight distribution ($M_w/M_n = 1.22-1.35$) was maintained. At room temperature with [Ph₃C][B(C₆F₅)₄], the yttrium analog (**89c**) displayed poor activity for ethylene NB copolymerization and the lute-tium analogue (**89d**) was inactive for the polymerization.

Utilizing [Cp₂*SmMe(THF)] and [Cp₂*SmH]₂ (90 and 91, Figure 25), Yasuda and coworkers²¹¹ described the synthesis of block copolymers containing polyethylene (insertion mechanism) with several polar monomers (noninsertion mechanism) such as MMA, methyl acrylate (MA), ethyl acrylate (EA), δ -valerolactone (VL), and ϵ -caprolactone (CL) via sequential addition. Ethylene was first polymerized $(M_{\rm w}/M_{\rm n} = 1.39 - 2.01, M_{\rm n} = 6600 - 27\,000\,{\rm g\,mol^{-1}})$ followed by addition of the respective polar monomer to form a diblock copolymer; however, reversal of monomer addition led to no block copolymer formation. Thus, a PE-block-PMMA, PE-block-PMA, PE-block-PEA, PE-block-PVL, and PE-block-PCL were synthesized and showed good material properties such as deep coloration with dyes. In a later report, the structurally related 92 (Figure 25) was also shown to be a viable block copolymerization catalyst for ethylene, MMA, and CL.²¹² Furthermore, Desurmont et al.²¹³ reported on the synthesis of diblock copolymers poly(1-pentene)/PH and PMMA/PCL using the structurally similar bridged Cp-bearing yttrium and samarium catalysts 93 and 94 (Figure 25) via sequential monomer addition.

It had been previously shown that Cp_2^*Sm is active for ethylene homopolymerization involving coordination of ethylene by two Sm^{II} centers followed by electron transfer to form a telechelic initiator (Scheme 12).²¹⁴ Desurmont *et al.*²¹⁵ cleverly applied this observation to the synthesis of triblock copolymers of ethylene and polar monomers. Thus, triblock copolymers of PMMA-*block*-PE-*block*-PMMA, PCL-*block*-PE-*block*-PCL, and PDTC-*block*-PE-*block*-PDTC (PDTC = poly(2,2-dimethyltrimethylene carbonate)) were prepared through sequential monomer addition with 95 and 96 (Figure 25).

3.23.6 Late Metal Olefin Polymerization Catalysts

3.23.6.1 Nickel and Palladium *a*-Diimine Catalysts

3.23.6.1.1 Polymerization of α-olefins

In the mid-1990s, Johnson et al.²¹⁶ reported the synthesis and olefin polymerization activity of α-diimine complexes of nickel and palladium. These systems were unique among late metal catalysts in their ability to produce high molar mass materials, rather than oligomers, from both ethylene and higher α -olefins. Furthermore, the metal centers were shown to migrate along polymer chains ('chain walking'),²¹⁷ allowing access to polyolefins with a wide variety of microstructures simply by varying ligand substitution patterns, temperature, or pressure. Shortly after the initial reports, conditions were disclosed which allowed the nickel catalysts 97 and 98 (Figure 26) to polymerize 1-hexene and 1-octadecene in a living fashion.²¹⁸ Upon activation with MAO or MMAO at -10 °C and low monomer concentrations, 97 and 98 resulted in living systems furnishing polymers of $M_n = 19\,000 - 91\,000\,\mathrm{g\,mol^{-1}}$ and narrow molecular weight distributions (M_w/M_n as low as 1.09). The systems were also shown to exhibit a linear increase in M_n with time. Branching density was less than that calculated for perfect sequential 1,2-insertions as a result of ω,1-enchainment, or 'chain-straightening'.²¹⁹ PH with as few as 118 branches/1000 carbons (vs. 167 expected for perfect 1,2-insertions) and poly (1-octadecene) with as few as 39 branches/1000 carbons (vs. 56 expected) were produced at -10 °C. Branching density was controlled by reaction conditions and catalyst structure, with 98 producing more linear polymers than 97. Studying several palladium and nickel complexes, Merna et al.^{220,221} reported living 1-hexene polymerization behavior with 97/MAO and 99/MAO. These values are considerably narrower than those reported by Brookhart for similar reactions at 23 °C, although the reason for the improvement is not clear.







Scheme 12 Formation of a telechelic initiator for ethylene polymerization.



Figure 26 Nickel α-diimine precatalysts for olefin polymerization.

A siloxy-substituted analog of 97 (100, Figure 26) was synthesized by Yuan *et al.*²²² who studied its application for the living polymerization of 1-hexene at -11 °C and up to

16 °C. At the higher temperature, the polydispersity increases somewhat ($M_w/M_n = 1.12-1.21$), and the increase in molecular weight is only linear for the first 40 min. In addition, the

polymer has a different microstructure, with branching greatly decreased at $16 \,^{\circ}$ C relative to $-10 \,^{\circ}$ C (83 vs. 132 branches/ 1000 carbons, respectively).

Utilizing a structural variant of **97** featuring a cyclophane diimine ligand (101, **Figure 26**), Camacho and Guan²²³ reported the first living polymerization at elevated temperatures with nickel. When activated with MMAO, **101** furnished PHs with narrow molecular weight distributions ($M_w/M_n = 1.13-1.22$) up to 75 °C and branching densities (52–58 branches/1000 carbons) approximately one-half of those reported for **97**. The authors attribute the improved behavior to the cyclophane framework which very effectively blocks the axial sites of the nickel center preventing chain transfer.

Rose *et al.*²²⁴ employed the chiral, C_2 -symmetric nickel diimine complex **102** (Figure 26) to control polymer microstructure for living polymerization of α -olefins. A hallmark of the original nickel diimine catalysts is the ability to undergo successive β -hydride eliminations/reinsertions, commonly referred to as 'chain walking'.²² This may lead to 'chain-straightening' with α -olefins, generating regioirregular polymers with less branching than expected. Careful tailoring of reaction conditions (low temperatures and high monomer concentration) with catalyst **102** generates high selectivity for ω ,2-enchainment, generating predominantly methyl branches at regular intervals between methylene units (illustrated for 1-hexene in Scheme 13). The technique is applicable to a range of α -olefins, but selectivity for ω ,2-enchainment was shown to decrease with increasing chain length (96 mol.% ω ,2-enchainment for 1-butene vs. 70% for 1-octene).

Suzuki *et al.*²²⁵ have explored α -diimine complexes of both nickel and palladium (**103a–103e**, **Figure 26**) for the polymerization of 1-hexene at very high pressures (up to 750 MPa). While nickel catalysts displayed nonliving behavior, the palladium catalysts **103d** and **103e** (**Figure 26**) were living for 1-hexene polymerization and polydispersities decreased at higher pressures (M_w/M_n = 1.27–1.29 at 0.1 MPa vs. 1.11–1.17 at 500 MPa with **103e**).

Using diimine complexes of palladium, Gottfried and Brookhart²²⁶ have demonstrated conditions which allow for living polymerizations of 1-hexene and 1-octadecene at 0 °C where quenching with Et₃SiH is required to prevent chain coupling. Relative to 104b, catalyst 104a (Figure 27) exhibited improved living behavior for 1-hexene polymerization. This was attributed to the ability of the nitrile donor to compete with 1-hexene for the open coordination site in 104b. Over the course of 3 h, both 104a and 104b showed a linear increase in M_n with time and furnished PHs with narrow molecular weight distributions ($M_w/M_n = 1.10-1.15$) and branching densities of 75–85 branches/1000 carbons. Catalyst 104b was likewise applied to the living polymerization of 1-octadecene. The M_n

106 Ar = 4-tBuPh



Scheme 13 ω ,1- and ω ,2-enchainment of 1-hexene.



Figure 27 Nickel and palladium precatalysts for olefin polymerization.

was observed to increase linearly over the first 3 h at 0 °C; however, the molecular weight distribution increased as well $(M_w/M_n = 1.34 \text{ after 3 h})$. This was attributed to precipitation of the polymer at this temperature, which also limits the accessible molecular weights to ~40 000 g mol⁻¹. Borkar *et al.*²²⁷ reported on a structurally similar diimine palladium complex to **104a** bearing a five-membered ester chelate arising from 1,2-insertion of MMA into the cationic palladium precusor (**104c**, Figure 27). Over the course of 22 h, catalyst **104c** displayed 'quasi-living' behavior for 1-hexene polymerization showing an increase in M_n with time.

It was also discovered that addition of carbon monoxide (CO) in the presence of 1-hexene and **104c** afforded an alternating copolymer.²²⁷ Taking advantage of this, a PH-*block*-poly (1-hexene-*alt*-CO) diblock copolymer was made through sequential monomer addition. Similarly, a PE-*block*-poly (E-*alt*-CO) diblock copolymer was also synthesized through sequential monomer addition.

3.23.6.1.2 Propylene polymerization

α-Diimine complexes of nickel were the first late transition metal catalysts reported for the living polymerization of propylene.²¹⁶ Upon activation with MMAO at –10 °C, catalyst 97 (Figure 26) afforded PP with a narrow molecular weight distribution (M_w/M_n = 1.13; M_n = 160 000 g mol⁻¹) and M_n was shown to increase linearly with conversion. The material obtained had 159 branches/1000 carbons, far less than the theoretical value of 333 for sequential 1,2-insertions, which was attributed to chain-straightening. As branching decreased, T_g values decreased as well (as low as –55 °C), illustrating the dramatic effects of enchainment mechanism on physical properties.

Killian *et al.*²¹⁸ demonstrated the living nature of nickel catalysts 97 and 98 (Figure 26) with the synthesis of well-defined di- and triblock copolymers of α -olefins. At –15 °C, activation of 97 with MAO followed by sequential addition of monomers afforded PP-*block*-PH with monomodal, narrow molecular weight distributions (M_w/M_n = 1.11–1.13), which exhibited less branching than predicted, due to partial chain-straightening. Triblocks were prepared by activation of 97 or 98 with MMAO at –10 °C followed by reaction with 1-octadecene to afford a semicrystalline, chain-straightened

block as observed in homopolymerizations with that monomer. Sequential addition of propylene resulted in poly(1octadecene)-*co*-PP, which was followed by formation of a third poly(1-octadecene) block as propylene was removed (Scheme 14). The resultant materials exhibited elastomeric properties as expected based on the 'hard–soft–hard' triblock structure of the polymers.

Living polymerization of propylene was also achieved by Yuan et al.²²² with 100 (Figure 26). At -11 °C, 100/MAO produced PP with narrow molecular weight distribution $(M_w/M_p = 1.17 - 1.19)$ and a nearly linear increase in molecular weight over 2 h. Minimal chain-straightening was observed (316 branches/1000 carbons) and the polymer was moderately syndio-enriched ([rr] = 0.54). Exploiting the living nature of 100, di- and triblock copolymers were synthesized.²²² At -15 °C, 100/MAO polymerized propylene and generated a syndio-rich polypropylene block. Following removal of excess monomer under vacuum, addition of 1-hexene at the same temperature generated a diblock copolymer with $M_{\rm w}/M_{\rm n}$ = 1.18 and $M_{\rm n}$ = 46 400 g mol⁻¹. Triblocks were produced with this catalyst in a similar fashion. Polymerization of 1-hexene first, followed by introduction of propylene (with 1-hexene still present), followed by venting and then allowing the residual 1-hexene to react allowed for formation of a $(M_{\rm n} = 31\,100\,{\rm g\,mol^{-1}})$ shorter PH-b-poly(propylene-ran-(1-hexene))-b-PH triblock copolymer.

The cyclophane Ni catalyst 101 (Figure 26) was employed by Camacho and Guan²²³ in a dramatic demonstration of propylene chain-straightening. At temperatures up to 50 °C, 101/MAO showed good activity for propylene polymerization, with narrow molecular weight distributions $(M_w/M_n = 1.06 - 1.16)$. In addition, M_n was shown to increase linearly with time at 50 °C. The PPs contain 104-113 branches/1000 carbons, indicative of extensive chain-straightening. This implies that the cyclophane ligand geometry favors a 2,1-insertion mechanism.

Utilizing the chiral, C_2 -symmetric nickel complex 102 (Figure 26), Cherian *et al.*²²⁸ polymerized propylene in a living fashion at temperatures up to 22 °C in the presence of MAO, with a narrow distribution of molecular weights ($M_w/M_n \le 1.11$). Both the regio- and stereocontrol of enchainment are temperature dependent, allowing access to a wide



Scheme 14 Synthesis of 1-octadecene/propylene triblock copolymers using 98/MMAO.



iPP-block-rirPP-block-iPP-block-rirPP-block-iPP

Scheme 15 Synthesis of propylene-based block copolymers using 102/MAO.

variety of polymer microstructures from a single monomer. At low temperatures (-78 °C), no chain-straightening is observed furnishing highly isotactic PP, but the percentage of 3,1-enchainment increases up to 56.2% at 22 °C producing an amorphous and regioirregular PP. Uniquely, this catalyst has the ability to maintain living behavior at a variety of temperatures, but with variable tacticity and levels of chain-straightening. Utilizing this temperature dependence, 102/MAO was used to synthesize regioblock PPs having good elastomeric properties.²⁸ Both a triblock and a pentablock copolymer were synthesized by simply varying the reaction temperature during the course of the polymerization (Scheme 15). For example, an iPP-block-rirPP-block-iPP $(M_n = 109\,000\,\mathrm{g\,mol^{-1}}, M_w/M_n = 1.14)$ and an *iPP-block*rirPP-block-iPP-block-rirPP-block-iPP $(M_{\rm n} = 159\,000\,{\rm g\,mol^{-1}})$ $M_{\rm w}/M_{\rm n}$ = 1.39) pentablock copolymer were prepared by toggling the reaction temperature between -60 and 0 °C. TEM revealed no microphase separation. However, the pentablock copolymer exhibited an exceptional strain at break of 2400% and good elastomeric recovery out to strains of 1000%.

In an attempt to obtain higher regio- and isoselectivity at low reaction temperatures, Rose *et al.*³⁰ introduced new chiral, C_2 -symmetric nickel diimine complexes featuring cumyl-derived ligands. Each of the complexes (105a–105f, Figure 27) exhibited higher regioselectivity than 102 at -60 °C in the presence of MAO. Of the complexes studied at -78 °C, 105f furnished isotactic PP with the highest melting temperature ($T_m = 149$ °C). In addition, a linear increase in M_n with polymer yield is observed at 0 °C. Regioblock polypropylenes were produced with 105f/MAO (Figure 27) that exhibited improved elastomeric performance at elevated temperatures (e.g., 65 °C) over block copolymers synthesized with 102/MAO.³⁰

Using Pd complexes containing diimine ligands (104b, Figure 27) at 0 °C, Gottfried and Brookhart²²⁶ observed a relatively linear increase in polypropylene M_n with time up to approximately 40 000 g mol⁻¹. However, living systems were not obtained when the palladium ester chelate catalyst 104a was employed due to slow initiation relative to propagation. This initiation problem could be circumvented utilizing 104b because the weakly bound nitrile group is more easily

displaced by propylene. Consistent with previous results, PPs generated by this catalyst are chain-straightened, containing approximately 253 branches/1000 carbons.

3.23.6.1.3 Ethylene polymerization

First-generation nickel α -diimine catalysts such as 97 (Figure 26) do not polymerize ethylene in a living fashion due to relatively facile chain transfer. Schmid *et al.*²²⁹ have investigated modifications of this framework to prevent chain transfer by enhancing the steric bulk about the metal center. When 106 (Figure 27) was activated with MAO at ambient temperature, molecular weight distributions were decreased markedly (M_w/M_n as low as 1.3) for short reaction times and ultra-high molecular weight (>4 500 000 g mol⁻¹), highly linear PE was produced.

Further investigating ethylene polymerization behavior with this class of catalysts, Camacho *et al.*²³⁰ extended the study of hindered diimine catalysts with cyclophane complex **101 (Figure 26)**. Upon activation with MMAO, **101** is highly active for production of branched PEs (66–97 branches/1000 carbons) with relatively narrow polydispersities (M_w/M_n as low as 1.23 at 50 °C). Most significantly, these catalysts exhibit impressive thermal stability, with good activities even up to 90 °C. However, the polydispersity increases, and the activities decrease somewhat at higher temperatures. Interestingly, a related alkyl cyclophane Ni complex demonstrated almost no activity for ethylene polymerization.²³¹

In a subsequent report, Popeney *et al.*²³² found a significant effect on polymer properties and reactivity upon fluorination of the cyclophane ligand (107, Figure 28). The fluorinated nickel complex (107) showed improved thermal stability relative to its nonfluorination counterpart (101). After 70 min at 105 °C, 107/TIBA produced high molecular weight PE ($M_n = 190000 \text{ g mol}^{-1}$) with a unimodal molecular weight distribution ($M_w/M_n = 2.7$). The palladium complex bearing the fluorinated cyclophane (108, Figure 28) was observed to produce higher molecular weight polymer than variations of the catalyst containing nonfluorinated ligands. Upon activation with TIBA at 35 °C, 108 yielded PE with a narrow polydispersity ($M_w/M_n = 1.3$) and high molecular weight ($M_n = 264000 \text{ g mol}^{-1}$). Both the nickel (107) and palladium


Figure 28 Nickel and palladium precatalysts for olefin polymerization.

(108) complexes exhibited a significant decrease in chain branching compared to their nonfluorinated counterparts. The authors postulate that the fluorine atom stabilizes the electrophilic metal center through electron donation. This type of stabilization is well known in early metal polymerization systems, but this report represents the first example of positive fluorine interactions in late metal olefin polymerization.

To achieve living polymerization of ethylene with palladium catalysts 104a and 104b (Figure 27), Gottfried and Brookhart²³³ demonstrated that specific reaction conditions, particularly quenching reactions with Et₃SiH to prevent chain coupling, were crucial. At 5 °C, highly branched (~100 branches/1000 carbons), amorphous PEs with very narrow molecular weight distributions $(M_w/M_n < 1.1)$ were produced, and $M_{\rm n}$ was shown to increase linearly over at least 6 h. At 27 °C, $M_{\rm n}$ of 237 000 g mol⁻¹ could be obtained in 2 h with broadened molecular weight distributions ($M_w/M_p = 1.19$). To ensure rapid initiation of 104a, high pressures of ethylene (400 psig) were required to displace the chelated carbonyl group, which is retained in the highly branched PE product. Compound 104b exhibited similar activity at high pressures, while also yielding polymers with relatively narrow polydispersities $(M_w/M_p = 1.15 \text{ at } 5 \circ \text{C})$ at 1 atm ethylene. A telechelic polymer could be produced with 104a by addition of alkyl acrylates before the silane quench.²²⁶ Acrylates undergo one insertion into the growing chain, forming stable chelates, but do not insert further, allowing for clean end-functionalization to generate polymers with two distinct ester end groups. Additionally, aldehyde end groups could be generated by quenching with 4-penten-1-ol. The vinyl group inserts,

followed by Pd migration down the chain, and finally β -hydride elimination to generate the difunctional polymers are shown in Scheme 16.

Given that palladium diimine catalysts produce highly branched, amorphous materials with ethylene and produce semicrystalline polymers from long-chain α-olefins via a 'chain-straightening' mechanism, copolymers containing these two segments are an attractive goal. Gottfried and Brookhart²²⁶ investigated this block copolymer synthesis in detail. Using 104b (Figure 27), block copolymers of ethylene and 1-octadecene were prepared by opposite orders of addition furnish PE-*block*-poly(1-octadecene) to and poly(1octadecene)-block-PE. In all cases, materials with narrow molecular weight distributions were obtained $(M_w/M_n = 1.06 - 1.22)$. Depending on the order of monomer addition, the copolymer microstructures differed. When ethylene is introduced first, the number of ethyl and propyl branches decreases substantially relative to the case where 1-octadecene is added first.

Extending the study of **104a**, Zhang and Ye²³⁴ modified the palladium ester chelate by immobilization on a polyhedral oligomeric silsesquioxane (POSS) support (**109**, Figure 28), which furnished POSS end-functionalized PEs. The M_n was shown to increase linearly with time. In a subsequent report, Zhang and Ye²³⁵ immobilized the palladium ester chelate on silica nanoparticles as a versatile surface-initiated living ethylene polymerization technique for grafting from silica nanoparticles. After cleavage of the PE brushes from the silica nanoparticles, the polymers were found to possess narrow PDIs ($M_w/M_n \sim 1.18$).

Utilizing a triacrylate, Zhang *et al.*²³⁶ synthesized a trinuclear palladium α -diimine catalyst (110, Figure 28) for the production of star PE. At 5 °C in the presence of ethylene,



Scheme 16 Synthesis of telechelic polyethylene.

110 produced three-arm star polymers with narrow molecular weight distributions $(M_w/M_n = 1.05 - 1.12)$ and molecular weights $(M_n = 32\ 000 - 135\ 000)$ that increased over the course of 5 h. Cleavage of the star polymer revealed arm molecular weights $(M_n = 11\ 000 - 44\ 000\ g\ mol^{-1})$ that were approximately 3 times smaller than the corresponding star polymer. Analysis of the intrinsic viscosity of the polymer was consistent with star polymers exhibiting more compact chain conformation.

To synthesize graft copolymers, Brookhart and Matyjaszewski combined living insertion polymerization with living atom transfer radical polymerization (ATRP) techniques. Palladium diimine chelate complexes have been previously used for living polymerization of ethylene, affording end-functionalized, branched polyethylenes.²³⁷ Catalyst **111** (Scheme 17) builds on this strategy by appending an acrylate ester forming a PE macromonomer that was incorporated into a living ATRP of *n*-butyl acrylate to generate poly(*n*-butyl acrylate)-*graft*-PE. Graft copolymers of moderate molecular weight ($M_n =$ up to 115 000 g mol⁻¹) were obtained with

approximately 4–5 grafts per chain and relatively narrow molecular weight distribution (M_w/M_n as low as 1.4).

Combining living insertion polymerization with living ATRP techniques, Zhang *et al.*²³⁸ generated block copolymers with a functionalized palladium diimine catalyst. Catalyst **112** (Scheme 18) appended with bromo-functionality forms a PE macroinitiator that was incorporated into a living ATRP of *n*-butyl acrylate or styrene to generate poly(*n*-butyl acrylate)-*block*-PE and PS-*block*-PE diblock copolymers (Scheme 18).

3.23.6.1.4 Other monomers

To generate a series of poly(E-*co*-P) comb polymers, Rose *et al.*²³⁹ have polymerized poly(E-*co*-P) macromonomers. Using a nonliving titanium bis(phenoxyimine) catalyst (**113**, **Scheme 19**), poly(E-*co*-P) macromonomers featuring one unsaturated chain end were synthesized. The monomers contained a mixture of allyl (polymerizable) and propenyl (unpolymerizable) end groups. The macromonomers were then homopolymerized using a living nickel diimine catalyst,



Scheme 17 Graft copolymer synthesis using living insertion polymerization and ATRP.



Scheme 18 Synthesis of poly(*n*-butyl acrylate)-*block*-PE and PS-*block*-PE diblock-copolymers.



Scheme 19 Synthesis of poly(E-co-P) comb polymers.

97/MAO (Figure 26, Scheme 19), to generate poly(E-*co*-P) comb polymers featuring approximately 7–14 arms/molecule after fractionation from the unpolymerizable residual macromonomer; these values correspond well to the theoretical values based on reaction stoichiometry. The molecular weight distributions remained relatively low ($M_w/M_n = 1.51-1.90$, $M_n = 74\,000-209\,000\,\mathrm{g\,mol}^{-1}$).

Beyond unfunctionalized olefins, 97 is also capable of polymerizing olefin monomers that incorporate polar functional groups. Copolymers of polar monomers with olefins are attractive due to enhanced physical properties such as biocompatibility and ease of processing.³⁷ Rieth et al.²⁴⁰ synthesized polyolefin elastomers by addition of small amounts of ureidopyrimidone (UP)-functionalized hexene to polymerizations of 1-hexene. Nickel catalyst 97/Et₂AlCl (Figure 26) was used, exploiting the dual ability of Et₂AlCl to activate the nickel center and to protect the Lewis basic nitrogen functional groups. Polymers incorporating ~2% UP-functionalized monomer were obtained with narrow molecular weight distributions $(M_w/M_p = 1.2 - 1.4)$. The resultant polymers exhibited reversible, noncovalent cross-linking through hydrogen bonding interactions and thus have elastomeric properties at room temperature.

In addition to simple linear α -olefins, Park *et al.*²⁴¹ reported the polymerization of a number of 1,6-dienes catalyzed by palladium complexes to afford polymers with *trans*-1,2disubstituted five-membered rings. In a subsequent report, 114/NaBArF₄ was shown to polymerize 5-allyl-5-crotyl-2,2dimethyl-1,3-dioxane in a living fashion (Scheme 20).²⁴² A linear increase in M_n with monomer conversion was demonstrated with molecular weight distributions remaining relatively narrow ($M_w/M_n = 1.20-1.24$). Later, Takeuchi *et al.*²⁴³ reported that 97/MMAO was capable of polymerizing 9,9-diallylfluorene (Scheme 20) yielding a polymer with $M_n = 6100 \text{ g mol}^{-1}$ and $M_w/M_n = 1.36$ after 3 h. The resultant polymer contained predominately sixmembered rings with *cis* geometry as evidenced by ¹³C NMR spectroscopy.

The copolymerization of ethylene and diethyl diallylmalonate was investigated by Xiang et al.²⁴⁴ in 2009 using 115 (Figure 29). Due to extensive chain walking, ethylene homopolymerization produces polymer with a hyperbranched structure. Incorporation of the diethyl diallylmalonate reduces the amount of branching in the polymer produced because the catalyst is unable to chain-walk through the resultant five-membered ring. At 35 °C, 115 produced PE containing 97 branches/1000 carbons with $M_{\rm w} = 78000 \,{\rm g \, mol^{-1}}$ and a narrow molecular weight distribution $(M_w/M_n = 1.44)$. Upon incorporation of diethyl diallylmalonate (0.40 M), molecular weight $(M_{\rm w} = 25\,000\,{\rm g\,mol^{-1}})$ and polydispersity $(M_w/M_p = 1.20)$ decreased along with branch density, which was reduced to 81/1000 carbons. Therefore, polymer topology can be tuned from hyperbranched to linear as a function of diethyl diallylmalonate incorporation.

Finally, Kiesewetter and Kaminsky²⁴⁵ applied a combinatorial screening approach to identify catalysts for the copolymerization of NB with ethylene. Catalysts **116a** and **116b** (Figure 29) were identified and they furnished poly (E-*co*-NB) with 9–62 mol.% NB incorporation and relatively narrow molecular weight distributions (M_w/M_n as low as 1.4) indicating 'quasi-living' behavior.



Figure 29 Nickel and palladium complexes for olefin polymerization.

3.23.6.2 Nickel *α*-Keto-*β*-diimine Catalysts

Bazan and coworkers^{246,247} recently described the synthesis and olefin polymerization behavior of a nickel α-keto-β-diimine complex. At 0 °C, activation of 117 (**Figure 29**) with MAO in the presence of 1-hexene furnished *a*PH possessing $M_n = 157000 \text{ g mol}^{-1}$ and $M_w/M_n = 1.2$. Over the course of 120 min, molecular weights of the polymers obtained from the polymerization were observed to increase while polydispersities remained narrow. Microstructural analysis of the polymer by ¹³C NMR spectroscopy revealed mainly butyl (81.9%) and methyl (12.0%) branches; signatures arising from 2,1-insertions were not detected.

In addition to polymerizing 1-hexene in a living fashion, Bazan and coworkers^{246,247} reported that 117/MAO (Figure 29) was living for propylene polymerization. At 0 °C, 117/MAO furnished high molecular weight PP $(M_n = 138000 \text{ g mol}^{-1})$ with narrow polydispersity $(M_w/M_p = 1.1)$. Over the course of 120 min, molecular weights of the polymers obtained from the polymerization increased while molecular weight distributions remained narrow. Analysis of the resultant polymers showed no evidence of 2,1-insertions. The material is best described as an ethylenepropylene copolymer; however, observed propylene sequences are moderately isotactic ([m] = 0.77).

Bazan and coworkers^{246,247} have also shown that 117/MAO (Figure 29) is living for ethylene polymerization. At 10 °C, 117/MAO produces branched PE (19 branches/1000 carbons) with $M_n = 260\,000\,\mathrm{g\,mol^{-1}}$ and $M_w/M_n = 1.1$. Due to the small amount of branching, the PE exhibits a $T_{\rm m}$ = 122 °C. At 32 °C, high molecular weight ($M_{\rm p} = 1.112000 \,\mathrm{g \, mol^{-1}}$) branched PE (47 branches/1000 carbons) is obtained with a slightly broadened polydispersity $(M_{\rm w}/M_{\rm n} = 1.3).$ The carbonyl functionality leads to an increase in activity of approximately 2 orders of magnitude for ethylene polymerization over the analogous β -diimine catalyst (118, Figure 29) with no carbonyl functionality. The increase in reactivity was attributed to the attachment of a Lewis acid (from the aluminum cocatalyst) to the exocyclic oxygen site on the propagating cationic species.

3.23.6.3 Other Nickel Catalysts

Hicks *et al.*²⁴⁸ have also investigated a series of anilinotropone-based nickel catalysts **119a–119c** (Figure 30). Upon activation by Ni(COD)₂, high activities and long lifetimes were observed for the polymerization of ethylene, particularly in the aryl-substituted cases, **119b** and **119c**. Over time, the M_n was shown to increase in a nearly linear fashion with polydispersities remaining relatively narrow (as low as 1.2) at room temperature. However, increasing both the



Figure 30 Nickel precatalysts for olefin polymerization.

reaction temperature and time leads to a subsequent increase in polydispersity.

In 2009, Yang *et al.*²⁴⁹ reported the synthesis of α -aminoaldimine nickel complexes (**120a–120e**, **Figure 30**) for ethylene polymerization. After 3 h at 25 °C, **120d**/MAO produced polyethylene with high molecular weight ($M_n = 164\ 000\ \text{g}\ \text{mol}^{-1}$) and narrow molecular weight distribution ($M_w/M_n = 1.31$). Increasing reaction time to 24 h resulted in an increased molecular weight ($M_n = 393\ 000\ \text{g}\ \text{mol}^{-1}$) while maintaining a narrow polydispersity ($M_w/M_n = 1.23$).

Finally, Bazan and coworkers^{250,251} have investigated nickel diimine variants 121a–121g (Figure 30). At 20 °C, 121a/Ni (COD)₂ produced PE with low branching (12–19 methyl branches/1000 carbons) and M_n was observed to increase linearly with time up to 30 min. Additionally, the molecular weight distributions remained narrow for all the catalysts studied (M_w/M_n =1.1–1.4). Investigation into the role of the ligand revealed that as the steric bulk increased an increase in polymerization activity was observed.

Utilizing **121**, Bazan and coworkers^{250,251} achieved the first quasi-living copolymerization of ethylene with a polar monomer, 5-norbornen-2-yl acetate. Upon activation with Ni (COD)₂, **121a–121g** (Figure 30) incorporated 1–17 mol.%

5-norbornen-2-yl acetate into a polyethylene backbone. Molecular weight distributions were relatively narrow $(M_w/M_n = 1.2-1.6)$, and the M_n exhibited a nearly linear increase with conversion. To synthesize block copolymers with different ratios of ethylene, Diamanti et al.²⁵² adopted a strategy based on a pressure-jump technique. Polymerization of 5-norbornen-2-yl acetate and 50 psi ethylene generates an amorphous copolymer with approximately 25% polar monomer incorporation. After a given reaction time (8-45 min), the ethylene pressure was increased to 1100 psi leading to the formation of an essentially PE block (Scheme 21) with relatively narrow polydispersities ($M_w/M_n = 1.3-1.6$). Analysis of GPC and DSC data is consistent with diblock formation. TEM analysis demonstrated that the materials are microphase separated, consistent with blocks of distinct compositions. Tapered copolymers (TCP) have also been prepared with this system that allows depletion of 5-norbornen-2-yl acetate under a constant ethylene pressure.²⁵³ It was observed that as 5-norbornen-2-yl acetate concentration depletes semicrystalline properties are obtained after specific reaction times, consistent with the fact that ethylene-rich segments are formed indicating pseudo-diblock copolymer formation. This strategy was used to make pseudo-tetrablock copolymers by addition of a second



Scheme 21 Synthesis of ethylene/5-norbornen-2-yl acetate block copolymers using 121a.



Scheme 22 Synthesis of PE-graft-PMMA copolymers using 121c and ATRP.

batch of 5-norbornen-2-yl acetate after a prescribed time.²⁵⁴ Tensile testing revealed a strain at break of about 1000% at 65 °C with 80% elastic recovery.

In a later report, Schneider *et al.*²⁵⁵ combined living insertion polymerization with living ATRP techniques to synthesize graft copolymers. Polymerization of ethylene followed by copolymerization with 5-norbornen-2-yl-2'-bromo-2'-methyl propanoate using **121c** (Figure 30) activated with Ni(COD)₂ furnished a PE macroinitiator. Subsequent polymerization with MMA by living ATRP methods furnished PE-graft-PMMA copolymers (Scheme 22).

3.23.6.4 Other Palladium Catalysts

The field of palladium-mediated living olefin polymerization was advanced in 1995 by Safir and Novak²⁵⁶ with the design of σ , π -bicyclic Pd catalyst **122** (Figure 31), which is both highly air- and moisture-stable, due to chelation by the appended olefin, but exhibits good activity for living polymerization. This unique, robust living behavior was demonstrated by the synthesis of well-defined block copolymers of NB and diethyl 7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate. A subsequent retro-Diels–Alder reaction on this polymer afforded a discrete PNB-*block*-poly(acetylene) copolymer.

While investigating another palladium complex, Mehler and Risse²⁵⁷ reported on the polymerization of NB in a controlled fashion with catalyst **123** (Figure 31) to obtain saturated polymers. Renewed chain growth was observed with sequential addition of monomer, but only for low conversion. At 0 °C, narrow molecular weight distributions were obtained for short reaction times ($t_{rxn} = 20$ min; 54% conversion; $M_{\rm n} = 21400 \,{\rm g}\,{\rm mol}^{-1}$; $M_{\rm w}/M_{\rm n} = 1.07$), but broadened as conversion increased ($M_{\rm w}/M_{\rm n} = 1.34$ at 100% conversion). Breunig and Risse²⁵⁸ also showed that **123** polymerized a wide variety of ester-functionalized NBs, in some cases with narrow molecular weight distributions, and with linear increase in $M_{\rm n}$ over time. Sequential addition of an NB monomer with different substitution pattern afforded diblock copolymers of moderate molecular weight.

3.23.6.5 Monocyclopentadienyl Cobalt Catalysts

In 1991, Brookhart *et al.*²⁵⁹ identified Cp^{*} cobalt complex **124** (Figure 31) as a competent catalyst for polymerization of ethylene in a controlled fashion to low molecular weights $(M_n = 13\ 600\ \text{g mol}^{-1};\ M_w/M_n = 1.17)$. Soon thereafter, aryl or silyl groups were introduced in the catalyst framework that prevent chain migration and allow for the production of a variety of end-functionalized PEs under living conditions.²⁶⁰ Reaction of **125a–125e** (Figure 31) with ethylene led to the formation of aryl-substituted PEs with quite narrow molecular weight distributions $(M_n$ up to 21 200 g mol⁻¹; $M_w/M_n = 1.11-1.16$). Triethylsilane-capped PEs were furnished with catalyst **126** $(M_n = 16\ 100\ \text{g mol}^{-1};\ M_w/M_n = 1.15)$.

3.23.7 Outlook and Summary

The last decade has seen significant new advances achieved in the field of living olefin polymerization. Many efficient and selective catalysts are now available for the living polymerization of ethylene in addition to living and stereoselective



Figure 31 Palladium and cobalt precatalysts for olefin polymerization.

polymerization of α -olefins, resulting in the creation of unlimited new polymer architectures, such as block copolymers and end-functionalized macromolecules. The ability to synthesize such polymers will allow the detailed study of the effect of polymer microstructure on the mechanical and physical properties of this new class of materials.

As we wrote in our previous reviews, 2^{-4} the main challenge facing this new field is that these expensive metal complexes only form one polymer chain during the polymerization reaction, resulting in economically nonviable materials for commodity applications. Significant research in developing catalytic systems that can produce multiple chains per metal center must be conducted. One strategy to accomplish this goal is to add excess amounts of an inexpensive metal complex that will rapidly transmetallate the active living catalyst, producing many chains per metal center.94-96,261-265 This strategy can then be used to create multiple block copolymers per metal center by varying polymerization conditions.^{83,266} A second strategy is to add an external agent at specific intervals during the living polymerization to terminate a chain and begin a new one.¹⁷⁰ Third, metal complexes that transmetallate at rates slower than monomer enchainment but faster than chain formation have the potential to produce block copolymers when two different polymerization catalysts are used. 25,26,267-269 Finally, nonliving catalysts that can be induced to introduce blocks on a timescale faster than that of chain formation can be used to make block copolymers.²⁴

Future research will continue to uncover new living systems capable of making unique polyolefin structures, and these advances will greatly expand the range of polyolefin materials. New strategies for developing catalyst systems capable of furnishing multiple chains per metal center will allow commodity polyolefin production from living catalysts. Undoubtedly, the future for specialty materials is a bright one in light of continued new developments in the field of living olefin polymerization.

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3.24 Copolymerization of Alkenes and Polar Monomers by Early and Late Transition Metal Catalysts

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3.24.1	Introduction	779
3.24.2	Coordination of Polar Groups to Transition Metals: Challenges for the Copolymerization of Olefins	
	with Polar Comonomers	781
3.24.2.1	Early Transition Metals: Inhibition by σ -Coordination	781
3.24.2.2	Late Transition Metals: Coordination and Insertion of Olefins	781
3.24.2.2.1	Influence of the olefin coordination equilibrium	782
3.24.2.2.2	Insertion of olefins into alkyl-metal bonds	782
3.24.2.2.3	Competing σ -coordination of polar olefin comonomers	783
3.24.2.2.4	Coordination of acrylonitrile: an example for the challenge to copolymerize ethene with polar functionalized olefins	783
3.24.3	Methods for the Synthesis of Polar Copolymers with Early Transition Metals	784
3.24.3.1	Direct Copolymerization of Polar Momoners and α -Olefins	784
3.24.3.1.1	Borane-containing olefins	784
3.24.3.1.2	Silicon-containing olefins	786
3.24.3.1.3	ω-Functionalized olefins	789
3.24.3.2	Copolymerization of Sterical Demanding Polar Olefins and α -Olefins	792
3.24.3.2.1	Ether-functionalized olefins	792
3.24.3.2.2	Amino-functionalized olefins	792
3.24.3.2.3	Norbornyl ester-derivatized olefins	794
3.24.3.3	Copolymerization of Polar Olefins and α -Olefins with Protecting Groups	794
3.24.3.3.1	Trialkylsilyl-protected olefins	794
3.24.3.3.2	Lewis acidic protective groups – aluminium alkyl compounds	796
3.24.3.3.3	Lewis acidic protective groups – titanium-based compounds	807
3.24.4	Late Transition Metals in the Copolymerization of Functional and Nonpolar Olefins	808
3.24.4.1	The Strictly Alternating Copolymerization of Carbon Monoxide and α -Olefin Comonomers	808
3.24.4.1.1	General information	808
3.24.4.1.2	Polymerization mechanism for the α -olefin carbon monoxide copolymerization with chelating bis-phosphine	
	palladium catalysts	808
3.24.4.1.3	Influence of the catalyst structure on the ethene carbon monoxide copolymerization	810
3.24.4.1.4	Propene carbon monoxide copolymerization: regio- and stereoselectivity	811
3.24.4.1.5	The terpolymerization of ethene, propene, and carbon monoxide	813
3.24.4.1.6	Introduction of functional groups into olefin carbon monoxide copolymers	813
3.24.4.2	α -Diimine Catalysts for the Synthesis of Branched Functional Copolymers	813
3.24.4.2.1	General information about α -diimine late transition metal catalysts	813
3.24.4.2.2	The copolymerization of ethene and polar functionalized olefins with α -diimine-based catalysts	814
3.24.4.3	Phosphine Sulfonate-Based Catalysts: Synthesis of Linear Copolymers of Ethene and Functionalized Olefins	816
3.24.4.3.1	General information for the phosphine sulfonate catalyst system	816
3.24.4.3.2	Complex formation	816
3.24.4.3.3	Homopolymerization of ethene	817
3.24.4.3.4	Copolymerization of ethene and polar comonomers: mechanism for the copolymerization of polar	
	comonomers with phosphine sulfonate-based catalysts	818
3.24.4.3.5	Examples of polar olefins in the copolymerization with ethene	818
3.24.5	Conclusion	820
References		820

3.24.1 Introduction

To date, polyolefins – specifically polyethene (PE) and polypropene (PP) – are the most important commercial polymers. Due to the combination of their excellent chemical and physical properties and their low production costs, these materials find extremely broad application. Since the discovery of a coordinative insertion polymerization by Ziegler in 1953, great efforts have been made to optimize both heterogeneous and homogeneous polymerization catalysts to further improve their activities and stabilities and to introduce the possibility of producing polyolefins with a wide variety of tacticities. In the case of stereoselective polymerization with PPs, today polymeric products can be achieved with specific tacticities ranging from atactic through syndiotactic and isotactic, and almost every combination in-between.^{1,2} Thus, PP properties

779

ranging from waxes to elastic up to thermoplastic behavior with high strength and stiffness can be afforded. Variation of the polymer properties for PE by control of the branching degree was achieved by Brookhart and coworkers who developed a variety of nickel and palladium α -diimine catalysts that are able to produce highly branched PE with the so-called 'chain walking' mechanism.³ Unfortunately, these catalysts are not stable against hydrogen that is used as a chain termination agent in order to control the molecular weight. Subsequently, hydrogen-stable, terphenyl-based α -diimine catalysts were developed by Meinhard *et al.* combining this important feature with the high stability toward functional groups and polar solvents of the parent catalyst system.⁴

An alternative approach to modulate the polymer properties is to produce a copolymer, from two monomers where one monomer gives rise to a hard segment and the other affords a softer segment. A block-like structure can be achieved by using two different catalysts that are capable of polymerizing only one of the two monomers and a chain shuttling agent that is able to transfer a growing polymer chain between the different catalytic centers.^{1,5} As can easily be seen, all of these polymers have one major drawback - a lack of polar functionality along the polymer backbone. Polar functional groups are, for example, very important for a good adhesion on substrates such as glass or ceramic, for a good printability or dyeability. Introduction of functional groups into a polymer chain can be achieved principally in two ways; one approach is a direct incorporation during the polymerization process through a direct copolymerization of an α-olefin with a polar comonomer or by end-group functionalization via a controlled termination reaction with polar compounds. The second method is the chemical modification of preformed polymers. The great advantage of the good chemical resistance for these polyolefins becomes a huge drawback in possible postmodification reactions. Under normal reaction conditions, a postmodification process is not possible in most cases. One possibility is a free radical grafting process with compounds containing polar groups,

for example, maleic anhydride. This free radical grafting reaction is typically carried out at temperatures of up to 200 °C. These harsh conditions also lead to polymer degradation and crosslinking.^{6,7} Another postmodification proceeds via carbenes that can react in their singlet state, suppressing significantly free radical side reactions such as degradation or crosslinking. Carbenes can be formed in a thermal manner by using diazoesters like ethyldiazoacetate or catalytically.⁶ For the aforementioned end-group functionalization during the polymerization process, several chain transfer agents are available. There are electron-deficient/neutral and electron-rich chain transfer agents that are known to proceed by different pathways (Figure 1).⁸

As electron-deficient or neutral chain transfer agents, silanes, boranes, and alanes are known and extensively investigated in single-site-catalyzed olefin polymerization in order to obtain heteroatom-functionalized chain ends. Electron-rich chain transfer agents, such as phosphines and amines, have also been studied on organolanthanide-mediated polymerization systems.⁸

Block copolymers consisting of an α-olefin block and a polar polymer block can be produced with a catalytic system that is able to polymerize the α -olefin by a coordinative insertion polymerization process and the polar comonomer in a coordinative group transfer polymerization or a radical process. This kind of polymerization with group 4 and rare earth metal metallocene complexes is not covered in the scope of this chapter. Further information on this topic can be found in the literature.9 Another possible reaction route, which will be the focus of this review, is a direct catalytic copolymerization of α-olefins and polar comonomers, leading to randomly distributed copolymers. Principally all catalysts known to polymerize α -olefins can be used for this kind of copolymerization; however, especially in the case of the early transition metal catalysts, the polar group typically leads to a poisoning of the catalyst. Possible ways to avoid a deactivation of the catalyst is to use only weakly coordinating functional groups, or to protect the polar groups by using sterically demanding substituents or by



Figure 1 Catalytic cycle for single-site-mediated olefin polymerization in the presence of: (left): electron-deficient chain transfer agents. P = polymer chain, E = Si, B, Al; R = alkyl, aryl; (right): electron-rich chain transfer agents. P = polymer chain, E = P, N; R = alkyl, aryl.

adding additional Lewis acids such as tri-iso-butylaluminum (TIBA). Over the past few years, reduction of Lewis acidity in early transition metal-based catalysts by ligand modification led to interesting new developments in homo- and copolymerization reactions with polar monomers. This concept is also viable for late transition metal-based catalysts, which are known to be more stable toward polar groups and thus are able to produce copolymers without any protection techniques. However, decreasing polymerization activities observed with increasing concentration of the polar comonomer still remains a challenge. Additionally, formation of intermediate catalyst resting states by 'backbiting', a coordination of functional groups in the growing polymer chain to the catalyst, imposes severe consequences for the reaction mechanism. Despite these problems, drastic advancements in the unproinsertion tected copolymerization of fundamental functionalized olefins (FOs), such as methyl acrylate (MA), acrylonitrile (AN), and others, has been achieved in the past few years.^{3,10} Due to the large number of reports on late transition metal-catalyzed copolymerization reactions, the discussion will be restricted to the three best-known and most important catalyst systems. These are the copolymerization and terpolymerization of olefins with carbon monoxide by bisphosphine palladium complexes as well as a-diimine and phosphine sulfonate-based palladium catalysts.

3.24.2 Coordination of Polar Groups to Transition Metals: Challenges for the Copolymerization of Olefins with Polar Comonomers

3.24.2.1 Early Transition Metals: Inhibition by σ -Coordination

In the case of the Lewis acidic early transition metal polymerization catalysts, there is always a significant competition between the desired η^2 -coordination (π -coordination), leading to a migratory insertion polymerization, and the direct coordination of the polar group (σ -coordination). In most of the cases, the more Lewis acidic early transition metals undergo a fast deactivation after addition of the polar comonomer. As will be later discussed in detail in Section 3.24.3.3, one possibility to overcome a fast deactivation via the direct coordination of the polar comonomer to the active site of the metal is realized by a protection group technique. There exist only a few publications concerning the coordination of the polar comonomers in the case of the early transition metal catalysts. One concerns an NMR spectroscopic study using the depicted ethers with $Cp_2ZrMe_2/B(C_6F_5)_3$ as catalyst system (Figure 2), and clearly shows the dependency of the electronic and steric effect of the protection group upon the ability of a η^2 -coordination versus a direct coordination of the functional group.¹¹ Increasing steric encumbrance leads to



Figure 2 σ - and π -coordination of various ethers on a zirconocene cation.

reduced coordination of the ether group to the cationic zirconium center. The silylethers are, in addition to the increased steric bulk on the oxygen functionality, less Lewis basic because silicon is known to efficiently delocalize the π -electrons of the oxygen atom and hence coordination via the oxygen atom is inhibited.

3.24.2.2 Late Transition Metals: Coordination and Insertion of Olefins

The two most prominent examples of catalysts in the late transition metal-catalyzed ethene homopolymerization are the Ni- or Pd-based α -diimine 1 and phosphine sulfonate-based 2 catalysts (Figure 3).

Despite the fundamental similarity of employing the same metals, different catalyst structures entail different reaction pathways leading to drastically varying polymer architectures and hence polymer properties. The α -diimine system, on the one hand, normally produces branched to highly branched PE.³ On the other hand, phosphine sulfonate-based Pd(II) catalysts produce highly linear PE.¹² This behavior can be attributed to the reaction mechanism itself. Prominent feature in the α-diimine catalyst system is the chain walking mechanism where the metal can move along the polymer chain by a series of fast β -hydride eliminations, reorientation, and reinsertion steps. The equilibrium of chain walking as well as coordination and insertion of ethylene in the chain propagation is dependent on the catalyst structure as well as the reaction conditions (Scheme 23). In progression from the 2,6-di-iso-propylsubstituted catalysts of Brookhart and coworkers³ to the terphenyl system of Meinhard et al.,⁴ the branching is significantly reduced (from 50-100 branches to 8-40 branches per 1000 carbon atoms) (Figure 4).

The high activity and stability as well as the high obtained molecular weights of these complexes can be attributed to a blocking of the axial positions, which protect the growing polymer chain toward incoming molecules (e.g., ethene or hydrogen).

By comparison of the α -diimine catalysts with the phosphine sulfonate-based palladium catalyst system, the change from a symmetric to an asymmetric ligand structure is apparent on first sight. Here (as well as in other ligand systems; Section 3.24.4.1.4), it could be shown that this leads to major differences in reactivity. Despite the partially open catalyst structure, these complexes are of remarkable stability and activity in



Figure 3 Generalized structure of the α -diimine 1 and phosphine sulfonate 2 catalyst systems, various possibilities for substitution and ligands (R₁, R₂, L) can be found in the literature.



Figure 4 2,6-Di-*iso*-propyl 3- and terphenyl 4-based α -diimine catalysts, various possibilities for substitution and ligands (R₁, R₂, L) can be found in the literature.



Figure 5 Highly sterically challenging phosphine sulfonate by Skupov *et al.*¹³

the production of PE with a high degree of linearity (1–10 branches per 1000 carbon atoms). This contradicts, on the first glance, the principle for protection of the active site by steric bulk of the ligand. Again it was shown that catalysts activity as well as structure and molecular weight of the obtained homopolymers are dependent on the catalyst. Confusingly, steric bulk of the ligand in the proximity of the metal center has a controversial influence. The report from Skupov *et al.*¹³ on an extremely bulky phosphine sulfonate 5 (Figure 5) shows exceptionally high molecular weights and high activity in the homopolymerization of ethene, in line with the observations of Brookhart.

However, the direct comparison of phenyl-, naphthyl-, anthracenyl-, and phenanthryl-substituted phosphine sulfonate-based catalysts showed both a reduction of obtained molecular weights and catalyst activity.14 Detailed experimental and theoretical investigations showed that the asymmetric nature of the phosphine sulfonate ligand leads to a site preference for the additional ligands (olefins, base, and growing polymer chain/alkyl group), which destabilizes alkyl groups (or the growing polymer chain) on the position trans to the phosphorus ligand and additionally protects the catalyst from decomposition or chain termination.¹² Change of the metal from neutral Pd(II) to neutral Ni(II) complexes with phosphine sulfonate ligands is possible and leads to ethene polymerization catalysts. Unfortunately, in contrast to the Pd (II) complexes, no copolymerization with polar comonomers could be performed.15-1

Three effects for the polymerization reaction with polar functionalized olefins have to be considered; each of them attributed to different spots in the reaction pathway. First, the coordination of the olefin to the metal center has to be noted. Here, the binding strengths of the respective comonomers have to be considered, along with the resulting equilibrium between coordinated ethene and the respective functionalized olefin. Following step after this coordination of olefins is their insertion into the metal–alkyl bond of the catalyst. Functionalization can have a significant influence on the insertion rate as well as on the orientation of the monomer during the insertion. This can lead to a control of the insertion regioselectivity. Lastly, the ability of polar functionalized olefins to form σ -bonds via their polar groups instead of π -bonds via the olefin has an influence of the reactivity and can lead to unfortunate restrictions in the olefin pool.

3.24.2.2.1 Influence of the olefin coordination equilibrium

A key requirement for insertion polymerization of olefins is their ability to form π -coordination complexes with metal complexes. In electron-deficient late transition metal complexes, the coordination of electron-rich olefin monomers is stronger than that in olefins with electron withdrawing (EWG) functional groups. Confirmation for this logic supposition was provided via density functional theory (DFT) calculations. It was shown that the strength of the coordination is proportionally linked to the energy level of the olefin HOMO (highest occupied molecular orbital), which is normally represented by the π (C=C) orbital. The reason is the strong electron donation from this π (C=C) orbital to a vacant d_{σ} orbital of the metal. This dominates the back donation from the metal d_{π} orbital to the $\pi^*(C=C)$ (LUMO, lowest unoccupied molecular orbital) orbital of the olefin. Functionalization of an olefin with an EWG lowers the energy of the HOMO and thus the overall strength of the coordination. An overview concerning calculated HOMO/LUMO energies and coordination energies in some complexes can be found in the literature.^{10,18} Additionally, the calculations showed a strong influence of the coordination strength for ethene on the overall charge of the metal complex. In all reports, the binding strength to the electron-rich monomer decreases in the following order: cationic > neutral > anionic metal complex.¹⁹

Brookhart and coworkers³ showed that the incorporation of olefins in copolymerization experiments with α -diimine complexes is in first approximation dependant on the equilibrium of the employed olefin monomers. The insertion rate into the metal–carbon bond as well as the formation of coordinative resting states by coordination of functional groups is neglected for now. Furthermore, it could be shown that this equilibrium is a result caused by the respective monomers, their concentrations, and the reaction conditions.

3.24.2.2.2 Insertion of olefins into alkyl-metal bonds

Experimental observations as well as theoretical calculations show that the insertion rate of polar functionalized olefins and ethene are usually comparable. Some electron-poor functionalized olefins have reduced insertion barriers compared to ethene, resulting in a faster insertion.²⁰

In asymmetrically substituted olefins, the regioselectivity of the insertion reaction is a critical point that has to be considered. Again theoretical calculations as well as experimental observations agree on a predominant 2,1-insertion mechanism



Scheme 1 Regioselectivity of the insertion for functionalized olefins.

for late transition metal-catalyzed copolymerization reactions (Scheme 1).

The regioselectivity can be assumed as a cooperative result of steric and electronic effects. The latter can be explained as follows:

- In EWG functionalized olefins, the LUMOs are relatively stable but possess similar coefficients for the sp^2 carbon orbitals ($2p_z$). Furthermore, the calculations show no remarkable charge separation within the olefin molecule. Therefore, it can be assumed that steric reasons lead to the favorable 2,1-insertion.
- Electron-rich olefins (e.g., propene and methyl vinyl ether), on the other hand, show a different insertion behavior (no predominant insertion and 1,2-insertion, respectively). The substituted olefins now show a considerable charge separation where the positive charge is mainly located on the substituted carbon atom. This results in a negation of the steric preferences in some olefins. However, with high steric hindrance, the 1,2-insertion is again unfavorable and the 2,1-insertion predominantly occurs.²⁰
- Additionally, control of the regioselectivity via the ligand structure or chain end control have to be considered for the orientation and insertion of substituted olefins. Interesting examples herefore can be found in the chiral copolymerization or carbonlyation of olefins with carbon monoxide.²¹

3.24.2.2.3 Competing $\sigma\text{-}coordination$ of polar olefin comonomers

Despite the fact that late transition metal catalysts are exceptionally stable to polar functionalities and polar solvents (in comparison to early transition metal catalysts), there are several points to be considered upon addition of functional groups to a reaction mixture.

As in early transition metal-catalyzed copolymerization reactions, functionalized olefins can form either σ - or π -coordination compounds with late transition metal complexes (Scheme 2). The σ -coordination prevents π -coordination of olefins and thus lowers the overall copolymerization rate. The rate drop is directly proportional to the σ -coordination strength. Application of a large excess of the nonpolar olefin can reduce this negative influence of σ -coordination by increasing the concentration of competing olefin.







Figure 6 Backbiting of the growing polymer chain to form a five-membered chelate in a bis-phosphine Pd system for the copolymerization of C0 with ethene (anion omitted).

In copolymerization experiments with polar comonomers (e.g., carbon monoxide or MA), an interesting phenomenon can be observed. This is the so-called 'backbiting' mechanism, where the growing polymer chain tilts back and the metal is stabilized by a chelating coordination (usually five- or six-membered ring) of a functional group on the polymer chain. Details for this reaction will be explained further in Section 3.24.4.1.2(ii) (Figure 6).

Due to these stable catalyst resting states, a further monomer coordination and insertion is retarded, which results in an overall decrease in polymerization rate. Depending on the nature of the coordinating functional group, the polymerization is either slowed or completely halted. Brookhart and coworkers³ showed this for α -diimine catalysts where a significant rate reduction could be observed for oxygen-containing functional comonomers and the copolymerization was usually halted in presence of nitrogen containing functional groups. Additionally, the incorporation of EWG functionalized olefins disfavors following insertions of these comonomers due to the strong EWG character of the polar functionalities in α -position of the growing polymer chain due to 2,1-insertion.^{22,23}

3.24.2.2.4 Coordination of acrylonitrile: an example for the challenge to copolymerize ethene with polar functionalized olefins

Not only the highly Lewis acidic early transition metal-based polymerization catalysts suffer from poisoning by coordination of functional groups. Even in late transition metal-based complexes, the possible σ -coordination in certain functional groups has a negative impact on polymerization reactions. The prominent example here is the still ongoing search for active acrylonitrile (AN) copolymerization catalysts. This reaction can serve as an ideal example to illustrate the challenges in late transition metal-catalyzed insertion polymerizations with polar functionalized comonomers. The metal-mediated copolymerization of AN has numerous appearances in literature; however, in most cases, the reaction mechanism seems to be of ionic or radical nature.

Deubel and Ziegler^{24,25} showed by theoretical investigation that the coordination behavior of AN has a dependence on the formal charge of the metal center of the catalyst. That means in cationic α -diimine complexes the AN favors σ -coordination, whereas in neutral salicylaldiminato ligand-based Pd(II) or Ni(II) complexes the probability of σ - and π -coordination is equal. Concerning the insertion regioselectivity, 2,1-insertion is assumed due to the reasons presented in Section 3.24.2.2.2. Wu et al.²² investigated the insertion reaction of AN in symmetric (N^N) chelating ligands. It was shown that the first insertion of an AN unit into the Pd-Me bond takes place in a facile manner but no second insertion occurs as AN is not able to break the relatively strong bridging unit in the resulting PdCHEtCN-Pd aggregates. Furthermore, the formed complexes cannot react with ethene at room temperature. Cleavage of these aggregates by addition of a Lewis acid $(B[C_6F_5]_3)$ is possible, but the EWG in α -position inhibits the insertion reaction. In general, these experiments showed that AN coordination can compete with ethene coordination despite its weaker π -coordination and insertion rate. A second report concerning neutral (P^P) chelating ligands also showed the initial first AN insertion product (2,1-insertion) but no further reaction with ethene or CO.²⁶

By way of comparison, Groux *et al.*²⁷ studied the complexation of AN in neutral and anionic salicylaldiminato complexes. Here, it could be shown that these complexes can oligomerize AN. Furthermore, the oligomerization could be slightly enhanced by the introduction of a negatively charged substituent, which results in an overall negatively charged Pd complex. Unfortunately, these complexes have a high tendency to agglomerate in trimeric structures inhibiting polymerization and oligomerization (**Figure 7**).

Overall, it can be concluded that the insertion of AN is not a limiting factor in this system and that it occurs in a 2,1-fashion. Copolymerization with other monomers could not be achieved under the mild conditions required for the handling of these AN insertion complexes.

To date, the only example of an AN copolymerization reaction with ethene was reported by Kochi *et al.*²⁸ Here, the phosphine sulfonate-based Pd catalyst was able to give several AN insertions in a linear PE backbone (Scheme 3).

The resulting polymer can possess AN end groups on either side and the insertion ratio is approximately 1:1:2 (start:end: backbone AN units). The PE backbone structure of these small



Figure 7 Generic structure of trimerization products occurring during the oligomerization of acrylonitrile as observed by Groux *et al.*²⁷



Scheme 3 Copolymerization of acrylonitrile with ethene promoted by a phosphine sulfonate catalyst.

copolymers is highly linear and therefore a radical copolymerization process was excluded as radically polymerized copolymers would posses internal branching. A very recent comparison of different catalyst systems by DFT calculations indicate the high barrier for β -hydride elimination in phosphine sulfonate Pd(II)-based catalysts as the critical feature enabling the copolymerization of ethene and AN. Other systems show either no incorporation, insertion and agglomeration, or fast decomposition of the catalyst after incorporation of an AN unit.²⁹

In summary, it can be concluded that the monomer insertion itself is not the main obstacle in the search for catalysts capable of the copolymerization of AN and, for example, ethene. However, the major challenges lie in the prevention of σ -coordination of nitrile groups and AN to the metal that lowers the ratio of π -coordinated AN needed for the reaction by a strong blockage of the coordination sites as well as the reduced olefin insertion rate into nitrile-substituted metal–alkyl groups and the stability of insertion products. This example nicely illustrates the three important prerequisites for insertion polymerization of olefins with polar comonomers: (1) the coordination equilibrium, (2) the insertion rate and regularity, and (3) inhibition by σ -coordination and backbiting/aggregation.

3.24.3 Methods for the Synthesis of Polar Copolymers with Early Transition Metals

3.24.3.1 Direct Copolymerization of Polar Momoners and α -Olefins

3.24.3.1.1 Borane-containing olefins

The use of borane-containing monomers in the copolymerization of olefins with early transition metals was investigated by Chung et al. in the late 1990s.³⁰⁻³⁴ The initial idea for the borane approach was based on the unique location of boron in the Periodic Table. As an element of Group 13, it has electron-deficient properties, thus giving the chance to coexist in copolymerizations with early transition metals with minimal risk of poisoning the catalyst. Additionally, it is a nonmetallic element, adjacent to carbon, resulting in a similar behavior. So the borane-containing copolymers behave in a similar manner to the hydrocarbon homopolymers. This results, on the one hand, in the possibility to incorporate high amounts of comonomer in the resulting copolymer and, on the other hand, in a very similar behavior, compared to the corresponding hydrocarbon homopolymer, during the polymerization process.

A further advantage of borane-containing polymers is the easy access to a broad variety of functional groups via conversion of the borane groups under mild chemical conditions. In addition, the borane groups, or the newly formed functional groups can serve as initiator to obtain grafted copolymers. With these techniques, Chung *et al.* produced a wide range of functional copolymers.^{30,32–37} Scheme 4 illustrates some modification routes emerging from the borane-containing polymer.

3.24.3.1.1(i) Direct copolymerization of aliphatic α -olefins and borane-containing monomers with early transition metal catalysts

Chung *et al.* compared different catalytic systems with respect to their catalytic activity and their borane incorporation during copolymerization reactions.^{35,38,39} For this purpose, they used



Scheme 4 Possible modifications of the borane-containing polymer.



Figure 8 Used zirconocenes for the incorporation of borane-containing monomers.

a heterogeneous Ziegler–Natta-type catalyst (TiCl₃·AA (aluminum activated)/Et₂AlCl), as well as the homogeneous complexes ethene-bis(1- η^5 -indenyl)zirconium dichloride 6, and bis (η^5 -cyclopentadienyl)zirconium dichloride 7 (Figure 8).

As the borane-containing comonomer, 5-hexenyl-9-borabicyclo[3.3.1]nonane (5-hexenyl-9-BBN) was used together with ethene or one of the higher homologs up to 1-octene. In the copolymerization with ethene and the different catalytic systems, there is a significant difference in activity as well as in the amount of incorporated borane monomers.35 The highest activity and incorporation level of borane were observed for the strained ansa-metallocene Et(Ind)₂ZrCl₂ 6. Upon activation, this metallocene incorporates about 50-60% of the borane monomer and an increased amount of borane in the feed leads to proportional inreased borane incorporation in the polymer. A further and unexpected observation was a higher activity with larger amounts of borane in the feed. This observation shows that there is obviously no retardation of the catalyst activity due to the borane groups. The higher activity is explained by the so-called 'positive comonomer effect'.⁴⁰⁻⁴⁵ In the case of heterogeneous systems, the positive comonomer effect is often ascribed to a better fragmentation of the catalyst support with addition of higher α -olefins and thus, leading to more accessible active sites.^{40,41} Next to the positive comonomer effect, with homogeneous systems, a negative comonomer effect is also described. The change in activity is reported to depend on the ligand and the comonomer structure.44 Cp₂ZrCl₂ 7 is also able to incorporate the borane monomer; but compared to the ansa-matallocene 6, the incorporated amount is very low even at high amounts of borane in the feed. The heterogeneous Ziegler-Natta system has a very low

activity in the copolymerization of ethene and 5-hexenyl-9-BBN and does not incorporate the borane monomer. With the Ziegler-Natta systems, Chung et al. performed kinetic studies concerning the copolymerization of aliphatic a-olefins with different chain lengths and 5-hexenyl-9-BBN.³⁹ The authors observed that, in general, the borane monomer behaves as a higher α -olefin in the Ziegler-Natta catalyst. To determine the reactivity of the different monomers, a batch polymerization with a 1:1 molar ratio of the particular α-olefin and 5-hexenyl-9-BBN was performed and the amount of incorporated borane in the polymer during the polymerization process was analyzed. In the case of 1-octene, the incorporated amount of borane in the polymer after a short reaction time (minutes) is \sim 30%. This implies only a slight higher activity for 1-octene. Using 1-butene, the amount of incorporated borane monomer initially is clearly lower and in the case of propene nearly no borane is incorporated in the beginning of the reaction and only a slight increase is visible during the polymerization. Thus, leading to the following activity behavior:

propene \gg 1-butene > 1-octene > 5-hexenyl-9-BBN.

In a continuous polymerization process, this observed activity behavior directly influences the obtained microstructure of the polymer. Thus, a copolymerization of propene and the borane monomer leads to a copolymer, because of the preferred incorporation of propene, with long propene sequences. This copolymer forms crystalline phases similar to those obtained in pure isotactic PP. The borane groups are located in the amorphous part of the copolymer and so even under heterogeneous and mild conditions a modification of the borane groups (e.g., conversion to alcohol functionalities) can be performed quantitatively. This behavior leads to a polar modified polymer that can co-crystallize with pure isotactic PP and thus be used in polymer blends in order to optimize the PP adhesion to other materials such as aluminum and glass.

3.24.3.1.1(ii) Direct copolymerization of aromatic α -olefins and borane-containing monomers with early transition metal catalysts Beside the early transition metal-catalyzed copolymerization of aliphatic α -olefins with borane-containing monomers,



Scheme 5 Synthesis of 4-[B-(*n*-butylene)-9-BBN]styrene.

Chung *et al.* investigated the copolymerization of aromatic α -olefins and borane-containing monomers. Therefore, the synthesis of new borane-containing styrene monomers (Scheme 5) and their copolymerization with styrene were undertaken.^{36,37}

To obtain syndiotactic copolymers, the half-sandwich titanocenes, Cp*Ti(OMe)₃/methylaluminoxane (MAO), Cp*TiCl₃/MAO, and CpTiCl₃/MAO, are used. In these systems, the monomers (styrene and borane-containing styrene) are reported to have very similar reactivities. Hence, this leads to a lower crystallinity of the resulting polymers with increasing amount of borane monomers, as a result of shorter styrene sequences. This behavior stands in contrast to the copolymerization of propene and 5-hexenyl-9-BBN, where nearly independent of the amount of borane, the propene monomer inserts more readily, always leading to long crystalline PP sequences (see above). In the case of the copolymer from styrene and the borane 8, the amount of borane comonomer can be directly used to control the melting point of the resulting polymer. For syndiotactic polystyrene, a melting point of about 270 °C requires processing temperatures over 300 °C, which is close to the point of decomposition. With the incorporation of 2.1 mol% of 4-[B-(n-butylene)-9-BBN]styrene 8 into the syndiotactic polystyrene and postsynthesis modification of the borane groups to hydroxyl groups, the obtained polymer shows a melting point of about 250 °C. This reduced melting point ensures a good processability of the polymer without thermal decomposition.

3.24.3.1.2 Silicon-containing olefins

3.24.3.1.2(i) Homo- and copolymerizations with silicon-containing monomers on Ziegler–Natta-based catalytic systems

Alongside borane-containing monomers, there are several reports concerning homo- and copolymers comprising silicon in the side chain. These respective silicon-containing monomers are analogous to the borane-containing monomers and show only weak interaction with the early transition metal catalysts. Likewise, they can easily undergo functional group transformations. The first homopolymerization experiments have been reported by Natta et al. with allylsilane and allyltrimethylsilane.^{46,47} The obtained poly(allylsilane) is crystalline with a melting point of 127-128 °C and can be crosslinked with oxygen or water. Poly(allyltrimethylsilane) is obtained in high molecular weight with an AlEt₃/TiCl₄ catalytic system. It is reported to be somehow inhomogeneous with a large insoluble fraction (in xylene), which has a high melting point of 350-360 °C. This high melting point is assigned to an isotactic structure based on X-ray scattering experiments. Later, Itoh et al. prepared polyvinylsilane and a copolymer of vinylsilane and ethene with a Ziegler-Natta system.⁴⁸ The observed lower activity compared to a homopolymerization with ethene was assumed to be a result of catalyst poisoning. In addition, dimethyldiallylsilane and methylphenyldiallylsilane were also homopolymerized with a Ziegler-Natta system.49 These two silane monomers were copolymerized with propene by Nametkin et al. with a AlEt₃/TiCl₄ catalytic system.⁵⁰ With an increasing amount of silicon, the copolymers show improvements in the thermomechanical behavior and the copolymers with methylphenyldiallylsilane are characterized by a high, specific elongation (600-700%). Longi et al. prepared copolymers of propene and allylsilane in a copolymerization with a Ziegler-Natta catalyst.⁵¹ After treatment of these polymers with potassium hydroxide inter- and intramolecular crosslinks of Si-O-Si are obtained.

3.24.3.1.2(ii) Homo- and copolymerizations with silicon-containing monomers and metallocene-based polymerization catalysts.

In addition to the Ziegler-Natta systems, there are also some reports of homo- and copolymerizations with silicon-containing monomers with metallocene-based polymerization catalysts. In 1994, Zeigler et al. employed different metallocenes for the preparation of isotactic, syndiotactic, and atactic poly(allyltrimethylsilane).⁵² Polymerization of allyltrialkylsilanes with a higher steric demand leads to a decrease in polymer yield and molar mass. With allyltriphenylsilane on a MAO-activated metallocene, only oligomers can be obtained, whereas with allyltrimethylsilane, and the same catalyst under the same polymerization conditions, a true polymer is formed.⁵³ Usage of metallocenes like rac-Et(Ind)2ZrCl2/MAO leads to an activity decrease with increasing amounts of allyl- and vinyltrimethylsilane.⁵⁴ The molecular weight of the poly(allyltrimethylsilaneco-ethene) is hardly affected by increasing amounts of silane comonomer. The lower molar mass is assumed to be a result of a charge build-up from silicon in the transition state (Figure 9), leading to a faster β -hydride elimination.⁵⁵

NMR spectroscopic end-group analysis confirmed this possible influence of silicon because of a high incorporation degree of the silane monomers as terminal vinylidene groups



P = polymer chain



with a Cp₂ZrCl₂/MAO catalytic system. In the case of a *rac*-Et(Ind)₂ZrCl₂/MAO catalyst, however, the end-group analysis reveals an increased incorporation degree of allyltrimethylsilane with an increasing amount of silane comonomer in the feed. In this case, allyltrimethylsilane acts as a real comonomer. The sharp decrease in molar mass must therefore be due to a different effect of the silane comonomer.⁵⁵

Lipponen and Seppälä achieved copolymerization of a silane monomer with ethene without a sharp decrease in molar mass by increasing the distance between silicon and the unsaturated chain end.56 Therefore, 7-octenyldimethylphenylsilane was synthesized and copolymerized with ethene by rac-dimethylsilyl-bis(2-methyl-1-n⁵-indenyl)zirconium dichloride/MAO and Et(Ind)₂ZrCl₂/MAO. During the polymerization, a positive comonomer effect analogous to the polymerization of borane-containing monomers on metallocenes can be seen. Only a small decrease in molar mass with increasing amount of silane monomer is obtained and the incorporation level of silane monomer increases. The polymerization of this silane monomer shows that a longer spacer between the silicon atom and the double bond effectively suppresses the electron donating effect of silicon. In addition, the polarized silicon-carbon bond does not deactivate the catalyst. The poly(propene-co-7octenyldimethylphenylsilane) can easily (and in good yields) be converted into other functional groups (e.g., alkoxy or halosilane groups) or directly be used as a adhesion promoter in a composite of microsilica and PP.

Another promising approach to copolymerize allyltrimethylsilane and ethene was performed by Liu and Nomura.⁵⁷ Therefore, nonbridged half-titanocenes 9–12 (Figure 11) were used and copolymers without the drastic decrease in molar mass with increasing amount of silane comonomer as was seen for zirconocene complexes such as Cp₂ZrCl₂ 7 or *rac*-Et(Ind)₂ZrCl₂ 6 were obtained (Figure 10).⁵⁵

The incorporation level of the silane monomer reach values up to 60 mol% in the case of catalyst 10 and a concentration of the silane monomer in the feed of $1.05 \text{ mol } l^{-1}$. The same catalysts can also effectively incorporate vinyltrimethylsilane into a PE backbone.⁵⁸ Until this publication, there were no reports of ordinary metallocenes being able to coordinate and as a result polymerize or copolymerize this bulky silane monomer. Catalyst 11 shows the best activities and the highest incorporation levels of the silane comonomer. At a silane concentration of 1.1 moll⁻¹ and an ethene pressure of 6.1 bar an activity of $3730 \text{ kg}_{\text{polymer}} \text{ mol}_{\text{Ti}}^{-1} \text{ h}^{-1}$ is obtained. The corresponding copolymer has an $M_{\rm n}$ of 573 000 g mol⁻¹ and a silane content of 11.9 mol%. Upon increasing the concentration of silane comonomer to 2.3 mol l⁻¹, the activity decreases to $820 \text{ kg}_{\text{polymer}} \text{ mol}_{\text{Ti}}^{-1} \text{ h}^{-1}$, the molar mass to an M_{n} of 304 000 g mol⁻¹, and the silane content in the copolymer increases to 21.4 mol%. This demonstrates a decrease in molar mass with an increasing amount of vinyltrimethylsilane in the feed, but it is not as dramatic as in the case of the common metallocene polymerization catalysts and allyltrimethylsilane.



Figure 10 Molecular weight decrease for the polymerization of allyltrimethylsilane with different metallocenes. Polymerization conditions: top: $V_{\text{total liquid}}$ $_{\text{phase}} = 50 \text{ ml}$, cat = $2.5 \times 10^{-6} \text{ mol}$, Al/Zr = 2000, $T_p = 80 \text{ °C}$; $pC_2H_4 = 1.2 \text{ bar}$, $t_p = 60 \text{ min}$; bottom: $V_{\text{total liquid phase}} = 30 \text{ ml}$, cat = $0.1 \times 10^{-6} \text{ mol}$, Al/Zr = 30 000, $T_p = 25 \text{ °C}$; $pC_2H_4 = 4.1 \text{ bar}$, $t_p = 10 \text{ min}$.



Figure 11 Nonbridged half-titanocenes.

Amin and Marks copolymerized alkenylsilanes and ethene with homogeneous mono- or bi-nuclear organotitanium complexes (Figure 12),^{59,60} which are known to be efficient α -olefin polymerization agents and in addition being able to effect silanolytic chain transfer.^{59,61}



Figure 12 Organotitanium complexes for an efficient α -olefin polymerization with alkenylsilane incorporation and silanolytic chain transfer.

In these systems besides the expected insertion of the α -olefins, an intra- or intermolecular silanolytic chain transfer takes place (Scheme 6).⁶⁰ The proposed mechanism shows the formation of a copolymer in the steps I and II. In addition to further insertion reactions of ethene (V), this copolymer can undergo an intra- (III) or intermolecular (IV) silanolytic chain transfer that is proposed to occur via a four-centered σ -bond metathesis transition state. All produced polymer species can subsequently take part in further enchainment or silanolytic chain transfer reactions.





A simultaneous introduction of branching and versatile reactive functionalities into polyolefins is possible with these systems. By controlling the amount of intermolecular silanolytic chain transfer that leads to an increasing amount of long-chain branching (LCB), the possibility to control the microstructure and thus the properties of the resulting polymer is achieved. Both the chain length of the alkenylsilane monomer and the nuclearity of the organotitanium catalyst have an influence on the incorporation level of the alkenylsilane and the amount of intermolecular silanolytic chain transfer. In the copolymerization with ethene, the longer-chain alkenylsilanes have a lower incorporation level because of a greater steric hindrance during the coordination and insertion processes at the catalytic center. Hence, the incorporation level increases in the following order:

$$C_8H_{15}SiH_3 < C_6H_{11}SiH_3 \approx C_4H_7SiH_3 < C_3H_5SiH_3$$

Indeed this leads to more short-chain branches in the case of the shorter alkenylsilanes but the efficiency of the long-chain branch (polymeric branch) is higher for the longer alkenylsilanes. Thus, the gel permeation chromatography multiangle laser light scattering (GPC-MALLS)-derived LCB data indicate that the ratio of LCB to total branch content increases in the order

$$C_3H_5SiH_3 < C_4H_7SiH_3 \approx C_6H_{11}SiH_3 \approx C_8H_{15}SiH_3$$

These LCB trends are also reflected in the melting temperatures of the resulting polymer because of a dramatic decrease with higher LCB density.⁶⁰ The second effect on the polymer microstructure, the nuclearity of the organotitanium complexes leads to higher molecular weights for the binuclear organotitanium complexes. As plausible explanations, a higher probability for a reinsertion of a silyl end-capped macromonomer or a higher probability for the silanolytic chain transfer of a polymer chain because of the neighboring active centers are mentioned.

For the polymerization of vinylic monomers with a Si–O–Si linkage, only few reports can be found. Trimethylsilyloxydimethylvinylsilane is reported not to afford a copolymer with a metallocene and ethene due to the deactivation of the active species.⁵⁴ A related report concerns a direct copolymerization of propene and ethene with the monovinyl-functional silsesquioxane **16** as Si–O–Si-containing comonomer by Tsuchida *et al.*⁶² For this purpose, a silsesquioxane with a polymerizable unsaturated chain end and different MAO-activated metallocenes (Figure 13) was used.

The incorporated amount of the comonomer in the poly (ethene-*co*-silsesquioxane) with an M_n of $100\,000\,\mathrm{g\,mol^{-1}}$ is about four monomer units. The copolymer with propene produced with the Cp₂ZrCl₂/MAO system is a viscous liquid with a low molar mass ($M_w = 2200\,\mathrm{g\,mol^{-1}}$). The thermostability of the obtained copolymers in air is improved compared to the thermostability of the analog PE and oligopropene. Later, Zheng *et al.* copolymerized a similar norbonenyl-based silos.⁶³ With higher concentrations of the comonomer, incorporation levels of up to 3.4 mol% with ethene and of up to 10.4 mol% with propene can be achieved. The improvement of the thermostability in air for the ethene copolymers show an increase of 90 °C in the onset of decomposition temperature based on



Figure 13 Copolymerization of a silsesquioxane and ethene, or propene with different metallocenes.

5% mass loss compared to an ethene homopolymer with a similar molecular weight.

3.24.3.1.3 @-Functionalized olefins

3.24.3.1.3(i) Copolymerization of ω -functionalized alcohols, amines, and esters with ethene or propene on early transition metal complexes

Introduction of a spacer between the double bond and the functional group is another possible technique to inhibit a deactivation of the Lewis acidic catalyst by the functional group. However, in the case of most polar olefins, the spacer alone is not enough to inhibit the deactivation of the early transition metal complexes. To achieve a good catalyst activity and a high incorporation level of the polar comonomer additional techniques such as steric protection (Section 3.24.3.2) or protection of the polar functional groups with strong Lewis acidic compounds such as alkyl aluminum compounds (Section 3.24.3.3.2) are used. The importance of combining the protection of the olefin, for example, by MAO with the introduction of a longer spacer between the olefin and the polar group can be seen by the change of activity for a system with varying either the concentration of the comonomer (Table 1, Runs 1–3)⁶⁴ or the amount of aluminum compound (Table 1, Runs 4–6).⁶⁵

An example for the successful application of steric protection of the functional group together with a longer spacer was given by Xu and Chung.⁶⁶ In this study, $Cp*TiMe_3/B(C_6F_5)_3$ was employed without additional aluminum compounds in the polymerization of several styrene derivatives (Figure 14).
 Table 1
 Effect of Al/Zr and Al/10-undecen-1-ol (Un-OH)

 molar ratio on propene/10-Un-OH^a or ethene/10-Un-OH^b
 copolymerization with Et(Ind)₂ZrCl₂/MAO

Run	Al/Zr	Al/10-Un-OH	Activity (kg-P) mol ⁻¹ (Zr) h ⁻¹
1	4000	1.15	110
2	4000	1.92	800
3	4000	5.82	2600
4 ^{<i>c</i>}	1890	2.52	500
5 ^d	3780	5.04	2200
6 ^{<i>d</i>}	12600	16.08	6700

^aruns (1-3): $V_{\text{toluene}} = 300 \text{ ml}$, $\text{cat} = 4.8 \times 10^{-6} \text{ mol}$, $T_p = 30 \,^{\circ}\text{C}$, $pC_3H_6 = 3.0 \text{ bar}$, $t_p = 60 \text{ min}$;

 bruns (4-6): $V_{total~liquid~phase}\!=\!160\,ml,~cat\!=\!2.56\times10^{-6}\,mol,~T_p\!=\!25\,^\circ\text{C};~\rho\text{C}_2\text{H}_4\!=\!2.0$ bar,

 $c_{t_0} = 20 \text{ min};$

 $d_{t_0}^{i} = 10$ min pretreatment time of 10-Un-OH with MAO = 60 min.

In comparison to the homopolymerization reaction of styrene, utilization of the dimethylamino-functionalized styrene compound 18 with only small protecting methyl groups on the nitrogen atom, the relative activity is decreased below 1% compared to styrene homopolymerization. With a larger protection group such as a trimethylsilyl group 19, the relative activity is increased to 14%. The longer spacer in the compounds 20 and 21 leads to relative activities of 27% and 63%, respectively (to styrene homopolymerization). This behavior demonstrates the importance of the combination of the spacer length and the employed protecting strategy to achieve a good polymerizability of polar monomers without a significant deactivation of the active species.

Löfgren et al. studied the metallocene-catalyzed copolymerization of ethene with polar olefinic comonomers containing functional groups (alcohols, carboxylic acids, and esters) experimentally and by using molecular modeling techniques.⁶⁷ The effect of the spacer can be seen in the case of the copolymerization of 5-hexen-1-ol or 10-undecen-1-ol (Un-OH) with ethene on a bis(n-butylcyclopentadienyl)zirconium dichloride/MAO catalytic system. Both the activity and the incorporation level of the comonomer increase with a longer spacer. To confirm these results, a molecular dynamic simulation was employed to determine the probability for σ -oxygen coordination of an already inserted alcohol comonomer. Therefore, the distances between the functional group and the double bond for the different conformers of 10-Un-OH 56 and 5-hexen-1-ol 57 (Figure 25) and their energies were calculated (Figure 15).

As it is clearly demonstrated, the monomer with the longer alkyl chain has more conformers, but the minimum distance of the polar group to the olefin is about 4 Å with an energy of more than 3 kcal mol⁻¹ over the global minimum. In the case of the monomer with the shorter alkyl chain, several possible conformers exist with a minimum distance between 3 and 4 Å together with energies below 2 kcal mol⁻¹ over the global minimum. This observation is in accordance with the experimental results, which show a higher activity for the alcoholic comonomer with the longer spacer. Hence, the longer spacer reduces the interaction with the catalyst and thus leads to a higher activity.



Figure 14 Styrene-based monomers for the homopolymerization with a Cp*TiMe₃/B(C₆F₅)₃ catalyst system without aluminum compounds.



Figure 15 The energies of the various conformers of comonomer 56 (left), or comonomer 57 (right) as a function of the corresponding distances between the functional group and the olefin group. The C–O distance measured is indicated as a gray line in the molecular structures. Reproduced from Ahjopalo, L.; Löfgren, B.; Hakala, K.; *et al. Eur. Polym. J.* **1999**, *35*, 1519.⁶⁷

3.24.3.1.3(ii) Copolymerization of ω -halo- α -olefins with α -olefins on early transition metal complexes

The first examples of a polymerization of α -olefins bearing halogen atoms in the side chains with Ziegler-Natta catalysts were published around 1960, for example, for trifluoroalkyl-substituted ethenes⁶⁸ and halostyrenes.⁶⁹ Deactivation of the catalyst is widely observed in all of these systems. By addition of Lewis bases to the Ziegler-Natta systems, Bacskai suppressed the dehydrohalogenation reaction of the Lewis acid with the ω-halo-α-olefin leading to a diene and hydrogen halide. The latter is able to deactivate the catalyst and reduce molar masses of the polymer.⁷⁰ Clark and Powell reported on the polymerization of ω -halo- α -olefins with TiCl₃/AlEt₂Cl as a catalyst system.⁷¹ Decreased deactivation can be achieved by increasing the size of the halogen atom and the distance between the double bond and the halogen atom. A good compatibility of halogenated organic compounds with Ziegler-Natta systems can also be seen by the experiment of Bruzaud et al. Here, a higher activity in the case of 1-hexene homopolymerization on a zirconocene/MAO system in methylene chloride was observed because of a better activation process.⁷² Overall, an enhanced compatibility of chlorinated olefin derivatives compared to the above-mentioned polar olefin monomers (Section 3.24.3.1.3(i)) can be seen.

Hence, homo- and copolymerizations with propene or ethene and ω -halo- α -olefins were also carried out on a zirconocene/MAO catalytic system. First copolymerization experiments of 11-chloroundec-1-ene with 1-hexene using a *rac*-Et(Ind)₂ZrCl₂/MAO catalyst system in methylene chloride and toluene show a complete deactivation with the former solvent because of fast side reactions; however, in the case of

toluene, a polymer is produced, but the chloroalkane side group undergoes a Friedel Crafts alkylation activated by MAO. With heptane as solvent successful homo-, co-, and terpolymerizations without side reactions are reported.⁷² 5-Chloropent-1-ene as the chlorinated comonomer with a shorter spacer results in complete deactivation. The reason for this is presumed to be an interaction of the chloro atom of the last-inserted comonomer via a seven-membered chelate to the metal cation. The deactivation mechanism of vinylchloride on Group 4 metal olefin polymerization catalysts was investigated by Stockland and Jordan⁷³ Their investigation includes an NMR spectroscopic experiment of Cp₂ZrMe₂/B(C₆F₅)₃ with up to two equivalents of vinylchloride and a polymerization experiment of vinylchloride together with Et(Ind)₂ZrCl_{2/}MAO as catalytic system.⁷⁴ The first of these experiments with two equivalents of vinylchloride leads to a dichlorospecies of the metallocene together with propene formation and subsequent oligomerization by another remaining active catalytic center (Scheme 7).

The reason for the appearance of the dichlorospecies and the oligopropene is a very fast β -chloride elimination reaction, which itself is much faster than the coordination and insertion of a further vinylchloride monomer. In the polymerization experiment with MAO, the chloro species can be realkylated by MAO either to produce further propene from vinylchloride or to oligomerize free propene to atactic oligopropene, respectively (Scheme 8).

Beside this study several other reports on β -functional group elimination reactions with early transition metal catalysts have been published.^{75,76} These results show clear tendencies for termination reactions if the spacer between the olefin and the

$$Cp_2Zr \xrightarrow{\mathsf{MeB}(\mathsf{Ar}^{\mathsf{F}})_3}_{\mathsf{Me}} + 2 \qquad Cl \qquad \mathsf{Cp}_2ZrCl_2 + B(\mathsf{Ar}^{\mathsf{F}})_3 + PF$$

$$A_r^{\mathsf{F}} = C_{\mathsf{e}}F_5$$

Scheme 7 Reaction of vinylchloride with Cp₂ZrMe₂/B(C₆F₅)₃.



Scheme 8 Polymerization study of vinylchloride with Et(Ind)₂ZrCl₂/MAO.

functional group is insufficiently long to suppress elimination reactions.

3.24.3.2 Copolymerization of Sterical Demanding Polar Olefins and $\alpha\text{-Olefins}$

Several sterically hindered monomers have been reported to be polymerizable without further protection. Unfortunately, a clear differentiation between the addition of Lewis acids as cocatalyst and protecting agent cannot always be made. Hence, only reports with a clear sterical protection are discussed in the following section.

3.24.3.2.1 Ether-functionalized olefins

Published results of unprotected ether-functionalized α -olefins are very limited. Reports on reactions lacking protection are restricted to NMR spectroscopic experiments by Stojcevic and Baird who examined the influence of the sterical demand for different olefinic ethers on their coordination to zirconium-containing catalysts.⁷⁷ The results are discussed in Section 3.24.3.1.3. More promising in this context is the use of trialkylsilyl-protected ethers. Hence, it is discussed in Section 3.24.3.3.1.

However, Byun and co-workers have reported on the copolymerization of 4-allylanisole and ethene using different zirconocenes and only low amounts of MAO with monomer to aluminum ratios of 1:1 or even 5:1.78 The resulting polymerization activities are moderate to high. The most active catalyst with an ether to aluminum ratio of 2:1 is Cp*2ZrCl2 and achieves an activity of $187 \text{ kg}_{\text{polymer}} \text{ mol}_{Zr}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$. (Under equivalent conditions, an activity of 260 kg_{polymer} mol_{Zr}⁻¹ h⁻¹ bar⁻¹ was observed for ethene homopolymerization and even $430 \text{ kg}_{\text{polymer}} \text{ mol}_{\text{Zr}}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$ for the copolymerization of ethene and allylbenzene.79) Pretreatment time of the comonomer with MAO has only a marginal influence on the polymerization performance. Variation of the Al/Zr ratio at constant monomer concentrations has three different results. While an increase of the Al/Zr ratio results in an increase of the polymerization activity, the allylanisole incorporation in the

copolymer decreases, due to the higher steric hindrance of the protected monomer. At the same time, the molecular weight of the polymer also decreases, as a result of an increase in chain transfer reactions from the catalyst to the aluminum compounds. Variations in the Al/anisole ratio up to 0.2 results in an allylanisole incorporation of 17.9 mol%, a molecular weight of only $3500 \,\mathrm{g}\,\mathrm{mol}^{-1}$ and a polymerization activity of $8 \,\mathrm{kg}_{\mathrm{polymer}} \,\mathrm{mol}_{Zr}^{-1} \,\mathrm{h}^{-1} \,\mathrm{bar}^{-1}$.

In 1998, Stehling and co-workers reported the polymerization of the new olefinic vinyl ether 23 (Scheme 9).⁸⁰ The polar monomer can be copolymerized with propene or 4-methylpent-1-ene using *rac*-Et(THInd)₂ZrMe₂/[HNMe₂(C₆H₅)][B (C₆F₅)₄] resulting in copolymers with molecular weights of 28 000 g mol⁻¹ and 6000 g mol⁻¹, respectively, without the addition of further aluminum alkyls. The interesting feature about this polymer is an internal initiating group for a living radical polymerization reaction, which allows preparation of well-defined graft copolymers with styrene at 123 °C (Scheme 9).

3.24.3.2.2 Amino-functionalized olefins

Amino-functionalized polyolefins attract huge interest due to their exceptional properties, for example, in their utilization as antioxidants⁸¹⁻⁸³ potential and application for as hole-transporting organic materials in light-emitting diodes.⁸⁴A further interesting property of poly(amino)olefins is the possibility for guarternization of the amino functionalities.^{85,86} Thus, the amino-functionalized polyolefin is converted to an ammonium-functionalized polyolefin with increased solubility in polar solvents such as water or alcohols as well as having increased affinities to polar substances, such as dyes.⁸⁷

However, the Lewis basic nature of amino groups complicates insertion polymerization in presence of such functionalized olefins. Nonetheless, beside the protected monomers (Section 3.24.3.3), reports on the polymerization of unprotected amino-functionalized olefins have also been published. These reports are generally limited to tertiary amines and activities depend on the steric demand of the alkyl groups. The first report by Waymouth *et al.* concerns the polymerization of 5-(N,



Scheme 9 Copolymerization of propene and 23 followed by radical graft polymerization of styrene.

N-di-*iso*-propylamino)-pent-1-ene **27** by Cp*₂ZrMe₂/B(C₆F₅)₃ and Et(THInd)₂ZrMe₂/B(C₆F₅)₃ without the addition of aluminum alkyl agents, however the observed activities were low.⁸⁷ Following reports deal with the detailed analysis of the influence of nitrogen-substituted olefins on the polymerization reaction using Cp*₂ZrMe₂/[CPh₃][B(C₆F₅)₄] without addition of any aluminum-containing compound.⁸⁸ Best results for the sterical protection were achieved for di-*iso*-propyl-substituted amines in the sequence dimethyl **24** < diethyl **25** < diphenyl **26** < di-*iso*-propyl **27** (Figure 16). The spacer length between the olefin functionallity and the amino group in an α-amino-ω-olefin is also very important (Table 2). Alteration of the olefinic substituent, for example, from pentene **27** to butene **28** results in a four-fold decrease in polymerization activity.

Copolymerization reactions of **27** (Figure 16) with 1-hexene and 4-methyl-pent-1-ene afford good results using *rac*-Et(THInd)₂ZrMe₂ and Cp*₂ZrMe₂ after activation with *N*,*N*-dimethylanilinium tetrakis(pentafluorophenyl)borate [HNMe₂Ph][B(C₆F₅)₄].⁸⁹ Although the activity dropped significantly even at addition of small quantities of amines, copolymers with variable amounts of amino functionalities could be produced. In the case of the copolymerization of **27** with hex-1-ene using *rac*-Et(THInd)₂ZrMe₂, determination of the copolymerization parameters shows an almost ideal copolymer with a slight preference for the amine incorporation. For the **27**/4-methyl-pent-1-ene copolymerization, the amine incorporation is clearly favored for both tested catalysts. The melting points of the resulting copolymers decrease compared

to the corresponding homopolymers, accompanied by a significant increase of the decomposition points already at low comonomer incorporation levels (Table 3).

Another approach to polymerize several sterically protected styrene-based amines (Figure 14) was reported by Xu and Chung.⁶⁶ Catalysts for this study were a large number of half-titanocenes with or without the addition of aluminum compounds. Among those systems, Cp*TiMe₃/tris-(2,2',2"-nonafluorobiphenyl)borane showed the best catalytic performance $(activity = 7.9 \times 10^3 \text{ kg}_{polymer} \text{ mol}_{Ti}^{-1} \text{ mol}_{monomer}^{-1} \text{ h}^{-1}, \text{ syndio-}$ tacticity = 94.5%) in the polymerization of 4-(N,N-bis)(trimethylsilyl)amino)styrene 19 without addition of aluminum alkyls. A successive comparison of the polymerization reactions with different functional olefins and $[CPh_3][B(C_6F_5)_4]$ as cocatalyst shows that the polymerization performace is clearly dependent on the sterical demand of the amino group as well as the spacer length between the olefinic group and the amino functionality (despite the separation by the rigid phenyl group; as discussed in Section 3.24.3.1.3). Even though the methyl-substituted amine 18 can be polymerized with this catalyst system, activities are low. In the case of the most sterically encumbered amine 21, activities are 700 times higher $(7 \times 10^3 \text{ kg}_{\text{polymer}} \text{ mol}_{\text{Ti}}^{-1} \text{ mol}_{\text{monomer}}^{-1} \text{ h}^{-1})$ in addition to an increased syndiotacticity by more than 50%.

Beside these studies, other research groups reported on the polymerization of amine-containing monomers by early transition metal catalysts with an aluminum alkyl: polar monomer ratio of < 1. First reports of these were made by Giannini *et al.* in the



Figure 16 Amine-containing monomers.

 Table 2
 Amine monomers polymerized with the Cp*₂ZrMe₂/borate system^a

Monomer	n _{catalyst}	C _{Monomer}	Reaction time	Conversion ^b	Activity ^c	M _n ^d
	mM	M	min	%	h∙c[M] ⁻¹	g mol⁻¹
24	9.8	1.9	60	8.5	9	NA
25	9.7	1.7	30	75.2	155	920
26	10.9	0.5	45	90.7	111	826
27	3.2	3.0	30	99.0	619	1278
28	7.1	2.1	40	71.3	151	3046

^aConditions: 6 ml toluene solutions, T=22 °C, N₂ atmosphere in a drybox.

^bPercent conversion of monomer, determined by GC after indicated time.

^cActivity in amount of monomer consumed per amount of catalyst, concentration of monomer, and hour.

^dDetermined from ¹H NMR vinylidene end-group analysis.

Table 3	Thermal transit	ion data for	homo- and	copolymers
synthesized	with rac-Et(Ind)	2ZrMe2/bora	ate	

Polymer	T _m ª ℃	Dec. temp ^b °C	M _n ^c g mol⁻¹
Poly(4M1P) ^d	223	342	16200
Copolymer(2.5% amine/4M1P) ^e	186	385	>14 000 ^f
Copolymer (12.5% amine/ 4M1P) ^e	159	400.6	>14 000 ^f
Poly(amine) ^g	115	401.7	>14 000 ^f

^aPeak melting points reported.

^bDetermined in N₂ as the onset of 100% degradation.

^cDetermined by ¹H NMR spectroscopic vinylidene end-group analysis.

^dlsotactic poly(4-methyl-1-pentene).

^eThe copolymers are isotactic poly[4-methyl-1-pentene-*co*-5-*N*,*N*-(di-*iso*-propylamino) pent-1-ene).

The upper limit of detection for this technique for the amine polymers is about 14 000. 9sotactic poly[5-*N*,*N*-(di-*iso*-propylamino)-pent-1-ene].

4M1P, 4-methylpent-1-ene.

late 1960s.^{85,90} The polymerization of several aminofunctionalized olefins with methyl, ethyl, and isopropyl substituents on the nitrogen atom combined the different spacer lengths ranging from propene up to pentene was successfully realized with an aluminum-activated TiCl₃ catalyst system in presence of excess polar monomer. Secondary amines, even if highly sterically hindered (e.g., 5-*N-tert*-butylaminopent-1-ene), caused catalyst deactivation. Again the importance of the spacer length between the amino group and the double bond has to be noted. While 4-(*N*,*N*-di-*iso*-propylamino)but-1-ene was copolymerized with ethene in low yields, 3-(*N*,*N*-di-*iso*-propylamino)prop-1-ene could not be polymerized at all. 5-(*N*,*N*-di-*iso*-propylamino)pent-1-ene could be copolymerized with ethene by a homogeneous or SiO₂-supported Me₂Si(Ind)₂ZrCl₂/MAO catalyst system.⁹¹

As in the case of 4-(*tert*-butyldimethylsilyloxy)styrene (Section 3.24.3.3.1), Kim *et al.* have been successful with the syndiotactic homopolymerization of 4-(*N*,*N*-dimethylamino) styrene and 4-(*N*,*N*-diethylamino)styrene using Cp*titanatrane/ modified methylaluminoxan (MMAO) catalyst system **31** (Scheme 10) with excess of functional monomer. The activities for the polymerization reactions are good compared to the polymerization of nonfunctionalized styrene but the molecular weights are drastically reduced. Best results were obtained for poly(4-(diethylamino)styrene), with a molecular weight of

84 kg mol⁻¹, an activity of 2.9×10^4 kg_{polymer} mol_{catalyst} ⁻¹ mol_{monomer} ⁻¹ h⁻¹ and a polymer decomposition temperature of 372 °C. By the addition of hydrochloric acid, syndiotactic poly(4-(*N*,*N*-dimethylamino)styrene)- and poly(4-(*N*, *N*-diethylamino)styrene)-hydrochloride can be achieved.

Due to the fact that most polymerization reactions with early transition metal complexes contain an excess of aluminum alkyl reagents compared to the functional group, a protective complexation of the amine by the aluminum alkyl is likely. Hence, these reports will be disregarded here and are discussed in Section 3.24.3.3.2(i).

3.24.3.2.3 Norbornyl ester-derivatized olefins

Due to their rigid structure, ester-functionalized norbornenes show a suppressed backbiting of the functional group after monomer insertion. Hence, it is reported that methyl-5-norbornene-2-yl-ester **32** (Figure 17) can be copolymerized with ethene, propene, 1-butene, and dicyclopentadiene with vanadium-based Ziegler–Natta catalysts and an alkyl aluminum/functional olefin ratio of ~1.⁹² Only one of the two heteroatoms in the ester functionality can be effectively protected by Lewis acids. The obtained copolymer exhibits a functional monomer incorporation of 1–3% and can be modified by vulcanization via the dicyclopentadiene comonomer units resulting in a polymer with a breaking elongation of 300%.

3.24.3.3 Copolymerization of Polar Olefins and $\alpha\text{-Olefins}$ with Protecting Groups

3.24.3.3.1 Trialkylsilyl-protected olefins

The first approach to protect hydroxyl groups in alcoholic olefins from deactivating reactions with the catalyst systems stems from classic organic protection group chemistry. This involves masking of the hydroxyl groups by hydrolyzable silyl protection groups. Already in the 1960s, Giannini *et al.* used TMS groups to protect alcohols and secondary amines from undesired deactivation reactions in the TiCl₃/AlR₂Cl-catalyzed polymerization reaction.⁹⁰ Following this report, several examples of Si-masked hydroxyl and amino alkenes have been

Figure 17 Functionalized norbornene derivatives.



Scheme 10 Polymerization of polar functionalized styrene derivatives by Cp*titanatrene/MMAO 31.

investigated with only little improvement of comonomer incorporation, obtained molecular weight of the polymers and conversion. However, an influence of the chosen monomer on the polymerization behavior can be found.

Wendt *et al.* examined the influence of the steric demand for silyl groups on the copolymerization of ethene with trialkylsilyl-protected [2.2.1]hept-5-ene-2-methanol **33** (Figure 17) using differently substituted ⁱPr[CpInd]ZrCl₂ catalysts after activation with MAO.⁹³ The resulting order showed an increasing polymerization activity in the sequence *iso*propyldimethylsilyl < triethylsilyl < *tert*-butlydimethylsilyl < thexyldimethylsilyl < tri-*iso*-propylsilyl. This sequence corresponds with the increasing steric demands of the silyl protecting groups. Similar results were found for the copolymerization of trimethylsilyl- and tri-*iso*-propylsilyl-protected 10-undencen-1-ol **56** (Un-OH, Figure 25) with several metallocene catalysts.⁹⁴

Comparison of the copolymerization performance of trialkylsilyl- and TIBA-protected derivatives of olefin **33** (Figure 17) with ethene under otherwise identical conditions shows higher polymerization activity together with lower comonomer incorporation in case of TIBA protection compared to trialkylsilyl protection.⁹⁵ This behavior can be explained by the steric demands of the protection groups. The less sterical demanding silyl groups result in higher comonomer incorporation while the overall catalyst activity decreases due to deactivation. On the other hand, the TIBA protection with higher steric encumbrance results in reduced deactivation, together with decreased comonomer incorporation due to the size of the protection group.

An interesting homopolymerization of 4-trimethylsilyloxy-1,6-heptadiene using Cp*₂ZrCl₂/[CPh₃][B(C₆F₅)₄] as catalyst was reported by Kesti *et al.* (Scheme 11).⁸⁷ This system produces poly[methene-3,5-(1-trimethylsilyloxy)cyclohexanediyl], which can be converted to the corresponding alcohol by treatment with aqueous HCl. Also, 5-*tert*-butyldimethylsilyloxy-1-pentene can be polymerized at low temperatures with M_w of up to 10 000 g mol⁻¹.

Related polymers can be achieved by homopolymerization of 4-*tert*-butyldimethylsilyloxystyrene with 31/MMAO (Scheme 10), which has also been reported to be active in the polymerization of the corresponding amines (Section 3.24.3.2.2).⁹⁶ The resulting syndiotactic poly(4-*tert*-butyldimethylsilyloxystyrene) (M_w = 330 000 g mol⁻¹, activity = 4.4×10^4 kg_{polymer} mol_{catalyst}⁻¹ mol_{monomer}⁻¹ h⁻¹, T_{decomp} = 367.7 °C in nitrogen atmosphere)

can easily be converted into the corresponding polyalcohol under acidic conditions.

The silyl protecting approach can also be used for α -olefin- ω -amines.^{85,90} Schneider *et al.* reported the homo- and copolymerization of *N*,*N*-bis(trimethylsilyl)-1-amino-10-undecene and ethene using **39**/MAO (Figure 19) as catalyst system with a high catalytic activity.^{97,98} The resulting silylaminofuctional LLDPE (linear low-density PE) can be converted to the amine by aqueous deprotection and contains high amounts of comonomer (Scheme 12).

The influence of TMS- and methyl-substituted amines was studied by Xu and Chung⁶⁶ The polymerization of the aforementioned amino-functionalized styrene derivatives **18–21** (Figure 14) shows that, upon substitution of a methyl group with a TMS group, the polymerization activity is increased by a factor of 300 due to the better steric protection of the amine. Further increase in polymerization activity can be achieved by the introduction of a longer spacer in addition to the rigid phenyl group, which separates the olefinic group from the amino-functionalized part of the monomer. For example, introduction of two methylene groups by change from **19** to **20** leads to a more than two-fold increase in activity as well as an increase of syndiotacticity from 76.5% to 90.5%.

Silyl protection has also been used to circumvent known solubility and gelation problems.⁹⁹ The silyl group effectively suppresses formation of polymeric μ -bridged aluminum alkoxides, due to the weaker dative coordination of the silyl ether to the aluminum compound compared to the partially covalent interaction of the corresponding alcohols with aluminum alkyls. Hence, the copolymerization of Un-OH 56 with tetradec-1-ene and oct-1-ene using a sterically protected hafnocene dimethyl spezies **37** (Figure 19)/[B(C₆F₅)₄][Me₂NHPh] results in copolymers with high molecular weights (up to 480 000 g mol⁻¹) and a low polydispersity index (PDI ~ 1.3–1.4).

However, the importance of further protection for silyl-protected polar olefins with aluminum alkyls (Section 3.24.3.3.2) is difficult to judge. Löfgren and co-workers found that 10-undecenyl trimethylsilyl ether can be copolymerized with ethene by Et(Ind)₂ZrCl₂/MAO at similar activities compared to the corresponding alcohol.¹⁰⁰ Although the latter is known to be protected by aluminum alkyls, no interaction of the trimethylsilyl ether with aluminum alkyls was observed.¹⁰¹

In an NMR spectroscopic study, Stojcevic and co-workers could show that the trialkylsilyl-protected alkenols 10triphenylsilyloxy-dec-1-ene and 10-trimethylsilyloxy-dec-1-ene



Scheme 11 Polymerization of 4-trimethylsilyloxy-1,6-heptadiene under the formation of cyclic polymer.



Scheme 12 Polymerization of TMS-protected 1-amino-10-undecene followed by aqueous deprotection.

do not coordinate to Cp₂ZrMe₂/[B(C₆F₅)₃] via the protected oxygen functionality. The steric hindrance also leads to a very weak π -coordination of the olefin resulting in a slow homopolymerization.⁷⁷ Nevertheless, a copolymerization of both monomers with ethene or propene using *rac*-Et(Ind)₂ZrCl₂/MAO is possible (Section 3.24.3.3.2(iii)).

Recently developed catalysts exhibit promising properties in the copolymerization of trialkylsilyl-protected alkenols with α -olefins. The titanium-based tridentate catalyst 47 (Figure 21) is able to copolymerize *tert*-butyl(dec-9-enyloxy) dimethylsilane and ethene with high activities, even if deficient amounts of aluminum compounds are used to protect the ether functionality (Section 3.24.3.3.2(iii)).¹⁰² Comonomer incorporation of up to 4.2 mol% and molecular weights of up to 100 000 g mol⁻¹ are reported, with polymerization activities 3 times higher than that for the corresponding reaction using Et(Ind)₂ZrCl₂ as catalyst precursor.

3.24.3.3.2 Lewis acidic protective groups – aluminium alkyl compounds

Most reactions occurring between the active catalyst species and polar monomers are simple Lewis acid/base reactions. The active catalyst usually consists of a reasonably strong Lewis acid, while the functional groups of the polar olefinic monomers such as alcohols or amines are Lewis bases. The approach to polymerize such polar olefinic monomers via coordination polymerization pathway with early transition metal complexes results in formation of the acid-base adduct. This adduct is no longer active for the desired olefin polymerization reaction. Most commonly used protection groups are aluminum-based organic compounds due to their cheap and wide commercial availability and their ubiquitous application as impurity scavenger in common polymerization processes. In principle, other Lewis acids could be used as well, but beside titanocene complexes, no examples are reported in literature. The use of [Ph₃C][B(C₆F₅)₄] as protecting agent as proposed by Wilén et al.83 has not been confirmed.

Due to their ubiquitous presence in transition metal-catalyzed polymerization reactions, alkyl aluminum compounds as protective groups are extensively studied. Their effect is based on the reaction of aluminum alkyl compounds with Lewis basic (and therefore catalyst poisoning) oxygen or nitrogen atoms of the monomers (Scheme 13). As a result, coordinative poisoning of the catalyst is prevented in subsequent polymerization reactions.

$$(H_n^{O})^{O} = \frac{AIR_3}{(H_n^{O})^{O}} = \frac{AIR_3}{(H_n^{O})^{O}} =$$

Scheme 13 Exemplary reaction of aluminum alkyls with functional monomers (R = alkyl, E = AIR₂, alkyl, trimethylsilyl).

Due to the widespread usage of aluminum alkyls in olefin polymerization reactions (e.g., as water scavenger or for catalyst alkylation), it is often difficult to assess the influence of changes in the reaction conditions on a specific observance in the copolymerization behavior. The choice of an appropriate aluminum compound is crucial for a satisfactory incorporation of polar monomers into polyolefins. MAO, often used for catalyst activation, is not always able to protect the catalyst from deactivation.¹⁰³ This can be attributed to insufficient complexation^{103,104} and a nonuniform composition of the commercial MAO solutions.¹⁰⁵ The contained trimethylaluminum (TMA) can also lead to increased chain transfer from the catalyst to the present aluminum compounds.¹⁰⁶ Hence, isobutyl modified MAO, for example, exhibits better protective characteristics.¹⁰⁷ Therefore, and due to the difficult examination of MAO containing reaction mixtures,¹⁰⁵ the addition of further well-defined aluminum compounds like TMA, triethylaluminum (TEAL), tri-n-butylaluminum (TNBA), TIBA, and tri-n-octylaluminum (TOA) has been examined.^{103,106,108–111}

The nature of the alkyl group in aluminum alkyl compounds has a huge influence, not only on the polymerization activity, but also on the polymer microstructure. Imuta *et al.* reported that TMA- or TEAL-protected allyl alcohol produces end-hydroxylated poly(ethene) in the copolymerization with ethene by 35/MAO (Figure 19).^{106,109} This can be explained by formation of a dormant zirconium species with an oxygen atom attached to the zirconium, followed by a chain transfer from zirconium to aluminum. While the small aluminum compounds such as TEAL and TMA predominantly lead to this chain transfer reaction, larger compounds such as TIBA allow further ethene insertion following incorporation of the allyl alcohol monomer (Scheme 14).¹⁰⁶ A similar mechanism was also proposed for the polymerization of α -olefin- ω -amines, which also lead to terminal amino-functionalized polymers by using TMA.¹⁰⁸

Kawahara et al. undertook a more detailed study of homopolymerization of alkyl aluminum-protected Un-OH 56







Scheme 15 Possible mechanism of the formation of alcohol compounds.

(Figure 25).¹¹⁰ The aluminum alkyls employed in this study were TMA, TEAL, TNBA, and TIBA, while Et(Ind)₂ZrCl₂/MAO was applied as the catalyst system. Neither dimers nor oligomers of the Un-OH were detected in this reaction. Instead, beside the starting material, a number of saturated alcohols can be found. The composition of the produced alcohols is controlled by the nature of the aluminum alkyl used for the protection of the starting material. In the case of TMA, only small amounts of dodecan-1-ol can be found, most likely due to a coordination of the oxygen atom of the monomer to the metallocene active center because of the reduced steric bulk of TMA. By this, coordinative insertion of the monomer is suppressed. TEAL produces up to 78 mol% 10-methyl-dodecan-1-ol, which occurs following a reaction pathway via the steps 1-6 to result mainly in the product E (Scheme 15). Usage of TNBA results in a mixture of 45 mol% undecan-1-ol B, formed via the steps 2 and 3-7 and 55 mol% 10-methyl-tetradecan-1-ol F, via the 1-6 pathway. In contrast to this, TIBA produces predominantly B undecan-1-ol in 91 mol% via steps 2 and 3-7 and only 8 mol% of pentadecan-1-ol. The analysis of the reaction kinetics for these experiments shows that the reaction rate increases with growing steric demand of the aluminum alkyls in the order TMA << TEAL < TNBA, TIBA. While the consumption of the alkenol was limited for TMA, it proceeds until completion for the other aluminum alkyls. Formation of all detected alkenols and alcohols can be explained by a complex reaction mechanism based on olefin coordination-insertion

steps, elimination reactions, as well as transfer reactions to the aluminum compounds (Scheme 15).

3.24.3.3.2(i) Influence of the polymerization conditions on the catalyst performance

A pretreatment of the functional monomer with the protective aluminum compound tends to have an important influence on the polymerization performance.^{65,78} This is attributed to the formation of protected polar monomer prior to the polymerization reaction, hence decreasing the hazard of catalyst poisoning by residual unprotected monomer. During this reaction, dimers or tetramers of polar functional olefins are believed to be formed (e.g., **Figure 24** and **Figure 29**).^{95,105,112} The appropriate pretreatment time for an effective monomer protection clearly depends on the structure and functionality of the monomer as well as on the nature of the aluminum compound. However, pretreatment times longer than 60 min show no significant improvement in polymerization performance.^{65,78}

Seppälä *et al.* studied the influence of reaction temperature on the copolymerization of ethene and Un-OH using Et(Ind)₂ZrCl₂/MAO.⁶⁵ In the range of 30–70 °C, a significant dependency of the polymerization activity can be found. Surprisingly, for the comonomer incorporation a maximum of 9 wt.% is observed at 50 °C, while incorporation at 30 °C and 70 °C is ~6 wt.%. At higher temperature also, catalyst decomposition has to be taken into account. A decrease in activity for the copolymerization of ethene and TIBA-protected 2,7-octadienyl methyl ether with Me2Si(Ind)2ZrCl2/MAO is observed by increasing the temperature from 45 °C to 60 °C. The optimal polymerization activity in this reaction was found for catalyst 38/MAO with higher thermal stability (Figure 19) at 90 °C.103 Similar temperature-dependant deactivation is noted for the bis(phenoxy-imine)-based zirconium complex 45 (Figure 20).¹¹³ Here, an increase of the polymerization temperature from 0 °C to 75 °C results in a continuous decrease of polymerization activity while a maximum of comonomer incorporation is reached at 50 °C. Santos et al. reported that an increase of polymerization temperature in the copolymerization of ethene with MAO-pretreated 10-undecenoic acid by Cp2ZrCl2/MAO increases only the ethene consumption in the beginning of the reaction whereas the incorporation of the polar comonomer is only slightly affected.¹¹⁴ However, the influence of the temperature on the catalyst stability as well as on the stability of the protected monomer in regard to MAO dissociation is difficult to estimate and has not been studied separated from other effects.

It is self-evident that the concentration of the monomers has an influence on their copolymerization behavior. High concentrations of the nonpolar olefin such as ethene or propene results in higher polymerization activities due to the increased incorporation of these monomers.^{91,100,115} Hence, the incorporation level of the polar monomer is accordingly low. To achieve high incorporation rates of the polar comonomer, low concentrations of the nonpolar monomer have to be chosen, which in turn results in low polymerization activities due to the higher steric demand of the aluminum-protected functionalized monomers.

3.24.3.3.2(ii) Electronic and steric influence of the catalyst system on the polymerization behavior of polar olefins

In principle, all Group 4 catalysts are able to polymerize higher α -olefins and can also be used to polymerize polar olefinic monomers in the presence of aluminum alkyl compounds. However, there are significant differences regarding their

tolerance toward functional monomers. While all catalysts show a reduction of the polymerization activity when exposed to functional group-containing olefins, the extent of this decrease varies over a wide range.

Compared to conventional Ziegler-Natta systems, metallocenes exhibit an outstanding tolerance toward polar monomers.⁶⁵ This can be explained by an enhanced steric protection of the metal center from the ligand framework. Hence, closed metallocenes with a narrow gap aperture¹¹⁶ like the unbridged (Ind)₂ZrCl₂ show a smaller negative influence in polymerization performance by addition of polar monomers in comparison to the ansa-metallocenes Et(Ind)₂ZrCl₂, Me₂Si(Ind)₂ZrCl₂, and Me₂Si(2-Me-Ind)₂ZrCl₂ (Figure 18).¹¹⁷ The case of Me₂Si(2-Me-4,5-benz[e] indenyl)₂ZrCl₂ 40 (Figure 19) shows that not only the steric but also the electronic properties of a catalyst have to be taken into account, as this catalyst is a much stronger Lewis acid in comparison to the corresponding indenyl complexes. Hence, reaction with the Lewis basic alcohol occurs more readily, even though it is protected by pretreatment with MAO. From these considerations, it is not remarkable that constrained geometry catalysts such as complex 13 (Figure 12) are much more sensitive to functional groups due to their open structure.¹¹⁵

Among metallocenes, the so-called 'Kashiwa' catalysts, for example complexes **35** and **36** (Figure 19), exhibit a remarkable tolerance toward functional groups.^{118,119} This tolerance can be explained by the high steric hindrance of the ligand system. Upon activation with MAO, this catalyst is able to copolymerize Un-OH and ethene without further addition of aluminum alkyl. High comonomer contents can be achieved under appropriate conditions. Also, the polymerization of numerous other functionalized monomers such as epoxides, succinic anhydrides, alcohols, and carboxylic acids as well as several norbornene derivatives have been claimed in the patent literature.¹¹⁹

Bis(phenoxy-imine)titanium chloride complexes also exhibit a remarkable tolerance toward functional groups.^{113,120,121}



Figure 18 Copolymerization diagram for co(ethene-Un-OH) with different metallocenes. Reproduced from Ahjopalo, L.; Löfgren, B.; Hakala, K.; *et al. Eur. Polym. J.* 1999, *35*, 1519.⁶⁷

SiEt₃

^tBu



Figure 19 Examples for sterically protected metallocene catalysts capable for the polymerization of polar functional olefins.



Figure 20 Fujita catalysts employed for the polymerization of polar monomers.

Terao *et al.* reported the copolymerization of ethene and 5-hexene-l-yl-acetate.¹²⁰ While the corresponding zirconium complex is practically inactive in the copolymerization reaction, the titanium complexes such as **42–44** (Figure 20) produce copolymers with an exceptional high activity of up to 515 kg_{polymer} mol_{catalyst} ⁻¹ h⁻¹ (**42**), molecular weights of up to 500 000 g mol⁻¹ (**43**) and a comonomer content of up to 3.2 mol% (**44**). DFT calculations for this system show that the energy difference between ethene- and carbonyl-coordinated complexes is significantly lower than that for reference compounds such as Cp₂TiCl₂. This can be attributed to the reduced Lewis acidity of the catalyst due to the stronger back bonding of the [O⁻,N]-ligands. Related catalyst systems have also been claimed to polymerize monomers such as MA, 4-ethyl pentenoate, norbornene carboxylate, and Un-OH.¹²²

Similar results were observed for the copolymerization of ethene and Un-OH or 5-hexen-1-ol, respectively, using 46/MAO (Figure 20) as catalyst system.¹²¹ In this report, copolymerization of ethene and 10-undecenoic acid with the same or even higher activities as in the copolymerization with Un-OH are achieved. The overall activity for the hydroxyland acid-functionalized monomers is only slightly reduced compared to ethene homopolymerization. Beside this, polymerization activities of 42 are several times higher than those observed in the Et(Ind)₂ZrCl₂/MAO system.

The recently developed tridentate titanium complexes 47 and 48 (Figure 21) base on the same principle, the incorporation of an electron donating ligand, which reduces the Lewis acidity of the titanium center.¹⁰² These catalysts are able to produce copolymers of ethene and functionalized



Figure 21 Tridentate $[O^-NS^R]$ TiCl₃ catalyst precursor developed by Yang and co-workers.



Figure 22 (a) Titanium-ketimide complexs used by Dias *et al.*; (b) Constrained Geometry Catalyst developed by van Tol and co-workers.

olefins, such as alcohols, carboxylic acids, and even phosphines with high activities and good comonomer incorporation ratios.

Replacement of a Cp-group by an ketimide moiety was successfully carried out by Dias *et al.* in several titanium complexes for the copolymerization of Un-OH and ethene.¹²³ These reported compounds **49–51** (Figure 22) are all active in copolymerization reactions, even though (Cp)(N=C^tBu₂) TiCl₂), with the lowest activity in the homopolymerization of ethene exhibits the highest tolerance toward the polar function.

Recently, several titanium(III) complexes have also been reported to copolymerize polar monomers with a good tolerance toward functional groups. Jensen and co-workers employed $Cp*TiMe_3/[Ph_3C][B(C_6F_5)_4]$, which is reduced in situ by the addition of zinc powder.^{124,125} The catalytically active species is presumably a Ti(III) complex able to polymerize styrene (>95% syndiotactic, 170000 g mol⁻¹) and to mediate the polymerization of methyl methacrylate (MMA) by a group transfer protocol-like pathway (>65% syndiotactic, 70 000 g mol⁻¹). Additionally, it mediates the copolymerization of MMA and styrene to yield a random 80% co-isotactic poly[styrene-co-(methyl methacrylate)], which contains 4% MMA. The mechanisms for both homopolymerizations using metallocene catalysts are principally known. While the homopolymerization reaction of styrene occurs via a single-site 2,1-insertion pathway, the homopolymerization of MMA is believed to proceed via a 1,4-insertion conjugated addition mechanism (group transfer polymerization (GTP) like), which in principle also could proceed via a 2,1-olefinic insertion. Hence, it is likely that the copolymerization occurs by a combination of these two mechanisms (Scheme 16). The crucial step in this mechanism follows a GTP which, might be possible due to the lower Ti oxidation state. Noncoordinative reaction mechanisms were excluded by control experiments.

The well-characterized CpTiCl₃/MAO system was reported to copolymerize MA and styrene with low molecular weight (7800 g mol⁻¹) but high comonomer content (50%).^{126,127} A similar mechanism to the one depicted in **Scheme 16** was proposed by Cunningham and Fassihi as shown in **Scheme 17**, based on competitive coordination of the styrene and the MA.¹²⁷

The constrained geometry system $[(1,2,4-tri-^iPr-3-EtNMe_2)Cp]TiCl_2$ **52** (Figure 22)/MAO has been claimed to copolymerize ethene with 5-hexen-1-ol and 5-norbornene-2-carboxaldehyde with low activities but high amounts of comonomer incorporation compared to conventional metallocene catalyst systems.¹²⁸

Recently, the application of phenoxy-imine-type vanadium (III) complexes 53–55 (Figure 23) for the copolymerization of ethene with polar hydroxyl group-functionalized α -olefins, such as Un-OH, 5-hexen-1-ol, and 3-butylene-1-ol, has been reported.¹²⁹ The resulting polymers are random copolymers with a Un-OH incorporation of 13.9 mol%, molecular weights of up to 177 000 g mol⁻¹, and remarkable activities of up to 12.8 kg_{polymer} mmol_V⁻¹ h⁻¹.







Scheme 17 Competition between methyl acrylate (MA) and styrene in copolymerization using CpTiCl₃/MAO (R = alkyl).¹²⁷



Figure 23 Vanadium(III) complexes developed by Mu et al.¹²⁹

3.24.3.3.2(iii) Functionalized olefins suitable for alkyl aluminum-protected polymerization

As already mentioned in Sections 3.24.3.1.3 and 3.24.3.2, the structure of the polar monomer has a crucial influence on the polymerization behavior. Hence, the choice of a suitable monomer is of great importance for the success of a copolymerization reaction. Beside steric protection of the functional group, the length of the alkyl spacer between the olefinic and the polar functionality has a huge influence on the polymerization, several examples of polymerization reactions of different functionalized monomers will be discussed in detail, ordered by their functionality.

Alcohols Alcohols can be well protected by aluminum alkyls (even if sterically hindered) and are extensively studied. The influence of the steric hindrance for the monomer as well as the aluminum compound, the spacer length between the olefinic end group and the functional group, the catalyst structure as well as the ratios catalyst:aluminum compound: comonomer, and the reaction conditions have been investigated.

For an efficient protection of the functionalized monomer, which results in polymerization reactions with good activities, molecular weights, and comonomer incorporations, an aluminum alkyl:alcohol ratio of at least 1:1 is required.^{103,112} At this component ratio, aluminum-bridged, dimeric complexes of the monomer are proposed (Figure 24). NMR spectroscopic examinations for the reaction of Un-OH with different amounts of MAO and TEAL suggest the formation of tetrameric Al₄(R')_n(OR)_{12-n} (n = 6, 4), containing a central aluminum surrounded by six oxygen atoms (Figure 24(b)).¹⁰⁵

The second important factor, which has an influence on the copolymerization reaction, is the structure of the applied monomer. Löfgren and co-workers intensively studied the structural effect of different alcohols as well as other polar monomers on their copolymerization reactions with simple nonfunctionalized α-olefins. A study of several α-hydroxy-ω-olefins of different chain length and different steric demands (Figure 25) shows that the length of the alkyl spacer between the olefinic and the hydroxyl group of the monomer has an influence on its polymerization performance.⁶⁴ In comparison of Un-OH 56 (Figure 25) and 5-hexen-1-ol 57 (Figure 25, Hex-OH), the influence of the chain length on the polymerization activity can be detected, which has already been discussed in Section 3.24.3.1.3.¹¹⁷ However, the effect of the chain length on the comonomer reactivity, which is determined by the comonomer incorporation in the resulting copolymer, is clear. Shorter chains result in reduced monomer reactivities, most probably due to



Figure 24 Assumed structure of the complex formed by (a) 33 (Figure 17) and TIBA at a monomer: alumium alkyl ratio of 1:1,¹¹² (b) TEAL and Un-OH.¹⁰⁵



Figure 25 Several different alcoholic olefins studied by Löfgren et al.

the high sterical demand of the aluminum-protected hydroxyl group. The detrimental factor leading to a stronger reduction of the polymerization activity for primary and secondary alcohols compared to tertiary ones is explained by the increasing steric protection. However, in terms of comonomer incorporation, the chain length is more important. Hence, it is not surprising that 2-methyl-3-buten-2-ol **58** (Figure 25) cannot be incorporated at all (even though the catalyst activity during the polymerization is high), while 12-tridecen-2-ol **59** (Figure 25) exhibits the highest incorporation among the investigated polar olefin comonomers.

Similar results, especially with Un-OH as reference substance, have been reported in numerous publications with focusing different subjects such as monomer structure,^{101,115,130} catalyst structure,^{65,91,113,115,119,121} structure of the aluminum alkyl,^{104,106,107,110,115,131,132} and amount of the aluminum alkyl.^{65,105,107,112,131,133-135} As most of these publications do not deliver new insights or are discussed elsewhere in this publication, they will be disregarded in this chapter.

Additionally, polymerization reactions of nonlinear monomers are reported in the literature. Copolymerization of the norbornene derivative **33** (Figure 17) with ethene was examined for Cp₂ZrCl₂, Et(Ind)₂ZrCl₂, and Me₂Si(Cp)₂ZrCl₂ produce copolymers with ethene after activation with MAO, showing high comonomer incorporation (up to 6.2 mol%) and reasonable polymerization activities.¹³⁶ Similar results were found by in the co- and terpolymerizations of TIBA-protected **33** (Figure 17) with ethene and norbornene by different zirconocene catalysts upon MAO activation.^{91,95,112} The melting points of the copolymers for **33** (Figure 17) and ethene can be varied from room temperature to more than 100 °C depending on the molecular weight and the comonomer content. The same observation applies to the glass transition temperature of the terpolymers of ethene, norbornene, and 33 (Figure 17), which can vary from 23 °C to 124 °C. The similar terpolymerization of ethene, norbornene, and TIBA-protected 3-buten-1-ol using Et(Ind)₂ZrCl₂/MAO result in polymers with different degrees of crystallinity adjustable by the amount of norbornene in the terpolymer feedstock.¹³⁷

Un-OH can also be copolymerized with propene on a MAO-pretreated glass surface by Et(Ind)₂ZrCl₂.¹³⁸ Parts of the resulting copolymer are chemically bonded to the surface, as shown by extraction experiments, scanning electron microscopy (SEM) microscopy as well as Fourier transformation infrared spectroscopy (FTIR) analysis. Similar results were reported for the copolymerization of ethene with Un-OH by the same catalyst system on the organically modified silicate montmorillonite (OMMT) resulting in PE-Un-OH/OMMT nanocomposites which consist of well-exfoliated OMMT dispersions and controlled degrees of PE functionalization.¹³⁹

Monomers containing phenol groups with sterically hindered hydroxyl functionalities have attracted special interest due to their ability to act as antioxidants.¹⁴⁰ The majority of commercial antioxidants exhibit low molecular weights, a feature which is problematic for the usage as additives in plastics. Contamination by leaching of the polymer additives into the human environment could be reduced by usage of macromolecular antioxidants or incor poration of such functional groups into polymers.¹⁴¹⁻¹⁴³ The first reports on polymer-bound phenolic stabilizers for the preparation of poly[propene-*co*-4-(hept-6-enyl)-2,6-di-*tert*-butylphenol] show much higher stability of the resulting copolymer toward irradiation than commercial available poly(propene) containing non-polymer-bound stabilizers.¹⁴⁴ In the copolymerization reactions of



Figure 26 Different polymerizable phenolic monomers.

ethene and 6-tert-butyl-2-(1,1-dimethylhept-6-enyl)-4methylphenol 61 (Figure 26) by different MAO-activated zirconocenes and Ziegler-Natta catalyst systems, an interkinetic profile was obtained for esting the copolymerization. This showed an initial increase of the polymerization rate upon phenol addition, followed by a subsequent decline indicating a decay process.^{145,146} For the unusual increase in reactivity, different possible explanations are presented: (1) the reaction of the phenolic monomer with excess TMA contained in MAO results in a decay of TMA, which therefore cannot interfere with the active catalyst by the formation of the inactive Me-bridged dinuclear species or chain transfer reactions;¹⁴⁷ (2) the aluminum compound formed in the reaction of the phenolic monomer with TMA can act as an additional cocatalyst; and (3) the phenolic monomer increases the dielectric constant of the reaction medium and therefore enhances the reactivity of the metallocene. The obtained copolymers exhibit increased thermooxidative stabilities compared to the homopolymers. For example, poly[propene-co-tert-butyl-2-(1,1-dimethylhept-6enyl)-4-methylphenol] shows an 70-120-fold increase in thermooxidative stability at 110 °C in air even at low comonomer contents. Similar results were observed for the copolymerization of ethene with a range of 2,6di-tert-butylphenol-based olefins (62a-d in Figure 26).¹⁴⁸ All monomers can be copolymerized by rac-Et (THInd)₂ZrCl₂/MAO even though the results for 62a and 62d are the best. The copolymers again show increased thermal stabilities compared to the homopolymers. However, an initial increase in polymerization activities upon the addition of these polar monomers has not been reported.

The styrene derivative 4-methene-(3,5-di-*tert*-butyl-4-phenoxy)styrene **63a** (Figure 26) and its methylsilylated analog **63b** were successfully copolymerized with styrene by indenyltitanium trichloride/MAO from Wilén and co-workers.¹⁴⁹ The produced copolymers exhibit relatively high syndiotacticity, molecular weight, and thermal stability compared to PS.

Copolymerization of another interesting vitamin E analog polar olefin was reported in the same work. This is a novel tocopherol-based olefin 64 (Figure 27), which can be copolymerized with ethene using the *rac*-Me₂Si(THInd)ZrCl₂/MAO catalyst system with reasonable activities ($2500 \text{ kg}_{polymer} \text{ mol}_{Zr}^{-1} \text{ h}^{-1}$) and molecular weights ($41\,000 \text{ g} \text{ mol}^{-1}$).¹⁴⁹ However, the



HO

thermooxidative stability of the polymer is only slightly increased by this comonomer.

64

Other interesting new aspects for the copolymerization of alkenols with α -olefins and early transition metal catalysts are occasionally delivered by the development of new polymerization catalysts. For instance, the catalyst system developed by Kashiwa et al. possesses a steric crowding, which even copolymerization of unprotected enables alkenols (Section 3.24.3.3.2(ii)).^{109,118} Bis(phenoxy-imine)-based titanium and zirconium Fujita-type complexes have been used for the copolymerization of α-olefins and Un-OH, which show only slightly decreased polymerization activity (Figure 20).^{113,121} In contrast to this, usage of titanium ketimide complexes 49-51 (Figure 22) shows a drastically decreased copolymerization activity for ethene and Un-OH compared to the homopolymerization.123 Vanadium(III) catalysts bearing bidentate anionic [N^O]-ligands (53-55, Figure 23) are capable of copolymerizing Un-OH, 5-hexen-1-ol, and 3-butylene-1-ol with ethene with good polymerization activities.¹²⁹

Ethers Weak interaction of ether functionalities and aluminum alkyls results in poor protection of the ether group, especially for the sterically encumbered MAO protection reagent,¹⁰¹ which is also observed for silyl ethers. Therefore, this weak interaction with the protecting agent leads to similar catalyst deactivation compared to the respective alcohol, which is protected by MAO as shown by Löfgren et al.¹⁰⁰ The first publication on the polymerization of ether-functionalized olefins using Ziegler-Natta catalyst systems reports on the homopolymerization of 7-phenoxy-1-heptene and 4-allylanisole with TiCl₃/Et₂AlCl in 94% and 15% yield, respectively.¹⁵⁰ In addition, metallocene catalysts have also been applied for the polymerization of olefinic ethers, but their polymerization requires steric protection by silvloxy groups (Section 3.24.3.3.1) and sterically protected unbridged metallocenes (Cp*₂ZrMe₂).⁸⁷

Also, the influence of the steric demand of ethers on their polymerization behavior was systematically studied by Stojcevic and Baird using rac-Et(Ind)₂ZrCl₂ as catalyst.⁷⁷ The examined monomers CH2=CH(CH2)8OR (R=Me, PhCH2, Ph₃C, Me₃Si, and Ph₃Si) have been copolymerized with ethene and propene upon catalyst activation by an excess of MAO. The expected higher activity and polar monomer incorporation for increasing steric encumbrance of the groups R could not be observed. While the ether incorporation in the copolymerization reactions with ethene is generally very low, better results can be achieved in propene copolymerizations. The highest comonomer incorporation is observed for R=Me, the least sterically hindered olefin used in this study, followed by R = TMS. Moreover, the obtained molecular weights are highest for these two copolymers, and for all copolymers even higher than for propene homopolymerization under the same conditions. This effect is explained by a contact ion pair of the catalyst cation and the MAO anion, which is eventually separated by ether-functionalized molecules. Successful test of this hypothesis was carried out by addition of the saturated n-decyl methyl ether, which gives similar results in the copolymerization of propene with 1-hexene.

The copolymerization of ethene with TIBA-precomplexed allyl ethyl ether and allyl propyl ether has been catalyzed by **38**/MAO (**Figure 19**) and related zirconocenes.¹³⁵ While the incorporation level of the allyl ethyl ether was highly dependent on the TIBA:ether ratio, in case of the allyl propyl ether, the TIBA concentration had a negligible effect. However, for the latter case, the polymerization temperature had a high influence with an optimum at 45 °C. Furthermore, the copolymerization of TIBA-protected 2,7-octadienyl methyl ether with ethene has been reported recently.¹⁰³ Different catalysts were employed, with the sterically protected zirconocene **38** (**Figure 19**) as the most active upon MAO activation. In this case, the catalyst even outperforms a late transition metal nickel α -diimine catalyst system (Section 3.24.4.2).

Copolymerization of ethene with a number of hydrolyzable ethers (65–68, Figure 28) by the metallocene 41/MAO (Figure 19(b), Section 3.24.3.3.2) and the constrained geometry catalyst 13/MAO (Figure 12, Section 3.24.3.1.3) has been reported.¹⁵¹ The resulting copolymers are partially degradable, especially under basic, but also acidic conditions.

Carboxylic acids Even though (co)polymerization of carboxylic acid-functionalized olefins (together with nonpolar olefins in case of copolymerization) is much more difficult than the polymerization of alcohol- or ester-functionality bearing olefins, several successful attempts have been reported. Especially, Löfgren and co-workers published intensive studies on oxygen-functionalized olefins. To summarize their results on the copolymerization of ethene and 10-undecenoic acid, it can be stated that (co)polymerization is possible under several conditions. Careful choice of the comonomer structure, especially in terms of intrinsic steric protection of the functional group, as well as the distance between the double bond and the polar group is of critical importance.^{64,117,130} 10-undecenoic acid, protected with an excess of MAO, gives access to a metallocene-catalyzed copolymerization with ethene at relatively low activities.¹³⁰ For an effective protection of the carboxylic acid functionality, a monomer:aluminum alkyl ratio of 1:2 is necessary.^{95,112,114} In contrast to the alcohol-functionalized compounds, dimer formation of two functionalized olefinic monomers and containing four aluminum alkyls is proposed (Figure 29). These olefin/aluminum alkyl complexes are obviously bulky. Therefore, the efficient protection of the carboxylic acid functionality leads to increased polymerization activities, but also to low comonomer incorporation due to the increased steric demand.

Several Ziegler–Natta catalyst systems have been reported to (co)polymerize carboxylic acid containing monomers, for example, in the copolymerization of aluminum-protected 10-undecenoic acid with propene^{152–157} or 1-hexene and 4-methyl-1-pentene¹⁵⁰ with α -olefins using TiCl₃/Et₂AlCl as catalyst system.

Due to the low polymerizability of carboxylic acids by metallocene catalysts, only a limited number of successful copolymerization reactions have been published. Beside copolymerization reactions of 10-undecenoic acid with ethene^{117,130} and propene,⁶⁴ co- and terpolymerization reactions of norbornenecarboxylic acid 34 (Figure 17) with α -olefins have been reported.^{95,112}

Recently, new catalysts have been employed, which exhibit good tolerance toward carboxylic acid-functionalized



Figure 29 Proposed 2/1 dimer structure formed by the reaction of TIBA and norbornene carboxylic acid.



Figure 28 Comonomers bearing hydrolytically cleavable ether functions used by Wilson et al.¹⁵¹
monomers with a-olefins, for example, in the copolymerization of 10-undecenoic acid with ethene using bis(phenoxyimine)-based zirconium and titanium complexes 42-46 (Figure 20) and a 2:1 ratio TIBA:OH.¹²¹ The polymerization activities for these reactions are only slightly lower than for the corresponding ethene homopolymerization and interestingly even higher than for the copolymerization reaction of ethene and Un-OH or Hex-OH. Catalysts 47 and 48 (Figure 21) are reported to copolymerize ethene and 10-undecenoic acid upon MMAO-activation with polymerization activities comparable with the corresponding Un-OH copolymerization and molecular weights around 30 000 g mol⁻¹, while the comonomer incorporation is only low with 1.5 mol%.¹⁰² The copolymerization of pentadec-14-enoic acid and ethene by 35 (Figure 19, Section 3.24.3.3.2) upon MAO activation has been claimed to polymers produce with molecular weights of 71 000 g mol⁻¹.¹¹⁹

Carboxylic acid chlorides Even though several copolymerization reactions of carboxylic acids have been reported, only one publication on the copolymerization of carboxylic acid chlorides and α -olefins can be found in literature. Kaya *et al.* observed the copolymerization of propene with 10-undecenoyl chloride using *rac*-Et(Ind)₂ZrCI₂/MAO.¹⁵⁸ This copolymerization reaction exhibits a lower activity, molecular weight, and comonomer content in the polymer compared to the corresponding carboxylic acid.

Esters Early examinations for the polymerization of ω -ester- α -olefins by different Ziegler-Natta catalyst systems have been reported. Using TiCl₃ activated with ⁱBu₂AlCl or Et₂AlCl, it is possible to homopolymerize a variety of different ester-functionalized olefins. Among the reported monomers, the polymerization activity is in direct correlation to the respective sterical protection of the functional group and higher activities are observed with increasing steric hindrance.159 Corresponding results can be found for functional olefins with decreasing chain lenght.^{160,161} Copolymerization of 2,6dimethylphenyl-10-undecenoate with 1-dodecene, 1-octene, 1-hexene, propene, and ethene is also possible under the applied conditions, ¹⁶² as well as the preparation of terpolymers with ethene and propene.¹⁶³ Employment of a VOCl₃/AlEt₂Cl catalyst system is feasible as well for these terpolymerization reactions, which result in a higher degree of ester incorporation. Production of several other ester-containing copolymers has been claimed in the patent literature. Among these are copolymers of 2,6-dimethylphenyl-10-undecenoate, phenyl-10-undecenoate, and ethyl-10-undecenoate with propene and ethene, as well as MMA-containing copolymers,164 methyl-10-undecenoate copolymers with 1-octene, 165,166 copolymers of allyl-17-octadecenoate with ethene and propene,167 and block or random copolymers of n-butyl-10-undecenoate with propene, 1-hexene, and 4-methyl-1-pentene.¹⁵⁰

Regarding metallocene-based catalysts, several reports concerning the copolymerization of functionalized olefins with simple α -olefins have been published. In course of their extensive studies on the metallocene-catalyzed polymerization of aluminum-protected oxygen-containing monomers, Löfgren *et al.* also examined ester-functionalized olefins.^{64,101,117,130} Decomposition reactions could be observed in the reaction of ester functionalities and MAO.¹⁰¹ For example, during the reaction of *tert*-butyl undecenoate with MAO, slow formation of alkene fragments can be observed by NMR spectroscopic experiments, which are formed via the free acid and subsequent alkyl-oxygen cleavage, followed by reaction of the resulting tert-butyl cations with a further equivalent of MAO. An analogous reaction is not observed in the case of methyl-9-decenoate. Therefore, this functional olefin could be copolymerized with ethene using ("BuCp)₂ZrCl₂/MAO as catalyst system with comparatively low polymerization activities even at low comonomer concentrations in the feed.¹³⁰ Despite the observed slow decomposition reaction explained above, tertbutyl-10-undecenoate was found to exhibit better properties in terms of polymerization activities in the copolymerization with propene using Et(Ind)₂ZrCl₂/MAO compared to methyl-9-decenoate due to the increased sterical protection of the functional group.⁶⁴ However, activities are still notably lower than the corresponding acids due to the weaker interaction between the functional group and the aluminum alkyl.

New interesting results for the polymerization of ester-functionalized α -olefins were recently reported by Terao *et al.* with the ethene/5-hexene-1-yl-acetate copolymerization by different bis(phenoxy-imine)titanium complexes **42–46** (Figure 20).¹²⁰ Depending on the catalyst structure high activities (up to 515 kg_{polymer} mol_{cat.}⁻¹ h⁻¹), high molecular weights (up to 500 000 g mol⁻¹) or high polar monomer contents (up to 3.2 mol%) could be obtained. Additionally, two reports on the copolymerization of styrene and MMA have been published using Ti(III) catalysts as discussed above (Section 3.24.3.3.2).^{126,127}

Ketones α -Olefins bearing keto functionalities show also only weak interactions with aluminum compounds resulting in insufficient protection for the successful polymerization by transition metal catalysts.⁶⁴ Additionally, undesired side reactions, for example, the keto-enol tautomerization of 2,2dimethyl-11-dodecen-3-one in combination with MAO were reported.¹⁰¹

Epoxides Imuta *et al.* demonstrated the copolymerization of epoxides such as 1,2-epoxy-9-decene with ethene by the sterically protected zirconocene **36** (Figure 19) upon MAO activation.¹¹⁹ The monomer was reacted with TIBA prior to polymerization and the resulting polymers exhibit molecular weights of about 130 000 g mol⁻¹.

Carboxylic acid anhydride Only one case of a copolymerization of carboxylic acid anhydrides has been reported with the copolymerization of pentapropenyl succinic anhydride and ethene by **36 (Figure 19)** upon MAO activation, resulting in copolymers with molecular weights of 250 000 g mol⁻¹.¹¹⁹

Amines As reported in Section 3.24.3.2.2, sterically demanding amines can be polymerized without further protection under certain conditions. However, aluminum-protected amines are usually employed to suppress catalyst deactivation reactions. Even if protected, distinct differences in reactivity can be found for the primary, secondary, and tertiary amines due to their intrinsic steric protection. Under the same conditions, the copolymerization activities of ethene with 10-undecenylamine, N-methyl-10-undecenylamine, and N,N-dimethyl-10-undecenylamine increase from 950 to 1700 and 2100 kg_{polymer} mol_{Zr}⁻¹ h⁻¹, respectively, using a four-fold excess of aluminum alkyls.¹⁶⁸ Surprisingly, a decrease in polymerization activity can be observed upon changing the monomer from N,N-dimethyl- to N,N-di-sec-butyl- to N, N-di-iso-propyl-protected 10-undecenylamines.

Hagihara *et al.* reported the copolymerization of allyl amine with propene by *rac*-Me₂Si(Ind)₂ZrCl₂/MAO using a TMA or TIBA protecting approach.¹⁰⁸ However, only low activities and enhanced chain transfer reactions to the TMA are observed. This functional olefin can also be copolymerized with ethene by **35** (**Figure 19**) upon MAO activation.¹⁶⁹ Use of TIBA is preferred over TEAL for the protection, as higher molecular weights (up to 25000 g mol^{-1}) and overall higher amine incorporation levels were achieved. This can be attributed to a lower extent of chain transfer reactions with TIBA compared to TEAL (Section 3.24.3.3.2(i)).

An interesting group of amino-functionalized α -olefins are the polymerizable hindered amine light stabilizers (HALS) introduced by Wilén and co-workers.^{82,83,170} Several olefinic 2,2,6,6-tetramethylpiperidine derivatives were copolymerized with α -olefins to result in polyolefins with internal light stabilizer functionalities and show no leaching during usage. For this purpose, several structurally different HALS containing monomers **69–75** (Figure 30) were tested in the copolymerization with ethene and propene by Ziegler–Natta systems as well as different homogeneous and supported metallocene catalysts. The resulting copolymers clearly exhibit higher thermooxidative and light stabilities, as, for example, observed for poly(ethene-*co*-2-(but-3-enyl)-2,6,6-trimethylpiperidine) after aging at 115 °C.⁸³

Copolymerization of different HALS-substituted norbornene derivatives **76–78** (Figure 30) and ethene using a vanadium-based Ziegler–Natta catalyst system shows only very low activities, and the resulting polymers partially bear high amounts of the comonomer.¹⁷¹ These copolymers also show good characteristics in aging tests.

Copolymers ethene and 4-(7-octen-1-vl)-N, of N-diphenylaniline 79 (Figure 31) were successfully synthesized by Et(Ind)₂ZrCl₂/MAO.⁸⁴ The copolymerization reactions proceed with good activities (up to 25.7×10^3 kg_{polymer} mol_{Zr} ⁻¹ h⁻¹ bar ⁻¹), resulting in polymers that exhibit molecular weights of around 100 000 g mol⁻¹, high comonomer incorporation (up to 6.1 mol%) as well as high thermal stability and good hole-transporting abilities for the stable green emission of (tris(8-hydroxyquinolinolato) aluminum (Alq₃). Therefore, these polymers are promising materials for optoelectronic device applications. For their potentially interesting photochemical and electrochemical properties, other related amino-functionalized α -olefins are also known 9-(Bicyclo[2.2.1]hept-5-en-2-ylmethyl)-9H-carbazole 80 (Figure 31) can be copolymerized with ethene by PhC(CpFlu)ZrCl₂ and Ph₂C(CpInd)ZrCl₂, respectively, using a large excess of MAO, which is also prereacted with the polar monomer.¹⁷² Similar results were obtained by the polymerization of N-(vinylphenyl)carbazole 81 (Figure 31).¹⁷³

Imides For this class of olefin monomers, only VCl₄/AlEtCl₂ is reported to be applicable in the copolymerization of aluminum-protected imides, such as *N*-vinylsuccinimide/AlEtCl₂, with ethene and propene.¹⁷⁴

Amides Homo- and copolymers of sterically hindered ω -amides- α -olefin using TiCl₃/Et₂AlCl as catalyst system have been reported by Holler and Youngman.¹⁵⁰ For precomplexation reactions more than one equivalent of aluminum alkyls is necessary. Copolymerization of butyl- and phenyl-substituted 10-undecenamide with 1-hexene, 4-methyl-1-pentene or 1-dodecene resulted in copolymers with an amide incorporation of typically 6–10%.







Figure 31 1-olefins suitable for photochemical and electrochemical macromolecular materials.



Figure 32 Structures of the polymerized oxazoline derivatives 2-(9-decen-1-yl)-1,3-oxazoline 82, 2-(9-decen-1-yl)-4,4-dimethyl-1,3-oxazoline 83, and 2-[4-(10-undecene-1-oxy)phenyl]-1,3-oxazoline 84.

Löfgren and co-workers reported the copolymerization of ethene and propene with several long-chain olefinic amides (methyl-, *tert*-butyl-, dimethyl-, diethyl-, and di-*iso*-propyl-substituted 10-undecenamides) using Et(Ind)₂ZrCl₂/MAO and Me₂Si(2-Me-Ind)₂ZrCl₂/MAO.¹⁶⁸ Here, the copolymerization reactions show a dramatic decrease of activity in all cases compared to related amino-functionalized olefins.

Oxazolines Reports on the copolymerization of α -olefin- ω -oxazolines with α -olefins are rare. Due to two heteroatoms in the monomer the deactivation of the catalyst is very likely. However, copolymerization reactions of the functionalized oxazolines **82–84** (Figure 32) with propene have been reported.^{158,175}

Although a high amount of MAO was used in these copolymerization reactions, only low activities could be achieved, with best obtained results for the sterically most demanding monomer **83**. Increasing comonomer content leads to a decrease of the polymer melting points as a summary effect resulting from the decrease in isotacticity, reduced polymer chain length and higher comonomer content. As 2-oxazolines are known to undergo thermal ring-opening addition reactions with carboxylic acids, crosslinked polymer blends are obtained by blending oxazoline-functionalized polyolefins with polystyrene bearing carboxylic functionalities at elevated temperatures (**Scheme 18**).¹⁷⁶

Phosphines and phosphonates Due to their highly Lewis basic character, reports on the polymerization of phosphines using early transition metal catalysts are very rare. Copolymerization of ethene and diphenyl(undec-10-enyl) phosphine was reported very recently by Yang *et al.*¹⁰² This polymerization is performed using 47 (Figure 21), a catalyst which exhibits a remarkable tolerance toward polar functional groups (Section 3.24.3.3.2(ii)). Beside this, the application of the TiCl₃/Et₂AlCl catalyst system has also been reported in the same reaction.¹⁵⁰ Holler and Youngman demonstrated the polymerization of dimethyl-10-undecenylphosphonate using

 $\rm TiCl_3$ and $\rm Et_2AlCl$ as catalyst system resulting in a small amount of an insoluble polymer. 150

Thioether Copolymerization of 3-(penten-1-yl)thiophene with ethene by the constrained geometry catalyst 13 (Figure 12) upon MAO activation was reported by Zhang and Hessen in 2002.¹⁷⁷ The presence of the Lewis basic comonomer has no detrimental effect on catalyst productivity or polymer molecular weight compared to the corresponding ethene homopolymerization. An interesting application of this copolymer is the usage as a macromonomer in the FeCl₃-mediated copolymerization with 3-hexylthiophene. This results in poly(3-hexylthiophene) grafted on the pendant thienyl groups of the poly[ethene-*co*-3-(penten-1-yl)thiophene], which is a potential material for light-emitting diodes and nonlinear optical materials (Figure 33).

3.24.3.3.3 Lewis acidic protective groups – titanium-based compounds

An interesting protection approach was introduced by Novak and Tanaka^{178,179} Instead of aluminum alkyls, titanocene complexes of the polar comonomers are used. This is especially usefull for the protection of acrylate and methacrylate comonomers, which are difficult to protect by other methods due to enolate formation. The resulting complexes Tim **85** and



Figure 33 Poly(3-hexylthiophene) grafted on the pendant thienyl groups of poly[ethene-co-3-(penten-1-yl)thiophene].



Scheme 18 Crosslinking of oxazoline containing polymers by ring-opening reaction (PP, polypropene; PS, polystyrene).



Figure 34 Titanocene-protected methacrylic acid 85 (Tim) and acrylic acid 86 (Tia).

Tia 86 exhibit a good protection of the carboxyl group (Figure 34).

In principle, such protection using the carboxylate salt is feasible, but an exchange of the metal cation coordinated to the carboxylate salt has to be taken into account. This would lead to a transfer of the protected olefin between the titanocene and the active catalyst. Copolymerization experiments of Tim/Tia with ethene lead to the desired titanocene-protected copolymers in yields comparable to ethene homopolymerization. Hydrochlorination of the protected polymer regenerates the protecting Cp₂TiCl and the free carboxylic acid of the polymer (Scheme 19).

3.24.4 Late Transition Metals in the Copolymerization of Functional and Nonpolar Olefins

3.24.4.1 The Strictly Alternating Copolymerization of Carbon Monoxide and α -Olefin Comonomers

3.24.4.1.1 General information

The copolymerization of carbon monoxide and α -olefins (mainly ethene and propene; **Scheme 20**) is the prominent example for an olefin/polar comonomer copolymerization system suitable for industrial application. This process was employed by Shell and BP in industrial pilot plants, but the resulting copolymers could unfortunately not be commercially established in the market. The successful implementation in an industrial process was the result of a combination of high catalyst activities and inexpensive monomers as well as the facile control of the reaction and the product properties.

Polyketones, in general, are a versatile class of polymers, which complement nonpolar polyolefins by regular incorporation of ketone functionalities as polar structural motives which causes a high degree of crystallinity. Beside difficulties in polymer processing due to the high melting point close to the decomposition temperature, these copolymers possess numerous interesting properties and are, for example, nontoxic and photodegradable. Additionally, a wide range of polymer analogue modifications as well as the copolymerization with an



Scheme 20 Reaction Scheme for the copolymerization of ethene and carbon monoxide; Pd-based catalysts with bis-chelating phosphine ligands (P^P) and weakly coordinating counterions X.

enormous selection of functional olefins can be employed for additional control of the polymer properties.

Radical copolymerization of ethene and CO (ECO) is possible; however, harsh reaction conditions have to be employed and the resulting copolymer is poorly defined, a common problem in these processes.^{180,181} The first observations concerning the formation of strictly alternating ECO oligomers with the catalyst K₂Ni(CN)₄ in water have been reported by Reppe and Magin¹⁸² Subsequent attempts to improve the Ni catalyst systems were only marginally successful due to the high affinity of Ni toward CO. The general breakthrough was reported by Sen and Lai¹⁸³ with palladium complexes in the presence of phosphines. This system was improved by Drent^{184,185} using chelating bis-phosphines (mainly bis-diphenylphosphinopropane (dppp)), which results in extraordinary performance regarding catalyst stability and activity.

3.24.4.1.2 Polymerization mechanism for the α -olefin carbon monoxide copolymerization with chelating bis-phosphine palladium catalysts

3.24.4.1.2(i) General information on the catalyst structure

The active catalyst species for the copolymerization reaction of olefins and carbon monoxide is Pd(II) in a square planar complex environment. Usually bis-chelating phosphines are employed to provide stabilization, catalyst solubility, as well as steric protection. Furthermore, the remaining substituents bear the functionalities required for the insertion polymerization, namely the coordinated olefin or CO monomer as well as an alkyl or acyl group for the migratory insertion (from the growing polymer chain). These active catalysts are either employed as single component catalysts (SCCs) or can be obtained from precursor complexes in situ (Section 3.24.4.3.2).¹⁸⁶ Nonchelating phosphines are generally inferior, as the catalyst activity is greatly reduced by a possible isomerization from the polymerization active cis to the inactive trans form (Scheme 21). Thus, the growing polymer chain and the coordinated monomer form a dormant trans-configuration intermediate until further isomerization reactivates the catalyst.



Scheme 19 Copolymerization reaction of Tim with ethene and subsequent deprotection by hydrochloric acid.



Scheme 21 Chelating and nonchelating bis-phosphine palladium complexes in the strictly alternating copolymerization of ethene and carbon monoxide (X_1, X_2 = olefin or growing polymer chain).

3.24.4.1.2(ii) Initiation and termination reaction

Initiation and termination of the α -olefin carbon monoxide (OCO) copolymerization are a complex interaction of several reactions. These depend strongly on the employed reaction conditions and additives, with the most important factor being the choice of solvent.^{185,187} Lewis acids of weakly coordinating anions (e.g., HOTf=trifluoromethanesulfonic acid; HX, X=weakly coordinating anion) are normally employed in the *in situ* preparation of active complexes to generate [(P^P)Pd²⁺][X⁻]₂ species. Alternatively, AgX salts are applicable to abstract chloro ligands from suitable precursors (such as (P^P)PdCl₂). Further details concerning the control of the initiation/termination process as well as the activation of precursor complexes can be found in literature.^{185–189}

In general, oligomers and polymers with keto [K] or ester [E] end groups are obtained in protic solvents (e.g., methanol). Thus, [E–E], [K–K], and [K–E/E–K] terminated chains can usually be found in a polymer sample. In aprotic solvents, the chain termination occurs by β -hydride elimination creating a vinyl-terminated polymer.^{185,187,190} As the reactions are

usually carried out in mixtures of methylene chloride and methanol (small amounts of water are also possible as activators; for problems, see next paragraph) together with possible additives like benzoquinone (oxidant), only the end-group formation in presence of protic solvents is explained below (Figure 35).

The polymerization reaction is initiated by either a (P^P) Pd-H⁺ or a (P^P)PdOMe⁺ species, which are formed during initiation or chain termination. Sequential insertion of ethene and carbon monoxide into a Pd–H bond leads to a Pd–C(=O) Et [K] group. Carbon monoxide insertion into a Pd–OMe bond results in formation of a PdC(=O)OMe [E] end group. After consecutive copolymerization of CO and olefin, the chain termination occurs by either methanolysis or protonolysis upon reaction with the polar solvent. The ratio of [K] and [E] end groups is dependent on the actual employed reaction environment.

Especially water is problematic for the reaction as it can lead to the decomposition of the palladium compound, for example, in the reaction of $Pd(OAc)_2$ with a phosphine by partial oxidation to the phosphine oxide $R_3P=O$. On the other hand, it can act in an analogous manner as methanol as an activator for the copolymerization reaction. Intermediary $[Pd-H]^+$ catalytic species, which can be formed, for example, by water gas shift reactions, are also highly reactive and can decompose to Pd (0).¹⁹¹ This reaction can be prevented by the addition of oxidants such as benzoquinone, which reoxidizes decomposed Pd (0) to active Pd(II). However, this compound is also involved in the formation of ester-terminated oligomers or polymers, mainly [E-E], by oxidation of the growing polymer chain with methanol.

3.24.4.1.2(iii) Chain propagation

The propagation mechanism of the OCO copolymerization (as explained in the simple case of ECO) takes place in a strictly alternating fashion as a result of thermodynamic and kinetic



Figure 35 Possible pathways for the formation of keto [K] and ester [E] end groups in initiation and termination reactions during strictly alternating ethene/carbon monoxide copolymerization. GPC, growing polymer chain.

restrictions.¹⁹² It was shown that the consecutive insertion of two CO monomers is thermodynamically not possible at the present reaction conditions. Subsequent insertion of two successive ethene molecules cannot take place for kinetic reasons.¹⁸⁵ An observation, which is on first glance surprising as the same catalysts can dimerize ethene to butenes in the absence of CO at even higher reaction rates. In a limited feed of CO only copolymerization takes place until complete CO consumption, followed by a switch to exclusive ethene dimerization to butenes.¹⁹³ This is established for (P^P) chelating bis-phosphine catalysts can incorporate higher levels of ethene at increased ethene pressure (Section 3.24.4.3.4).¹⁹⁴

The abundant literature data on the chain propagation reaction itself shows a defined and consensual accepted reaction mechanism.¹⁸⁸ After activation of a precursor or chain termination, the active species is created, which possesses either a Pd–C(=O)R (acyl group) **87** or a Pd–carbon (alkyl group) **89** (Scheme 22). Due to the strength of the CO coordination to the metal, the 'vacant' coordination site will usually be occupied by CO molecules (alternative coordination of ethene, solvent molecules, or weakly coordinating counterions).

Starting from a Pd–acyl species 87, the copolymerization can only proceed with a coordinated ethene molecule, as double insertion of CO is not possible for thermodynamic reasons. Insertion of ethene yields the β -keto alkyl complex that is stabilized by 'backbiting', a coordination of the keto functionality to the 'vacant' coordination site, forming the β -keto chelate 88. Due to this strong stabilization, the binding force of ethene is insufficient to replace the coordinated oxygen functionality. Thus, only CO coordination can follow, leading to the alkyl complex 89, with successive CO insertion to 90. Again this intermediate is stabilized by 'backbiting' forming a γ -keto chelate. In this case, ethene is able to replace the polar group and closes the reaction circle. Chain termination takes place as detailed in the previous section.

3.24.4.1.3 Influence of the catalyst structure on the ethene carbon monoxide copolymerization

The insertion polymerization is strongly dependant on the steric and electronic environment at the metal center of the catalyst and can be greatly influenced by an appropriate ligand design. Three major approaches for a catalyst modification by ligand design have been employed. First, the dppp ligand backbone can easily be derivatized and substituted. Second, exchange of substituents at the phosphine groups permits the modification of the steric and electronic environment in close proximity to the metal center. Additionally, in the last modification protocol, one or both phosphine functionalities are exchanged for different heteroatom donor functionalities, such as phosphites or sulfonates (Section 3.24.4.3). It should be noted that due to the large number of different reported (P^P) chelating ligands in the literature, only a pertinent selection will be discussed here.

3.24.4.1.3(i) Backbone modification

The fundamental (P^P) chelating dppp ligand presented by Drent et al. can be improved by modification of the ligand backbone (Figure 36).¹⁹³ Variation of the backbone length in α - ω -bis-phosphines starting from dppp lowers the resulting catalyst activity in the ECO copolymerization. This observation can be attributed to an influence of the spacer bridge on the P-Pd-P angle in the respective catalysts and influences the conformation of the aryl groups on the phosphine. This alters the sterical hindrance on the metal center depending on the ring size.^{195,196} Bianchini et al.¹⁹⁷ presented dppe (1,2-bis(diphenylphosphino)ethene)-based 91 ligands such as cyclo-tetraphos [cis, trans, cis-1,2,3,4-tetrakis(diphenylphosphino)-cyclobutane] 91c, which show activities comparable to standard dppp 92-based catalysts (Figure 36). The significant increase of activity is attributed to a rigid ligand backbone conformation. The chelate ring in these complexes prefers an envelope configuration, whereas in catalysts based on 91 the ligand usually assumes a twisted configuration. This effects the alignment of the aryl substituents and the available coordination sphere at the palladium center and is presumably the reason for the enhanced catalytic activity



Scheme 22 Mechanism of the strictly alternating ethene/CO copolymerization.



Figure 36 Structures of chelating phosphine ligands accessible by ligand backbone modification.

of **91**-based complexes with a rigid backbone structure. Other ligand systems similar to **91** like *o*-dppbe [*o*-bis(diphenylphosphino)benzene] **91b** or *cis*-dppe (*cis*-bis(diphenylphosphino) ethene) **91a** confirm the necessity of a rigid backbone for an enhanced activity (not as high as for **91c** presumably for electronic reasons; Figure 36).

An additional method to improve the activity of 92-based catalysts is the introduction of two methyl groups to obtain *meso*-CH₂(CH₃CHPPh₂)₂ 93 (Figure 36). This enhancement is explained by the so-called *meso* effect, which is attributed to a change in electronic and steric properties of *meso* compared to *racemic* CH₂(CH₃CHPPh₂)₂ complexes, resulting in different copolymerization productivities.¹⁹⁵ Steric influence is again based on a specific arrangement of the ligand backbone and the aryl groups on the phosphorus atom.¹⁸⁸

3.24.4.1.3(ii) Modification of the substituents on the phosphine groups

Variation of the substituents on the coordinating phosphine groups alters the steric environment on the metal center, as well as the electronic influence of the phosphines. Modification of 92 was reported by Drent and Wife. Here the introduction of *o*-OMe groups on the aryl substituents results in catalysts with improved reactivity and stability.¹⁹⁸ A similar example is the exchange of the aryl substituents in bis(diarylphosphino)methane 94a and the derived ligand bis (diarylphosphino)-*N*-methyl-amine 94b (Figure 37).

It was shown that different bulky o-functinalized aryl substituents can significantly increase the activity of corresponding catalysts, up to the activity of catalysts based on 92. Possible substituents herefore include, for example, OMe, Me, Et, and ⁱPr. Combined with a backbone substitution effect, 94b-based catalysts display enhanced activities, which are attributed to the combination of an electronic effect by the amino functionality in the backbone as well as increasing sterical hindrance. The latter factor has the most important influence on the catalyst activity and overcompensates the negative effect of the small backbone spacer in 94-based catalysts compared to their dppp analogs.¹⁹⁹ Dependence of observable effects on the substitution position at the aryl groups was exemplified, for example, in the case of a sulfonated ligand 95 (Figure 37). Here, o-methoxy- as well as p-methoxy-substituted meta-sulfonated bis-phosphines were used in copolymerization reactions.²⁰⁰



Figure 37 Structure of chelating bis-phosphine ligands accessible by modification of the phosphine aryl groups.

The drastic decrease of activity in case of *para* substitution compared to the *ortho* position shows the crucial effect of the latter one due to the proximity to the metal center. Different examples by Meier *et al.* addressed the substitution of one phenyl group in dppp against a 2-hydroxyethyl functionality, which results in interesting ligands for propene carbon monoxide (PCO) copolymerization due to differences in reactivity and selectivity between the *racemic* and *meso* form.²⁰¹ Ligands bearing bis-phosphines with CF₃-substituted aryl groups are especially interesting for (PCO) or copolymerization of higher olefins with carbon monoxide (OCO) if substituted asymmetrically.²⁰²

3.24.4.1.4 Propene carbon monoxide copolymerization: regio- and stereoselectivity

Exchange of ethene by higher α -olefins, usually propene, leads to new copolymer structures and properties due to the introduction of side groups into the polymer backbone. This directly influences the polymer properties, for example, the crystallization behavior and the solubility of the resulting polymers. Change from a symmetric monomer (ethene) to a substituted olefin leads to different possibilities of olefin orientation upon coordination to the polymerization catalyst and in the end to a control of the regioselectivity. Usually a 1,2- insertion is preferred over the 2,1-insertion of propene and higher α-olefins (Scheme 1). Both possibilities and the degree of discrimination can be recognized by distinct structural motives in the copolymer backbone. Considering two consecutive insertions and the orientation of their alkyl groups in respect to the central carbonyl group, head-to-tail, head-to-head, and tail-to-tail structures can be observed (Figure 38). The orientation is dependent on the structure of the employed catalyst. ¹³C NMR spectroscopic investigations can be used to determine the degree of regioregularity by analysis of the percentage of uniform head-to-tail monomer incorporation. Deviations from a strictly regular monomer incorporation lead to a changed polymer microstructure resulting in different melting behaviors.

Furthermore, in case of highly regioregular polymers, the stereoselectivity of the monomer insertion can be controlled by



Figure 38 Regioselectivity in propene/CO copolymerization reactions.



Figure 39 Tacticity in regeoregular propene carbon monoxide copolymers.

a chiral complex or induced enantiofacial selectivity through the coordinated polymer chain. This results in a stereocontrol of the side groups in the copolymer chain and isotactic, syndiotactic, or atactic copolymers (Figure 39). The following examples show the control of regio- and stereoregularity in PCO copolymers.

3.24.4.1.4(i) Control of the regioregularity

Regioselectivity in PCO copolymerizations catalyzed by dppp-based complexes can be controlled, for example, by an exchange of the phenyl substituents for isopropyl groups. This leads to complete polymer regioregularity for this dipp (1,3-propanediyl-bis(di-*iso*-propylphosphine)) catalyst system, unfortunately, accompanied by a decrease of the molecular weights for obtained copolymers.²⁰³ Further investigations showed the significant influence of the Lewis basicity of the phosphines and a well-balanced sterical encumbrance on the metal center to achieve high regioselectivity, activity, and molecular weights.^{204,205}

3.24.4.1.4(ii) Control of the stereoregularity

The stereoregularity of copolymers depends on the differentiation of the monomer incorporation due to the enantiofacial selectivity of the catalyst. As already mentioned, this can lead to a control over the polymer tacticity, which can be observed by detailed analysis of the ¹³C NMR polymer spectra, as signals of different pentads can be recognized and assigned. In isotactic polymers, the enantioselectivity is also important as the polymer is chiral and can be either the RRRR- or SSSS-enantiomer. The absolute configuration on the asymmetric backbone carbon atoms can be determined by comparison of polymer circular dichroism (CD) spectra with small chiral ketones or NMR spectroscopic investigation with optically active NMR



Figure 40 Linear and spiroketal structure of propene/carbon monoxide-based polyketones.

shift reagents.^{204,206} These optically active polyketones will be addressed with more detail in the following section.

Depending on the reaction conditions of PCO and OCO copolymerizations, polyketones are obtained either in a linear or in a spiroketal structure. The equilibrium of the keto- and ketal structure depends on the energetic difference between both forms, which is fairly small in OCO copolymers of higher olefins (the stability of the spiroketal form increases with the length of the α -olefin). Investigation of the dynamic behavior was carried out by NMR spectroscopy in solution and in the solid state.²⁰⁶ The spiroketal form can be converted into the linear poly(1,4-ketone) at higher temperatures or by treatment with 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) and precipitation (Figure 40).

Biggest influence on the enantiofacial differentiation in chiral copolymerization catalysts is due to the employment of chiral chelating ligands. This is often combined by an asymmetric substitution pattern as, for example, in (R,S)-BINAPHOS-based catalysts where the ligand is bound by phosphine and phosphite donor atoms. This system is able to produce high-molecular-weight PCO copolymers with extremely high molar optical rotation (Figure 41). Combined with a highly simplified ¹³C NMR spectrum, a high degree of regioand stereoselectivity (uniform head-to-tail incorporation, isotactic structure) of the resulting polymers is indicated. The mechanism of the polymerization was analyzed in detail to



Figure 41 Structure of the chiral chelating (R,S)-BINAPHOS phosphine phosphite ligand.

investigate the reasons for this selectivity. Isotope labeling studies confirmed that different phosphorus donor atoms (phosphine and phosphite) lead to a preferred location of the alkyl group or the growing polymer chain *trans* to the phosphine donor. Combined with a *cis–trans* isomerization process (referred to the phosphine donor), a uniform polymerization with high stereoregularity is achieved.²⁰⁷

This study excellently addresses several interesting points in the copolymerization by catalysts with asymmetric ligands. (1) The asymmetric structure leads to nonequivalent coordination sites, which favor or disfavor the stability of coordinated groups. (2) Additionally, enantiofacial selectivity introduced by the chiral ligand structure is enhanced by the stereochemistry of the conjugated growing polymer chain.²⁰⁷ The latter case is also critical for the stereoselective copolymerization with achiral catalysts.²⁰⁸ Furthermore, the asymmetric substitution pattern can lead to reduced termination by β -hydride elimination due to the energetically nonfavored position *trans* to the phosphite in (R,S)-BINAPHOS, resulting in highmolecular-weight polymers.²⁰⁷

3.24.4.1.4(iii) Optically active 1,4-polyketones

Sterio- and regioselective copolymers based on propene and carbon monoxide are interesting, as this is one of the few examples where optically active polymers can be obtained from an achiral monomer feed. Usage of enantioselective chiral polymerization catalysts, for example, JOSIPHOS,21 DUPHOS206 or BINAPHOS²⁰⁹ allow the synthesis of chiral polyketones with an enantiomeric excess higher than 90%. Interestingly, the resulting pure chiral isotactic polyketones show a lower melting point compared to the isotactic mixtures of both enantiomers. This indicates a chiral recognition of the opposing enantiomeric forms, which influences the crystallinity of the polymer.²¹⁰ Furthermore, the resulting copolymers can easily be reduced to the optically active 1,4-polyols.²⁰⁶ The reaction and influence of the catalyst as well as the chain-end influence could be studied in the formation of low-molecular-weight products in presence of high amounts of oxidants.

3.24.4.1.5 The terpolymerization of ethene, propene, and carbon monoxide

The strictly alternating ECO copolymerization affords highly crystalline polymeric materials with high melting points close to decomposition temperature, which are also insoluble in common organic solvents. To overcome this huge processing problem, a terpolymerization of ethene and CO with higher α-olefins like propene was studied. Incorporation of the higher olefin comonomer introduces side chains in the polymer backbone, which hamper the arrangement of the polyketone chains. This decreases the degree of crystallinity, lowers the melting point, and increases the solubility of the polymers. Depending on catalysts and polymerization conditions, the polymer properties can be controlled between thermoplastic behavior and properties of thermoplastic rubbers.^{211,212} Terpolymerization in a batch experiment with CO and a precharged mixture of propene and ethene leads to a range of polymer properties, strongly depending on the ethene/propene ratio. If the ethene content is below \sim 50%, thermoplastic elastomers are obtained. A further increase leads to the formation of crystalline thermoplastic terpolymers with a loss of elasticity. Due to the different reactivities for ethene and propene, the

polymerization can lead to gradient copolymers and heterogeneous polymer blends. Fractionized analysis of a terpolymerization reaction shows an increase of the amount of propene/CO units with reaction time and decreasing ethene concentration.^{211,212}

As an alternative to this batch process, the pulse-feed polymerization (PFP) was developed.²¹³ During this process, ethene is added discontinuously to an ethene/propene/CO terpolymerization reactor at defined time intervals. Considering the faster reaction of ethene compared to propene, this technique allows the control of ethene incorporation in the terpolymers with ethene/CO-rich regions. By this polymerization process, terpolymers with up to 70% ECO content can be obtained, which are still highly soluble in organic solvents in contrast to terpolymers produced by the process above with equally high ECO contents. The terpolymers are created homogenously and no different polymer fractions could be isolated by fractionation experiments.

3.24.4.1.6 Introduction of functional groups into olefin carbon monoxide copolymers

Beside these basic reactions with ethene and propene, numerous other monomers can be employed in the co- and terpolymerizations with CO. Due to the huge number of publications, the reader is referred to literature for more information. For example, copolymerization with norbornene, norbornene derivatives, and styrene as well as functionalized monomers such as alcohols, carbonic acids, carbamates, amides, or epoxides is possible. Functionalities are usually required to be separated from the olefin by an alkyl spacer.^{188,214–216}

Several interesting copolymerizations with unusual functional comonomers are, for example, the incorporation of benzo-15-crown-5-functionalized olefins, sacharides, vitamins, amino acids, dipeptides, and stereoids as well as mesogenic groups. Thus, highly interesting functionalities for applications in biochemistry, pharmacy, and engineering are accessible.^{217–223}

3.24.4.2 α -Diimine Catalysts for the Synthesis of Branched Functional Copolymers

3.24.4.2.1 General information about α -diimine late transition metal catalysts

The α -diimine-based Pd(II) complex system is one of the most versatile highly active catalyst systems, which combines an easily accessible structural variability with a great robustness against solvent impurities or functional groups due to the low Lewis acidity of the palladium center. Although usually applied for ethene homopolymerization, branched PE is also accessible with a great structural variability. This feature was nicely characterized by Guan *et al.*²²⁴ A characteristic trait of this catalyst system is the chain walking mechanism leading to branched polymer structures (Scheme 23). Facile β -hydrogen abstraction, subsequent reorientation, and reinsertion of the resulting olefin mark this reaction. As the result, the metal center can 'walk' along the polymer chain until chain propagation is resumed by coordination and insertion of the next olefin.

Progress in the development of this catalyst system led from simple di-*iso*-propyl-substituted α -diimines to hydrogen-stable terphenyl ligands (**Figure 4**. The substituents in terpenyl-based ligands can also be bridged to obtain cyclophane structures. The remarkable tolerance of the α -diimine palladium system is



Scheme 23 Chain walking mechanism responsible for branch formation in α -diimine-based late transition metal-catalyzed polymerization reactions.

discussed in numerous review articles.^{3,10,186,225} For example, activity for ethene homopolymerization can be retained in the presence of functional additives or solvents. The tolerance toward functional groups includes, for example, ethers, esters, and organic acids, with the exception of nitriles or most nitrogen-functionalized additives and solvents, which inhibit polymerization. An example for this stability is the synthesis of microstructured polymers by aqueous emulsion and suspension polymerizations of olefins. In addition to solvent stability, this system is able to copolymerize olefins with polar comonomers such as acrylates (see below). For more detailed information regarding the properties and the control of the homopolymerization of ethene with this system, the reader is referred to literature.^{3,226,227}

3.24.4.2.2 The copolymerization of ethene and polar functionalized olefins with α -diimine-based catalysts 3.24.4.2.2(i) Methyl acrylate: ethene copolymerization

The copolymer structure and the reaction mechanism of α -diimine complex-catalyzed copolymerization reactions with functionalized α -olefins are now described in detail for the ethene-MA copolymerization system.^{3,226,227} This will serve as a general example for a copolymerization of ethene with polar comonomers. In other specific cases, the nature of the relevant steps may vary, but the general concept is applicable.

Brookhart and coworkers²²⁶ investigated the copolymerization of MA and ethene with 2.6-di-iso-propyl-substituted α -diimine palladium catalysts 3 (Figure 4, Section 3.24.4). Upon activation of (N^N)PdMeCl precursors with sodium salts of noncoordinating counter ions in presence of acrylates formation of an insertion product is observed. This structure is exceptionally stable and can act as a preformed active catalytic species (SCC; Section 3.24.4.3.2). Additionally, copolymerization of ethene with acrylates is possible as well. It could be shown by simultaneous refractive index and UV detection GPC that acrylate is uniformly incorporated in the copolymer. ¹H and ¹³C NMR spectroscopies showed that the polymer is a highly branched copolymer, similar to the ethene homopolymers accessible with the same catalyst under similar conditions. The acrylate units are incorporated predominantly on the end of the branches. Only a small part of the resulting ester units, proportional to the ethene pressure, is incorporated directly in the polymer backbone (Scheme 24).

Kinetic studies could elucidate the nature of the acrylate incorporation mechanism and led to an understanding of the copolymerization mechanism. All critical intermediates are observable by low-temperature NMR spectroscopy (Scheme 25). MA replaces the labile ether ligand in the $[(N^N)Pd(OEt_2)Me]$ complex 96 by π -coordination



 $Ar_{4}^{F} = 3,5 - C_{6}H_{3}(CF_{3})_{2}$

Scheme 24 Formation of a single component catalyst by insertion of methyl acrylate into a (N^N)PdMe⁺ species and copolymerization of ethene and methyl acrylate.





(-80 °C) 97 and undergoes a 2,1-insetion reaction into the Pd–Me bond to 98 at -80 °C. The resulting four-membered chelate complex isomerizes to the five-membered chelate complex 99 by β -hydride elimination. At -20 °C another rearrangement takes place to give the stable six-membered chelate 100.

The high stability of the MA backbiting in 100, together with the facile β-hydride elimination and reinsertion to chelated reaction intermediates can explain the decrease of polymerization activity in the presence of MA (which is proportional to the MA concentration). As described above (Section 3.24.4), the coordination of ethene and MA are competing reactions. The low binding constant of MA to the metal limits the proportion of MA incorporation with respect to ethene incorporation. Additionally, a linear dependence of the MA incorporation on the MA concentration in the reaction solution could be proven. Increasing MA concentration lowers the overall turnover number (TON) of the catalysts by a reduction of the ethene TON, together with a stationary MA TON. On the other hand, an increase of the ethene pressure leads to both, an increased activity for MA and ethene. The monomer concentration has no effect on the branched structure of the polymer, which suggests a fast 'chain walking' mechanism compared to a slower propagation reaction. Also, the number of ester-terminated branches is not dependant on the monomer concentrations, but their length is reduced by a rising ethene pressure. Olefin insertion rate analysis showed the MA insertion to occur at lower temperatures compared to ethene incorporation (-80 °C and -20 °C, respectively) proving no influence on the overall copolymerization rate from the insertion reaction. These results show that the major limitations for the copolymerization reactions can be found in the low binding strength of acrylates and the formation of stable chelate reaction intermediates.^{226,227}

Nickel-based a-diimine catalysts inhibit copolymerization under similar conditions compared to corresponding palladium catalysts. DFT calculations showed that Ni a-diimine catalysts are principally capable for ethene/MA copolymerization, but also an increased catalyst poisoning by a stronger backbiting through O-coordination. However, this copolymerization can be carried out with Ni α-diimine catalysts under harsh conditions.¹⁰ The resulting copolymer structure varies from a relatively linear copolymer (30 Me branches per 1000 carbons) to highly branched structures with $\sim 1\%$ acrylate units incorporated in the polymer backbone.¹⁰ Low-temperature NMR spectroscopic studies also showed a major difference in the insertion reaction. Here, the insertion resulting in the four-membered chelate complex occurs at -40 °C, but the following reorganization to the five- and six-membered chelate complex is slow (room temperature over 1 day) compared to that with the corresponding palladium catalysts (which occurs

readily at -60 °C), due to a strong Ni–carbonyl interaction in these respective complexes.¹⁰

3.24.4.2.2(ii) Methyl methacrylate incorporation

The additional methyl group in MMA compared to MA has drastic influences on the resulting homopolymers, for example, high stability and rigidity. These polymers are usually accessible by anionic or radical pathways in the presence of metal catalysts. Polymerization reactions with this monomer via an insertion polymerization mechanism is a huge challenge as the coordination ability of 1,1-di-substituted olefins is significantly reduced compared to mono-substituted olefins. α-Diimine catalysts, very useful for the copolymerization of ethene and MA, were investigated in this copolymerization reaction.^{228,229} It could be observed that 1,2-insertion of MMA results in a stable five-membered chelate complex 101 (Scheme 26). This structure has no substituents on the α -carbon and possesses two methyl groups on the β-carbon atom and β-hydrogen abstraction is not possible. Furthermore, the coordination of MMA to the metal is considerably weaker, resulting in the solely formation of branched PE in reaction mixtures containing ethene and MMA. In addition, the barrier for the insertion reaction is increased. The above-mentioned stable MMA 1,2-insertion products can initiate the homopolymerization of ethene as well as the copolymerization of CO and alkenes.²²⁸

Additionally, copolymerization with Ni α -diimine catalysts is possible by usage of alkyl aluminum compounds as protective agents for the polar group in functionalized olefins. Although this method is not desired due to additional costs of alkyl aluminum compounds as a ratio of monomer/protecting agent of 1:1 to 1:2 are required.²²⁹ Transfer of this protection principle with alkyl aluminum compounds to a wide variety of other functional olefins is possible. For more information about the available monomer pool, the reader is referred to literature.²²⁹

3.24.4.2.2(iii) Vinyl acetate: coordination and decomposition of insertion products

Reaction of α -diimines with vinyl acetate (VAc) unfortunately does not result in polymerization reactions. The low coordination ability to a cationic Pd complex for this functional olefin is due to an increased sterical hindrance. The, compared to ethene, higher π (C=C) frontier orbital (HOMO) energy should promote a π -coordination to the metal. Unfortunately, effective σ -coordination via the oxygen atom is also possible and is assumed to be a severe restriction to the incorporation. Furthermore, the insertion rate of VAc into metal–alkyl bonds is reduced compared to ethene and can occur either in a 2,1-fashion (Pd–Me bond; Scheme 27) or in both 1,2- and 2,1-fashions (Ni–Me bond). By insertion of VAc a stable five-membered chelate structure 102 is again obtained (at







Scheme 27 Insertion reaction of vinyl acetate and decomposition of the resulting chelate complex (Pd system).

0 °C), which is not able to initiate polymerization reactions. An additional limitation for the utilization of this system is a reorganization and elimination of propene and acetate at higher temperatures (60 °C). This decomposition occurs for both, Pd and Ni α -diimine catalysts. Detailed information for this reaction can be found in literature.¹⁰

3.24.4.2.2(iv) Acrylonitrile, vinyl halides, and vinyl ethers: challenges for α -diimine catalysts

As already mentioned above (Section 3.24.4), the reaction of AN with α -diimine catalysts is problematic. The favorable σ -coordination of AN in combination with aggregation of insertion products prevent the copolymerization of AN with ethene as well as the homopolymerization of ethene.¹⁰ Vinyl halides are reported to give insertion products, subsequent reorganization followed by β-halogen abstraction and loss of propene for (N^N)PdMe complexes. This has been mainly reported for (N^N)Pd bipyridine complexes, but these results seem to be also consistent with calculations and observations for α -diimine Pd complexes. Another interesting but problematic functional monomer group is vinyl ethers. Reaction of these olefins with α -diffice complexes results in 1.2-insertion. followed by β-OR elimination to the resulting (N^N)Pd allyl complex (Scheme 28). Usage of silyl ethers (triphenylsilyl or trimethylsilyl vinyl ether) makes insertion copolymerization possible. In addition, these vinyl silvl ethers are increasingly stable toward B-OR elimination and cationic polymerization. two common problems with vinyl ethers comonomers. For instance, the trimethylsilyl ether can be copolymerized next to significant amounts of cationic polymerization and triphenylsilvlether can be incorporated by a-diimine-based catalysts without problems.230

3.24.4.3 Phosphine Sulfonate-Based Catalysts: Synthesis of Linear Copolymers of Ethene and Functionalized Olefins

3.24.4.3.1 General information for the phosphine sulfonate catalyst system

Modified triphenylphosphines are widely applied in coordination chemistry and catalysis. Introduction of sulfonate groups on the phosphine ligand provides the highly interesting triphenylphosphine sulfonate ligand system. The usually meta-sulfonated phosphines are employed, for example, in the biphasic hydroformylation (Rône-Poulenc process).²³¹ Application of sulfonated phosphines in polymerization chemistry are limited and can be found in the aqueous copolymerization of ethene and carbon monoxide (Section 3.24.4.1.3). o-Sulfonated triphenylphosphines are quite rare in literature. These ligands can be applied in classic catalytic reactions, for example, the Heck reaction²³²⁻²³⁶ and late transition metal-catalyzed polymerization reactions. In the latter case, phosphine sulfonates are usually employed as palladium complexes for homo- and copolymerization reactions. Nickel complexes can additionally be used for ethene oligomerization and polymerization. Polymerization of ethene with benzene-sulfonate complexes originates from Murray in 1987²³⁷ and was continued by Drent et al.,^{238,239} who already reported the palladium-based copolymerization of ethene with polar comonomers, attracting interest in numerous research groups. This led to a rapid development of this catalyst system.¹⁰ The commonly employed o-sulfonated arylphosphines with two functional aryl groups are readily available and provide ample possibilities for modification (Figure 42).

3.24.4.3.2 Complex formation

In general, several pathways can lead to active polymerization complexes. These possibilities can serve as a common principle with possible transfer to other late transition metal-catalyzed



Figure 42 Substitution pattern of the commonly applied *o*-sulfonated arylphosphine ligand system, $R_1 = Alk$; $R_2 = Alk$, Ar, OAlk.



R = t-Bu, SiMe₃, SiPh₃, Ph

Scheme 28 Mechanism for the 1,2-insertion and β -OR elimination reaction of α -diimine Pd complexes and vinyl ethers. Increasing stability of the complexes in the row R = Ph, *t*-Bu < SiMe₃ < SiPh₃ leads to possible copolymerization reactions with vinyl silyl ethers, prefereantally with R = SiPh₃.

reactions requiring activation of catalyst precursors. Both the now in detail discussed *in situ* activation and the preformation of stable active catalyst species have their own advantages and disadvantages.¹⁸⁶

3.24.4.3.2(i) In situ complex formation

This protocol was originately applied by Drent et al. in the in situ reaction of phosphine sulfonate ligands with a palladium precursor, for example, (Pd(OAc)₂ or Pd(dba)₂ [dba = dibenzylidene acetone]) (ratio, phosphine/ Pd = 1.1/1).^{238,239} Following investigations on the nature of the active species showed that most likely (P^O)Pd(OAc) acts as reactive intermediate. Unfortunately, Pd(P^O)₂ can be formed from the palladium precursor as undesired side product. In the nonalternating copolymerization of CO and ethene, these bis-chelated complexes showed only low degrees of multiple ethene insertions. It was proposed that under reaction conditions, the complex acts as a bis-phosphine catalyst by a cleavage of the Pd-O (sulfonate) bonds. The resulting phosphine complex cannot promote the multiple insertion of ethene (Section 3.24.4.1).¹⁹⁴

3.24.4.3.2(ii) Complex preformation

Originating from the above-mentioned observation that phosphine sulfonates can form dormant bis-chelated complexes promoting undesired side reactions (reversible Pd–O bonding leading to bis-phosphine coordinated complexes with different reacivity), the successive development step was the synthesis of stable active single component catalysts and discrete palladium complexes for the *in situ* activation with only one phosphine sulfonate ligand.

The reaction of dicyclopentadiene with Na₂PdCl₄ in the presence of ethanol produces the dimeric [(Cp-OEt)PdCl]₂ (Cp-OEt = $1-\eta^2$, $5\eta^1$ -6-ethoxy-exo-5, 6-dihydrodicyclopentadiene) moiety, which can be reacted with (P^O) chelating ligands in the presence of Na2CO3 to the active single component catalysts [(P^O)Pd(Cp-OEt)] 104.194 An alternative approach is the reaction of (COD)PdMeCl (COD = 1,5-cyclooctadiene) with the phosphine sulfonate ligands in the presence of an amine base (e.g., $EtN^{i}Pr_{2}$), which forms the stable anionic [(P^O)PdMeCl][HNEt'Pr2] complexes. Chloride abstraction and replacement by a suitable base (e.g., pyridine and lutidine) affords the directly active single component catalysts $(P^{O})PdMe(B)$ **103** (B = base).^{10,240} **103** can be alternatively accessed by reaction of (tmeda)PdMe₂ (tmeda = N, N, N', N'-tetramethylethylene diamine) with two equivalents of ligand via a dimeric tmeda-bridged [(P^O)Pd]2tmeda intermediate and formation of methane. Again addition of a suitable base to replace tmeda results in the formation of the active catalysts. Additional similar procedures can be found in the literature.²⁴¹ The nature of the base has considerable influence on copolymerization reactions, as shown by Guironnet et al. where replacement of pyridine bases by dimethyl sulfoxide led to a drastic increase of MA incorporation (Section 3.24.4.3.4).²³

An extensive overview about employed phosphine sulfonate ligands and the reported combination of substituents and bases can be found in literature.¹⁰ The most commonly used ligand is the benzenesulfonic acid-derived 2-[bis(2-methoxyphenyl)phosphine]-benzenesulfonate or its toluene sulfonic acid-based analogue. Upon reaction with a



Figure 43 Structure of the common neutral palladium phosphine sulfonate catalysts with *o*-OMe aryl substituents.

palladium-methyl precursor and introduction of pyridine or lutidine as the coordinating base the stable and active catalysts of class 103 are obtained (Figure 43).

3.24.4.3.3 Homopolymerization of ethene

For a better understanding of the catalyst system, the key characteristics in the homopolymerization of ethene is briefly explained before copolymerization reactions with functional olefin comonomers are addressed. Commencing with the first report by Murray in 1987, this catalyst system was employed in the oligomerization and homopolymerization of ethene.²³⁷ Current catalyst systems produce PEs with high degrees of activity and linearity (1–10 branches per 1000 carbon atoms). The activity varies over a wide range and the obtained polymers show molecular weights of 10^3 – 10^6 g mol⁻¹. Activity, polymer structure, and obtained molecular weights are strongly dependant on the steric bulk of the employed ligand.

Investigations on complex 5 with the greatest degree of steric bulk near the palladium center (Figure 5, Section 3.24.4)¹³ show exceptionally high molecular weights for the resulting PE together with high activities. These findings are in line with reports by Ittel et al.³ and suggest that high steric bulk, which blocks the axial positions toward incoming ethene leads to an increased molecular weight of the resulting polymers by retarding chain termination. However, as mentioned above (Section 3.24.4), comparison of phenyl, naphthyl, anthracenyl, and phenanthryl substituents on phosphorus shows only a decrease of catalyst activity and molecular weights with respect to the phenyl-based catalysts. Unfortunately, the molecular structures of the catalysts with high steric bulk could not be obtained for direct comparison especially of the steric demand in the axial positions.¹⁴ Concerning the reaction mechanism, the asymmetric (P^O) coordination of phosphine sulfonate ligands has an important influence which leads to a site preference of additional ligands as well as to a differentiation of the respective opposing positions. This could be shown by detailed experimental and theoretical investigations (Figure 44).



Figure 44 The asymmetric substitution pattern on phosphine sulfonate catalysts.

The phosphorus has a strong *trans* effect, leading to an enhanced migration ability of the growing polymer chain in the opposing position (X_1) to the stabilized *cis*-position (X_2). Thus, in the catalyst resting state, the alkyl group is always located on the position *cis* to phosphorus and upon *cis*-*trans* isomerization the now destabilizing *trans* effect facilitates migratory insertion of the alkyl group, which again leads to the stabilized conformation.^{10,12} This effect also has a significant influence on the polymer architecture, as the β -hydride elimination is drastically reduced compared to other systems causing the formation of essentially linear PE. Similar Ni complexes are also able to homopolymerize ethene but cannot promote the copolymerization with polar commoners.^{14,15}

3.24.4.3.4 Copolymerization of ethene and polar comonomers: mechanism for the copolymerization of polar comonomers with phosphine sulfonate-based catalysts

As explained above (Section 3.24.4), a change from ethene as coordinating ligand in metal catalysts to polar functionalized olefins leads to drastic differences in its coordination behavior. This is due to a modification of the frontier molecular orbital energy, as well as by introduction of steric demand originating from substituent(s) in the olefin monomer. Theoretic investigations on the copolymerization mechanism by Ziegler²⁴² (on MA/ethene) and Nozaki et al.²⁹ (on AN/ethene) indicate the same critical aspects as for the homopoylmerization of ethene. Most importantly, the high energy barrier for the β -hydride elimination causes formation of linear copolymers and stabilizes the complex to facilitate the insertion in α -substituted alkyl groups with EWG functionalities. The numerous reports on possible copolymerization reactions with these highly interesting catalysts make it to date the most variable and promising system for the incorporation of fundamental and highly challenging functional olefin comonomers. All reported cases show a high stability of the complexes, which is possibly a stabilizing effect of employed coordinating bases and relatively minor difficulties in the competing coordination of olefins and polar functional groups. However, polymerization activities are low and clearly depend on the concentration of functionalized olefins. This can be shown, for example, in the case of a reported MA insertion product by Guironnet et al. in a phosphine sulfonate system (Scheme 29).²³ In this case, no strong backbiting is observed and the formation of four-membered chelates is very weak, predominantly resulting in an olefin adduct.

3.24.4.3.5 Examples of polar olefins in the copolymerization with ethene

3.24.4.3.5(i) Methyl acrylate

MA can be polymerized with neutral, phosphine sulfonate catalysts to linear ethene MA copolymers (Scheme 30).



Scheme 29 Catalyst resting state in the MA insertion polymerization with phosphine sulfonate-based catalysts.



Scheme 30 Copolymerization of ethene and MA by (P^O)Pd-based phosphine sulfonate catalysts.

Copolymer analysis showed a very low branching (1 branch per 1000 carbon atoms) and a relatively high MA incorporation. Analogous to the α -diimine catalyst system, it was shown that the incorporation of MA is dependent on the acrylate concentration and insertion occurs in a 2,1-fashion. Numerous different substitution patterns were tested and it could be shown that steric bulk near the phosphorus atom promotes a high incorporation and productivity.^{10,13,238} However, too large bulky substituents can again decrease MA incorporation.¹³ Guironnet et al.^{23,243} showed the activity and acrylate insertion to be also dependant on the coordinated base. Replacement of the usually applied pyridine or lutidine by the weakly coordinating dimethyl sulfoxide ligand raised the acrylate incorporation to 52%, which includes double acrylate insertion reactions at low ethene pressures and high temperatures. Additionally, this catalyst showed to promote the homooligomerization of MA. In comparison to other functionalized comonomers, MA represents the most effective copolymerization system with phosphine sulfonate-based catalysts. The high stability can also be observed by a recent report on the direct incorporation of acrylic acid.²⁴⁴

3.24.4.3.5(ii) Vinyl acetate, acrylonitrile, vinyl halides, and other comonomers

Phosphine sulfonate-based catalysts are also active for the copolymerization of these highly interesting classes of comonomers. Kochi et al. showed that a low incorporation of VAc can be achieved ($\sim 2\%$). The coordinating bases can also be lutidine and dimethyl sulfoxide. NMR spectroscopic analysis showed incorporation of VAc in the main chain together with two VAc end groups.¹⁸ Similar to this report, the copolymerization of AN could also be reported for the first time (Scheme 3). AN is incorporated into the copolymer in low ratios (2-9%).²⁸ Vinyl fluoride (VF) was copolymerized with ethene by Weng et al.²⁴⁵ This copolymerization of VF facilitated compared to other vinyl halides, as its tendency toward radical copolymerization is reduced and β-halide abstraction is also more difficult. Again, VF was incorporated into a linear PE with low incorporation ratios and relatively low molecular weights. The possibility to increase the incorporation ratio in an tetrameric catalyst aggregate based on a di-ortho-sulfonated arylphosphine could be reported.^{246,247} Furthermore, copolymerization of vinyl ethers with OEt, O'Bu, O'Bu, or OPh groups with ethene is possible at low incorporation ratios and activities.²⁴⁸ Other successful copolymerization reactions include NIPAM, N-vinyl-2-pyrrolidinone, 249 vinyl sulfones, 250 styrene derivatives,²⁵¹ and functionalized allyl copolymers.²⁵² In conclusion, it can be noted that this list of possible copolymerization reactions represents significant advances in the copolymerization of ethene and functionalized olefin comonomers. Despite the overall low activities and low functional olefin incorporation ratios, the phosphine sulfonate catalysts

proved to be the most versatile system for this type of copolymerization. Due to the recent insights into the polymerization mechanism, additional developments can be expected in the near future.

3.24.4.3.5(iii) The nonalternating copolymerization of ethene and carbon monoxide

In addition to the wide variety of true coordination/insertion polymerization reactions with polar functional monomers, the phosphine sulfonate catalyst system is capable of the nonalternating copolymerization of olefins and CO. First discovered by Drent *et al.*²³⁹ with *in situ* formed catalysts, Nowack *et al.*¹⁵ later prepared the first single component catalysts **104**. In the course of this development, the reaction was studied in detail concerning the mechanism that leads to the additional incorporation of ethene units (Figure 45).

In principle, this observation is remarkable as cationic (P^P)-chelated Pd complexes only give strictly alternating polyketones. By DFT calculations, it was shown that the formation of chelated palladacycles by backbiting of the acyl-oxygen atom is disfavored due to the neutral palladium catalyst. Enhanced back donation from the palladium leads to a weakening of these structures together with a facilitated decarbonylation. Both effects give rise to an enhanced coordination and insertion of ethene for this catalyst system. Combined with the results from the ethene homopolymerization reactions, where the ready cis-trans isomerization could be observed, this explains the high incorporation of ethene into polyketones. Another important factor is the introduction of o-alkoxy functionalities in the aryl ligands. Steric restraints facilitate the copolymerization and promote the nonalternating polymer structure, but electronic repulsion of the o-alkoxy groups seems to enhance the above-mentioned decarbonylation reaction.253,254

All these theoretically investigated factors could be observed in experimental screening reactions. The first publication by Drent²³⁹ indicated that the degree of nonalternation is increased by introduction of *o*-methoxy

functionalities at the aryl ligands. Nowack *et al.*¹⁵ could show that the preformation of the catalyst is of crucial importance to the polymerization. Complexation of a second phosphine sulfonate ligand leads to neutral bis-chelated complex structures that are very stable and can only produce strictly alternating polyketones. It was proposed that the opening of the sulfonate oxygen chelate leads to a bis-phosphine catalyst system, only capable to copolymerize ethene and CO in a strictly alternating fashion (Figure 46).

In this study, it could also be shown that *o*-alkoxy groups are crucial due to electronic reasons. o-Methyl groups, which are of similar size compared to methoxy functionalities, show only a very low degree of nonalternation like the parent phenyl-based catalysts. In a mechanistic study of the nonalternating CO/ethene copolymerization, a strong dependence on the ethene partial pressure and the reaction temperature could be proven.²⁵⁵ NMR spectroscopic studies at room temperature showed no significant additional ethene incorporation into the copolymer chain. β-Chelated intermediate structures could also be observed. Unlike in (P^P)-chelated systems (Drent system; Section 3.24.4.1) both comonomers are able to cleave these chelated structures. This is presumably due to a weak coordination of CO to the neutral catalyst. Addition of toluene sulfonic acid comparable to the Drent system is problematic, as the acid can destabilize the phosphine sulfonate complex by protonation of the sulfonate moiety, leading in the end to catalyst decomposition. Benzoquinone, on the other hand, has no influence on the insertion of additional ethene units, but increases the productivity of the catalyst, presumably by the reoxidation of Pd decomposition products.255

Beside these examples based on phosphine sulfonates, Bianchini *et al.*²⁵⁶ reported the use of phosphanylferrocenecarboxylate complexes able to incorporate excess ethene units into polyketones. These catalysts act as monodentate phosphines in the presence of large amounts of TsOH causing the protonation of the carboxylate. The activity and the degree of extra ethene insertion are unfortunately very low.



Figure 45 Mechanism of the nonalternating ethene carbon monoxide copolymerization including alternating and nonalternating pathways.



Figure 46 Proposed chelate cleavage in bis-chelated (P^O)Pd(O^P) complexes.

3.24.5 Conclusion

Functionalized polyolefins possess highly interesting properties, such as enhanced dyeability, thermostability, or optoelectronic and electrochemical behaviors, which makes them potential candidates as high-performance materials. However, their synthesis by transition metal-catalyzed polymerization reactions still features tremendous problems due to catalyst deactivation reactions. For copolymerization reactions catalyzed by early transition metal complexes several strategies have been developed to avoid these problems. The application of weakly coordinating polar olefins has been successfully employed for borane- and silicon-containing olefins. The resulting polymers can easily be converted into other functional groups in polymer analogous reactions. In terms of Lewis basic olefinic monomers, the application of long alkyl spacers between the olefinic and the polar functionality of the monomer, together with a protection technique, ensures polymerizability without complete deactivation. For the latter approach, the employment of bulky substituents at the heteroatom as well as an increased steric hindrance at the metal center has been proven to be suitable. Furthermore, the protection of the functionality by Lewis acids (e.g., aluminum alkyl compounds) prior to the polymerization has been widely applied. However, the employment of less Lewis acidic catalyst systems, being less prone to catalyst poisoning by the polar functionalities, appears to be the most effective approach. This effect can be observed for early as well as late transition metal catalysts. In comparison to early transition metal complexes, late transition metal-based polymerization catalysts possess significantly increased stability toward functional groups or polar solvents. Protection and spacer influence as general principles for the copolymerization with functional olefins are also applicable to provide facile and effective copolymerization reactions. Additionally, the excellent functional group tolerance allows direct unprotected copolymerization of ethene with functional commodity olefins like MA. Drastic effects of the formal complex charge on coordination and incorporation of functional olefins can be observed and exploited in catalyst design. Application of asymmetric catalysts can induce site selectivity and additional tools for reaction control. All in all these features provide ample possibilities for catalyst tuning. Early and late transition metal-based copolymerizations complement each other in the copolymerization of nonpolar olefins with polar functionalized olefins. Careful choice and design of the catalyst and functional monomer provide means

to create functionalized high-performance copolymers suitable for special applications.

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Alkene/CO Copolymerization 3.25

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3.25.1	Introduction	825
3.25.2	Alternating Copolymer of Ethylene and CU	825
3.25.2.1	Reaction Mechanism	825
3.25.2.2	Ligands Employed for the Alternating Copolymerization of Ethylene and CO	827
3.25.2.2.1	Bidentate diphosphine ligands	827
3.25.2.2.2	Bidentate diimine or bipyridine ligands	828
3.25.2.2.3	Unsymmetrical bidentate ligands	828
3.25.3	Nonalternating Copolymer of Ethylene and CO	
3.25.4	Alternating Copolymerization of Mono-substituted Ethylene and CO	831
3.25.4.1	Stereochemical Aspects	831
3.25.4.2	Alternating Copolymer of Propylene and CO	832
3.25.4.2.1	Synthesis of isotactic poly(propylene-alt-CO) using achiral ligands	832
3.25.4.2.2	Synthesis of isotactic poly(propylene-alt-CO) using chiral ligands	832
3.25.4.3	Alternating Copolymer of Styrene and CO	833
3.25.4.3.1	Synthesis of syndiotactic poly(styrene-alt-CO)	833
3.25.4.3.2	Synthesis of isotactic poly(styrene-alt-CO)	834
3.25.4.3.3	Synthesis of poly(styrene-alt-CO) with other structural control	835
3.25.4.4	Other Olefin/CO Copolymers Consisting of Propylene, Styrene, or 1,@-Dienes	835
3.25.4.5	Copolymerization of Functionalized Olefins with Carbon Monoxide	835
3.25.4.5.1	Copolymerization of olefins possessing a functional group at a remote position with CO	836
3.25.4.5.2	Copolymerization of fundamental polar vinyl monomers with CO	836
3.25.5	Copolymerization of Imines with Carbon Monoxide	838
3.25.6	Chemical Transformation of Polyketones	839
3.25.7	Physical Properties and Industrial Application of the Olefin/CO Copolymers	840
References	An and the second se	840

3.25.1 Introduction

Ethylene/CO copolymer or ethylene/propylene/CO terpolymer is a thermoplastic synthetic resin which possesses engineering plastic property, high crystallinity, excellent mechanical property, and chemical resistance. The polyketones were commercially available for several years as Carilon® by Shell and Ketonex® by BP.¹ They can be produced either by radical polymerization or by coordination-insertion polymerization: while radical polymerization provides branched nonalternating copolymers in which the incorporation ratio of ethylene/CO is larger than 1, completely alternating linear copolymers are produced when transition metal complexes are employed as catalyst. Most commonly used are palladium(II) species in addition to a few examples of nickel(II) and rhodium(I). $^{2-4}$ It is notable that the synthesis of a linear but nonalternating copolymer with ethylene/CO>1 was recently reported by using a new class of Pd catalyst (Figure 1).⁵

Not only ethylene but also substituted ethylenes, such as propylene, 1-hexene, or styrene, can be employed for the copolymerization. Because the melting point of the ethylene/CO alternating copolymer is almost as high as its



Figure 1 Alternating and nonalternating ethylene/CO copolymers.

decomposition temperature, decreasing the melting point of the copolymer was essential to obtain a melt-processible material. Thus, for practical usage, a third monomer like propylene or higher 1-alkene is mostly added.

In addition, olefins bearing functional groups, such as esters, alcohols, and carboxylic acids, are also applicable to copolymerization, owing to the less oxophilic, 'soft' nature of the Pd catalysts. The reactivity of the substituted olefins heavily depends on the ligands employed as catalysts.

When a copolymer consists of mono-substituted ethylene and CO, there exist two factors to be controlled to obtain regular structures; they are regioselectivity which is reflected as headhead, head-tail, or tail-tail structures and enantiofacial selectivity which corresponds to isotactic or syndiotactic structures.

In this chapter, the transition-metal-catalyzed synthesis of completely alternating ethylene/CO copolymer will be reviewed in relation to the catalyst design and reaction mechanisms. Next, synthesis of nonalternating copolymers will be discussed. Reactions of mono-substituted ethylene with CO will be discussed together with the stereochemistry of the products and finally applicable functional olefins will be described.

Alternating Copolymer of Ethylene and CO 3.25.2

3.25.2.1 Reaction Mechanism

The catalytic systems mostly used for the ethylene/CO copolymerization and ethylene/propylene/CO terpolymerization are palladium complexes of the type $[Pd(L^{L'})(S)_2]X_2$, where $L^{L'}$ { $L= \text{or} \neq L'$ } is a *cis*-chelating bisphosphine ligand such as 1,3-bis (diphenylphosphino)propane (DPPP); S is a solvent molecule, methanol, for example; and X is an anion with low coordination capability. An oxidant is often used together with the palladium complexes, especially for the reaction in methanol. As shown in Scheme 1(a), the initiation step is reported to be a carbonyl insertion to a Pd–OMe bond ($A1 \rightarrow A2$), followed by the subsequent alternating insertion of olefins and CO. Chain transfer occurs by protonolysis of A4 to regenerate Pd–OMe species A1 providing a polymer with saturated alkane chain end. Alternatively chain transfer takes place via methanolysis of Pd–C(=O)–(polymer) (A3) generating Pd–H and a polymer with ester chain end, MeO(C=O)–(polymer). The olefin insertion to

the resulting Pd–H bond gives an alkylpalladium species to which CO and olefin insert in an alternating manner. An oxidant is added to prevent the Pd^{2+} species from reduction into the inactive Pd^{0} when a bisnitrogen ligand is employed. For styrene/CO copolymerization, the oxidant can be avoided by using fluorinated alcohols instead of methanol. Alternatively, as described in Scheme 1(b), alkylpalladium complexes, represented as $[Pd(L^L)(CH_3)(S)]X$ (A4), are employed in some cases, especially for the reactions in aprotic solvents. Carbonyl insertion to the Pd–Me bond (A5 \rightarrow A6) initiates the reaction. In this system, chain transfer results from β -hydride elimination which occurs less frequently compared to the methanolysis in methanol. The counter-anion X is a noncoordinating anion such as CF_3COO^- , $4-CH_3C_6H_4SO_3^-$,

From Pd dication in MeOH (a)



From alkyl-Pd cation (b) in an aprotic solvent



Scheme 1 Initiation, propagation, and chain transfer of the olefin/CO alternating copolymerization initiated by a palladium dication or an alkylpalladium cation.

and BAr_4^- (Ar = 3,5-(CF₃)₂C₆H₃) to facilitate the olefin coordination.

3.25.2.2 Ligands Employed for the Alternating Copolymerization of Ethylene and CO

Considering the detailed polymerization mechanism described in **Scheme 2**, a *cis*-chelating bidentate ligand with the L-Pd-L' bite angle around 90° seems to be the ligand of choice. As shown, substitution of the chelating ketone carbonyl by the incoming carbon monoxide (B1 \rightarrow B4) takes place prior to the CO migratory insertion (B4 \rightarrow B5). The substitution takes place via either associative (B2) or dissociative (B3) mechanism. Similarly, ethylene insertion is triggered by substitution of coordinating carbon monoxide by ethylene (B6 \rightarrow B9), again via either associative (B7) or dissociative (B8) mechanism. In all species, the L-Pd-L' angle is kept to be 90°. It should be noted that ethylene insertion (B9 \rightarrow B10) requires the highest energy in all of the steps. Thus, if the ligand does not form a strong bidentate chelate, the ethylene–acylpalladium intermediate B9 may isomerize to complex B11 in which the two ligands, the acyl group and ethylene, are *trans* to each other. This species does not undergo ethylene insertion because the acyl group and ethylene must be *cis* to each other for migratory insertion. Instead, methanolysis proceeds providing shorter esters.

For ethylene/CO copolymerization, *cis*-bidentate ligands are widely used; examples are (un)substituted DPPP, diimines, or (un)substituted bipyridines and unsymmetrical bidentate ligands represented as phosphine–Z where Z is either neutral or anionic oxygen atom, sp²-neutral nitrogen atom, or sulfide. Details for each ligand are described as follows.

3.25.2.2.1 Bidentate diphosphine ligands

The above consideration is nicely demonstrated by the following data. Six catalyst systems were prepared from Pd(NCMe)₂ $(4-CH_3C_6H_4SO_3)_2$ and bidentate ligands of the formula $Ph_2P(CH_2)_mPPh_2$ (m = 1-6) as cited in **Table 1**.² The productivity was in the order of m = 3 > 4 > 5 > 2 > 6 ~ 1 and the molecular weight was in the order of m = 3 > 2 > 4 > 5 ~ 6 = 1. Thus, copolymers are given in high productivity with the ligands providing



Scheme 2 Coordination-migratory insertion mechanism for olefin/CO copolymerization catalyzed by palladium complexes.

 Table 1
 Effect of the spacer length of bidentate diphosphine ligands

 on the molecular weight and productivity of ethylene/CO cooligomers or copolymers

Ligand Ph ₂ P(CH ₂) _m PPh ₂	H(CH ₂ CI n =	H ₂ CO) _n OCH ₃ Productivity (g poly g ⁻¹ Pd h ⁻¹)
Ph ₂ P(CH ₂)PPh ₂ (DPPM)	2	1
$Ph_2P(CH_2)_2PPh_2$ (DPPE)	100	1000
$Ph_2P(CH_2)_3PPh_2$ (DPPP)	180	6000
Ph ₂ P(CH ₂) ₄ PPh ₂ (DPPB)	45	2300
$Ph_2P(CH_2)_5PPh_2$	6	1800
Ph ₂ P(CH ₂) ₆ PPh ₂	2	5



stable chelate $(m = 2 \sim 4)$ while shorter cooligomers are given when the chelate structure is less stable (m = 1, >5).

Since the discovery of the effectiveness of Pd–DPPP catalysts,² various DPPP-like ligands have been designed and successfully employed to catalyze the CO/ethylene copolymerization. Common ligand variations have generally involved substitution(s) at either the phenyl rings or the saturated carbon backbone. Introduction of a methoxy substituent in the *ortho* position of each phenyl group provided excellent results in terms of both productivity and catalyst stability.²

A considerable increase in productivity, even by 50%, was observed when methyl groups were introduced in both 1-positions of the DPPP backbone, particularly with $R_{r}S(S,R)$ stereochemistry as in meso-2,4-bis(diphenylphosphino) pentane (meso-BDPP).⁶ The combined use of DPPP-like ligands with dinitrogen ligands such as 2,2'-bipyridine (BPY) and 1,10phenathroline (PHEN), in the presence of a non-coordinating counter-anion and BQ, has been reported to give higher productivities. Thus, the bis-chelated Pd(II) precursors, [Pd(PP) $(N^{N})](PF_{6})_{2}$, are more efficient than the corresponding mono-chelated (PP)P(II) complexes under comparable experimental conditions.^{7,8} Addition of excess $B(C_6F_5)_3$ to (dppp)Pd (OAc)₂ in CH₂Cl₂ was also reported to improve the reactivity.⁹ The product polyketone was found to contain fluoroaryl groups from the borane in the chain ends, suggesting the chain initiation from Pd-C₆F₅.

Another direction of catalyst development is the catalyst separation and recovery. Water-soluble DPPP derivatives containing *m*-sodium sulfonatophenyl groups have been developed for liquid–liquid two-phase separation.^{10,11}

3.25.2.2.2 Bidentate diimine or bipyridine ligands

Dinitrogen ligands based on sp²-nitrogen such as BPY and PHEN in **Figure 2** and their alkyl-substituted derivatives form efficient catalysts for alternating ethylene/CO copolymerization, but the activity is generally low in comparison with diphosphine catalysts. The reverse occurs for the vinylarene/CO copolymerization of vinylarenes, such as styrene, for which dinitrogen catalysts are much more efficient than diphosphine catalysts.¹²

Either monochelated $[Pd(N-N)(RCOO)_2]$ or bis-chelated $[Pd(NN)(N'N')][X]_2$ precursors (NN is either equal or different to N'N' and X = PF₆⁻, TFA⁻, OAc⁻) have been used to copolymerize CO and ethylene. The bis-chelated catalysts are more efficient than the corresponding monochelated derivatives and the best combination of ligand and anion was obtained with BPY or PHEN and PF₆⁻.¹³ Irrespective of the

Figure 2 DPPP and its derivatives and bipyridine-type ligands employed in CO/olefin copolymerization.

precursor, the catalytically active species was proposed to contain one chelating ligand, while the second molecule is important for increasing the stability of the catalysts toward the decomposition to palladium metal and improving the molecular weight.⁷ The complex $[Pd(phen-SO_3Na)(H_2O)_2]$ $(BF_4)_2$, obtained by reacting $[Pd(MeCN)_4](BF_4)_2$ with the water-soluble PHEN derivative PHEN-SO_3Na, was found to be an active catalyst for the copolymerization of CO and ethylene in aqueous solution.¹⁰

3.25.2.2.3 Unsymmetrical bidentate ligands

Unsymmetrical bidentate ligands, which can be illustrated as P-O, $P-O^-$, P-N, and P-S, have been employed together with Pd(II) salts to copolymerize ethylene and CO. The examples are shown in **Figure 3**. In the presence of these catalysts, however, the productivity in polyketones is at least 2 orders of magnitude lower than that obtainable with DPPP-like ligands. Moreover, only a few systems selectively give high molecular weight polyketones. Among the ligands cited in **Figure 3**, the phosphine–sulfonates 1 and 2 exhibit unique performance as will be discussed in the following sections.

3.25.3 Nonalternating Copolymer of Ethylene and CO

The transition metal-catalyzed alternating copolymerization of ethylene with carbon monoxide has been widely investigated to produce a variety of γ -polyketones.^{1,3,4} However, the resultant alternating γ -polyketone generally suffers from low processibility due to its insolubility in common solvents and very high $T_{\rm m}$ (≈ 260 °C), both of which are attributed to high crystallinity induced by dipolar interactions between carbonyl groups. The incorporation of a small amount of propylene in addition to ethylene is one solution to obtain a melt-processible alternating ethylene/CO copolymer.¹⁴ The problem of processibility can also be avoided by reducing the CO content in the copolymer by producing nonalternating copolymers. Conventionally, radical¹⁵ process has been employed for the synthesis of such nonalternating copolymers; however, they generally provide branched polymers.

Despite numerous reports on the transition metal-mediated copolymerization of ethylene and CO,^{1,3,4} most of them afforded strictly alternating copolymers. The alternating nature can be attributed to (i) the formation of five-membered



Figure 3 Unsymmetrical bidentate ligands used for ethylene/CO copolymerization.



Scheme 3 Mechanism of the alternating copolymerization of ethylene with carbon monoxide.

cationic palladacycle **C1**, which kinetically favors CO insertion over ethylene insertion to form six-membered chelate complex **C2**,^{16–20} and (ii) thermodynamically disfavored double insertion of CO (**Scheme 3**).²¹ Nonalternating copolymers can be obtained if ethylene is incorporated into the five-membered chelate complex **C1**. Until recently, however, there has been no catalyst that provides nonalternating ethylene/CO copolymers. Even under high ethylene/CO ratio conditions, copolymerization produces exclusively error-free γ -polyketone until all the carbon monoxide is consumed.

In 2002, Drent *et al.* reported the first example of nonperfectly alternating copolymerization of ethylene with carbon monoxide via the coordination polymerization mechanism.²² They showed that a mixture of $Pd(OAc)_2$ and a phosphine– sulfonate ligand (1a, 1b) produced ethylene/CO nonalternating copolymers with CO contents of 42–49%. Since this discovery, many investigations have been performed based on the phosphine–sulfonate ligand.^{23–27} The Pd complexes bearing a phosphinoarylsulfonate (1) and a phosphinoalkylsulfonate (2) shown in Figure 4 were found to be active for nonalternating copolymerization, in which the former complex is more active than the latter one.²⁵ The complexes (1a)Pd (CP-OEt) and (1a)Pd(Codyl*) exhibited catalytic activities as high as 100–600 g mmol⁻¹ h⁻¹ and a molecular weight (M_n) of around 150 000.^{23,25} It should be noted that polyethyleneblock-poly(ethylene-alt-CO) can also be obtained because the Pd phosphine–sulfonate catalysts produce linear polyethylene.²⁴

The incorporation ratio of ethylene can be controlled by changing the reaction conditions. For example, the multiple insertion of ethylene is enhanced with an increase in the ethylene/CO ratio, although the catalytic activity is reduced.²²⁻²⁴ Moreover, the introduction of a bulkier *o*-alkoxy group or *o*-methyl group on the aryl substituent led to a significant increase in the amount of ethylene incorporation into the copolymer. Thus, it has been possible to produce nonalternating copolymers with as little as 10 mol.% CO incorporation.²⁴ It should be noted that the multiple ethylene insertion decreased significantly when the ratio of the ligand and Pd was 2:1. Rieger *et al.* reported that the dimeric bisphosphine–sulfonate catalyst [P–O]Pd[P–O]^{23,25,28} produced only a pure form of the alternating copolymers.²³



Figure 4 Catalysts employed for the nonalternating copolymerization of ethylene with carbon monoxide.

The origin of the multiple ethylene units was investigated through experimental²⁵ and theoretical^{26,27} studies (Scheme 4). The formation of multiple ethylene units can be understood as a result of ethylene insertion into the five-membered palladacycle D1. This insertion is facilitated because of the following reasons: (i) The relative stability of chelate complexes D1 over D2_{cis}, D2_{trans}, D3_{cis}, and D3_{trans} is lower than those of the corresponding cationic complexes, since the back-donation from palladium to ethylene or CO is likely to be enhanced in the case of neutral Pd phosphine–sulfonate complexes.^{26,27} Thus, opening the chelate structure of D1 by ethylene becomes easier as compared to the analogous cationic Pd systems.²⁹

(ii) The decarbonylation from Pd-acyl complexes bearing a phosphine-sulfonate ligand (D4) is more favorable than that from cationic Pd-acyl complexes bearing DPPP.^{26,27} The facile decarbonylation could be attributed to the instability of the six-membered chelate structure (D4) arising from the relatively weak Pd-O chelate bond trans to phosphorus atom. This is also supported by experimental results that the formation of D4 was not observed by NMR analyses.^{22,25} The introduction of bulky substituents on the phosphorus atom of phosphine-sulfonate ligands also weakens the chelate structure of D4 to promote decarbonylation followed by multiple ethylene insertion. Regarding these two reasons, the concentrations of ethylene adducts D2_{cis} and D2_{trans} should be higher than those of the corresponding cationic complexes. As a result, ethylene insertion is facilitated because of the higher concentration of the precursor ($D2_{trans}$).

Recently, Bianchini *et al.* have found that Pd(II) complexes bearing phosphanylferrocenecarboxylic acids (Figure 5) catalyzed the nonalternating copolymerization of ethylene with CO, albeit with low activities (~ 10 g mmol⁻¹ h⁻¹), molecular weight (M_n up to 13 400), and ratio of adjacent ethylene units (CO content 48%) as compared to those by Pd phosphine–sulfonate catalysts.³⁰ It was suggested that the ligands worked as a monodentate phosphine to generate cationic Pd(II) catalysts in the presence of excess 4-CH₃C₆H₄SO₃H in MeOH.

The physical properties of the nonalternating ethylene/CO copolymers have been investigated. The melting points of ethylene/CO nonalternating copolymers were much lower than those of perfectly alternating copolymers ($T_m \approx 260$ °C) and decreased with increasing multiple ethylene units. For example, copolymers with CO contents of 35^{23} and $10\%^{24}$ exhibited melting temperatures of 220 and 118 °C, respectively. This tendency could be attributed to the relatively weakened interactions between the polymer chains.



Figure 5 Ligands employed for the palladium-catalyzed nonalternating copolymerization of ethylene with carbon monoxide.



Scheme 4 Plausible explanations for multiple insertions of ethylene.

3.25.4 Alternating Copolymerization of Mono-substituted Ethylene and CO

3.25.4.1 Stereochemical Aspects

Although the activity is lower compared to ethylene, substituted ethylenes, such as 1-alkenes or vinylarenes, are also applicable to the alternating copolymerization with CO. The propylene/CO and styrene/CO copolymers possess side chains, which are methyl and phenyl groups, respectively, and thus there exist possible regioisomers and stereoisomers. Several mechanistic studies proposed that the key step to determine the regio- and stereochemistry is the olefin insertion to acylpalladium species. Polymers with high regioregularity are produced if the olefin insertion reaction is regioselective to either 1,2 or 2,1-mode. As described in **Scheme 5**, the propylene insertion is mostly 1,2-mode and the styrene insertion is often 2,1-mode.

There are two types of tacticity control: chain-end control and enantiomorphic-site control. For easier understanding, here the explanation starts with styrene/CO copolymerization and then propylene/CO will be referred. For styrene/CO copolymerization, syndiotactic copolymers are obtained if efficient chain-end control to the unlike diad controls chain propagation. (Regarding the nomenclature of like and unlike: The meso and racemo nomenclatures commonly used for vinyl monomer diads are not applicable to the head-to-tail polyketone because the junction unit between the two stereocenters, $-CH_2-C(=O)-$, is not symmetric. Poly(α -amino acid)s and poly(propylene oxide) are other examples of polymers with asymmetric (W. V. Metanomski, Compendium of Macromolecular Nomencla-ture, IUPAC Macromolecular division). Accordingly, the words like and unlike, which are used in organic chemistry, are applied; like (l) is used for the diad consisting of the same configuration (analogous to meso) and unlike (u) for the opposite (analogous to racemo).) Syndiotactic copolymers are prepared if efficient chain-end control to the unlike diad operates the chain propagation. This is the case for styrene/CO copolymerization when achiral dinitrogen ligands,

such as BPY or PHEN, are employed. On the other hand, isotactic copolymers arise from enantiofacial selection by the catalyst. Using chiral catalysts which differentiate one of the two enantiofaces of olefins, isotactic copolymers are produced for both propylene/CO and styrene/CO. Isotactic copolymers could be produced using an achiral catalyst if efficient chain-end control prefers like diad to unlike. In fact, propylene/CO copolymerization catalyzed by Pd complexes of 1,3-bis(diethylphosphino)propane³¹ or bis(diarylphosphinomethyl)-1,2-phenylene complexes gives stereoregular and isotactic polyketone.³² It should be noted, however, that this like selectivity might be attributed to the enantiomorphic-site control if the achiral ligands create chiral complexes upon their coordination.³³ Anyway, for propylene or styrene, the stereoregular olefin/CO copolymers reported to date are isotactic poly(propylene-alt-CO), isotactic poly(styrene-alt-CO), and syndiotactic poly(styrene-alt-CO) (Scheme 5). Terpolymers of propylene/ethylene/CO and styrene/ethylene/CO have also been produced in which the α -olefin side chains are either atactic or isotactic (vide infra).

Unlike polypropylene or polystyrene, there exist asymmetric centers in the main chain of the propylene/CO and styrene/CO copolymers. Thus, one enantiomer of a chiral catalyst should produce the corresponding enantiomer of the isotactic polyketone so far as the stereoregularity arises from the catalyst control. In other words, optically active catalyst possibly produces optically active polyketones.

Asymmetric synthesis polymerization is the reaction that produces polymers with configurational chirality in the main chain, starting from prochiral monomers.^{34,35} Even if effective chiral induction takes place in the polymerization of a vinyl monomer (1-substituted ethene), the resulting stereoregular (e.g., isotactic) polymer is hardly optically active because the polymer chain has a plane of symmetry if one ignores the trifling difference of the chain ends (**Figures 6(a)** and **6(b)**). On the other hand, the alternating copolymer of vinyl monomers with carbon monoxide possesses true chiral centers in the polymer main chain due to the absence of plane of symmetry.



Scheme 5 Tactic polyketones synthesized by the alternating copolymerization of olefins with CO.



Figure 6 Isotactic polypropene (a, b) and isotactic poly(propylene-*alt*-CO) (c, d). A σ -plane exists in polypropene; in other words, (a) and (b) are essentially the same. On the other hand, (c) and (d) are enantiomers.

Accordingly, there exist two enantiomers, namely *RRRR*— and *SSSS*—, for the isotactic polyketone (Figures 6(c) and 6(d)).

3.25.4.2 Alternating Copolymer of Propylene and CO

3.25.4.2.1 Synthesis of isotactic poly(propylene-alt-CO) using achiral ligands

The first propylene/CO alternating copolymer was obtained using $Ar_2P(CH_2)_3PAr_2$ (Ar = phenyl and 2-methoxyphenyl), but the regioregularity and stereoregularity were low as assignable by ¹³C NMR spectroscopy in the region of the carbonyl resonances.³⁶ The head-to-head and the tail-to-tail enchainments exhibit peaks at 214–216 and 207–208 ppm while the peaks around 211–213 ppm are attributed to the head-to-tail structure. The sharpness of the δ 211–213 peak, which corresponds to the *like–like* triad, provides an indication of the degree of isotacticity present in the polymer.

In the 1990s, investigations into bisphosphine ligand design opened a new area for alternating propylene/CO copolymerizations, namely, the ability to synthesize highly isotactic polyketones. Representative ligands on Pd dication employed for these copolymerizations are shown in **Figure 7**. While having the same 1,3-propanediyl backbone as previously used complexes, simple replacement of the aryl groups in Ar₂P(CH₂)₃PAr₂ by ethyl groups to give Et₂P(CH₂)₃PEt₂ improved the regioselectivity of polymerization, and thus completely regioregular, isotactic-rich copolymer was obtained although quantitative evaluation of the tacticities is not included in the literature.³⁷ Another achiral ligand, bis(diarylphosphinomethyl)-1,2-phenylene, also provided the regioregular highly isotactic CO/propylene polyketone (82% for *like*-diads).^{37,38}

3.25.4.2.2 Synthesis of isotactic poly(propylene-alt-CO) using chiral ligands

Chiral ligands were first employed to improve isotacticity in propylene/CO alternating copolymerization, by exploiting catalyst control over the enantiofacial selection of propylene. The first attempted synthesis of isotactic poly(propylene-*alt*-CO) using an optically active ligand involved 2,2-dimethyl-4,5-bis (diphenylphosphinomethyl)-1,3-dioxolane (DIOP); however, the product was both regioirregular and stereoirregular.³⁹ Isotactic poly(propylene-*alt*-CO) was produced by using 6,6'-dis-ubstituted-2,2'-bis(dialkylphosphino)-1,1'-biphenyl ligands (up to 100% h–t polymer, with 96% for the *like*-diads).³⁷ Unlike DPPP, a chiral dimethyl-substituted DPPP, 2,4-bis(diphenylphosphino)pentane (*rac*-BDDP in Figure 1), provided a highly isotactic copolymer.^{40,41} Highly isotactic poly(propylene-*alt*-CO)



Figure 7 Ligands employed for the synthesis of isotactic poly(propylene-alt-CO).

of the asymmetric center in the main chain.

was also produced using Pd complexes of chiral ligands Me-DuPHOS (1,2-bis(2,5-dimethylphospholano)benzene),⁴² BINAPHOS (2-(diphenylphosphino)-1,1'-binaphthalen-2'-yl 1,1'-binaphthalen-2,2'-diylphosphite),^{43,44} and JOSIPHOS-type ligand (1-[2-(diarylphosphino)ferrocenyl]ethyldialkylphophine) (**Figure 7**).^{45,46} Notably, not only the C2-symmetric ligands but also C1-symmetric ones efficiently produced the corresponding isotactic polyketone. The highest productivity for propylene/CO alternating copolymerization, 1797 g of copolymer per gram of palladium per hour, has been reported using the catalyst system Pd(OAc)₂/JOSIPHOS/BF₃•OEt₂ in CH₂Cl₂–MeOH at 50 °C under 7.5 MPa of CO pressure ($M_n = 14\,000$, >99% h–t, >97.5% for *like*-diads).

As mentioned before, a pair of enantiomers exist for isotactic polyketones. It should be noted that high isotacticity does not necessarily mean high polymer enantiopurity, since both *RRRR*— and *SSSS*— chain segments can exist in the same polymer in amounts determined by the nature of its stereoerrors. For the asymmetric centers in the main chain of poly (propylene-*alt*-CO) prepared using a catalyst system containing ligand Me-DuPHOS, almost complete enantioselectivity (preferential existence of one chain stereoisomer) was confirmed by ¹³C NMR analysis utilizing a chiral shift reagent.⁴² Shorter units of the copolymer that contain one propylene unit or two propylene units were prepared by Cy-BIPHEP,⁴⁷ the results also supporting the exclusive formation of a single poly(propylene-*alt*-CO) enantiomer.

More practically, the molar absorption for the carbonyl group by circular dichroism (CD) can be used as an indicator for the enantioselectivity of the poly(propylene-*alt*-CO) chain. High values, such as $\Delta\varepsilon + 1.73$ with a catalyst system Cy-BIPHEP³⁸ and $\Delta\varepsilon -1.66$ with a catalyst system containing BINAPHOS,⁴⁴ were reported using (CF₃)₂CHOH as a solvent. Although the presence of higher order polymer structures, for example, helical structures, would affect CD absorption, the absence of such structures was confirmed by comparing the CD spectrum of the polyketone to that of (*S*)-3-methyl-2,5-hexanedione, a single configurational unit analog.⁴⁸ Accordingly, the molar absorption of poly(propylene-*alt*-CO)

Depending on the reaction conditions, poly(propylenealt-CO)s can be isolated as either the true polyketone, poly (1-methyl-2-oxo-propanediyl), or as a polyspiroketal, poly [spiro-2,5-(3-methyltetrahydrofuran)] (Figure 8).⁴⁹ The latter polymer can be transformed into the thermodynamically more stable polyketone either thermally or by dissolution in (CF.) CHOH (abbreviated as HFIP).^{31,42} There are no solvents other than HFIP which stabilize the polyketone form and the reason is not clarified yet. The ketal formation is unique for highly isotactic copolymers generated from propylene or other higher aliphatic 1-alkenes. A helical structure was suggested by CD spectrum for a spiroketal having azobenzene side chains. Asymmetric alternating copolymerization of CH2=CH-(CH2)4-O-C6H4-N=N-C6H5 with CO provided a 3:1 mixture of polyspiroketal and polyketone upon reprecipitation from methanol and CHCl₃. Strong Cotton effect of the azobenzene moiety around 340 nm was indicative of the helical orientation of the azobenzene moiety in the polyspiroketal structure.50

Alkene/CO Copolymerization

833

3.25.4.3 Alternating Copolymer of Styrene and CO

3.25.4.3.1 Synthesis of syndiotactic poly(styrene-alt-CO)

The first styrene/CO alternating copolymers were obtained using $[Pd(bpy)(S)_2|X_2$ or $[Pd(phen)(S)_2|X_2$ complexes as catalysts where S is a solvent, mainly methanol, and X is a noncoordinating anion.⁵¹ The triad stereochemical composition can be estimated by ¹³C NMR peak using the enchained styrene *ipso*-carbon peak at 136–138.³⁷ For copolymers of *para*-substituted styrenes with CO, the peaks due to the main-chain carbons at δ 42–45 (CH₂), 52–55 (CH), 210 (C=O) are used to discuss the stereoregularity because there are two *ipso*-carbons for the substituted styrenes.

Successful chain-end control for the high syndiotacticity may be attributed to the exclusive 2,1-insertion of styrene, which is in sharp contrast to the predominant 1,2-insertion of aliphatic 1-alkenes such as propylene. The stereocontrol by the



Figure 8 Formation of a spiroketal structure.



Scheme 6 Stereocontrol in the styrene/CO alternating copolymerization.

asymmetric center of the enchained styrene unit (located at the β -position to the metal after insertion of CO) seems rather surprising, because it seems too distant to control the direction of the next incoming styrene monomer. It is proposed that the asymmetric center of the acylpalladium propagating species controls the orientation of the polymer chain carbonyl which is bound to palladium, and that this carbonyl interacts with the inserting styrene to control the stereochemistry of insertion (Scheme 6, TS1).³ Thus, mediated by the carbonyl, effective chain-end control seems to be performed. The chain growth process of styrene/CO copolymerization with a bipyridine acetyl palladium complex has been monitored by ¹H and ¹³C NMR over the first three alternating insertion sequences by using 4-tert-butylstyrene, which exhibits more simple peaks as the substrate.⁵² Insertion of 4-tert-butylstyrene gave a 3:1 mixture of σ -benzyl complex and π -benzyl complex. After the subsequent insertion of CO, 4-tert-butylstyrene, and then another CO molecule, formation of a single diastereomer was confirmed at low temperature for the diad. Although the relative configuration was not determined, one can expect it should be unlike.

Alternatively, lower molecular weight model compounds of poly(styrene-*alt*-CO) were prepared in the presence of an excess oxidant using Pd(CF₃COO)₂/BPY in methanol. The high concentration of oxidant accelerates the chain transfer so that the shorter oligomers are obtained. Among various dimer, dimethyl 2,5-diphenyl-4products. а oxoheptanedioate, was obtained in a diastereomerically pure form.53 Interestingly, in contrast, the diastereoselectivity $(\sim 2:1)$ seen for the first two insertions of 4-methylstyrene in copolymerization with CO was much lower than the overall diastereoselectivity seen in the corresponding copolymer (~92% of uu triad, determined by ¹³C NMR when the catalyst system [Pd(CH₃)(CH₃CN) (ⁱPrN=CH-CH=NⁱPr)][B(3,5- $(CF_3)_2C_6H_3)_4$ in methanol was employed).^{54,55} Thus, the contribution of the growing chain to the stereocontrol is proposed in the latter case. So far, the highest level of uuselectivity up to 97-98% has been accomplished by using modified phenanthroline ligands.56,57

3.25.4.3.2 Synthesis of isotactic poly(styrene-alt-CO)

Brookhart first reported the asymmetric alternating copolymerization of 4-*tert*-butylstyrene with carbon monoxide using $[Pd(Me)(MeCN)(biox)][B(3,5-(CF_3)_2C_6H_3)_4]$ (Figure 9).⁵⁸ In this copolymerization, the enantioface of the olefin was selected by the chiral ligand instead of the chain end; as a result, the polymer was completely isotactic. Since one enantioface was



Figure 9 Ligands employed for the synthesis of isotactic poly(styrene-alt-CO).

discriminated against the other by the chiral catalyst, it is probable that the copolymer is also of high enantiopurity. The ligands employed for the isotactic copolymerization of styrenes with CO are summarized in **Figure 9**. Bidentate sp²-nitrogen ligands are most commonly used,^{39,59–62} along with the phosphine sp²-nitrogen bidentate ligand^{63,64} and phosphinephosphite BINAPHOS in **Figure 7**.^{43,44}

The enantioselectivities for styrene/CO copolymerizations were mostly estimated by molar optical rotation $[\Phi]_D$ or CD $\Delta \varepsilon$. By now, $[\Phi]_D = -536$ for 4-*tert*-butylstyrene/CO using a catalyst system [Pd(Me)(MeCN)(bisoxazoline)][B(3,5-(CF₃)₂C₆H₃)₄]⁵⁸ and $\Delta \varepsilon = -11.75$ for styrene/CO using a catalyst Pd(Me)(MeCN) $(\text{phospholeoxazoline})[B(3,5-(CF_3)_2C_6H_3)_4]^{65}$ are the highest reported values. A few studies involving the synthesis and characterization of oligomeric species have also been reported. Based on NMR analysis, Consiglio revealed that styrene insertion into the acylpalladium complex [(phospholeoxazoline)Pd(C(=O) Me)(MeCN)](CF₃SO₃) is both completely regioselective for 2,1-insertion and enantioselective.⁶⁶ This result is consistent with the fact that dimethyl (R)-2-phenylbutanedioate was obtained almost exclusively as the S-enantiomer (95% ee) when styrene/CO copolymerization with this catalyst was carried out in the presence of a high concentration of the oxidant benzoquinone. Highly stereoselective styrene/CO copolymerization was accomplished by using azabis(oxazoline) (Figure 9) with *ll* selectivity of over 99%.62

It is noteworthy that only low molecular weight oligoketones can be obtained with bisphosphine ligands in alternating styrene/CO copolymerizations. Drent has attributed this fact to the higher electron density on the Pd center when phosphine ligands rather than nitrogen ligands are used, because the growing styrene/CO copolymer has a higher tendency to terminate by β -hydride elimination than growing propylene/CO chains.³ The rather unusual fact that high copolymer can be prepared with catalyst system [(binaphos)Pd(Me)(MeCN)][B (3,5-(CF₃)₂C₆H₃)₄] is proposed to be attributable to the steric demand of this bulky ligand, which causes styrene to undergo 1,2-insertion rather than the more typical 2,1-insertion.⁶⁷ The continuous 1,2-insertion provided the h–t polyketone with high enantiofacial selection ($[\Phi]_D = -451$).

3.25.4.3.3 Synthesis of poly(styrene-alt-CO) with other structural control

When a bulky $P \sim N$ ligand was used, the electronically favored 2,1-insertion and the sterically favored 1,2-insertion compete with each other, providing a regioirregular styrene/CO copolymer.⁶⁴ Regiocontrolled but atactic copolymers were obtained using pyridine–imidazole⁶⁸ or diimine⁶⁹ ligands.

A stereoblock copolymer consisting of isotactic and syndiotactic 4-*tert*-butylstyrene/CO alternating copolymer was prepared by Brookhart.⁷⁰ First, copolymerization was initiated by using a Pd catalyst containing chiral bisoxazoline, to produce the isotactic block. Subsequently, addition of BPY to the system resulted in ligand replacement, so that the second block (formed by further copolymerization) was syndiotactic (Scheme 7). Similarly, *p*-methylstyrene/CO copolymer with atactic or isotactic stereoblock structure was successfully obtained by using substituted-diimine ligands.^{71,72}

3.25.4.4 Other Olefin/CO Copolymers Consisting of Propylene, Styrene, or 1, ∞ -Dienes

Using a mixture of two kinds of olefins, a terpolymer can be generated by alternating olefin/CO copolymerization. An olefin and carbon monoxide are incorporated in a completely alternating manner, and the order of the two olefins is mostly random. Asymmetric terpolymerization of styrene/ethylene/CO has been intensely studied by using [(phosphine-oxazoline)Pd(CH₃) (MeCN)](CF₃SO₃) as a catalyst.^{65,73} Ethylene was preferentially and randomly enchained in the terpolymer, in spite of the comparably higher reactivity of styrene for the copolymerization. The enantioselectivity for styrene in the terpolymerization is as high as that observed for the styrene/CO copolymerization.

Copolymerization of pent-1,4-diene or hex-1,5-diene with CO results in the cyclopolymerization to produce copolymers including cyclopentanone or cyclohexanone in the middle of the chain (Scheme 8).

3.25.4.5 Copolymerization of Functionalized Olefins with Carbon Monoxide

The incorporation of additional functional groups into the alternating and nonalternating polyketones would expand the range of available materials. However, most reports on the copolymerization of olefins with CO have dealt with the olefins without any polar functionality. Recent progress in this field has enabled the synthesis of highly functionalized polyketones by the copolymerization of functionalized olefins with CO. In this section, two types of copolymerization are described: (i) the copolymerization of olefins possessing a functional group at a remote position with CO, and (ii) the copolymerization of fundamental polar vinyl monomers with CO.





Scheme 8 Cyclocopolymerization of $1, \omega$ -diene and CO.



Scheme 7 Synthesis of stereoblock poly(styrene-alt-CO).

3.25.4.5.1 Copolymerization of olefins possessing a functional group at a remote position with CO

There have been several reports on the copolymerization of functionalized olefins with carbon monoxide. Catalysts consisting of Pd and DPPP were found to catalyze the copolymerization of CO with various functionalized olefins such as methyl 10-undecenoate, 10-undecenoic acid, 10-undecenyl alcohol, 3-butenol, and allylbenzene derivatives, as well as terpolymerizations of these functionalized olefins bearing benzo-15-crown ether, saccharide, amino acids, and steroids have also been employed for co- or terpolymerization.^{76–79} Norbornene⁸⁰ and other bicyclic olefins⁸¹ bearing ester groups have also been employed for copolymerization with CO. It should be noted that, when oxabicyclic diene was employed, the copolymerization accompanied by the retro Diels–Alder reaction proceeded to produce poly(ketovinylene)s (Scheme 9).

The asymmetric alternating copolymerization of olefin and CO has been achieved by using chiral ligands Me-DUPHOS and BINAPHOS for the functionalized olefins possessing hydroxyl,⁸² carboxy,⁸² carbamate,⁸³ amide,⁸³ fluoroaryl,^{84,85} epoxyalkyl,^{84,85} perfluoroalkyl,^{86,87} and *para*-chlorophenyl⁸⁸ groups (Figure 10).

3.25.4.5.2 Copolymerization of fundamental polar vinyl monomers with CO

In contrast to the above-mentioned monomers, fundamental polar vinyl monomers, whose polar group is directly attached to the olefin moiety, are difficult to be copolymerized with CO. Among many problems associated with metal-catalyzed copolymerization of polar vinyl monomers with CO, the most critical one is the formation of chelate intermediates after the insertion of vinyl monomers. It was reported that methyl acrylate,^{16,17,89-96} methyl vinyl ketone,⁹⁶ vinyl acetate,^{89,90} vinyl chloride,⁹⁷ and ethyl vinyl ether⁹⁸ can insert into cationic Pd-acyl bonds to give five-membered chelate intermediates with a polar group substituted at the α -position (E1); however, further insertion of the next monomers did not occur. The ligands employed for attempted copolymerization are summarized in Scheme 10. This could be attributed to the following three problems (Scheme 11): (i) CO coordination may be suppressed by the strong intramolecular ketone coordination in E1. Jordan et al. found that the Cl-substituted complex (E1, FG = Cl) has a short Pd-C bond as well as a Pd-O bond.⁹⁹ This may suggest that the α -electron-withdrawing group-substituted chelate structure is more stable than that of nonsubstituted chelate complexes, leading to a low tendency of E1 to form a chelate-opened structure (E2). (ii) The low nucleophilicity of the α-carbon arising from the electronwithdrawing group in E2 would be an obstacle for CO insertion. It is well known that electron-withdrawing substituents retard CO insertion into M-alkyl and M-aryl bonds.^{100,101} (iii) The formation of E4 and E1' is retarded due to the low coordination-insertion ability of polar vinyl monomers.

In 2007, Nozaki *et al.* reported that the mixture of Pd(dba)₂ and phosphonium sulfonate (1a, 1b) catalyzed the alternating copolymerization of vinyl acetate with CO (Scheme 12, top).¹⁰² The alternating structure of the obtained copolymers was unambiguously confirmed by NMR analyses and MALDI-TOF mass analysis. However, head-to-tail selectivity was found to be less controlled, which suggests that VAc insertion into the acyl-palladium bond may occur in both the 2,1-and 1,2-mode. The productivity was up to $3.0 \text{ g mmol}^{-1} \text{ h}^{-1}$ and the molecular weight (M_n) was up to 38000.















Scheme 11 Problems in the copolymerization of polar vinyl monomers with CO.



Scheme 12 Alternating copolymerization of vinyl acetate/CO and methyl acrylate/CO.



Figure 11 Initiators/catalysts used for the copolymerization of polar vinyl monomers with CO.

The alternating copolymerization of methyl acrylate with CO was also accomplished by using the same catalytic system (Scheme 12, bottom).¹⁰³ The activity of MA/CO copolymerization (up to 4.4 g mmol⁻¹ h⁻¹) and the molecular weight (up to $M_n = 30\,000$) of the copolymers were similar to those in the case of VAc/CO copolymerization. NMR studies revealed that the regiochemistry is strictly regulated, implying that the insertion of MA into the acyl-palladium bond occurs only in the 2,1-insertion mode.

Some control experiments have suggested both copolymerizations proceed via the coordination-insertion mechanism:^{102,103} (i) Chelate complexes shown in **Figure 11** also initiated and catalyzed the copolymerizations of VAc with CO and the copolymerizations of MA with CO, respectively. The obtained copolymers had an initiating chain end arising from the initiators. (ii) The addition of galvinoxyl hardly affected either the activity or the molecular weight of the obtained copolymer. (iii) The reaction initiated by AIBN afforded only poly(vinyl acetate) and poly(methyl acrylate).

3.25.5 Copolymerization of Imines with Carbon Monoxide

Polypeptides are the most ubiquitous biopolymers that have been used for a broad range of applications in materials, catalysis, and pharmaceuticals. For a long time, polypeptides have been synthesized from various amino acids, requiring multistep procedures for the preparation and subsequent activation using a stoichiometric amount of condensing agents to form peptide bonds.^{104,105} In contrast, the alternating insertion of carbon monoxide and imines into metal–carbon bonds would provide a new general procedure for the synthesis of polypeptides. Since the reaction is analogous to olefin/ CO copolymerization, the possibility for imine/CO copolymerization has been investigated by using palladium catalysts that have been widely used in olefin/CO copolymerization over the last decade.

In 1998, Sen¹⁰⁶ and Arndsten¹⁰⁷ independently reported the first observation of imine insertion into acyl palladiumcarbon bonds (Scheme 13). By using diphosphine and bipyridine as ligands, they observed the coordination of the imine through its nitrogen atom (F1) and CO insertion into the Pd-Me bond to yield acylpalladium intermediate F2. The insertion of imine into the Pd-Me bond of F1 did not occur. After the formation of acylpalladium complex F2, imine insertion proceeded in a direction that can form an amide bond. The resulting complex F3 possesses a square-planar geometry with the carbonyl oxygen of the amide coordinating as a fourth ligand. The chelation of the carbonyl group is directly analogous to that observed in palladium-catalyzed olefin/CO copolymerization intermediates (C1 in Scheme 3). These observations are consistent with theoretical calculations, suggesting that the insertion of an imine into acylpalladium proceeds through a four-membered ring transition state that is similar to the olefin insertion.¹⁰⁸

Further incorporation of CO and imine to complex F3 did not occur even at elevated temperature and pressure. This may be attributable to the strong chelation of the amide ligand in F3 effectively blocking the coordination site required for the coordination and insertion of CO. With the objective of breaking the strong chelate structure of F3, Arndtsen *et al.* investigated the use of chloride ions, which can coordinate to the palladium center (Scheme 14).^{109–111} Rather unexpectedly, an imidazoline derivative was obtained in the presence of Cl anions under a CO atmosphere. It is suggested that CO was inserted into the Pd–C bond of F3 followed by the subsequent reactions including β -H elimination, cyclization, and 1,3-dipolar cycloaddition with imine that is formed from F3.

Other metals such as nickel¹¹² and manganese¹¹³ have been investigated by Arndtsen *et al.* As in the case of Pd complexes, five-membered chelate complexes such as F3 have been formed via the reaction of alkylmetal complexes with CO and imines. The subsequent CO insertion into the five-membered chelate complex was observed in the case of manganese, and the resulting α -amido acyl complex was successfully characterized by X-ray crystallographic analysis. Cobalt complexes have also been investigated by Sen *et al.*¹¹⁴ because they are one of the most frequently used metal catalysts for the carbonylative polymerization of azirizines.¹¹⁵ However, the reaction of *N*-alkylbenzaldimines with CO in the presence of [Co (¹³CH₃C(O))(CO)₃(P(2–CH₃C₆H₄)₃)] or [Co₂(CO)₈] resulted in the formation of *N*-alkylphthalimidines.¹¹⁴

In 2007, Sun *et al.* reported the first copolymerization of imines with CO using a Co catalyst (Scheme 15).¹¹⁶ They found that an acylcobalt catalyst effectively catalyzed the co-polymerization of aldimines, ArCH=NMe, with CO.¹¹⁷ The



Scheme 13 Reactions of CO and imines with a Pd–Me complex.



Scheme 14 Formation of carboxylate-substituted imidazoline.



R = Ph, 4-MeC₆H₄, 4-MeOC₆H₄, 2,4,6-Me₃C₆H₂, *t*-Bu, C(Me)₂Et

Scheme 15 Alternating copolymerization of imines with carbon monoxide catalyzed by acylcobalt complex.

copolymerization was performed in dioxane under 55 bar of CO pressure at 50 °C for 6 h to obtain the alternating copolymer with M_n 1900–4100 with 73% yield. The alternating structure was confirmed by NMR and MS analyses. One end group is an acyl group while the other end group is presumed to be an imidazoline skeleton similar to that obtained in Scheme 14. When t-BuCH=NMe was used, copolymers with high molecular weights Mn of up to 28 800 was obtained. The low polydispersity index (1.18) and linear change in the molecular weight with the monomer-to-catalyst ratio suggested that the polymerization proceeded in a living fashion. They proposed a coordination polymerization mechanism in which the imine insertion occurs via a four-centered transition state. The unique properties of Nand C-disubstituted poly-a-peptides include good solubility in common organic solvents such as THF and chloroform and facile degradation by trifluoroacetic acid.¹¹⁷

3.25.6 Chemical Transformation of Polyketones

One of the unique features of the alkene/CO copolymer is the existence of multiple carbonyl groups in the main chain. Thus, versatile chemical transformations of the carbonyl groups were examined to provide new polymers (Scheme 16). The 1,4-diketone structure ethylene/CO copolymers can be transformed into pyrroles, thiophenes, and furans upon treatment with primary amines,^{118,119} phosphorus pentasulfide, and phosphorus pentoxide, respectively.¹²⁰

Derivatization was examined for optically active polyketones of propylene and CO. Diastereoselective reduction of poly



Scheme 16 Chemical transformation of polyketones to other functional polymers.

(propylene-*alt*-CO) was reported using metal hydride reagents. Using tetrabutylammonium borohydride as a reductant, (*S*)-poly(propene-*alt*-CO) was reduced into the corresponding polyol with the *S*/*R* ratio of 70/30 for the absolute configuration of the newly created chirogenic center. Baeyer–Villiger oxidation of (*S*)-polyketone with *m*-chloroperbenzoic acid provided poly (ketone/ester) in a ratio of ketone/ester = 82/18 with 73% isolated yield.^{42,121,122} An ester unit likely exists to distribute randomly in the product rather than to form a block copolymer of a polyketone and a polyester. This was suggested by methanolysis of the product polymer to give oligomers rather than methyl 3-hydroxybutyrate.¹²³ Because poly((*R*)-3-hydroxybutyrate) (PHB), the ester part of the current polymer,

is a well-known biodegradable polymer, further improvement of this oxidation is highly desired. The carbonyl group could be transformed into a C=C double bond. The methylenation of the (*S*)-polyketone using an organozinc–titanium reagent, CH₂(ZnI)₂–TiCl₃, provided the corresponding methylenated polymer.^{124,125} The reaction proceeded without any significant epimerization to give the highly isotactic product. The products, a new class of hydrocarbon polymers with main-chain chirality, are attainable only by this transformation but not by any other methods, such as ring-opening polymerization of 2-alkyl-1methylenecyclopropanes.

3.25.7 Physical Properties and Industrial Application of the Olefin/CO Copolymers

Completely alternating poly(ethylene-alt-CO) suffers from low processability due to its insolubility in common solvents and very high $T_{\rm m}$ (≈ 260 °C), both of which are attributed to high crystallinity induced by dipolar interactions between the carbonyl groups. In order to improve the processibility, terpolymer consisting of ethylene/propylene/CO is the major product in industrial production. Nonalternating copolymer of ethylene and CO is another candidate but is not in commercial production at this moment. Examples of unique physical and chemical properties of poly(olefin-alt-CO) made by ethylene/ CO copolymerization or ethylene/propylene/CO terpolymerization may be summarized as follows.⁴ It is classified as engineering plastic and shows high crystallinity, strong rigidity, and high impact strength. Recently, new fiber spinning technology has been developed by Asahi Kasei Fibers Co., dissolving poly(ethylene-alt-CO) in a concentrated aqueous solution of zinc chloride. The fibers thus obtained have potential application as a component of run-flat tires. The material also shows strong chemical resistance to acids, bases, and solvents. Its impermeability to hydrocarbons provides potential application to fuel tanks. Because the polyketones are photo-degradable due to the possible Norrish type I or II reactions, addition of UV absorber is sometimes required for industrial applications. None of the other polymers are vet to be applied to industry but are attractive anyway since they are extremely highly functionalized when compared to the conventional synthetic polymers.

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3.26 Cycloolefin Polymerization

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3.26.1	Introduction	843
3.26.2	Polycycloolefins: Homopolymerization	843
3.26.2.1	Poly(cyclopentene)	843
3.26.2.2	Polynorbornene by Early Transition Metal Catalysts	846
3.26.2.3	Polynorbornene by Late Transition Metal Catalysts	848
3.26.2.4	Properties and Applications	850
3.26.3	Cycloolefin Copolymers	851
3.26.3.1	Cyclopentene Copolymers	851
3.26.3.2	Norbornene Copolymers	853
3.26.3.2.1	Ethene-norbornene copolymers	853
3.26.3.2.2	Propene-norbornene copolymers	865
3.26.3.3	Other Cycloolefin Copolymers	869
3.26.3.4	Properties and Applications	869
3.26.4	Conclusions	870
References		870

3.26.1 Introduction

Many of the cycloolefins such as cyclobutene, cyclopentene, norbornene, cyclooctene, and their substituted compounds can be successfully polymerized or copolymerized.¹⁻⁴ Cyclohexene could not be polymerized until recently, because of the high ring stability and the twisted-chair conformation.⁵

A wide range of Ziegler–Natta catalysts, metallocene/methylaluminoxane (MAO), and other single-site catalysts were explored to produce polymers with new properties and applications.^{6–11} Much interest is focused on cyclopentene, norbornene, and cyclooctene homo- and copolymers because of the easy availability of the monomers and some excellent properties of the polymers.

There are two pathways for the polymerization of cycloalkenes. One is the double bond opening (addition polymerization) and the other is the ring opening (Scheme 1).¹²

Ring-opening metathesis polymerization (ROMP) gives polyalkenamers. These have typically been produced using heterogeneous catalyst systems based on molybdenum, tungsten, or ruthenium salts along with various cocatalysts and promoters.¹³ Polypentenamer from cyclopentene, Vestenamer® from cyclooctene, Norsorex® from norbornene, and Metton® or Telene® from dicyclopentadiene (DCPD) were developed to commercial products. In the past, well-defined catalysts such as those developed by Grubbs and Schrock were also used for ROMP.¹³

The ring-opening polymerization of cyclopentene and other cyclic olefins can give two structures, the *trans*-poly(cyclopentenamer) or the *cis*-poly(cyclopentenamer). Both microstructures were found with Ziegler catalysts.^{7,8} **Table 1** gives results of cycloolefin homopolymerization. Cyclopropene polymerized spontaneously above – 80 °C.¹⁴ Cyclobutene is also very active and polymerized easily with various catalysts. Homopolymerization by double bond opening can be achieved by vanadium and late transition metal catalysts.⁷ The use of heterogeneous Ziegler–Natta catalysts is accompanied by

ROMP, whereas homogeneous metallocene and single-site catalysts promote 100% addition polymerization of cyclopentene.⁹

The polymers obtained by 100% double bond opening feature two chiral centers per monomer unit and therefore are ditactic. Chiral metallocene catalysts produces tactic, crystalline homopolymers with extremely high melting points (for poly(cyclobutene) 485 °C, for polynorbornene about 600 °C) and decomposition occurs before melting. Whereas the atactic cyclic olefin polymers can be dissolved in hydrocarbon solvents at least to some extent, the tactic polymers are hardly soluble.¹⁵⁻¹⁷

By copolymerization of cyclic olefins, especially norbornene with ethene or propene, a cycloolefin copolymer (COC) can be produced.¹⁸ These new materials have been the focus of academic and industrial research. Ethene–norbornene copolymers (Topas[®]) are usually amorphous and show excellent transparency and high refractive index, making them suitable for optical applications.¹⁹ Zeonex[®] is an amorphous cycloolefin polymer (COP) with a cyclic structure in the main chain polymerized by ROMP of norbornene derivatives, followed by hydrogenation of double bonds, with properties similar to Topas[®].²⁰ Detailed information can be found in special reviews and books.^{21–25}

3.26.2 Polycycloolefins: Homopolymerization

3.26.2.1 Poly(cyclopentene)

There is a great interest in polymerizing cyclopentene because of its easy availability in the C_5 fraction of naphtha cracking. Homopolymerizations can be carried out by Ziegler–Natta catalysts, metathesis, metallocene, and late transition catalysts.^{12,26,27} The polymerization occurs by double bond or by ring-opening polymerization (see **Table 1**). Double bond opening leads to 1,3-*cis* and 1,3-*trans* enchainment.^{28–30} These polymers are ditactic and, therefore, structures such as erythrodisyndiotactic or isotactic and threodisyndiotactic or isotactic are possible (**Figure 1**).



Scheme 1 Addition polymerization (1) and ring-opening metathesis polymerization (ROMP) (2) of cyclic olefins.



		Ring ope	ening	
Monomer and catalyst system	Double bond opening (%)	trans (%)	cis (%)	Reference
Cyclobutene				
V _{(acac)3} AIEt ₂ CI	100	0	0	7
TiCl ₄ /AlEt ₃	5	65	30	7
WCI ₆ /AIEt ₃	30	40	30	7
Cyclopentene				
MoCl ₅ /AIEt ₃	0	0	100	8
WCI ₆ /AIEt ₃	0	100	0	8
VCI ₄ /AIMe ₂ CI	50-80	30-50		12
[Et(Ind) ₂]ZrCl ₂ /MAO	100	0	0	9
Cvclohentene				
MoCl ₅ /AIEt ₅	0	93	7	8
Cvclooctene (cis)				
WCI ₆ /AIEt ₃	0	85	15	8



Threodisyndiotactic

Figure 1 Microstructures of poly(cyclopentenes) obtained by double bond opening (addition polymerization).

The isotactic polymers are crystalline, have a low solubility, and have a melting temperature of $395 \,^{\circ}$ C. Collins and Kelly synthesized the oligomers by hydrooligomerization of cyclopentene in the presence of hydrogen with a *rac*-[Et(Ind)₂] ZrCl₂/MAO catalyst.^{28,31} Pure tri- and tetramers were isolated from the product mixture and their structure, including

stereochemistry, was established. The 1,3 insertion results from steric hindrance that makes probable β -hydrogen transfer to the zirconium center, olefin rotation, and *cis*-insertion (Figure 2).²⁸

Beside isotactic working bridged bis(indenyl)zirconocenes, syndiotactic *ansa*-cyclopentadienyl-fluorenyl or atactic biscyclopentadienyl or bisfluorenyl complexes are also used (Figure 3).³⁰



Figure 2 Proposed mechanism for *trans*-1,3-insertion of CPE through reversible chain transfer (P and P' = polymer chain). Reprinted with permission from Kelly, W. M.; Wang, S.; Collins, S. *Macromolecules* **1997**, *30*, 3151–3158. Copyright 1997 American Chemical Society.



Figure 3 Zirconocene complexes used for cycloolefin polymerization.

Zirconocene	Polymerization temperature	Polymerization time	Yield
	(°C)	(h)	(g)
$\begin{array}{c} Cp_2ZrCl_2\\ Et(Ind)_2ZrCl_2\\ Et(Ind)_2ZrCl_2\\ Et(IndH_4)_2ZrCl_2\\ [Ph_2C(Cp)(Flu)]ZrCl_2 \end{array}$	30	20	Traces
	10	90	13.6
	25	72	20.0
	22	10	24.5
	22	20	1.2

 Table 2
 Polymerization of cyclopentene with different zirconocene/MAO catalysts

Zirconocene amount, 10⁻⁶ mol; solvent, 200 ml toluene; MAO, 200 mg; cyclopentene, 100 ml in a 1-I glass autoclave.

Table 2 compares some different metallocenes for the polymerization of cyclopentene. There were found good yields for the isotactic working bis(indenyl)zirconocene, and low activities for the atactic working Cp_2ZrCl_2 and the syndiotactic working complex [Ph₂C(Cp)(Flu)]ZrCl₂.³²

The microstructures were studied using ¹³C-, COSY-, DEPT-NMR spectroscopy, and synchrotron radiation.³⁰ The C_2 -symmetric *rac*-[Et(Ind)₂]ZrCl₂/MAO catalyst produces a crystalline polymer and erythrodiisotactic oligomers. These isotactic polymers are crystalline, have a low solubility, and have a

melting temperature of 395 °C. The polymerization by these isotactic working catalysts is highly stereoselective. The physical properties of the polymers produced by Cp₂ZrCl₂/MAO and [Ph₂C(Cp)(Flu)]ZrCl₂/MAO reflect their almost atactic character.^{9,33} The wide-angle X-ray scattering (WAXS) of these polymers is characterized by an amorphic halo and a glass transition temperature at 65–67 °C measured by differential scanning calorimetry (DSC). The atactic poly(cyclopentene) is partially soluble in hydrocarbons.

McLain *et al.*³⁴ polymerized cyclopentene by late transition metal catalysts using MAO and borate-activated nickel and palladium diimine complexes. The nickel diimine complexes produce crystalline materials showing a *cis*-1,3 enchainment with a melting point of 240–330 °C. The hydroligomers were mainly atactic. Palladium catalysts gave pure atactic polymers. It is also possible to polymerize substituted cyclopentenes such as 3-methyl- or 3-ethyl-cyclopentene.

ROMP led to the ring opening of cyclopentene to a polypentenamer elastomer by breaking and reforming olefin double bonds with simultaneous opening of the unsaturated cycles of the monomers. *Cis-* and *trans-*structures are formed. Using the Grubbs catalyst $\text{RuCl}_2(\text{CHPh})(\text{PCy}_3)_2$ the poly(cyclopentene) shows 10% of *cis-* and 90% of *trans-*double bond contents.³⁵ The *trans-*product from the ring-opening polymerization can be produced by using WCl₆/AlEt₃ catalysts.³⁶

Substituted polycyclopropenes can be polymerized by palladium catalysts.^{37,38,40} The substitution decreases the activity, therefore the polymerization rate can be controlled. Cyclobutene polymers with high amounts of ring-opening units are obtained by Ziegler–Natta catalysts. Addition polymers of bicyclo(3.2.0)hept-6-ene are synthesized using early and late transition metal complexes.³⁹ It was shown that the catalyst [Pd(NCE)₄][BF₄]₂ gives a high-molecular-weight polymer with a very large extent of *cis-exo* linked repeating units.

Polymers with cycloaliphatic repeating units display good thermomechanical properties, high optical clarity, and low dielectric constants and are potentially suited for microelectronic and optical applications.⁴⁰

ROMP of 4-methylcyclopentene leads to the formation of a polymer with four different configurations, *cis-meso, cis-racemic, trans-racemic, trans-meso* stereochemical, owing to the relative positioning of the methyl substituents.⁴¹

The polycyclooctene by metathesis has been commercialized since 1980. The initial cyclic molecule undergoes ring opening and is converted stepwise to larger and larger rings and finally to a polyoctenamer. The elastomeric polymer is sold under the trade name Vestenamer[®] by Evonic in Germany. This polymer, used as blend component for rubber, contains high amounts of *trans* structures.⁴

Metathesis polymers of *endo*- and *exo*-DCPD prepared with WCl₆/Me₄Sn are atactic and contain both *cis* and *trans* olefin structures. Products obtained by ReCl₅ catalyst have in contrast

all-*cis* olefin linkages. The polymer tacticity was investigated and demonstrated after complete hydrogenation of the polymer.⁴²

The metathesis of DCPD to give the polymer Metton[®] has been operated in Canada by Hercules. Another trade product from the ROMP of cyclopentadiene is Telene[®]. As metathesis catalysts are used systems based on molybdenum, tungsten, or ruthenium salts.¹²

1,3-Cyclohexadiene (CHD) can be polymerized by a great variety of catalysts.⁴³ Using n-BuLi-based initiator, a typical amorphous powder of poly(CHD), which consisted of more than 90% of 1,4-units, was obtained. Ni-catalyzed poly(CHD) could have a *cis*-rich structure arising from a *syn*-coordinative mechanism. The obtained polymers are insoluble.

3.26.2.2 Polynorbornene by Early Transition Metal Catalysts

Sartori *et al.*⁴⁴ was one of the first who investigated the polymerization of norbornene (N) by $TiCl_4/(i-Bu)_3Al$ (Ti/Al = 1:2) catalyst. Tsujino *et al.*⁴⁵ reported on the analogous $TiCl_4/Et_3Al$ system, which produces a mixture of polynorbornene by double bond and ring opening (addition polymerization and ROMP, **Figure 4**).

The homopolymerization of norbornene using early transition metal catalysts drew new attention with the discovery of metallocene/MAO catalysts.^{30,46–48} It was found that most of the obtained polymers are insoluble in organic solvents, are crystalline, and show extremely high melting temperatures. Information about the microstructure was gathered by Arndt *et al.*^{49,50} who used the hydrooligomerization technique to produce saturated model norbornene dimers and trimers with metallocene catalysts known to produce atactic, isotactic, and syndiotactic poly(α -olefins) (see Figure 2).

The authors analyzed the structures and distributions of the oligomers and tried to correlate results with the metallocene structure and the polymerization mechanism, to extrapolate the polymer microstructure. It was shown that oligomers (and polymers) of different stereochemistries (tacticities) can be produced using metallocene catalysts.

Their investigations showed that norbornene was inserted into the metal–carbon bonds of the growing polymer chain (or into metal–hydrogen bonds formed by chain transfer) in a *cis-exo* manner. Due to the structure of norbornene, each insertion generates two chiral centers of opposite stereochemistry and therefore the resulting polymers are erythroditactic. The possible configurational base units (the erythroditacticities) of polynorbornenes are represented by configurations of erythrodiisotactic (only *meso* diads), erythrodisyndiotactic (only *racemic* diads), and erythroatactic (mixture of *meso* and *racemic* diads).

Detailed two-dimensional (2D) nuclear magnetic resonance (NMR) investigations on the hydrodimers formed by the different zirconocenes (see Figure 3) showed that all three



Figure 4 Different pathways for the transition metal-catalyzed polymerization of norbornene.



Figure 5 Structures of hydrodimers (a) and hydrotrimers (b) of norbornene according to Arndt *et al.*⁵⁰

catalyst precursors (when combined with MAO) yielded two diastereomeric hydrodimers, which were found to be the *meso* and *racemic* isomers shown in Figure 5. In contrast to polycy-clopentene, produced by metallocene catalysts, only 1,2-insertion (and no 1,3-insertion) is observed for polynor-bornene. The CH_2 -ring bridge prevents a β -hydrogen transfer.

Despite the catalysts' different stereoselectivity in α -olefin polymerization, all three favored the formation of the *meso*-hydrodimer. In the case of the achiral catalyst Cp₂ZrCl₂, this has to be attributed to chain end control since the Cp ligands do not induce stereopreference. From the *meso/rac* ratio, a difference in the free energies of activation ($\Delta G^{\#}_{meso} - \Delta G^{\#}_{rac}$) of 1.5 kJ mol⁻¹ at 30 °C has been calculated.

Of the three hydrotrimers that may result from a cis-exo insertion (Figure 5), Cp₂ZrCl₂ was found to produce only two: the mm and mr isomers (Table 3). No rr hydrotrimer is produced, showing that a racemic enchainment (r diad) formed by the first two insertions preferably is followed by a meso linkage (m diad). In addition, the high amount of mr isomer found in combination with the distribution of hydrodimers indicates that a meso enchainment formed by the first two insertions is preferably followed by a racemic one. Thus, it can be concluded that the penultimate unit has a rather strong influence on the monomer insertion (one has to bear in mind that every main chain atom of the growing polymer is a chiral center and that norbornene has to be considered as a bulky and rigid monomer). Based on the distribution of hydrodimers and trimers, a polymer formed by the same mechanism should have a heterotactic (mrmrmrm) structure disturbed by a significant amount of mm sequences.

Based on the mechanisms known from α-olefin polymerization, C_s-symmetric [Ph₂C(Cp)(Flu)]ZrCl₂ should produce an erythrodisyndiotactic polymer and therefore favor the formation of the rac-hydrodimer, while C2-symmetric rac-[Me₂Si(Ind)₂]ZrCl₂ should produce an erythrodiisotactic polymer and therefore preferably yield the meso-hydrodimer. Table 3 shows that both catalysts produce mixtures of mesoand rac-hydrodimers with a meso/rac ratio greater than 1. This can be explained by a change of the relative topicities of insertion from the first to the second insertion, and is in accordance with observations by Pino and Galimberti⁵¹ and Corradini and Guerra⁵² showing that the insertion into a metal-hydrogen bond of an active metallocene catalyst species is governed directly by steric interactions of the monomer with the ligand framework of the catalyst (direct stereocontrol), while further insertions are controlled by the orientation of the (bulky) growing polymer chain and its interactions with the ligand framework (indirect stereocontrol).

Arndt and Gosmann⁵³ reported on the crystal structure of a hydropentamer of norbornene from rac-[C₂H₄(IndH₄)₂]ZrCl₂ metallocene, which shows a trisubstituted central norbornene linking unit and consists of a stereoregular (erythrodiisotactic) trimer to which a stereoregular (*meso*) dimer is attached. Karafilidis *et al.*⁵⁴ extended this and characterized tetramers and pentamers obtained by the hydrooligomerization of norbornene with a *rac*-[Me₂C(Ind)₂]ZrCl₂/MAO catalyst (**Figure 6**). They propose C–H activation at the C7 carbon of the most recently inserted norbornene unit to be the root cause of the formation of trisubstituted units, and based on results of deuterium labeling experiments and molecular modeling,

Table 3Mol.% distribution of the hydrodimers and hydrotrimers of norbornene produced at 30 °C bymetallocene/MAO catalysts $1-3^{49}$

	Cp_2ZrCl_2 (1)	rac-[Me ₂ Si(Ind) ₂]ZrCl ₂ (2)	[Ph ₂ C(Cp)(Flu)]ZrCl ₂ (3)
	$C_{2\nu}$	<i>C</i> ₂	Cs
<i>meso</i> -hydrodimer	65 35	58 42	53 47
<i>mm</i> hydrotrimer (<i>mr</i> + <i>rm</i>) hydrotrimer 77	23 38	62 15	8
<i>rr</i> hydrotrimer	0	0	77



Figure 6 Mechanism of the formation of 2-*exo*,7'-*syn*-enchained units during norbornene polymerization by *rac*-[Me₂C(Ind)₂]ZrCl₂/MAO catalysts according to Karafilidis *et al.*⁵⁴ (R=H, Me; bis(indenyl) ligand and charge on Zr center are not shown).

assume that polynorbornene produced by some metallocene catalysts may have a regular structure involving such trisubstituted norbornene units.

The polymerization activity of the homopolymerization of norbornene is low because of the steric hindrance of zirconocene catalysts. Activities of 150 kg polynorbornene (mol Zr)⁻¹ h⁻¹ were reached using *rac*-[Et(Ind)₂]ZrCl₂ at 20 °C.³⁰

Half-sandwich complexes of titanium, when activated by a cocatalyst such as MAO, are even more active for the homopolymerization of norbornene than metallocenes.^{55,56} Peucker and Heitz⁵⁷ found that chromium-based half-sandwich complexes can also be activated to produce polynorbornenes and E–N copolymers.

3.26.2.3 Polynorbornene by Late Transition Metal Catalysts

Norbornene can be more easily polymerized by more open late transition metal catalysts based on palladium salts and complexes.^{56,58} Sen and Lai⁵⁹ found that the dicationic system [CH₃CN]₄Pd][BF₄]₂ is a very active catalyst for norbornene polymerization. After the discovery of MAO as cocatalyst, renewed interest grew up in the palladium-catalyzed polymerization of norbornene.60-68 Risse and coworkers16,61,62 investigated the homo- and copolymerization of norbornene and its derivates. Norbornene derivatives containing ester substituents were polymerized by Pd(II) catalysts. The transition metal catalyst was found to tolerate the ester functionality. The polymerization of the pure exo-isomers produced substantially higher yields than reactions of monomers containing a high proportion of the endo-isomer. Amorphous polymers with glass transition temperatures over the range of -40 to 268 °C were synthesized. An approximately linear relationship of molecular weight to

monomer conversion was established. This indicates that both chain transfer and chain termination reactions are rare.

Nickel-based catalysts were introduced for the synthesis of polynorbornenes with a narrow molecular weight distribution and low molecular weights.^{69–71}

Goodall *et al.*^{72,73} recognized the potential of polymers based on norbornene derivatives, and devised a toolbox of Pd- and Ni-based catalysts for their homo- and copolymerization. They used these highly active catalysts based on cationic 'naked-type' or neutral nickel and palladium complexes as well as cationic palladium systems to design several product groups of norbornene derivates by addition polymerization.

The 'naked' nickel and palladium catalysts are of the type used for the polymerization of butadiene.⁶⁹ A catalyst precursor in the presence of the monomer forms a catalytically active center bearing only monomer and the growing polymer chain as ligands. Among the simple olefins, norbornene can be considered to be a strong π -donor; therefore, cationic π -allyl complexes of nickel and palladium stabilized by cyclooctadiene (COD) ligands and noncoordinating counterions such as PF₆⁻ are prototypes of this class of catalyst precursors (Figure 7).

Similar active species based on di(2-ethylhexanoate)nickel, BF₃·Et₂O, and AlEt₃ in a 1:9:10 ratio forms, in the presence of butadiene, a catalyst precursor that may be activated by HSbF₆ to yield a cationic active species for norbornene



Figure 7 'Naked'-type nickel and palladium catalysts for norbornene polymerization according to Deming and Novak.⁷¹

polymerization. In a very similar mode, bis(1,4-cyclooc-tadiene)nickel(0) (Ni $(COD)_2$)/butadiene/HSbF₆ and di(2-ethylhexanoate)nickel/butadiene/HSbF₆ or Ni $(acetylace-tonate)_2$ /MAO give highly active catalysts for norbornene polymerization.

The polynorbornenes obtained from the Ni-based catalysts are soluble in common organic solvents such as toluene or hexane containing almost equal amounts of *mm* and *mr* triads.^{74,75}

By introducing α -olefins into the polymerization system as chain transfer agents, the molecular weight of the polynorbornenes from the Ni cation-based catalysts can be controlled: the insertion of an α -olefin is immediately followed by β -hydrogen elimination, and a vinyl-terminated polynorbornene and a Ni hydride are formed (**Figure 8**). The Ni hydride species serves as a starting point for another chain growth reaction.

Compared to its nickel analog, the palladium catalysts are less active and result in insoluble or hardly soluble polymers that are proposed to be erythodiisotactic. Similar insoluble polynorbornenes were produced by Arndt and Gosmann⁵³ using Pd(acac)₂ in combination with MAO.

In contrast to what has been shown for metallocene catalysts, for most nickel and palladium catalysts there is no influence of the ligand structure on the polymer microstructure and properties, although there is an influence on kinetic profiles and conversion during polymer formation.

Also neutral Ni and Pd compounds such as Ni(dpm)₂ (dpm = 2,2,6,6-tetramethyl-3,5-heptanedionate) or Ni(2-ethylhexanoate)₂ may be activated by $B(C_6F_5)_3$ and other boranes bearing highly electrophilic aryl groups, in the absence of any aluminum alkyl, yielding active catalysts for norbornene polymerization. These multicomponent catalysts produce slightly erythrodiisotactic polymer structures and feature pentafluorophenyl end groups, while polymers from the analogous palladium systems could not be investigated due their insolubility. Molecular weight regulation by α -olefins is possible, but it is accompanied by catalyst deactivation due to the reductive elimination of pentafluorobenzene. Another method for molecular weight regulation is the addition of small amounts of water or alcohols to induce protolysis of the growing chain. Therefore, these catalysts can be regarded as initiators rather than as true catalysts, forming multiple polymer chains.

Palladium allyl compounds⁷⁶ bearing a phosphine ligand and a leaving group were found to be single component catalyst precursors, yielding palladium cations that are highly active for norbornene polymerization (Figure 9).

The molecular weight of the polymers obtained depends upon the phosphine used, and the addition of α -olefins can



Figure 8 Mechanism of the molecular weight regulation by the use of 1-olefins as chain transfer agents in the addition polymerization of norbornene by Ni-based catalysts.



Figure 9 Multicomponent catalysts for norbornene polymerization based on cationic palladium–phosphine complexes (X=Cl, NO₂, O₂CCF₃; R=Ph, *n*-Bu, *t*-Bu, C₆F₅).

be used to induce chain transfer; nevertheless, the system is less susceptible to the α -olefin chain transfer method than the aforementioned Ni catalysts. A major advantage of this catalyst system is its tolerance toward polar groups, enabling its use in the copolymerization of functional derivatives of norbornene and for polymerization in suspension or emulsion.

Iron, cobalt, and chromium bis(imino)pyridyl complexes^{77,78} have been reported to be active for the polymerization of norbornene, especially when activated with MAO.

A wide range of transition metal catalysts can be used in the ROMP of norbornene. Analogously to cyclopentene, ROMP of norbornene leads to polymers with different microstructures. Polynorbornene with cis and trans, meso or racemic microstructures can be prepared by ROMP (Figure 10). Detailed investigations of the microstructure of ROMP polynorbornenes were carried out by ¹³C-NMR studies of Ivin and Rooney. 41,79,80 The polymerization of norbornene with ReCl affords a high-cis, mainly syndiotactic polynorbornene.⁸¹ The polymer is atactic with a *cis*-double bond content of more than 90% when WCl6/Me4Su or MoCl₅/Me₄Sn catalysts are used in dioxane as solvent.⁸² The cis content decreases to 50% if the solvent is changed to chlorobenzene. High-trans atactic polynorbornene can be prepared with RuCl₃(H₂O)₃ in a mixture of ethanol and chlorobenzene.

Similar microstructures are obtained when norbornene is replaced by norbornadiene. 5-and 6-substituted norbornene derivatives when polymerized by ROMP give more complex microstructures (Figure 11).⁸³ By ROMP it is possible, more easily than by Ziegler–Natta catalysts, to polymerize norbornenes with polar substituents such as carbomethoxy, carboethoxy, or trifluoromethyl groups.⁸⁴

3.26.2.4 Properties and Applications

Polynorbornenes may be grouped into two classes: those that are soluble in toluene and those that precipitate during polymerization. WAXS and ¹³C-NMR investigations, as well as high-temperature high-resolution ¹³C-NMR investigations of the soluble polymers, confirm the different structures of the polymers and enable a further classification.

The polymers generated by Ni(acac)₂/MAO and other 'naked' nickel-type catalysts are soluble in toluene and differ significantly from those derived from metallocene catalysts that are insoluble. Chemical shifts for the bridge carbon (C7) in the soluble polynorbornene were found between 33.8 and 34.3 ppm.^{74,85} Based on the assignment made by Al-Samak *et al.*⁸¹ for norbornene hydrotrimers (Figure 12), the chemical shift of 33.8 ppm belongs to *mm* and that of 34.2 ppm to *mr* and *rm* triads and an atactic polymer. Metallocene-based polynorbornenes show more *mm* triads and are more or less isotactic. Polynorbornenes synthesized by neutral nickel catalysts show in the ¹³C-NMR spectrum a peak at 35.0 ppm from C7 that indicates no substantial content of *mm* triads.⁷²

Tactic polynorbornenes produced by metallocene catalysts are crystalline and show a melting temperature of about 600 °C *in vacuo*, but they decompose before melting. This makes them unsuitable for a technical use. If different substituted polynorbornenes are copolymerized, materials are obtained that are soluble in toluene and have a melting temperature below 400 °C, the decomposition temperature. Homo- and copolymers with different alkyl or functional groups are commercialized by Promerus.⁸⁶

Using Ni- and Pd-based catalysts, they produce a range of tailor-made homo-, co-, and terpolymers based on substituted norbornenes for applications in electronic materials. Three



Figure 11 Four possible regular microstructures of polymer made from 5,6-disubstituted norbornene by ROMP.



Figure 12 ¹³C-NMR chemical shifts of bridge and bridgehead carbon atoms in norbornene hydrotrimers according to Arndt and Gosmann.⁵³

basic products have been developed at BF Goodrich:⁷³ Avatrel[™], Appear[™], and DUVCOR[™].

AvatrelTM is a group of dielectric polymers based on copolymers of alkyl norbornenes (>90 wt.%) and 5-norbornene-2-triethoxysilane (2–10 wt.%), in which an alkyl substituent is used to tailor the polymer T_g values and toughness, and the triethylsiloxy group is used to impart good adhesion to metals.⁸⁷ Dielectric polymers⁸⁸ are developed for electronic packaging, for example in multichip modules, where their low dielectric constants (2.4–2.6) enable close packing of conducting lines and thereby a high interconnect density. Their hydrocarbon nature causes a low water uptake and, therefore, a stable dielectric character, which gives them an advantage over polyimides, which are also used for these applications.

Appear[™] polymers have a similar composition and consist of >90 wt.% of an alkyl norbornene and <10 wt.% of an oxygen-containing norbornene derivative, which is used to increase chain–chain interactions and, thereby, the overall polymer properties. Applications for these polymers are flat panel displays⁸⁹ and optical wave guides, both of which are accessible due to the high optical transmission and low birefringence of the polymers, combined with their excellent moisture resistance and ability to be used at high temperature.

DUVCORTM polymers are used in photolithographic applications, primarily in deep UV (197 and 153 nm) positive photoresists.⁹⁰ While the cycloalphatic backbone of polynorbornene ensures a good transparency and a high reactive ion etch resistance, norbornene comonomers bearing functional substituents such as esters or ethers are used to tailor the adhesive properties of the material. A high amount (10–40%) of norbornene comonomers bearing acid-sensitive groups, for example, *t*-butyl carboxylic ester, is used to enable subsequent acid-catalyzed deprotection to change the solubility of the copolymer. Typically, photosensitive acid generators such as triarylsulfonium hexafluorophosphate are produced to induce cleavage of the ester moiety.

Other substituted polynorbornene copolymers have been developed for encapsulation, cover coating, and microelectronic applications.^{91,92} Elf Atochem is running a small plant for polynorbornene (Norsorex[®]) produced by ROMP in France. Norsorex[®] is used in the automotive industry for vibration and noise dampening and for soft seals and gaskets.

3.26.3 Cycloolefin Copolymers

The polycycloolefins are difficult to process due to their very high melting points and their low solubility in common organic solvents. By copolymerization of these cyclic olefins, especially of cyclopentene and norbornene with ethene or propene, COCs can be produced, representing a new class of thermoplastic amorphous materials. Early attempts to produce such copolymers were made by using heterogeneous TiCl₄/ AlEt₂Cl or vanadium catalysts, but real progress was made using metallocenes and other single-site catalysts that are about 10 times more active than vanadium systems and other Ziegler–Natta catalysts.

3.26.3.1 Cyclopentene Copolymers

Cyclopentene can be copolymerized with ethene or propene by heterogeneous and homogeneous Ziegler–Natta catalysts.⁹³ Crystalline or elastomeric copolymers are obtained depending on the cyclopentene content and the part of ring-opening or vinyl-type polymerization mechanism.⁹⁴ Metallocene/MAO catalysts are very active in the copolymerization of cyclopentene with ethene. In contrast to the homopolymerization of cyclopentene, the cyclic olefin is incorporated into the copolymer chain by 1,2-enchainment.

The polymerization activity increases with increasing reaction temperature and reaches 19 kg of copolymer by 1 mol of catalyst in 1 s by a low zirconocene *rac*-[Et(Ind)₂]ZrCl₂ concentration of around 10^{-6} mol l⁻¹ (Table 4).⁹⁵

The activities and the molecular weights of the obtained copolymers are not much influenced by the molar ratio of cyclopentene/ethene in the starting mixture. By low cyclopentene concentrations, there is a weak decrease but at higher concentrations activities are similarly high as for the homopolymerization of ethene. The amount of incorporated cyclopentene increases with decreasing polymerization temperature and increasing ratio of cyclopentene/ethene. Copolymers with 1.7-18 mol.% of cyclopentene units are obtained. The cyclic olefin is incorporated into the copolymer statistically. From the determined rates of incorporation, dependent on the reaction conditions, the copolymerization parameter r_1 (how much faster ethene is incorporated than cyclopentene when the last incorporation was an ethene unit) could be calculated to be around 80. The molecular weight distribution (M_w/M_n) of the copolymers is 2–4.

¹³C-NMR spectroscopy showed that cyclopentene is incorporated in the copolymer chain through a 1,2-insertion, without ring-opening metathesis. This is in contrast to the homopolymerization of cyclopentene where 1,3-insertion was observed. The 1,2-enchainment by only double bond opening is a result of an easy coordination to the zirconium center when the last insertion was an ethene unit. The β -hydride elimination of a cyclopentene unit at the end of the growing chain, which is needed to form a 1,3-enchained cyclopentene unit, is relatively slow compared to a next ethene insertion. Therefore, it is

Temperature (°C)	Cp/E	Time (min)	Activity (q copol (mol Zr) ⁻¹ s ⁻¹)	Cp in copolymer (mol.%)	<i>Μ</i> η (a mol ⁻¹)
	,	()		1 /	(0)
-10	0	150	470	0	244 000
-10	3.85	150	360	3.6	229 000
-10	7.7	150	380	4.7	233 000
-10	10.85	150	285	5.7	232 000
-10	15.3	150	840	6.8	223 000
+10	0	120	3260	0	175 000
+10	3.85	150	2400	1.8	178 000
+10	7.7	120	2900	2.7	165 000
+10	15.3	150	3330	4.0	158 000
+30	0	45	20 700	0	97 000
+30	3.85	45	12 200	1.4	99 000
+30	7.7	45	12 900	3.2	115 000
+30	15.3	63	19200	18.0	117 000

Table 4	Copolymerization	of cyclopentene a	and ethene,	activities,	and incorp	oration, a	is a function	of the	mole rat	io
cyclopenten	e/ethene (Cp/E) in	the reaction mixtu	ure at differ	rent tempe	ratures with	catalyst	rac-[Et(Ind)	2]ZrCl2		

Polymerization conditions: $[Zr] = 6.4 \times 10^{-7}$ to 6.4×10^{-6} mol I^{-1} , MAO: 2.2×10^{-2} mol Al I^{-1} , $[C_2H_4] = 0.296$ mol I^{-1} , solvent: toluene.

difficult to synthesize copolymers with more than 50 mol.% of cyclic olefin units. Higher incorporation rates up to 64 mol.% of cyclopentene were obtained if highly substituted cyclopentadienyl/fluorenyl zirconium complexes such as *rac*-dimethyl-silandiyl(ferroceno[2,3]inden-1-y)(cyclopentadienyl) zirconiumdichloride were used.⁹⁶

The copolymers show small cyclopentene blocks with 1,3-enchained units and isolated 1,2-enchained units. The *cis/ trans* ratio was quantified to be 10% *trans* of the 1,3-units and 2.9% *trans* of the 1,2-units, the main part was *cis* units.

Naga and Imanishi⁹⁷ studied the effects of the ligand structure of zirconocene catalysts on the copolymerization of cyclopentene (Cp) and ethene. They found that nonbridged zirconium complexes together with MAO as cocatalyst were not able to incorporate cycloolefin units into the polymer chain. Only bridged catalysts were able to do this. The copolymers obtained with *rac*-[Et(Ind)₂]ZrCl₂ contained not only *cis*-1,2-units but also 20–30% *cis*-1,3-units of cyclopentene. For other bridged zirconocenes, this was only found if the content of cyclic olefin units was higher than 20%. Only Cp-Cp-diad sequences were detected, no Cp-Cp-Cp triad sequences were found.

DSC measurements for these copolymers showed multiple melting endotherms and a broad composition distribution. A narrow copolymer composition distribution was obtained with *rac*- $[Me_2Si(Ind)_2]ZrCl_2$. One explanation for the broad composition or molecular weight distribution could be the fact that the chiral forms (*R*, *S*) and the small amounts of *meso* form of the zirconocene complex produce different micro-structures and molecular weights of the cyclopentene/ethene copolymers.⁹⁸

Copolymers with a high amount of cyclopentene units are mostly characterized by alternating sequences. Fujita and Coates⁹⁹ succeeded in the synthesis of highly alternating cyclopentene–ethene copolymer using a bis(phenoximine)titanium dichloride complex activated by MAO. The alternating copolymers show glass transition temperatures between –27 °C (27 mol.% Cp) and 10.1 °C (47 mol.% Cp) and have an atactic microstructure. Similar alternating copolymers were obtained by Lavoie *et al.*¹⁰⁰ using a constrained geometry titanium catalyst (dimethylsilylene[tetramethylcyclopentadienyl][*N-t*-butyl]titanium dichloride and modified MAO. The cyclopentene units are inserted by *cis*-1,2-enchainment. Such a cyclopentene–ethene copolymer with nearly 50 mol.% of Cp units shows a melting point of 182.5 °C and glass transition temperature of 16.3 °C.

It is also possible to copolymerize cyclopentene with propene.³² The activities for the copolymerization are between 45 and 135 kg copo (mol Zr)⁻¹ h⁻¹ (**Table 5**). The copolymers were investigated by ¹³C-NMR spectroscopy.

 Table 5
 Activities of the cyclopentene/propene copolymerization by different cyclopentene concentration and temperature with rac-[Et(Ind)₂]ZrCl₂

Temperature (°C)	Cyclopentene (mol I ⁻¹)	Time (h)	Activity (kg polymer (mol Zr) ⁻¹ h ⁻¹)
0	1.41	15.7	48
0	2.82	15.7	46
0	4.23	5	61
0	5.64	5	57
30	1.41	5	45
30	2.82	5	86
30	5.64	3.3	135

Polymerization conditions: $[Zr] = 6.25 \times 10^{-6} \text{ mol I}^{-1}$, MAO: $2.1 \times 10^{3} \text{ mol I}^{-1}$, 0.5 bar propene pressure.

If the isotactic zirconocenes *rac*-[Et(Ind)₂]ZrCl₂ or *rac*-[Me₂Si(Ind)₂]ZrCl₂ activated by MAO are used, the resulting copolymers contain 2–5 mol.% of Cp units incorporated by 1,2-enchainment mode.

The molecular weights of the copolymers are low and lie between 35 000 (0 °C) and $17000 \,\mathrm{g \, mol^{-1}}$ (30 °C copolymerization temperature).

The catalyst *rac*- $[Me_2Si(Ind)_2]ZrCl_2/MAO$ was used for the copolymerization of cyclopentene and propene by Arnold *et al.*¹⁰¹They obtained copolymers with a Cp content of 30.5 mol.% with a glass transition temperature of 19 °C.

The copolymerization parameters were investigated, and $r_{\rm p}$ was found to be 40. The insertion mode of the cyclopentene/ propene copolymerization was studied by Naga and Imanishi.¹⁰² The isoselective zirconocenes such as rac-[Et(Ind)₂]ZrCl₂, rac-[Me₂Si(Ind)₂]ZrCl₂, and rac-[Me₂Si(2-Me-Ind)₂]ZrCl₂ produced isotactic propene-cyclopentene copolymers with a narrow molecular weight distribution, whereas the syndioselective zirconocene [Ph2C(Cp)(Flu)] ZrCl₂ produced syndiotactic copolymers. It was found that the cyclopentene was incorporated as well by cis-1,2-insertion and cis-1,3-insertion, up to 62 mol.% of cyclopentene using the rac-[Et(Ind)₂]ZrCl₂ complex. A preferred cis-1,2-insertion was found by using rac-[Me₂Si(Ind)₂]ZrCl₂. More 1,3-insertion was found if the cyclopentene content in the copolymer increased and the copolymerization parameter $r_{\rm p}$ is less ($r_{\rm p}$ = 45.5 for rac- $[Et(Ind)_2]$ ZrCl₂ and $r_p = 70.0$ for *rac*- $[Me_2Si(Ind)_2]$ ZrCl₂).²⁷

Instead of cyclopentene, cycloheptene and cyclooctene can also be used with ethene for copolymerization.⁹⁵ The yield of copolymers obtained is about 4 times smaller than that obtained with cyclopentene. Copolymers with up to 4.5 mol.% of cycloheptene and 1 mol.% of cyclooctene could be produced using *rac*-[Et(Ind)₂]ZrCl₂/MAO as catalyst. Cyclohexene could not be copolymerized using *ansa*-metallocenes. Recently copolymerization of ethene with cyclohexene with efficient cyclohexene incorporation was reported to be catalyzed using nonbridged half-titanocenes containing aryloxo ligand by Wang *et al.*¹⁰³

The copolymerization parameter was calculated as $r_{\rm E} = 380$ (10 °C) and $r_{\rm E} = 500$ (30 °C). Molecular weights (around 20 000 g mol⁻¹) are low at a polymerization temperature of 30 °C and mostly independent of the cycloheptene content.

Alternating copolymers of cycloheptene and cyclooctene using a constrained geometry catalyst (CGC) with a benzindenyl ligand were obtained by Lavoie and Waymouth.¹⁰⁴

3.26.3.2 Norbornene Copolymers

Norbornene can be copolymerized with olefins such as ethene and propene. Among these new COCs, made accessible from metallocenes, 95,105 the ethene (E)–norbornene (N) copolymers are the most versatile and interesting ones (Figure 13, R=H).



Figure 13 E–N copolymers (R=H) and P–N copolymers (R=Me).

3.26.3.2.1 Ethene–norbornene copolymers

The group 4 metallocene catalysts^{95,105} showed much higher activity than traditional heterogeneous TiCl₄/AlEt₂Cl or vanadium catalysts, and the fine-tuning of ligand substituents allows to control copolymer structures, from random to alternating, and properties.^{105–109} After their first synthesis by Kaminsky and coworkers,^{95,105} ethene–norbornene (E–N) copolymers have been developed to commercial products Topas^{®108} from Ticona, while Mitsui produces APEL¹⁰⁹ by using vanadium-based catalysts.

A variety of metallocene catalysts having C_1 , C_2 , C_{2v} , and C_s symmetry were studied for E–N copolymerization. Subsequently, homogeneous organometallic catalysts, including half-sandwich and cyclopentadienyl-free group 4 metal catalysts, late transition metal catalysts, and more recently cationic rare earth metal half-sandwich alkyls, have been reported to catalyze E–N copolymerization.^{2,109}

Two trends common to almost all E–N copolymerizations by *ansa*-metallocenes are the following: (1) increase in norbornene concentration in a polymerization feed results in a decrease in catalytic activity, likely due to the facility of coordination to the active sites, and in an increase of norbornene content in the copolymer up to a plateau, which depends on the catalyst structure; and (2) molecular mass of the copolymer often increases with the increase of the norbornene content.

The resultant copolymer properties depend on different parameters, such as comonomer content and distribution throughout the polymer chain, as well as the configuration of the asymmetric carbons of the comonomer units. In E–N copolymers configuration at atoms C2/C3 in a ring can be either S/R or R/S, so two subsequent norbornene units can be either erythrodiisotactic (*meso*) or erythrodisyndiotactic (*racemic*). The possible stereochemical environments of norbornene in alternating sequences, diads, and triads are illustrated in **Figure 14**. Erythrodiisotactic and erythrodisyndiotactic microstructures of ENENE and ENNE segments can be obtained depending on the catalyst structure.^{110,111} The microstructure of the copolymer can be controlled by the appropriate choice of reaction conditions and catalyst structure.

3.26.3.2.1(i) Random ethene–norbornene copolymers by group 4 ansa-metallocenes

Ansa-metallocenes with C_2 and C_s symmetries (Figure 15) generate random copolymers containing norbornene microblocks.^{112–118} Copolymers with norbornene content well above 50 mol.% and T_g values as high as 220 °C can be synthesized. Metallocene symmetry and ligand substituents dictate polymerization activity, tacticity, and sequential distribution. The type of bridge has an influence on polymerization activity and norbornene content. Examples, most of them reported by Kaminsky *et al.*, are listed in Table 6.

Among the C_2 -symmetric metallocenes, rac-[Et(Ind)₂]ZrCl₂ (I-1) is the most active.¹¹⁴ E–N copolymers prepared with C_2 -symmetric I-1 contain mainly *meso* ENNE diads and small amounts of *meso-meso* NNN triads. On the other hand, the C_8 -symmetric [Me₂C(Cp)(Flu)]ZrCl₂ (II-1) based catalyst shows a high selectivity for producing E–N copolymers with *racemic* ENNE diads. Series of E–N copolymers were synthesized in the presence of zirconocenes with different symmetries and ligand patterns: rac-[Me₂Si(Ind)₂]ZrCl₂ (I-2), rac-[Me₂Si([*e*]-benz)₂]ZrCl₂ (I-3), rac-[Me₂Si(2-Me-[*e*]-Ind)₂]ZrCl₂



Figure 14 Alternating (NENEN), diad (ENNE), and triad (ENNNE) sequences, showing the possible configurations.



Figure 15 Structures of the group 4 ansa-metallocenes for ethene–norbornene copolymerization.

(I-4), besides the already mentioned I-1 and II-1.^{115–117} The $C_{\rm s}$ -symmetric II-1, as already known, turned out to be the most productive catalyst. Among the $C_{\rm 2}$ -symmetric catalysts, Me₂Si [(2-Me-[*e*]-Ind)₂]ZrCl₂ (I-4) was shown to be noticeably more active than the others of the series. The microstructure was dominated by metallocene symmetry and ligand type. Precursor I-3 produced copolymers with the highest norbornene content and the highest amount of *meso* ENNE sequences.¹¹⁷

The *C*_s-symmetric [Me₂C(Cp)(Flu)]ZrCl₂ (II-1), [Me₂Si(Cp) (Flu)]ZrCl₂ (II-5), and [Ph₂C(Cp)(Flu)]ZrCl₂ (II-6), and the *C*_{2v}-symmetric [H₂C(2,5-Me₂Cp)₂]ZrCl₂^{117,120} (III-2) showed higher activity than the *C*₂-symmetric metallocenes. Among these catalysts, the most active is complex III-2, while [Me₂Si (Cp)(Flu)]ZrCl₂ (II-5) shows the highest molecular mass.³² The presence of a methyl substituent on α-carbons and the absence of substituents on the β-carbons in compound III-2 are crucial to the high activity of this system. The lack of steric

Catal	yst						
Symr	netry	Activity ^a	[N]/[E]	N mol.% in copol	Т _д (°С)	M _w × 10 ⁻⁴ (g mol ⁻¹)	References
Cs	-1 -5 -6	2210 ^b 11 084 ^c 2410 ^b	25.1 19.0 25.05	>56 47 >56	175 129 184	12.7 43.1 14.0	114b 114e 114b
C_2	I-1	9120 ^d 32 ^e	0.20 24.0	26 55	72 173	22 /	32, 114 116, 117
	I-2	2320 ^d 1370 ^b 290 ^b	0.20 3.21 6.37	28 35 42	40 82 124	/ 18.8 19.8	32, 114 114b 114b
	I-3 I-4	28 ^e 38 ^e 70 ^e	24.0 24.0 24.0	58 54 60	168 194 148	 	116, 117 116, 117 116, 117
C ₁	IV- 5	520 ^f 2590 ^f 2730 ^g 690 ^h	2.5 10 10 10	35 53 ND 48	88 173 168 143	10.3 8.40 5.12 8.74	119 119 119 119 119

Table 6	Random E–N	copolymerization:	activities and	properties
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^a(kg pol (mol Zr)⁻¹ h⁻¹).

Polymerization conditions:

 ${}^{b}MAO/Zr = 1000$, $[Zr] = 5 \times 10^{-7} \text{ mol } I^{-1}$; $P_{F} = 2 \text{ bar}$, $T = 30 \circ C$.

 c MA0/Zr = 8600, [Zr] = 5 × 10⁻⁶ mol I⁻¹, P_F = 2 bar, T = 30 °C.

 d MA0/Zr = 200, [Zr] = 5 × 10⁻⁶ mol l⁻¹; P_E = 2 bar, T = 30 °C.

 $^{e}MAO/Zr = 2000$, [Zr] = 1.6 × 10⁻⁵ mol l⁻¹, P_F = 1.013 bar, T = 30 °C.

^{*t*}Dried MAO/Ti = 400, $[Ti] = 4 \times 10^{-4} \text{ mol } I^{-1}$, $P_E = 1 \text{ atm}$, $T = 40 \circ C$.

^gDried MAO/Ti = 400, [Ti] = 4×10^{-4} mol I⁻¹, P_E = 1 atm, T = 40 °C.

 h Ph₃CB(C₆F₅)₄/Ti = 1, Oct₃AI/Ti = 20, [Ti] = 4 × 10⁻⁴ mol l⁻¹, P_E = 1 atm, T = 40 °C.

hindrance on the reaction site facilitates the approach of the bulky norbornene to the reaction site and results in an increase of the norbornene content in the polymer. On the other side, compound [MeCH(Cp)₂]ZrCl₂ (III-3)¹²⁰ without methyl substituents was reported to have low activity and high norbornene incorporation ability.

Lee reported that the ethene-bridged complex [Et(2,5- Me_2Cp)₂]ZrCl₂ (III-1) could copolymerize ethene and norbornene with a higher comonomer incorporation ability than [Ph₂C(Fluo)(Cp)]ZrCl₂ (II-6) and with activity and comonomer incorporation much better than those obtained with the ethene-bridged complex, *rac*-[Et(Ind)₂]ZrCl₂ (I-1).¹²⁰

Random copolymers having a norbornene content between 48 and 60 mol.% showed $T_{\rm g}$ values that can reach about 200 °C. A linear correlation between the amount of norbornene incorporated and the $T_{\rm g}$ measured was found for not too high norbornene content.¹¹⁸ Comparison of $T_{\rm g}$ values of copolymers with high norbornene content¹¹⁷ led to the conclusion that there is no linear correlation between norbornene content and $T_{\rm g}$ values when copolymers with high norbornene content and different microstructures are considered.

Living α-olefin polymerizations are still quite rare despite the modern efficient examples recently developed.¹²¹ In contrast reports of E-N copolymerization in a (quasi) living manner exist with metallocene catalysts. Cherdron *et al.*¹⁹ first announced the possibility of controlling the reaction conditions to achieve 'quasi-living' E-N copolymerization. Tritto *et al.* have found that catalysts such as *rac*-[Et(Ind)₂]ZrCl₂ (I-1), Me₂Si(Me₄Cp)(N-^tBu)TiCl₂ (IV-1), *rac*-Et(4,7-Me₂Ind)₂ZrCl₂ (I-3), and 90% *rac*/10% *meso*-H₂C(3-^tBu-Ind)₂ZrCl₂ (I-9)/ MAO under usual conditions promote E–N copolymerization with both yields and molar masses increasing linearly with the polymerization time. The molecular mass of E–N copolymers, at temperatures between 30 and 50 °C and high norbornene feed fractions, increases with time for up to 1 h. The polydispersity can be as narrow as 1.1 at [N]/[E] feed ratios as high as 28.¹²² This indicates that very little chain transfer occurs and that E–N copolymerizations are quasi-living under these conditions. Chain growth over 1 h is unusual for olefin polymerization, the average lifetime of a growing ethene and propene polymer chain is typically less than seconds. The quasi-living character of the reaction depends on the type of catalyst used.

Detailed studies on chain termination and transfer reactions in E–N copolymerization promoted by several metallocenes were carried out by Bhriain *et al.*¹²³ It was confirmed that chain transfer reactions to monomer or to aluminumalkyls in *E-co*-N copolymerization processes are unlikely to occur. Chain ends groups were observed only when Me₂C(Ind(Cp)ZrCl₂/ MAO and *rac*-Et(2*-t*BuMe₂SiO-Ind)₂ZrCl₂/MAO were adopted.

3.26.3.2.1(ii) Alternating ethene–norbornene copolymers by group 4 ansa-metallocenes

Arndt and Beulich¹¹² and Herfert *et al.*¹²⁴ exploited the dual coordination sites of C_1 -symmetric metallocenes to control the sequence specificity in E–N copolymerization. Highly alternating stereoregular (isotactic) E–N copolymers were synthesized with the C_1 -symmetric, bridged metallocenes R₂C[(Flu)(3-R'Cp)] ZrCl₂ [R=Me or Ph, R'=Me or 'Bu] (II 2–4 and 6),^{112,124} in the presence of an excess of norbornene. The copolymers obtained are crystalline if the norbornene content is higher than 37 mol.% and have melting points of 270–320 °C. Elucidation of the

microstructure of these copolymers showed that the enchainement of norbornene units is isotactic.

The behavior of C_1 -symmetric pentalene metallocene (II-8) and (II-9) in E–N copolymerization was described by Kaminsky.¹²⁵ These *ansa*-metallocenes show a high thermostability up to polymerization temperatures of 105 °C, which is an important characteristic for industrial use. Moreover, the open angle between the aromatic rings of these metallocenes opens up the possibility to easily incorporate the bulky norbornene at high temperatures. The C_1 pentalene metallocenes showed increasing activities up to 50 mol.% of norbornene in the feed. Only at high norbornene concentration, the activities are low. Copolymers were alternating as with the other C_1 -symmetric metallocenes. More interestingly thanks to the steric hindrance of the phenylsubstituted pentalene ligand the molar masses reached M_w values up to 660 000– 800 000 g mol⁻¹ with II-8.

The *rac*- $[Me_2Si(2-Me_{e}]-benzind)_2]ZrCl_2$ (I-5) gave a mainly alternating isotactic copolymer with trace amounts of ENNE sequences and a surprising significant amount of norbornene (up to ~10%) belonging to NNN triads.¹²⁶

Isotactic alternating copolymers with norbornene content above 37 mol.% are semicrystalline. They feature T_g values of 100–130 °C and T_m values of 270–320 °C. They are still transparent owing to the small size of their crystalline regions (5 nm). Atactic alternating copolymers are amorphous with T_g values up to about 130 °C.

3.26.3.2.1(iii) Ethene–norbornene copolymers by group 4 constrained geometry catalysts

CGCs also copolymerize ethene and norbornene with lower activity than *ansa-zirconocenes*, but can give perfectly alternating copolymers. Harrington and Crowther prepared copolymers by $Me_2Si(3^{-t}BuCp)(NAdam)])TiCl_2$ (Adam = adamantyl), which are semicrystalline with remarkably high melting points (250 °C) and show a very simple ¹³C-NMR spectrum.¹²⁷ The authors suggested that the crystallinity was originated from an alternating and stereospecific structure of the copolymer chain.

 C_1 -symmetric, bridged monocyclopentadienyl titanium amido complexes Me₂Si(Cp')(N^tBu])TiCl₂ (Cp' = 2,4-Me₂Cp, 3-^tBuCp, indenyl) (IV 2–4) have also been shown to yield mainly alternating E–N copolymers by McKnight and Waymouth.¹²⁸ The catalyst having Cp' equal to Me₄Cp was the most productive one.

Molecular mechanics calculations and correlations between conformation and ¹³C-NMR chemical shifts demonstrated that E-N copolymers by Me₂Si(Me₄Cp)(N^tBu)TiCl₂ are alternating and atactic.¹¹⁰ Moreover, it was also found that the synthesis of E-N copolymers by $Me_2Si(Me_4Cp)(N^tBu)TiCl_2^{129}$ and MAO as catalyst at 50 °C in the presence of high norbornene feed fractions can be quasi-living. The molecular weight distribution (M_w/M_p) of 1.3 $(M_p = 100\,000\,\mathrm{g\,mol^{-1}})$ was the lowest polydispersity index obtained at 50 °C. When using a catalyst like Me₂Si(Me₄Cp)(N^tBu)TiCl₂, which allows for incorporation of long-chain branches in polyethene, E-N copolymers containing long-chain branches were obtained; the degree of long-chain branches decreased with increasing norbornene content in the copolymer: chain transfer to the monomer and formation of the vinyl terminated polymer chain are possible only at Mt-E*.



Figure 16 Structures of the group 4 constrained geometry catalysts for ethene–norbornene copolymerizations.

Recently, PhSiH₃ has also been found to be an efficient chain transfer agent for E–N copolymerization by Me₂Si $(Me_4Cp)(N^tBu)TiCl_2$. Silyl-functionalized E–N copolymers with high norbornene content have been produced efficiently. Thus, the steric bulk, which limits chain transfers to monomers or to metals in E–N copolymerization, does not limit chain transfer to silanolytic species.¹³⁰

Random E–N copolymers with high molar masses and high norbornene content were produced by Hasan *et al.*¹¹⁹ using the half-sandwich titanocene precatalyst Me₂Si(Flu)(N^{*t*}Bu)TiMe₂ (**IV-5**) activated with MAO free from Me₃Al (**Figure 16**). The catalytic activity increased with the [N]/[E] feed ratio for its high ability for homopolymerization of norbornene, which is ascribed to the open nature of active species due to the η^3 coordination between Ti and Flu ligand. The complex produces E–N copolymers with high molecular weights (up to 63 000 g mol⁻¹), narrow molecular weight distributions (M_w/M_n = 1.32), and an incorporation of norbornene up to 58 mol.% (**Table 7**).

The E–N copolymerization behavior with (IV-5) strongly depended on the activator used as well as on the polymerization temperature. The molecular weight of the copolymer decreased with raising the polymerization temperature in the dried MAO and MMAO systems, whereas it increased in the borate/Oct₃Al system. The 1-borate/Oct₃Al system was found to show the highest activity among the activator systems used. The enhancement of activity and M_n values in the borate/Oct₃Al system could be explained by relatively weaker counterion of [(^tBuNSiMe₂Flu)TiMe]⁺[B(C₆F₅)₄]⁻, which enhances the propagation rate of the copolymerization.

The ¹³C-NMR spectra of these copolymers showed new signals of triblock norbornene sequences, which have been assigned to *rac,rac*-NNN triads. The T_g values of the E–N copolymers obtained with (IV-5) were controlled up to 237 °C.

3.26.3.2.1(iv) Ethene–norbornene copolymers by group 4 half-sandwich catalysts

Nomura¹³¹ showed that nonbridged half-titanocenes containing anionic donor ligand of the type Cp/TiX₂(Y) [Cp' = cyclopentadienyl group; X = halogen, alkyl; Y = anionic ancillary donor ligands such as aryloxo, ketimide] displayed unique characteristics such as efficient incorporation of bulky olefins. Random E–N copolymers with high norbornene contents could be obtained with (Ind)TiCl₂(O-2 $_{c}$ 6-iPr₂C₆H₃) (V-1)

Table 7	Alternating	E–N copo	lymerization:	activities	and	properties
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Catal	vst						
Symmetry		<i>Activity</i> ^a	[N]/ [E]	N mol.% incorporated	T _g [T _m] (℃)	M _w ×10 ⁻⁴ (g mol ⁻¹)	Reference
<i>C</i> ₁	IV- 2	4694 ^{<i>b</i>}	2.0	34	67	40.1	128
	IV- 3	520 ^b	11.0	35	71	25.3	128
	IV- 4	1399 ^b	2.5	34	83	39.6	128
	11-2 11-4	1600° 145°	18.0 19.0	44 39	118 [243] 103 [255]	43.1 0.89	112 112

^a(kg pol (mol Zr)⁻¹ h⁻¹).

Polymerization conditions:

^bDried MAO/Ti = 2000, [Ti] = 2×10^{-5} mol I⁻¹; P_E = 0.9–4.9 bar, T = 40 °C.

 $^{c}MAO/Zr = 8600$, $[Zr] = 5 \times 10^{-6} \text{ mol } I^{-1}$, $P_{F} = 2 \text{ bar}$, T = 30 °C.

that exhibited higher norbornene incorporation than the Cp*-aryloxo analog (V-3), the 1,2,4-Me₃C₅H₂-aryloxo analogue (V-4), and the CGC (IV-1) (Figure 17).

The Cp-kemitide analog, CpTiCl₂(N=C'Bu₂) (V-5), exhibits both remarkable catalytic activity and efficient norbornene incorporation. The activity increased upon increasing initial norbornene concentration. The activity by V-5 increased at higher temperature (40, 60 °C) accompanied by increasing norbornene content in the copolymer. Copolymers with high molecular weights, unimodal molecular weight distributions, and high norbornene contents (58.8–73.5 mol.%) were attained at low ethene pressure (2 atm).

3.26.3.2.1(v) Ethene–norbornene copolymers by cyclopentadienyl-free group 4 metal catalysts

Highly alternating E–N copolymers could be obtained with bis(pyrrolide-imine) Ti complexes (named PI catalysts) (Figure 18), developed by Fujita and coworkers.^{132,133} These catalysts are the result of the combination of electronically flexible nonsymmetric imino-chelate lignands and group 4 transition metals¹³² and displayed a marked tendency to produce E–N copolymers with a stereoirregular structure despite the C_2 -symmetric nature of the catalysts.

The sterically open and highly electrophilic nature of the catalysts is probably responsible for the good norbornene



Figure 17 Structures of the group 4 half-sandwich catalysts for ethene-norbornene copolymerizations.



Figure 18 Structures of the cyclopentadienyl-free group 4 metal catalysts for ethene–norbornene copolymerizations.

incorporation in the E–N copolymers with high molecular weight, although they were not active for the homopolymerization of norbornene.

The E–N copolymerization with PI catalysts is living.¹³³ Particularly, the cylcohexyl substituent (VI-1) produces E–N copolymers with a narrow molar mass distribution $(M_w/M_n = 1.07-1.16)$ and with M_n value that increases linearly with the polymerization time. An M_n value up to 521 000 g mol⁻¹ was reached, this represents one of the highest reported values for a monodisperse E–N copolymers. Likewise, PI catalysts with phenyl (VI-2), 4-^tBu-cyclohexyl (VI-3), and cyclooctyl (VI-4) substitution give highly controlled E–N copolymerization. Copolymers with $M_n = 61 000-600 000 \text{ g mol}^{-1}$, $M_w/M_n = 1.07-1.23$, and norbornene content = 44.0–48.6 mol.% were achieved.

The highly controlled living copolymerization mechanism for E–N copolymerization with a PI catalyst/MAO is the result of the stabilization of an ethene-last-inserted species toward chain transfers. The coordination of highly nucleophilic and sterically encumbered norbornene to the ethene-last-inserted active species probably stabilizes the active species toward chain transfer and catalyst decay. Such a coordination would reduce the electrophilicity of the active site and, in addition, provide steric hindrance around the active site, which probably reduces all the possible chain transfers (e.g., hydrogen transfer to a reacting monomer, chain transfer to alkyl Al species). Thus, the achievement of the controlled living copolymerization probably results from the stabilization of a Ti-E* species toward chain transfers and its smooth change to a Ti-N* species stable toward chain transfers.

The living nature of the PI catalyst allowed the preparation of ethene- and norbornene-based block copolymers, including PE-*b*-poly(ethene-*co*-N) and poly(ethene-*co*-N)_a-*b*-poly(ethene-*co*-N)_b, in which each segment contains a different norbornene content consisting of crystalline and amorphous segments or two different kinds of amorphous segments.¹³³

A high-molecular-weight E–N copolymer with narrow molecular weight distribution ($M_n = 480\,000\,\mathrm{g\,mol^{-1}}$, $M_w/M_n = 1.38$, $T_g = 144$ °C) could be also obtained by bis(phenoxy-imine) Ti complexes (Ti–FI catalysts), which are known as high-performance olefin polymerization.

Unlike the PI catalysts, Ti–FI catalysts require the presence of steric bulk in proximity to the anionic donor and normally possess lower electrophilicity and a sterically less open nature. Among FI catalysts,^{132,133} the VII-1/MMAO system displayed the highest catalytic activity ($2360 \text{ kg} (\text{molTi})^{-1} \text{h}^{-1}$ and the highest norbornene incorporation (55 mol.%), and linear relationships between copolymer M_w and yields. Narrow molecular weight distributions were observed with VII-1, VII-2 and VII-3/MMAO, which indicated the quasi-living nature of these systems. The resulting copolymers are atactic alternating copolymers with a small amount of NN diad sequences.

3.26.3.2.1(vi) Ethene–norbornene copolymers by rare earth catalysts

Recently Hou reported the first example of efficient COC synthesis by rare earth metal catalysts. Cationic rare earth (group 3 and lanthanide) metal alkyls is an emerging new class of catalysts for the polymerization and copolymerization of various olefins including cyclic olefins.^{134,135} The combination of half-sandwich scandium bis(alkyl) complexes such as



$Ln = Sc, R_1 = R_3 = R_4 = R_5 = Me, R_2 = SiMe_3$	(VIII-1)
$Ln = Sc, R_2 = R_4 = R_5 = H, R_1 = R_3 = SiMe_3$	(VIII-2)
$Ln = Sc, R_1 = R_2 = R_3 = R_4 = R_5 = Me$	(VIII-3)
$Ln = Sc, R_1 = R_3 = R_4 = R_5 = Me, R_2 = SiMe_2C_6F_5$	(VIII-4)
$Ln = Y, R_1 = R_3 = R_4 = R_5 = Me, R_2 = SiMe_2C_6F_5$	(VIII-5)
$Ln = Lu, R_1 = R_3 = R_4 = R_5 = Me, R_2 = SiMe_2C_6F_5$	(VIII-6)

Figure 19 Structures of the rare earth catalysts for ethene–norbornene copolymerizations.

 $[Sc(\eta^5-Cp)(CH_2SiMe_3)_2(THF)] \quad ((VIII-1: Cp = C_5Me_4SiMe_3; VIII-2: Cp = 1,3-C_5H_3(SiMe_3)_2; VIII-3: Cp = C_5Me_5) (Figure 19) \\ with 1 equiv. of a borate compound such as [Ph_3C][B(C_6F_5)_4] \\ showed excellent activity for E–N copolymerization. 136$

Under appropriate conditions (25 °C and 1 atm ethene), the $[Sc(\eta^5-C_5Me_4SiMe_3)(CH_2SiMe_3)_2(THF)]/Ph_3C][B(C_6F_5)_4]$ system afforded an amorphous alternating E-N copolymer with $M_{\rm n} = 85\,000\,{\rm g\,mol^{-1}}$, $M_{\rm w}/M_{\rm n} = 2.19$, $T_{\rm g} = 118\,{}^{\circ}{\rm C}$, and norbornene content = 44 mol.%, with an activity as high as $25200 \text{ kg} (\text{mol Sc})^{-1} \text{ h}^{-1}$. The Cp ligands in these complexes showed a significant influence on the catalytic activity, which follows the order $(C_5Me_4SiMe_3) > (C_5Me_5) > (C_5H_3)$ (SiMe₃)₂-1,3). The analogous Sc complex with an unsubstituted Cp ligand $(Cp = C_5H_5)$ showed no activity for the copolymerization under the same conditions. The complex with (C5Me4SiMe3) ligand when activated with $[Ph_3C][B(C_6F_5)_4]$, a relatively small amount of norbornene used under 1 atm of ethene, and the reaction terminated in an appropriate period of time, produced a polymer mixture containing P(E-co-N)-b-PE as toluene soluble fraction.

Subsequently, E-N copolymerizations by a series of structurally characterized scandium, yttrium, and lutetium compounds of the type $[Ln(\eta^5-C_5Me_4SiMe_2R)(CH_2SiMe_3)_2(THF)]$ (Ln=Sc, Y, Lu) with R=Me, C₆F₅ as precatalysts were reported by Ravasio et al.¹³⁷ Complexes VIII-1 and VIII-4 showed excellent activities, whereas complex VIII-5 gave poor activity and VIII-6 was practically inactive. Weak stabilization of metal center by bulkier silvl group of the tetramethylcyclopentadienyl ring in complexes VIII-4 and VIII-5 allows controlled copolymerization ($M_w/M_n < 1.3$). Mainly atactic alternating E–N copolymers were obtained with the active catalytic systems. These copolymerizations were well described by first-order Markov statistics. Activity strongly depended on the nature of the metal and decreased in the series Sc (VIII-1-4), Y (VIII-5), and Lu (VIII-6) with the $(\eta^5-C_5Me_4SiMe_2C_6F_5)$ ligand. The molecular masses obtained by (VIII-1-4)/[Ph₃C] $[B(C_6F_5)_4]$ did not depend on the nature of the Cp ligand. By contrast, the Cp ligand influenced both the polydispersity and norbornene incorporation, which follow the order VIII-4 $(\eta^5-C_5Me_4SiMe_2C_6F_5) < VIII-1 (\eta^5-C_5Me_4SiMe_3)$. By replacing the $(\eta^5 - C_5 Me_4 Si Me_3)$ ligand with $(\eta^5 - C_5 Me_4 Si Me_2 C_6 F_5)$, it was found that the living character of mono(cyclopentadienyl) rare earth metal complexes improved.

The scandium complex **VIII-1** was used for the first time to achieve copolymerization of ethene with 5-norbornene-2-methanol and terpolymerization of ethene with norbornene and 5-norbornene-2-methanol with these highly sensitive family of catalysts.¹³⁸ The requirements for the success were (1) the preactivation by $[Ph_3C][B(C_6F_5)_4]$ and (2) the use of isolated Al^iBu_3 -protected monomer. Copolymers with high molar masses (M_n up to 330 000 g mol⁻¹) and good incorporation of functionalized norbornene derivative were obtained. More interestingly, terpolymers with very high molar masses (M_n up to 450 000 g mol⁻¹), with a broad range of composition, and with T_g values up to about 100 °C were prepared with excellent yields.

3.26.3.2.1(vii) Microstructure of ethene–norbornene copolymers

¹³C-NMR spectroscopy is surely the most powerful analytical tool for polymer microstructural investigations. A description of these copolymers as well as a detailed understanding of the processes and mechanisms involved in these copolymerizations proved difficult to be achieved. The spectra of copolymers with relatively high levels of norbornene are complex and the regions of signals may overlap, since the various stereosequences of triads and longer norbornene sequences originate splittings and shifts of the signals, which made even the norbornene content uncertain (Figure 20). A number of groups accepted the challenge of assigning the ¹³C-NMR spectra of E–N copolymers with various methodologies, which include synthesis of



Figure 20 ¹³C-NMR spectra of ethene–norbornene copolymer.

model compounds, NMR pulse sequences, synthesis of series of copolymers with different norbornene content, synthesis of copolymers selectively ¹³C-enriched, chemical shift prediction, and *ab initio* chemical shift computations.

Arndt was able to isolate and assign the signals of all the possible norbornene hydrodimers and hydrotrimers obtained by means of hydrooligomerization with ansa-metallocenes having different symmetries. These assignments have been very precious; the differences between dimers and trimers were used to understand the shifts.⁵⁰ However, the results of molecular mechanics show that dimers and trimers are not good models of polynorbornene and of its higher oligomers, due to strong steric interactions between nonadjacent units, which induce large deformations of the torsional angles and of the ring geometry. Fink et al. synthesized, isolated, and characterized hydrooligomers from dimers to pentamers of norbornene by I-8/MAO.⁵⁴ They found a new type of linkage in the tetramers and pentamers, similar to the one found by Arndt et al.⁵⁰ in a hydropentamer synthesized with I-1/MAO and characterized by means of X-ray.

Bergström *et al.*¹³⁹ by using ${}^{13}C^{-1}H$ correlations, HMQC (heteronuclear multiple quantum coherence) for one-bond correlations, and HMBC (heteronuclear multiple bond coherence) for two- or three-bond correlations were able to identify C5/C6 and C2/C3 of norbornene diads.

The comparison of spectra of copolymers with different norbornene content, obtained by catalysts with different symmetries, has helped to assign a number of resonances. However, use of this method alone is rather limited in the case of E–N copolymer spectra. ¹³C-NMR investigations based on a comparison between E–N copolymers of monomers with natural abundance of ¹³C and those obtained with

 $^{13}C_1$ -enriched ethene or $^{13}C_{5/6}$ -enriched norbornene allowed Wendt and Fink 140 to determine the number of C5/C6 or ethene signals and to make significant advances in their assignments.

The determination of the stable conformers by means of molecular mechanics and considering such conformation-dependent effects as the well-known γ -gauche effect allowed Li and Hou¹¹⁰ to achieve independent and complementary support to the chemical shift assignments. The results obtained with an rotational isomeric state (RIS) model of the E–N copolymers suggested for the first time and proved the occurrence of the splitting of the signals of *meso* and *racemic* alternating NEN sequences.

Tritto *et al.*¹⁴¹ extended the assignment of unknown signals of ¹³C-NMR spectra of E–N copolymers and analysis of the spectra based on a procedure devised for computing the molar fractions of the stereosequences that define the microstructure of an E–N copolymer. The copolymer chain was partitioned into fragments, according to the assignment level available, the molar fractions of such fragments were used to describe the chain microstructure: the observed peak areas of the greatest possible number of ¹³C-NMR signals assignable (on the basis of a list of known chemical shifts, and of additional hypotheses) are used in a computer program¹⁴¹ to generate and solve a set of linear equations where the molar fractions are the variables.

The various types of chain fragments (isolated, alternating, and blocks) defined in the calculation, which also distinguishes between *meso* (*m*) and *racemic* (*r*) alternating units and between *meso* (*M*) and *racemic* (*R*) ENNE sequences, along with most significant final assignments are illustrated in Figure 21 and are reported in detail in references [2, 141-143].



Figure 21 Most significant assignments of isolated, meso (m), and racemic (r) alternating units; meso (M) and racemic (R) ENNE sequences; and ENNE triads.

3.26.3.2.1(viii) Reactivity ratios

Several authors have calculated the E–N reactivity ratios according to the Fineman–Ross method. Examples are collected in **Table 9** along with those obtained from microstructural analysis by ¹³C-NMR spectra. McKnight and Waymouth¹²⁸ found that four CGCs give r_1 values between 2.0 and 5.1. The values found are consistent with values for ethene/octene copolymerizations ($r_1 = 2.6-4$) with the same catalysts and indicate a preference for the insertion of ethene over norbornene into an Mt-E* active center. In no case was it possible to accurately determine r_2 from the plots. However, the data were consistent with a value of r_2 very close to zero. The product of the reactivity ratios for all the CGC E–N systems approaches zero, indicating a tendency toward alternation.

Kaminsky and coworkers¹¹⁴ and Ruchatz and Fink¹¹⁸ have investigated the reactivity ratios of various metallocene catalysts known to incorporate more than 50 mol.% norbornene. Bridged zirconocenes I-1 and II-1 give r_1 values near 2.0 similar to the CGCs IV-1, IV-2, and IV-4. Catalyst Cp₂ZrCl₂ (XI) gives an r_1 value of 4.0, reflecting the steric influence of the unbridged cyclopentadienyl rings. The r_1 values for all the three catalysts indicate a preference for insertion of ethene over norbornene into an active Mt-E* center. For I-2 and XI Waymouth *et al.*¹⁰⁰ calculated an r_2 value of 0.03, while for II-1 the r_2 value is very close to zero. This clearly illustrates that these catalysts also disfavor a second norbornene insertion because of the steric influence of the last-inserted norbornene unit. Like the CGCs, these zirconocenes should have a tendency to produce alternating microstructures at high [N]/[E] feed ratios. Kaminsky¹¹⁴ found that bridged rac-Me₂Si(Ind)₂ZrCl₂ (I-4) yields copolymers with an r_1 value of 2.66 and an r_2 value 0.36, which are a clear indication of the random nature of the copolymers obtained.

All the C_1 -symmetric catalysts II-2, II-3, and II-4 have r_1 values between 2.7 and 3.3, the only r_2 values in the table is 0.001 for II-2.

More detailed information on copolymerization mechanisms was obtained by Tritto *et al.*¹⁴² (Table 8). They used a computer optimization routine, which allows to best fit the microstructural analysis by ¹³C-NMR spectra, to derive the reactivity ratios for both first- and second-order Markov models (M1 and M2, respectively). The theoretical equations relating copolymer composition and feed composition were fitted to the corresponding experimental data. The reactivity values agree with the reports that E–N copolymers obtained with IV-1/MAO are mainly alternating ($r_1 \times r_2 \ll 1$), the norbornene diad fraction is very low, and there are no norbornene triads or longer blocks ($r_2 \approx 0$).

The ranges of the reactivity ratios obtained at the lowest [N]/ [E] feed ratio are $r_1 = 2.34-4.99$, $r_2 = 0.0-0.062$. The r_2 values are in general smaller than those obtained for propene copolymerization. The highest $r_1 \cdot r_2$ values found for the copolymers prepared with catalyst I-4 confirm its tendency to give more random copolymers. The values of r_1 , r_2 , and $r_1 \cdot r_2$ for the E–N copolymers obtained with catalysts IV-1 and I-5 are comparable with those of alternating ethene–propene copolymers with metallocene catalysts. The results of the second-order Markov model showed that also all r_{11} values, as r_1 , are similar to those found for ethene and propene copolymerization with metallocene catalysts with low reactivity ratios. Differences in r_{12} and in r_{22} are illuminating, since they clearly show the preference of the insertion of E or norbornene into E–N–Mt and N-N-Mt, respectively. Parameter r_{12} increases in the order IV-1 < I-5 << I-1 < I-2, opposite to the tendency to alternate the two comonomers.¹⁴²

The r_{22} values are in general lower than those obtained for propene or other α -olefins, in agreement with the low homopolymerization activity of norbornene. The r_{22} value for catalyst I-5 is much greater than r_{12} ; this shows the tendency of this catalyst to insert a third norbornene after the second one. It was clear that the next-to-last E or norbornene monomer unit exerts an influence on the reactivity of the propagating Mt-E* or Mt-N* species, which depends upon the catalyst structure. The second-order Markov model must be used to describe E-N copolymerizations promoted by metallocenes I-1, I-2, and IV-1. A third-order or a more complex model may be required to fit the experimental data obtained with catalyst I-6, where more sterically hindered indene substitutions are dominant. At higher norbornene concentrations, copolymers with all catalysts may need more complex models. These results allowed the conclusion that E-N copolymerization is dominated by the bulkiness of the norbornene monomer and of the copolymer chain.

The pentad description of the microstructure of the alternating copolymers prepared with catalysts II-2 and II-3 allowed to test different copolymerization mechanisms.¹⁴³ Catalysts II-2 and II-3 are two of the typical C₁-symmetric catalysts, such as $Me_2C[(3-R-Cp)(Flu)]ZrCl_2$ (R=Me, ^{*i*}Pr, ^{*t*}Bu), which produce isotactic 'alternating' E-N copolymers.^{112,124} The analysis of these copolymers has been used to elucidate polymerization mechanistic details such as the importance of 'chain migration mechanism' versus 'chain retention mechanism'.112 Pentad level information on these copolymers was used to test M1 and M2 statistics as well as the two-site alternating mechanism (TSAM). It was clear that (1) sequences with even ethene units ENEEN are present in the two copolymers, thus ruling out the TSAM for E-N copolymerization with these catalysts; (2) the M1 statistics accurately describes the copolymer sample derived from catalyst II-2; and (3) the M2 statistics is necessary to describe the copolymer microstructure of the copolymer sample produced by II-3.

3.26.3.2.1(ix) Ethene–norbornene copolymers by late metal catalysts

Late transition metals are more tolerant to polar functionalities in the monomer and the formed polymer. On the other hand, late transition metals are often ineffective for the copolymerization of ethene with norbornene because the former as well as other 1-alkenes act as a chain transfer agent through β -hydrogen elimination. Hence, a catalyst for the copolymerization of ethene with functionalized norbornenes must be both tolerant of functional groups and resistant to β -hydrogen elimination.

Kaminsky *et al.* succeeded in E–N copolymerizations by using α -diimine palladium catalysts.^{144,145} The synthesis of these catalysts is easy and fast compared to that of *ansa*metallocenes. Two α -diimine catalysts with interesting performance, [(2,6-Me₂C₆H₃)₂GLY]Pd (**IX-1**, GLY = 1,2-ethanediimine = glycine derivate) and [(2,6-*i*-Pr₂C₆H₃)₂BUD]Pd (**IX-2**, BUD = 2,3-butanediimine) (Figure 22), were synthesized according to the literature,¹⁴⁶ and their behavior in E–N copolymerization was investigated in detail (Table 9). The catalytic activities ranged from 8 to 243 kg polymer (mol Pd)⁻¹ h⁻¹. High norbornene incorporation was

			Reactivity ratios										
Catalyst Symmetry		[N]/[E]	N _{cop} mol.%	First-order Markov model		Second-order Markov model				Finemann–Ross			
				r ₁	r ₂	r ₁ ×r ₂	r ₁₁	r ₁₂	r ₂₁	r ₂₂	r ₁	r ₂	References
C ₂	I-1 ^{<i>a,b</i>}	2.33 3.98	36.23 40.38	2.602 2.338	0.0275 0.0309	0.072 0.072	3.048 3.241	0.0247 0.0298	2.386 2.191	0.0081 0.0176			142 142
	I-2 ^{<i>a,b</i>}	2.33 3.98	33.85 40.52	2.717 2.871	0.0525 0.0618	0.143 0.177	3.046 4.174	0.0489 0.0622	2.519 2.543	0.1393 0.0339			142 142
	I-5 ^{<i>a,b</i>}	2.33 9.74	29.72 41.18	3.338 4.477	0.0071 0.0043	0.024 0.019	3.486 6.805	0.0061 0.0035	3.207 4.211	0.6179 0.0809			142 142
$C_{\rm s}$	IV-1 ^{<i>a,b</i>}	2.33 3.98	27.20 31.79	3.906 4.988	0 0	0 0	3.232 3.376	0 0	5.184 6.521	0 0			142 142
	II-6 II-1										2.61 2.93 1.8	/ / ~0	114 114, 128
C ₁	II-2 ^{<i>a</i>,<i>c</i>}	2.13 3.62	28.71 35.23	3.17 2.94	0 0	0 0	3.46 3.89	0 0	2.76 2.52	0 0	1.3	0.03	143 143
	II-3 ^{<i>a,c</i>}	2.33 4.00	23.93 30.95	5.34 5.00	0 0	0 0	5.93 6.93	0 0	3.61 3.33	0 0			143 143
	11-4 1V-2 1V-3										3.3 1.9 5.1	0.001	114 128 128
	IV-4										2.2		128

Table 8 Reactivity ratios of E–N copolymerizations

 a [Zr] = 0.010 mmol I⁻¹; [Al]/[Zr] = 3000; P_E = 1.013 bar; *T* = 30 °C; solvent = toluene. b From tetrad level analysis of ¹³C-NMR spectra. c From pentad level analysis of ¹³C-NMR spectra.



Figure 22 Structures of the late transition metal catalysts for ethenenorbornene copolymerizations.

achieved and activities were about one order of magnitude lower than for typical metallocene/MAO catalyst systems.

Catalysts **IX-1** and **IX-2** show notably different polymerization behaviors. Catalyst **IX-1** incorporates norbornene much better than ethene (**Table 9**). At higher x_Ns with **IX-1**, incorporation is nearly independent of feed composition and reaches a plateau of about $x_N = 0.60$. Polymerizations carried out at $x_N > 0.60$ yielded partially insoluble polymers.

In contrast, **IX-2** shows almost ideal copolymerization behavior at low to moderate values of x_{N_r} that is, the norbornene content of the polymer reflects the feed composition. The norbornene incorporation levels are low compared to those seen with **IX-1**. No norbornene block structures could be observed in the ¹³C-NMR spectra. The coordination sites of **IX-1** and **IX-2** are blocked by its isopropyl ligand aryl substituents and the ligand is inflexible because of its 2,3-butanediimine bridge system. Such steric bulk disfavors the formation of norbornene block sequences. In contrast, the lower steric bulk of the methyl substituent of the aryl ligands in **IX-1**, and its more flexible 1,2-ethanediimine bridge make norbornene block sequences more likely.

There is a comonomer feed composition effect seen on the polymerization activity of IX-1. Activity reaches a maximum at $x_N = 0.1$ and is 7 times higher than that for the homopolymerization of ethene. At higher x_N s, activity decreases. Catalyst IX-2 does not show such an effect. The E–N copolymer molecular weights obtained with the Pd catalysts range between 7000 and 502 000 g mol⁻¹. The molecular weights increase with higher x_N s, and reach a maximum for IX-1 by $x_N = 0.34$ and for IX-2 by $x_N = 0.1$. The polydispersities (M_w/M_n 's) of the copolymers formed with the Pd catalysts are generally lower than 2. Polymers produced at high x_N s are bi- or multimodal.

The T_g values of E–N copolymers produced with **IX-1** are very high and range from 98 to 217 °C. Copolymers produced at $x_N = 0.80$ and higher, as well as homo-polynorbornene, show no T_g or T_m values under 350 °C, and decompose at >350 °C. The T_g values of copolymers produced by **IX-2** range from –28 to 120 °C, due to their lower norbornene content.

Grubbs introduced (salicylaldimino)nickel methyl complexes¹⁴⁷ that yield linear polyethene with high molar masses. These catalysts operate without requirement of a cocatalyst and allow the incorporation of bulky cycloolefins as norbornene as well as functionalities into polyethene. Copolymerization of ethene with norbornene in both nonaqueous¹⁴⁷ and aqueous solutions could be carried out by (salicylaldimino)nickel methyl complexes.¹⁴⁸

Table 9Ethene–norbornene copolymerization with Pd diimine catalysts [$(2,6-Me_2C_6H_3)_2GLY$]Pd(IX-1) and [$(2,6-i-Pr_2C_6H_3)_2BUD$]Pd (IX-2)¹⁴⁵

Reaction c	onditions	1				Result	Results		
Catalyst	X _N ^b	[N]/[E] (mol I ⁻¹)	Pd (μmol)	Ac	X _N ^d	Т _g е (°С)	M, [↑] (g mol ^{−1})	M _w /M _n ^g	
IX-1	0.00	/	16.76	36	0.00	-75	1500 ^{<i>h</i>}	1.4	
	0.05	0.05	4.19	161	0.44	98	13 000	1.4	
	0.10	0.11	4.19	243	0.48	126	36 000	1.5	
	0.20	0.25	4.19	120	0.54	146	40 000	1.7	
	0.40	0.66	16.76	57	0.60	177	54 000	1.8	
	0.50	0.10	16.76	50	0.62	189	36 000	1.7	
	0.59	1.41	16.76	34	0.62	216	18000	1.7	
	0.80	4.00	16.76	11	i	i	12 000	1.7	
IX-2	0.00	-	7.77	185	0.00	-67	73 000	1.1	
	0.10	0.11	7.77	75	0.09	-28	502 000	1.7	
	0.20	0.25	7.77	63	0.16	10	358 000	1.7	
	0.40	0.66	7.77	57	0.29	63	248 000	1.6	
	0.49	1.00	7.82	48	0.34	83	231 000	1.5	
	0.59	1.44	7.82	37	0.40	97	157 000	2.7	
	0.81	4.11	7.82	8	0.40	120	22 000	6.3	

^aConditions: 200 ml toluene, 30 °C.

^bNorbornene molar fraction in feed.

^cActivity in kg pol (mol Pd)⁻¹ h⁻¹.

^dNot evaluable by ¹³C-NMR spectroscopy due to insolubility.

^ePolymer decomposes

Polymer molecular weight distribution is bi- or multimodal

ⁱPolymer is not soluble.

^gdetermined by GPC

^hdetermined by GPC



Figure 23 Examples of square planar nickel complexes with anionic *P*,*O*-chelate ligands used for the co- and terpolymerization of N, N–CO₂Et, N–CH₂OC(0)Me, N–CO₂Me, and NB–nBu with ethene and 1-alkenes.

The substitution pattern of these catalysts influenced, to some extent, the norbornene content of the resulting copolymers. Complex X-1 (Figure 23) could effectively promote the E-N copolymerization in water to yield the E-N copolymers with the maximum norbornene incorporation of 6 mol.% $(M_{\rm n} = 14 \, {\rm kg \, mol^{-1}})$. The (salicylaldiminato)nickel phenyl complex X-2, in combination with $[Rh(CH_2=CH_2)_2(acac)]$ as a phosphine scavenger (Ni/Rh = 2/1), was also effective for the copolymerization of ethene with norbornene in toluene or in aqueous emulsion, which afforded relatively highmolecular-weight random copolymers with norbornene contents up to 19 or 14 mol.% ($M_n = 77$ or 88 kg mol^{-1} , respectively).¹⁴⁹ The E-(N-CH₂OH) copolymers (N-CH₂OH content <5 mol.%) and E-(N-OC(O)Me) copolymers (N-OC(O)Me <4 mol.%) were obtained by X-3 at 40 °C and 100 psig ethene. The copolymerization of ethene with the methyl ester (N-CO₂Me) afforded the corresponding copolymers with cyclic comonomer incorporations less than 2 mol.%.

The (phenylimino)(propanamido)nickel benzyl complex $[(2,6-iPr_2C_6H_2)N=C(CH_3)C(O)=N(2,6-iPr_2C_6H_2)]$ Ni (CH₂Ph)(PMe₃) (Figure 24) in combination with Ni(COD)₂, served as an efficient catalyst for the copolymerization of

ethene with functionalized norbornene derivatives such as 5-norbornene-2-ol (N–OH) and N–OC(O)Me.¹⁵⁰ The E–(N–OH) copolymer with the maximum N–OH incorporation of 18 mol.% (M_n = 31 kg mol⁻¹) was obtained at 20 °C and 100 psig ethene. The E–(N–OC(O)Me) copolymer with the N–OC(O)Me content of about 17 mol.% (M_n = 30 kg mol⁻¹) was produced under the same conditions. The polymerizations are quasi-living as demonstrated by the narrow molecular



Figure 24 Palladium allyl complexes used for the copolymerization of norbornene or the functional derivatives N–CO₂Et, N–CH₂OC(0)Me, N–CH₂OH, and N–COOMe with ethene.

weight distributions of the resulting copolymers $(M_w/M_n = 1.2-1.4)$ and the increase of polymer molecular weight with polymerization time (8–90 min). By using the quasi-living nature of the (phenylimino)(propanamido)nickel benzyl complex/Ni(COD)₂ system, block copolymers P(E-*co*-(N–OC(O)Me))A-*b*-P(E-*co*-(N–OC(O)Me))B containing different ratios of ethene and N–OC(O)Me (comonomer content in block sequences changed from 25 mol.% (block A) to 1–2 mol.% (block B)) were synthesized through increasing the ethene pressure from 50 to 1100 psig during the polymerization reaction.¹⁵¹

Square planar nickel complexes with anionic *P*,*O*-chelate ligands (**Figure 23**) were used by Benedikt *et al.*¹⁵² for the co- and terpolymerization of norbornene, 5-norbornene-2-carboxylic acid ethyl ester (N–CO₂Et), 5-norbornene-2-methyl acetate (N–CH₂OC(O)Me), 5-norbornene-2-carboxylic acid methyl ester (N–CO₂Me), and 5-*n*-butyl-2-norbornene (N–*n*Bu) with ethene and 1-alkenes, respectively. Essentially alternating copolymers with norbornene derivatives with oxygen functionalities are noted to give lower (<19 mol.%) incorporation and reaction rates, as well as polymer molecular weights. In the terpolymerization with 1-alkenes the additional chain transfer pathways following 1-alkene insertion also decrease the polymer molar mass. The T_g values increase with the norbornene content.¹⁵²

Sujith *et al.*¹⁵³ introduced the bimetallic salicylaldiminenickel complexes{ $[(2,6-iPr_2C_6H_2)-N=CH-(2-anthracenyl-C_6H_3-O)-\kappa^2-N,O]Ni(\eta^3-CH_2Ph)$ } (bridge = *ortho*-C_6H_4 (**XI-1**); CH₂ (**XI-2**); *ortho*-C₆H₄(C₆H₄)₂ (**XI-3**)) for the copolymerization of ethene with norbornene and polar substituted norbornenes. High activities and high incorporations of polar norbornene are also observed for ethene/2-(acetoxymethyl) norbornene and ethene/2-(methoxycarbonyl)norbornene.

Interestingly, while in general incorporation of 2-(acetoxymethyl)norbornene is much more difficult than that of 2-(methoxycarbonyl)norbornene, Sujith *et al.*¹⁵³ observed similar ability of incorporation of the two polar norbornenes, with the relative order: XI-3 > XI-2 > XI-1. The effect of dinuclearity is more dramatic in the ethene/2-(acetoxymethyl) norbornene copolymerizations, and complex XI-3 (Figure 23) shows almost 3 times higher incorporations of the 2-(acetoxymethyl)norbornene than the mononuclear complex under the same feed ratio. The molecular weights were not sensitive to the bridge structure ($M_w = 20\,000-30\,000\,\mathrm{g\,mol}^{-1}$). The narrow molecular weight distributions ($M_w/M_n = 2.1-2.9$) observed indicated a single active species.

The phosphine-sulfonate (P-O)-chelating palladium complex $(2-MeOC_6H_4)_2P(C_6H_4(SO_3H)-2)Pd(allyl)$ (Figure 24) together with the $B(C_6F_5)_3$ activator was effective for the copolymerization of ethene with norbornene, giving the E-N copolymers with norbornene content up to 31 mol.%.¹⁵⁴ The analogous palladium species generated in situ by reaction of (Pd(DBA)₂) (DBA, dibenzylideneacetone) with the ligand (2-(MeO)-6-RC₆H₃)₂P(C₆H₄(SO₃H)-2) (XII-1, XII-2) showed similar or higher activities for the copolymerization of ethene with norbornene or functionalized norbornene derivatives. The norbornene derivative contents (N-CH2OC(O)Me: 38 mol.%, N-CO₂Et: 44 mol.%, N-OC(O)Me: 23 mol.%, and N-CH₂OH: 34 mol.%) in the corresponding copolymers obtained by the sterically less demanding XI-1/Pd(DBA)2 system were higher than those obtained by XII-2/Pd(DBA)₂. The copolymerization of ethene with norbornene in emulsion by the XI-1/Pd₂(DBA)₃ system was also reported, which afforded the atactic alternating E–N copolymers with the norbornene contents up to 44 mol.% (M_n = 3.0 kg mol⁻¹).

3.26.3.2.2 Propene–norbornene copolymers

Propene–norbornene (P–N) copolymers were expected to feature higher T_g values than E–N copolymers with the same norbornene content and molar mass since polypropene has a higher T_g value than polyethene.^{115–117} Moreover, differences in stereo- and regioregularity of propene units as well as in the comonomer distribution and the stereoregularity of the bicyclic units were expected to allow fine-tuning of copolymer microstructure and properties. However, compared to E–N copolymers, reports regarding P–N copolymers are very limited.^{155–159}

Arnold was the first to report on amorphous P–N copolymers with a norbornene incorporation up to 98 mol.% with the system I-2/MAO.¹⁵⁵ In contrast to the low polymerization activity, a surprisingly high norbornene incorporation was reported.

Then, Tritto et al.^{156,157} tackled the synthesis and microstructural studies of P–N copolymers with C_2 - and Cs-symmetric metallocenes and MAO as cocatalyst. Two ansa-metallocenes of C₂ symmetry, rac-[Et(Ind)₂]ZrCl₂ (I-1) and rac-[Me2Si(Ind)2]ZrCl2 (I-2), proven effective for producing prevailingly isotactic and regioregular polypropene as well as E-N copolymers with a tendency to alternate, were selected.¹¹⁶ While, as a metallocene of C_s symmetry they selected catalyst II-1, which yields prevailingly syndiotactic polypropene and is very active in E-N copolymerization (Table 10). Copolymerization activities and copolymer properties obtained with I-1 and I-2 at 30 °C are compared. The polymerization activities of I-1 and I-2 were found to be quite low especially when compared to those obtained for E-N copolymerization under analogous experimental conditions. Under similar polymerization conditions, II-1 allows for a lower norbornene incorporation than catalysts I-1 and I-2. The M_w values as well as T_g values of P–N copolymers are quite low in comparison to those of E-N copolymers.

A first assignment of the main ¹³C-NMR signals of P–N copolymers with norbornene content up to 35 mol.% (Figure 25) was obtained on the basis of distortionless enhancement by polarization transfer (DEPT) ¹³C spectra, comparison with isotactic polypropene (*i*-PP) and E–N copolymer spectra, and *ab initio* theoretical ¹³C-NMR chemical shifts, computed for the most relevant conformer populations estimated for an isotactic chain (P₄-N)_x.^{156,157} Such assignments were used to estimate the norbornene copolymer content and showed the presence of 1,3-propene misinsertions, which are formed in significant amount when increasing the [N]/[P] ratio of the feed.

The low activity was demonstrated to result from the difficulty of inserting a propene into the Mt-tertiary carbon bond formed after the norbornene insertion (Mt-N), which is even more sterically crowded than the sites formed after a propene (2,1) regioirregular insertion, less reactive than sites with a primary growing polypropene chain. Despite the relatively lower polymerization activity, at low

Catalyst Symmetry			[N]/[P]	P (bar)	Т (°С)	N		M 10-3	Reference
		<i>Activity</i> ^a				м _{сор} (mol.%)	T_g	$(g mol^{-1})$	
C_2	I-1	56 ^b	0.26	1	30	35	119	7.68	156
-2		33 ^b	0.67	1	30	33	139	20.40	156
		9 ^{<i>b</i>}	1.00	1	30	41	129	19.50	156
		310 ^c	0.15	8	70	22	42	/	160
		291 <i>°</i>	0.23	8	70	32	64	5.88	160
		249 ^c	0.36	8	70	32	79	7.22	160
		195 ^d	0.17	8	50	34	77	10.38	160
		145 ^d	0.24	8	50	39	82	10.92	160
		63 ^d	0.26	8	50	40	82	12.24	160
		48 ^{<i>e</i>}	0.22	5	40	42	104	15.06	160
		22 ^{<i>e</i>}	0.42	5	40	47	113	13.74	160
		9 ^{<i>e</i>}	0.53	5	40	53	121	13.54	160
	I-2	38 ^b	0.25	1	30	29	87	7.72	156
		8 ^b	0.67	1	30	32	108	14.6	156
		4 ^{<i>b</i>}	1.00	1	30	ND	115	12.31	156
	I-2	100 ^f	0.67	1	60	40	101	5.66	141
		60 ^f	1.00	1	60	56	140	1.86	141
		40 ^f	2.33	1	60	73	174	1.53	141
	I-5	180 ^d	0.10	5	40	16	12	7.1	161
		60 ^e	0.13	5	40	15	10	7.4	161
		30 ^e	0.29	5	40	16	22	5.0	161
Cs	IV-	1575 ^g	0.60	1	20	36	112	94.95	159
	5	865 ^g	1.13	1	20	58	198	137.98	159
		895 ^{<i>g</i>}	2.00	1	20	71	249	155.90	159

 Table 10
 P–N copolymerization: activities and properties

 $a(kg pol (mol Zr)^{-1} h^{-1}).$

Polymerization conditions:

$$\label{eq:main_state} \begin{split} {}^{b}\!MAO/Zr &= 2000, \ [Zr] &= 2 \times 10^{-5} \ \text{mol} \ I^{-1}. \\ {}^{c}\!MAO/Zr &= 2000, \ [Zr] &= 4 \times 10^{-4} \ \text{mol} \ I^{-1}. \\ {}^{c}\!MAO/Zr &= 2000, \ [Zr] &= 4 \times 10^{-4} \ \text{mol} \ I^{-1}. \\ {}^{c}\!MAO/Zr &= 2000, \ [Zr] &= 4 \times 10^{-4} \ \text{mol} \ I^{-1}. \\ {}^{c}\!MAO/Zr &= 370, \ [Zr] &= 1.5 \times 10^{-5} \ \text{mol} \ I^{-1}. \\ {}^{c}\!MAO/Ti &= 400, \ [Ti] &= 6.67 \times 10^{-4} \ \text{mol} \ I^{-1}. \end{split}$$





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norbornene/olefin ratio it is possible to obtain P–N copolymers that are relatively richer in norbornene than the E–N copolymers prepared in similar conditions. However, at higher norbornene/olefin feed ratios the great amount of 1,3-propene misinsertions clearly revealed that the steric hindrance of the Mt-tertiary carbon bond when norbornene is the last-inserted unit makes difficult the next propene insertion causing low polymerization activities, molecular masses, and T_g values.

Kaminsky *et al.* studied P–N copolymerization with the C_2 -symmetric I-2, two C_s -symmetric [Me₂C(Cp)(Flu)]ZrCl₂/MAO (II-5) and [Ph₂C(Cp)(2,7-di^tBuFlu)]ZrCl₂ (II-7) systems, and the constrained geometry catalyst IV-1. Copolymers and oligomers with a wide range of T_g values were produced with satisfying activities, while the activities for IV-1 were much lower. These studies confirmed that high reactivity of the cyclic monomer makes accessible P–N copolymers with higher norbornene incorporation, but with lower molar masses than E–N copolymers.^{158,160–162}

Hasan et al.¹⁵⁹ succeeded in the synthesis of P-N copolymers with high norbornene content up to 71 mol.% with catalyst (^tBuNSiMe₂Flu)TiMe₂ activated by Me₃Al-free MAO (dried MAO). They had previously reported that this metallocene when activated with dried MAO yields living propene and norbornene homopolymerization.¹⁶³ P-N copolymerizations were carried at 20 °C under atmospheric pressure of propene. Dimethylmetallocene IV-2 was activated by dried MAO, modified MAO (MMAO), and Ph₃CB(C₆F₅)₄/Oct₃Al. The system activated by Ph₃CB(C₆F₅)₄/Oct₃Al was the most active one and yielded the copolymer with the lowest molecular weight and broadest molecular weight distribution. Dried MAO vielded the copolymer with the narrowest polydispersity. The norbornene content in the copolymer was almost proportional to the [N]/[P] feed ratio and T_g value of the P–N copolymers increased linearly against the norbornene content in the copolymers, from 53 to 249 °C.

The influence of propene pressure and temperature on activity, norbornene content, M_{wv} and T_g of P–N copolymers by I-1 was assessed.¹⁶⁰ A decrease of norbornene content, M_{wv} and T_g was observed at high *T* and *P*. The great number of 1,3-propene insertions found especially at high temperature and pressure, occurring after an inserted norbornene unit, confirmed that the limiting step in P–N copolymerization is the difficulty to insert a P after N. Moreover, chain transfer reactions are likely to occur more often at a P-last-inserted-Mt bond: indeed, chain transfer reactions at an Mt-N bond are rather difficult because the β-H transfer would violate Bredt's rule, that is, the coplanarity of Zr-C(α)-C(β)-H. The M_w values of the P–N copolymers are quite low in comparison to those of E–N copolymers. The highest molar masses obtained at room temperature were in the range of 40 000 g mol⁻¹.

The 2-alkyl indenyl substitutions of C_2 -symmetric zirconocenes are key in increasing considerably the molar masses of the produced polymers. Boggioni *et al.*¹⁶¹ investigated the synthesis of P–N copolymers with *rac*-Me₂Si(2-Me-Ind)₂ZrCl₂ (I-4) for obtaining P–N copolymers with high norbornene content and high molar masses. Methyl 2 substitution on the indenyl ligand in I-4 has an unexpected and strong influence on the catalyst behavior in P–N copolymerization, causing a strong decrease in catalytic activity, molar fractions f_N , T_g , and M_n values (Table 9). P–N copolymers with maximum 16 mol.% of norbornene were obtained by I-4 in contrast to those highly alternating obtained by I-1.

The microstructural analysis by ¹³C-NMR of the copolymers gives evidence of the tendency of I-1 to alternate P and norbornene comonomers and of I-4 not to alternate the comonomers as well as information on the probability of insertion of norbornene and of the possible forms of P insertion (P_{12} , P_{13} , and P_{21}), see below. An interesting observation regards the unexpected amount of triads containing propene misinsertions or regioerrors, which are greater in the series from I-4 than from I-1. Regarding 1,3-enchained units, it is worth noting the relevant amount of $NP_{13}P_{12}$ in the series from I-4 and of $NP_{13}N$ in the series from I-1, reflecting the different tendency to alternate the comonomers of the two catalysts and the important penultimate effects with I-4.

Chain end group analysis revealed a greater amount of 2-butenyl end groups, arising from termination at an Mt-P₂₁, than of vinylidene groups arising from termination at an Mt-P₁₂. The greater amount of 2-butenyl end groups in samples with lower molar fractions of triads containing the P₂₁ unit and in samples obtained with I-1 gives an evidence that the limiting step in P–N copolymerization is the difficulty to insert a propene after N, which causes 2,1-insertions with subsequent isomerization to 1,3-propene insertions as well as chain epimerization in starved propene conditions with I-4. The great decrease in the tacticity of the PP blocks in the copolymers prepared with I-4 with increasing the norbornene content in the feed revealed that the difficulty of this catalyst in accommodating a norbornene into Mt-P₁₂N makes probable unimolecular epimerization events.

3.26.3.2.2(i) Microstructure of propene-norbornene copolymers

¹³C-NMR experiments and *ab initio* theoretical chemical shift calculations, combined with RIS statistics of the P–N chain, gave the first assignment of the ¹³C-NMR spectra of P–N copolymers.¹⁵⁷ The ¹³C-NMR spectrum of a P–N copolymer prepared with I-1/MAO, at [N]/[P] feed ratio of 0.26, along with the final signal assignment is displayed in Figure 25. The structure and carbon numbering of an isotactic P–N copolymer are also sketched. *Cis-2,3-exo* norbornene insertion is considered to occur into the metal–carbon bond as in E–N copolymerization. All propene consecutive monomer units have the methyls in erythro relationships as in an isotactic polypropene chain.

Recently, Boggioni *et al.*¹⁶² proposed a general scheme for describing the microstructure of P-N copolymers at triad level from ¹³C-NMR spectra. This scheme includes (1) definition of the possible triads composing the copolymer chain, (2) use of NMR techniques for assigning new signals, and (3) a best-fitting procedure to determine the copolymer microstructure.¹⁶² This procedure, which allows for a quantitative analysis of copolymer sequences as accurate as possible, has been applied to the analysis of the ¹³C-NMR spectra of a number of P-N copolymers prepared with catalyst precursors rac-[Et(Ind)₂]ZrCl₂ (I-1) and rac-[Me₂Si(2-Me-Ind)₂]ZrCl₂ (I-4). A complete description of the microstructure at triad level, including 1,3- and 2,1-propene insertions, has been attempted. New signals have been assigned such as those of the carbons of propylene in the alternating triad $NP_{12}N$ and of norbornene in tetrad NP12N P12, as well as the signals of P_{β} methyls in triad $NP_{12}P_{12}$ adjacent to a variable number of P_{12} units all in isotactic relationship and those of the $S_{\alpha\gamma}$ methine of a 1,3-propene-inserted units in the $NP_{13}P_{12}$ and of the methyl carbon atom of central monomer in $P_{21}P_{12}N$ and $NP_{21}P_{12}$. Although determination of all the triads has not been achieved, an estimate of the molar fractions of the major sequences with a standard deviation in the order of 2–4% has been obtained.

Shiono and coworkers¹⁵⁹ investigated by ¹³C-NMR spectroscopy the structure of the P-N copolymer produced with catalyst dimethyl IV-5. They observed several signals for each carbon due to the different comonomer sequences and stereoisomers of the norbornene unit. The signals around 26-30.4 and 30.26-35.42 ppm were tentatively assigned to carbons C5/C6 and C7, respectively. In particular, a broad resonance with several peaks at 31.2-32.1 ppm, which disappeared in the spectrum of polynorbornene, could be assigned to the C7 carbon of the norbornene unit in alternating and/or norbornene diad sequences. The signals at 33.3-35.4 ppm, visible also in the spectrum of polynorbornene, were assigned to NNN triads. The signals at about 36.4-41.4 and 43-53 ppm were therefore tentatively assigned to C1/C4 and C2/C3 carbons, respectively. Signals between 48 and 53 ppm were assigned to C2/C3 carbons of NNN triads. Moreover, the signals between 12.0 and 17.0 ppm, which appear at high norbornene content, were assigned to a methyl of propene unit connected to norbornene. Thus, the microstructure of these copolymers with a high norbornene content is random (Figure 26).

3.26.3.2.2(ii) Reactivity ratios and mechanisms

The microstructural analysis by ¹³C-NMR of the copolymers at triad level allowed to determine the reactivity ratios r_i and r_{ij} obtained from diads and triads.^{160,161} The highly alternating nature of the copolymerization with I-1 is evidenced by the high value of $NP_{12}N$ triads and from the low r_1 (= k_{P12P12}/k_{P12N}) and r_3 (= k_{P13P12}/k_{P13N}) values, as well as from the low r_{21} (= $k_{NP12P12}/k_{NP12N}$) and r_{23} (= $k_{NP13P12}/k_{NP13N}$) values, all close to zero.

The difficulty of catalyst I-4 to insert a norbornene into an Mt-P₁₂N bond appears from the vanishingly low content of $NP_{12}N$ triads and from the r_1 values greater than for I-1, but lower than in E–N copolymerizations. Thus, also for this catalyst norbornene insertions compete with propene insertions, but less than for I-1. The higher r_{11} and r_{21} values for I-4 with respect to I-1 are a clear indication of the different tendency to give alternating or random copolymers of the two catalysts. The r_2 values for I-4, greater than for I-1, and higher than r_1 values testify the difficulty to insert P after N.

The $r_{2"}$ (= $k_{NN/}k_{NP21}$) values higher than $r_{2'}$ (= $k_{NN/}k_{NP13}$) confirm the tendency of 2,1-propene insertion to isomerize to 1,3 especially in P–N copolymerizations with I-1. Interestingly, the r_2 , $r_{2'}$, and $r_{2"}$ values quite similar in copolymers from I-4 show that the norbornene-last-inserted unit slows down P₁₂ insertions so that all the possible forms of P insertions (P₁₂, P₁₃, and P₂₁) have similar probability of insertion. The high r_{23} values indicate that I-4 does not allow a norbornene insertion even into an Mt-P₁₃N bond, demonstrating a penultimate effect.



Figure 26 Available assignments of sequences of P–N copolymers.

3.26.3.3 Other Cycloolefin Copolymers

Properties of COC based on bicyclic monomers can be varied by varying the norbornene content or the structure of the bicycloolefin, this includes norbornadiene, DCPD, dimethanooctahydronaphthalene (DMON), or trimethano-dodecahydroanthracene (TMDA) (Figure 27)¹⁶⁴⁻¹⁷³ or by terpolymerization.¹⁷⁴

Copolymerizations of ethene with bicyclic olefins, such as 2,5-norbornadiene, 5-vinyl-2-norbornene, have been investigated with metallocene catalysts. The secondary groups do not interfere with metallocene copolymerizations and post-polymerization functionalization makes it possible to synthesize functionalized polyolefins.^{165–167}

DCPD, an inexpensive industrially available cyclic olefin, is a very promising and attractive monomer because it contains both a norbornene unit and a cyclopentene unit. If only one of the two double bonds in DCPD is selectively copolymerized with ethene, the remaining double bonds would be available for further functionalization.¹⁶⁸ Nevertheless, the copolymerization of ethene with DCPD has not been extensively studied.¹⁶⁹ A major problem often encountered in DCPD copolymerization appeared to be cross-linking, depending on concentration of comonomer and polymerization time.¹⁶⁹

Li and Hou¹⁷⁰ achieved the alternating ethene–DCPD copolymerization in a controlled manner over a wide range of temperatures (0–70 °C) by using the [Sc(η^5 -C₅Me₄SiMe₃) (CH₂SiMe₃)₂(THF)]/Ph₃C][B(C₆F₅)₄]. The highest catalytic activity (3.1 × 10⁶ g copol (mol Sc)⁻¹ h⁻¹ atm⁻¹) was achieved at 50 °C with a DCPD incorporation of *c*. 44 mol.%. Only the norbornene double bond was selectively copolymerized. Copolymer products had T_g values in the range of 101–125 °C. Ethene–DCPD–styrene terpolymerizations have also been achieved with excellent selectivity and activity, which afforded a new series of novel polymers that are difficult to be prepared with other catalyst systems.

The glass transition temperature of COC can be modulated through tuning of the norbornene content in the polymer chains. A limitation of E–N copolymers endowed with high T_g values is their brittleness: at high norbornene content, polymer chains are so rigid that chain entanglements are low, causing brittleness. One approach to have more ductile COC is the substitution of norbornene with a bulkier cycloolefin monomer. This would allow to obtain the same T_g values at a lower amount of cycloolefin incorporated and thus a higher amount of flexible ethene units in the polymer chain.

Kaminsky introduced higher condensed cyclic olefin comonomers, such as DMON or TMDA in the synthesis of COC.^{106,164} Metallocene catalysts showed significantly low activities in DMON/ethene copolymerization ((0.0004–0.94) × 10⁶ g (mol Zr)⁻¹ h⁻¹). Incorporation of the cycloolefin becomes more and more difficult with increasing monomer bulk. While reactivity ratio for norbornene is similar to that of propylene, reactivity ratios for DMON and TMDA are comparable to those of 1-butene and 1-hexene.

Copolymerization of ethene and 5,6-dihydrodicyclopentadiene (HDCPD), which is easily prepared through regioselective hydrogenation of DCPD, was realized [8-(η^5 -C₅Me₄)-2-Me(C₉H₈N)-κN]TiMe₂ (C₉H₁₀NH = 1,2,3,4-tetrahydroquinoline) (**IV**-6) activated with (Ph₃C)⁺[B(C₆F₅)₄]⁻ by Lee and coworkers.^{171,172} The copolymer was unambiguously characterized through analysis of 1D and 2D NMR spectra. The monomer reactivity ratios, r_E and r_{HDCPC} determined through the Fineman–Ross plot, are 2.3 and 0.008, indicating that a nearly alternating E–HDCPD copolymer is obtained at a high [HDCPD]/[E] feed ratio. The T_g value of E–HDCPD copolymer is lower than that of DCPD/ethene and E–N copolymers with the same content of cycloolefin.

Very recently, Lee and coworkers^{172,173} introduced the copolymerization of ethene with a regioselective partially hydrogenated tricyclopentadiene (HTCPD) by using the same catalytic system **IV-6**. The monomer reactivity ratios, $r_{\rm E}$ and $r_{\rm HTCPD}$, were 2.8 and 0.025, respectively. A nearly alternating copolymer with an HTCPD content of 45 mol.% was obtained with a satisfactory activity ($4.7 \times 10^6 \text{ g} \text{ (mol Ti)}^{-1} \text{ h}^{-1}$), with a $T_{\rm g}$ value of 177 °C, significantly higher than that of norbornene/ethene copolymer at the same cycloolefin content. Tensile stress–strain curves showed more ductile properties than a high- $T_{\rm g}$ E–N copolymer with similar $T_{\rm g}$.

3.26.3.4 Properties and Applications

E–N copolymers are usually amorphous and display a wide range of glass transition temperatures, from room temperature to about 220 °C. They are characterized by high chemical resistance, as well as by good processability.¹⁰⁷ They show excellent transparency and high refractive index, owing to their high carbon/hydrogen ratio, for example, the refractive index is 1.53 for a 50:50 E–N copolymer. These properties make them suitable for optical applications such as coatings for high-capacity CDs and DVDs, for lenses, medical equipments, blisters, toner binder, and packaging. During the past two decades progress in metallocene catalysts for cycloolefin copolymerization made possible the commercialization of E–N copolymers. A commercial plant for the production of COC material (E–N copolymer) was built in 2000 by Ticona in Oberhausen, Germany, with a capacity of $30\,000\,t\,a^{-1}$ (tons





per annum). Mitsui produces E–N copolymers using vanadium-based catalysts. The industrially produced copolymers have norbornene contents between 30 and 60 mol.% and $T_{\rm g}$ values of 120–180 °C. The copolymer densities are low and near 1. For many applications, these COC materials show better mechanical properties than comparable amorphous thermoplastics, and are processible by all conventional methods.

3.26.4 Conclusions

Norbornene polymerization is the most versatile among the cycloolefin addition polymerizations. The structure of the norbornene homo- and copolymers can be widely influenced by the symmetry and structure of the ligands on the transition metal complexes.

Ni- and Pd-based catalysts are most suitable and highly active for norbornene homopolymerizations or copolymerization with other cycloolefins. A range of tailor-made homo-, co-, and terpolymers based on substituted norbornenes for applications in electronic materials are produced and commercialized.

Single-site catalysts, such as metallocene compounds, CGCs, and nickel or palladium diimine complexes, used in combination with MAO or borate cocatalysts, are active for the copolymerization of norbornene with ethene.

E–N copolymers made by single-site catalysts are characterized by narrow molecular weight distributions, which make technical processing easier. The first commercial E–N copolymer products by early transition metal catalysts are already available. In contrast, late transition metal catalysts, which are more tolerant to polar functional groups, need further developments to be efficiently used in olefin–cycloolefin copolymerizations.

In comparison to the successful E–N copolymerization, copolymerizations of norbornene with higher α -olefins or styrenes and conjugated dienes, or of polycycloolefins still give low activity, low comonomer incorporation and molar masses. Thus, in the future, synthesis of new organometallic complexes, with various metal centers and with ancillary ligands with appropriate structure, will play an important role for their controlled copolymerization that would lead to COC with desired physical, mechanical, and optical properties.

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Biographical Sketches



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3.27 Alkyne Polymerization

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3.27.1	Introduction	875
3.27.2	Polymerization Catalysts	876
3.27.2.1	Mo and W Catalysts	877
3.27.2.1.1	Metal halide-based catalysts	877
3.27.2.1.2	Metal carbonyl-based catalysts	878
3.27.2.1.3	Metal carbene catalysts	878
3.27.2.2	Nb and Ta Catalysts	878
3.27.2.3	Rh Catalysts	882
3.27.2.4	Group 10 Metal Catalysts	884
3.27.2.5	Group 8 Metal Catalysts	885
3.27.2.6	Living Polymerization	885
3.27.2.6.1	Living polymerization by metal halide-based metathesis catalysts	885
3.27.2.6.2	Living polymerization by single-component metal carbene catalysts	887
3.27.2.6.3	Stereospecific living polymerization by Rh catalysts	888
3.27.3	Monosubstituted Acetylene Polymers	889
3.27.3.1	Aliphatic Monosubstituted Acetylene Polymers	889
3.27.3.2	Aromatic Monosubstituted Acetylene Polymers	933
3.27.3.3	Helical Polymers of Monosubstituted Acetylenes	933
3.27.3.4	Photoelectronically Functional Polyacetylenes	934
3.27.4	Disubstituted Acetylene Polymers	935
3.27.4.1	Polymerization of Disubstituted Acetylenes	935
3.27.4.1.1	Aliphatic acetylenes and monoarylacetylenes	935
3.27.4.1.2	Heteroatom-containing acetylenes	935
3.27.4.1.3	Diphenylacetylenes and analogues	935
3.27.4.2	Reactions of Disubstituted Acetylene Polymers	935
3.27.4.3	Functions of Disubstituted Acetylene Polymers	941
3.27.4.3.1	Gas-permeable polyacetylenes	941
3.27.4.3.2	Photoelectronically functional polyacetylenes	944
References		948

3.27.1 Introduction

Acetylene and its derivatives are polymerized using suitable transition metal catalysts to give high-molecular-weight (MW) polymers (Scheme 1). The monomers include acetylene, mono- and disubstituted acetylenes, and α, ω -diynes. The polymers possess alternating carbon–carbon double bonds along the main chain and exhibit unique properties, such as metallic conductivity, that are not expected with vinyl polymers.

In 1958, Natta *et al.*¹ polymerized acetylene for the first time using a Ti-based catalyst. This polymerization followed the insertion mechanism as in the case of polymerization of olefins. Because of the lack of processability and stability of polyacetylenes, early studies on polyacetylenes were motivated by only theoretical and spectroscopic interests. In 1977, Shirakawa *et al.*² discovered metallic conductivity of doped polyacetylene. This discovery greatly stimulated polyacetylene chemistry, and now polyacetylene is recognized as one of the most important conjugated polymers. Many publications are now available on the chemistry and physics of polyacetylene itself.³⁻¹⁶

Incorporation of various side groups into polyacetylene has been attempted to improve its stability and processability, and

to endow it with unique properties and functions. Early attempts led to the conclusion that only sterically unhindered monosubstituted acetylenes are polymerizable with the Ziegler-type catalysts. Conventional ionic and radical initiators lack the ability to provide high-MW polymers from substituted acetylenes. The first successful polymerization of a substituted acetylene was achieved in 1974.¹⁷ Group 6 transition metals were quite active for the polymerization of phenylacetylene (PA) to provide polymers with MWs over 10^4 . After this finding, there has been much effort to develop highly active catalysts, to tune the polymer properties, and also to precisely control the polymer structures. These energetic studies have produced a wide variety of polymers from acetylene derivatives including mono- and disubstituted acetylenes and $\alpha_{i}\omega$ -divnes. The alternating carbon-carbon double bonds in the main chain of these polymers endow the polymers with unique properties such as conductivity, nonlinear optical properties, magnetic properties, gas permeability, and photo- and electroluminescent properties, which are not accessible from the corresponding vinyl polymers.

Table 1 lists typical transition metal catalysts used for acet-ylene polymerization. It is clear that metals of various groups inthe periodic table are useful. The kind of monomers



Scheme 1 Polymerization of acetylene and its derivatives.

 Table 1
 Catalysts for the polymerization of acetylenes and the reaction mechanism

Group	4	5	6	8–10
Catalyst (monomer ^a)	Ti(O- <i>n</i> -Bu)₄−Et₃AI (HC≡CH)	NbCl ₅ , TaCl ₅ (RC=CR')	MoCl ₅ <i>n</i> -Bu ₄ Sn, WCl ₆ Ph ₄ Sn (HC=CB, BC=CB')	Fe(acac) ₃ –Et ₃ Al (HC=CB)
		TaCl ₅ – <i>n</i> -Bu₄Sn (PhC≡CC ₆ H₄- <i>p</i> -X)	$\begin{array}{l} M(CO)_6 - CCI_4 - hv (M = Mo, W) \\ (HC = CR, CIC = CR) \\ (RO)_2 Mo(=NAr) = CH - t - Bu \\ (HC = CCH_2) - C(CO_2 - Ft)_2) \end{array}$	$[(nbd)RhCl]_2$ $(HC=CPh, HC=CCO_2R)$ $(nbd)Rh^+BPh_4^-$ $(HC=CCH_0NHCOR)$
Mechanism	Insertion	Metathesis	Metathesis	Insertion

 a HC=CR and RC=CR' denote mono- and disubstituted acetylenes, respectively.

acac, acetylacetone; nbd, 2,5-norbornadiene.

polymerizable with a particular catalyst is rather restricted, and hence it is important to recognize the characteristic of each catalyst. Depending on the polymerization catalysts, there are two types of reaction mechanism (Scheme 2). One is the metathesis mechanism where the active species are metal carbenes, namely, species having a metal–carbon double bond, and the other is the insertion mechanism in which the active species are alkyl metals, namely, species having a metal–carbon single bond. These mechanisms can be distinguished from each other by the catalysts used but are rather difficult to distinguish from the polymer structure.

This chapter surveys the polymerization of substituted acetylenes focusing on the research during this decade. Monomers and polymers, polymerization catalysts, controlled polymerizations, and functional polyacetylenes are discussed. Readers are encouraged to access other reviews and monographs on the polymerization of substituted acetylenes^{6,18–44} and α, ω -diynes.^{45,46}

3.27.2 Polymerization Catalysts

After the first discovery of the highly active group 6 transition metal catalysts for the polymerization of substituted acetylenes,⁷ various kinds of catalyst systems based on group 4–10 transition metal complexes have been reported. Although there

Metal carbene (metathesis) mechanism



Metal alkyl (insertion) mechanism

Scheme 2 Propagation mechanisms and propagating species (M: metal).
have been a limited number of papers describing alternative polymerization methods such as radical, ionic, and γ -radiation-induced polymerizations,^{47–50} transition metal catalysts still have considerable advantages due to their high activity and processability. Typical transition metal catalysts are discussed in detail below, and the others including preliminary results are listed in **Table 3**.

3.27.2.1 Mo and W Catalysts

Group 6 transition metal catalysts based on Mo and W have been widely used for the polymerization of substituted acetylene monomers (**Table 2**).^{6,18,20–22,24,26} Based on the first successful example using metal halide catalysts with alkylating agents, a variety of group 6 transition metal catalyst systems have been developed. The following three types are summarized here: (1) metal halide-based catalysts, (2) metal carbonyl-based catalysts, and (3) metal carbene catalysts.

3.27.2.1.1 Metal halide-based catalysts

Metal halides, MoCl₅ and WCl₆, are one of the most convenient catalysts among group 6 transition metal catalysts, which can give high-MW polymers from various monosubstituted acetylenes, in particular monomers bearing bulky substituents. Less bulky monomers such as 1-alkyne and PA are successfully polymerized by MoCl₅ and WCl₆, but the polymer yields are relatively low with unsatisfactory MW ($M_{\rm p} < 1 \times 10^5$) due to unavoidable cyclotrimerization. The monomers sterically crowded on their carbon-carbon triple bond like tertbutylacetylene and ortho-substituted PAs selectively polymerize with MoCl₅ and WCl₆ to give high-MW polymers. The addition of appropriate organometallic cocatalysts such as n-Bu₄Sn, Ph₄Sn, Et₃SiH, Ph₃Sb, and Ph₃Bi into the catalytic systems enhances catalytic activity and allows fast polymerization even in the case of sterically less bulky monomers such as 2-octyne, 1-chloro-1-octyne, and disubstituted acetylenes.

WCl₄ catalyzes the polymerization of *tert*-butylacetylene and PA to give high-MW polymers with M_w over $1 \times 10^{5.51}$ In the presence of oxygen-containing compounds such as methyl acetate, acetylacetone, acetophenone, and 1,4-dioxane, the catalyst activity increases significantly, and thus allows a moderate condition to give the polymer in higher yield.

WOCl₄ is combined with Ph₄Sn (WOCl₄/Ph₄Sn ratio = 1:2) in 1,4-dioxane/benzene to afford poly(PA) efficiently, whose $M_{\rm w}$ reaches 1.1×10^6 (intrinsic viscosity [η] 1.23 dl g⁻¹) and whose *cis* content is 73%.⁵² High polymer yields can be achieved even in the case of a high monomer/catalyst ratio of 1260. The viscosity index, *a*, of poly(PA) formed by this catalyst was determined to be 0.61, indicating a sufficiently flexible chain.

Bulky aryloxo groups replace the chlorine ligand(s) of WCl₆ to improve the application range of acetylenic monomers. The catalyst systems such as WCl_n(dmp)_{6-n}/alkylating reagents (dmp = 2,6-dimethylphenoxo, n = 1-4) show high activity in the polymerization of *tert*-butylacetylene leading to very high MW ($M_n > 2 \times 10^6$) and narrow molecular weight distribution (MWD) ($M_w/M_n \cong 1.2$).⁵³ On increasing the number of aryloxo ligands on hexavalent W species, even less bulky 1-alkynes such as 1-butyne gave high-MW polymer with $M_n = 9.4 \times 10^4$ and $M_w/M_n = 3.5$. WCl₅(OAr) and WOCl₃(OAr), where Ar is a phenyl ligand with *o-tert*-butyl or *o*-chloro substituents, have proved to be single-component catalysts for the polymerization of PA at room temperature; the M_n reaches about 1×10^5 .⁵⁴

Metallocene and half-metallocene complexes also work as catalysts for the polymerization of substituted acetylenes; for example, a metallocene catalyst, Cp₂MoCl₂ (Cp = cyclopentadienyl), in conjunction with EtAlCl₂ (1:3 mole ratio), polymerizes PA into a polymer with $M_n = \sim 4 \times 10^{3.55}$ A half-metallocene-based ternary catalyst system, CpMoCl₄–EtMgBr–EtOH (1:2:2), polymerizes *o*-CF₃-PA in a living fashion to give a polymer whose M_w/M_n is 1.06; a

Table 2 Examples of group 5 and 6 metal halide catalysts and organometallic cocatalysts Metal chloride WCl₄ WOCl₄ MoCl₅ MoOCl₄ WCl₆ CpMoCl₄ WOCl₃(OAr) Cp₂MoCl₂ Me MoCl₃(thf) Me (n = 1 - 4)(thf = tetrahydrofuran) NbCl₅ TaCl₅ Me Me n(thf) Me Me (n = 1, 2)(n = 1, 2)Organometallic cocatalvsts n-Bu₄Sn, n-Bu₃SnCl, Ph₄Sn Ph₃Sb, Ph₃Bi Et₃SiH, Ph₃SiH Et₃Al, Et₂AlCl, EtAlCl₂ n-BuLi, Et₂Zn, EtMgBr

feature of CpMoCl₄ compared to MoOCl₄ is high stability against air and moisture. 56

3.27.2.1.2 Metal carbonyl-based catalysts

Mo and W hexacarbonyls, Mo(CO)₆ and W(CO)₆, alone do not induce polymerization of acetylenic compounds. However, UV irradiation of these catalysts in the presence of halogenated compounds can lead to the formation of active species for polymerization of various substituted acetylenes. Carbon tetrachloride (CCl₄) is used as a solvent in polymerization, and it plays a very important role in the formation of active species, and thus cannot be replaced by toluene, which is often used a solvent in polymerization catalyzed by metal chloride-based catalysts.^{6,18,20,21} Although these metal carbonyl-type catalysts are less active compared to metal halide-based counterparts, they can provide high-MW polymers. It is a great advantage that the metal carbonyl catalysts are very stable under air and thus are much easier to handle.

The use of a catalytic amount of Ph₂CCl₂ in metal carbonyl catalysts enables the omission of CCl₄. For example, the polymerization of PA with W(CO)₆ in the presence of Ph₂CCl₂ in toluene upon photoirradiation proceeds homogeneously to give a polymer with $M_n = \sim 2 \times 10^{4}$.^{57,58} High-MW polymers ($M_w > 10^5$) are attainable from sterically bulky aromatic and aliphatic acetylenes. It is also effective to use a catalytic amount of Lewis acids instead of CCl₄ in M(CO)₆-based catalysts (M = W, Mo).⁵⁹

An alternative metal carbonyl catalyst, (mesitylene)Mo (CO)₃₁ polymerizes substituted acetylenes in CCl₄ without photoirradiation.⁶⁰ It is argued that coordinating mesitylene is readily released by heating, and that the same active species as in the photoirradiation system would be formed. The acetonitrile complexes $M(CO)_3(NCCH_3)_3$ (M = W, Mo) polymerize various mono- and disubstituted acetylenes at room temperature.^{61,62} The arene and diene complexes, $(mesitylene)W(CO)_3$ and $(nbd)Mo(CO)_3$ (nbd = 2,5-norbornadiene), are tolerant to polar groups such as ester, ether, and nitrile in monomers. The halogenated complexes, $MI_2(CO)_3(NCCH_3)_2$ (M = Mo, W), are able to catalyze the polymerization of PA in toluene (see Table 3). Santhosh and Sundararajan⁶⁸ reported that (toluene)Mo(CO)₃ can also be activated by the addition of an electron acceptor, namely, chloranil. This catalytic system is applicable to ring-substituted PAs, such as *p*-BrPA, *p*-NO₂PA, and *p*-MeOPA.

Another type of metal carbonyl catalyst, MCl₂(CO)₃(AsPh₃) (M = Mo, W), that induces the ring-opening polymerization of norbornene and its derivatives has been shown to polymerize *tert*-butylacetylene and *ortho*-substituted PAs without photoirradiation or the use of CCl₄.¹⁵⁶ The reaction of *tert*-butylacetylene in the presence of seven-coordinate W (II) and Mo(II) compounds [MCl(M'Cl₃)(CO)₃(NCR)₂] (M = Mo, W; M' = Sn, Ge; R = Me, Et) leads to the formation of high-MW polymers ($M_n > 10^5$).^{88,157-159}

3.27.2.1.3 Metal carbene catalysts

Well-defined carbene catalysts show excellent activity for polymerization, and are isolable and thus informative to suppose the polymerization mechanism as metathesis type. The first example of isolated single-component carbene catalysts is Fischer and Casey carbenes (1 and 2, respectively, Figure 1), which polymerize PA, *tert*-butylacetylene, and cyclooctyne in low yields.¹⁶⁰ The bulk polymerization of PA with 1 gives a polymer with M_w 17 000 in 49% yield. In the case of *tert*-butylacetylene, 1 produced the corresponding polymer with high MW ($M_n = 260\,000$) and in 28% yield. Photoirradiation and/or addition of Lewis acids promotes the generation of active species. Casey carbene (2) is a less stable catalyst and thus more active compared to Fischer carbene. Rudler carbene (3) readily releases the intramolecularly coordinated double bond upon the approach of an acetylenic monomer, and is more active than the Fischer and Casey carbenes. Polymerization of 1-methoxy-1-ethynylcyclohexane and copolymerization of norbornene with *tert*-butylacetylene catalyzed by 3 have been reported.^{161–163}

The development of Mo and W alkylidene complexes (4), that is, the so-called Schrock carbene, has contributed to the rapid growth of polymerization chemistry of substituted acetylenes. Although the preparation of these catalysts is relatively difficult because of their low stability, in other words, high reactivity, they elegantly act as living polymerization catalysts for substituted acetylenes such as *ortho*-substituted PAs^{164,165} and α , ω -diynes.^{166–168} The details of the living polymerization are described below.

3.27.2.2 Nb and Ta Catalysts

Nb and Ta catalysts are very effective for the polymerization of acetylenic compounds bearing bulky substituents. In the case of sterically small substituted acetylenes, the side reactions such as cyclo- and linear oligomerization are unavoidable. For example, cyclotrimerization of linear 1-alkynes and PA readily occurs in the presence of NbCl₅ and TaCl₅. Bulky substituents can evade the cyclooligomerization to give the polymer successfully. Crowded disubstituted acetylenes such as internal 1-phenyl-1-propyne, 1-trimethylsilyl-1-propyne octvnes, (TMSP), and diphenylacetylenes (DPAs) are suitable for polymerization by group 5 catalysts.^{6,21,22} The simplest and most convenient catalysts are TaCl₅ and NbCl₅ in this class (Table 2), which can polymerize TMSP quantitatively without any coadditives in toluene at 80 °C to give a high-MW polymer $(M_{\rm w} = 10^5 - 10^6)$. The polymer formed is soluble in many common solvents such as toluene and chloroform.²⁴ A 1:1 mixture of TaCl₅ and Ph₃Bi works as a more active catalyst toward TMSP to produce a polymer whose M_w reaches 4×10^6 , which is the highest MW among those of the substituted polyacetylenes ever known. The polymerization of TMSP by NbCl₅ in cyclohexane affords polymer with narrow MWD ($M_w/M_n \sim$ 1.2) irrespective of conversion. The M_n increases in direct proportion to conversion, indicating the presence of a long-lived propagating species. Poly(TMSP) (PTMSP) exhibits extremely high gas permeability and hence its gas permeation behavior has been intensively studied (see Section 3.27.4.3.1).

DPAs are unable to polymerize with NbCl₅ and TaCl₅ alone. However, 1:1 mixtures of TaCl₅ and suitable cocatalysts such as n-Bu₄Sn, Ph₄Sn, and Et₃SiH afford poly(DPA)s in good to high yield. Poly(DPA)s are thermally very stable (up to ~500 °C based on thermogravimetric analysis (TGA)). Although simple poly(DPA) is insoluble in any solvent, totally soluble polymers can be obtained with TaCl₅–n-Bu₄Sn catalyst when substituents such as p-Me₃Si, p-t-Bu, p-n-Bu, p-PhO, and p-N-carbazolyl groups are introduced into aromatic rings on
 Table 3
 Various transition metal catalysts for polymerization of typical acetylenic monomers

Catalyst	Monomer ^a	References
Mo catalyst		
Mo(CO) ₆ –PhOH	PA (quant, $M_{\rm p} = 40700$)	63, 64
Mo(CO) ₆ -protic cocatalysts	PA. t-BuC=CH. 1.7-octadivnvl (all quant)	65
$M(CO)_6$ (activated by refluxing in solvent) (M = Mo, W, Cr)	PA (high vield, MW = 6000–17 000)	66
$C_{D_{2}}MO_{2}(CO)_{e}$ -PhOH, 3-chlorophenol, or iodine	PA internal alkyne, 1-alkyne	67
$M_0(CO)_4(nbd)$	PA monosubstituted acetylenes	61
wo(oo)4(ma)	ClC=C-n-Hex (quant $M = 238,000$)	01
	PA monocubetituted acetulanes CIC-CPh CIC-C-n-Hex (99%	61
100(00)3(013010)3	M = 855000	01
	PA (low yield < 15%)	61
	PA (10W y) = 0.00 (0.000)	60
	PA (qualit, WW = 5000-0000)	02
$\begin{bmatrix} MO(I)(GEOI3)(GO)_3(GT_3OI)_2 \end{bmatrix}$	PA(CUIV. = 45%, VIVV < 10000)	00
$IIIO(INO)_2(U_2OPII)_2$ -Lewis acid (IIOI4, SIIOI4, EIAIOI2)	$PA (80\%, M_W = 1000, WWD = 1.15)$	09
$MO_2(U_2\cup U_3)_4$ -Lewis acid (11U14, S11U14, GeU14, EIAIU12)	PA, t -Bub=UH (qualit, living mainter in GeUI ₄)	70
C/S -[MO(NU) ₂ U_1 (NUMP) ₂] U =ETAI U_1 2	PA, 3-nexene, t -BuG=CH (MWD = 1.10)	/1
CIS-[MO(NU) ₂ GI ₃ (<i>I</i> -PrOH)]·3 <i>I</i> -PrOH-ETAIGI ₂	PA, 2-nexyne, <i>t</i> -BuG≡CH	/1
$[Mo_2Cl_6(tht)_3]$ (includes isomer C_{2v} and C_s)	Acetylene, 2-butyne, 3-butyne, propargyl chloride, t -BuC=CH	72
	$(61\%, M_{\rm w} = 110000)$	
Mo(NMe ₂) ₂ (NHMe ₂)(dpma)	3-Hexyne	73
$M_2(Ot-Bu)_6$ (M = Mo, W)	Acetylene	74
$Mo(Ph_2PCH_2CH_2PPh_2)(C_7H_7)$	t -BuC=CH (M_w = 63 000)	75
MoBr ₃ -acidic or organometallic cocatalysts	<i>t</i> -BuC=CH (quant, M_n = 210 000)	76
$Mo(OEt)_5$ (with/without EtAICl ₂ or Et ₃ AI)	Propargyl alcohol and its derivatives	77
$(Me_3P)(PhH_2Si)Mo(=NAr)(NArSiPhH_2)$	PA (quant, Turnover number = 34)	59
MoO ₃ /siliceous mesoporous molecular sieves	1-Hexyne (64%, $M_{\rm W}$ = 30 000), other 1-alkynes	78
[(CF ₃) ₂ MeCO] ₂ Mo(=CHCMe ₂ Ph)(=N-C ₆ H ₃ -2,6- [/] Pr ₂)/siliceous	1-Hexyne (98%, $M_{\rm W} = 17000$)	78
mesoporous molecular sieves		
M/ catalyst		
WDr	t PuC - CH (augest M - 22,000)	76
	$P_{\text{D}}(0.00)$	70
$[Nd_{4}[W_{2}\cup I_{8}]]$	PA (92%)	79
$[W(OO)_3(U\Pi_3UN)_3] - [UP_2P_1]PF_6$	PA (40-45%, 1000) = 250000	00
$W(UU)_6 - P\Pi U = UH (COCATAIYST) - \Pi V$	PA and internal alkyne	81
	PA, I-nexyne	82
<i>trans</i> -[(CU) ₄ BrW≡CPN]	Acetylene, PA, 1-alkynes, Internal alkynes	83
$[(t-BuU)_3W \equiv C-t-Bu]$	PA (conv. = 100%, M_w = 20 000), $C_5H_{11}G \equiv CH$ (conv. = 100%,	84
	$M_{\rm w} = 25\ 000)$	
$Cl_3(dme)W \equiv C-t-Bu$	PA (69%, 32 000), <i>t</i> -BuC ≡ CH (82%, 300 000)	85
$WCl_5(o-4-t-Bu-C_6H_4)$	PA (66%, <i>M</i> _w = 150 000)	54
$WCl_5(0-2,6-Cl_2C_6H_3)$	PA (89%, <i>M</i> _w = 47 000), TMSA (15%), 1-hexyne (37%,	54
	<i>M</i> _w = 12 000), <i>t</i> -BuC=CH (34%)	
$WCl_5(o-2,6-di-t-Bu-C_6H_3)$	PA (78%, <i>M</i> _w = 230 000)	54
$WOCl_3(o-2,6-di-t-Bu-C_6H_3)$	PA (58%, <i>M</i> _w = 35 000)	54
$WOCl_3(o-2,6-Cl_2C_6H_3)$	PA (85%, <i>M</i> _w = 67 000)	54
$[NEt_4][W(CO)_5CI]$ –ZrCl ₄	PA	86
$[W(CO)_4(piperidine)_2]$ –ZrCl ₄	PA	86
$[W(CO)_4(bipy)]$ -ZrCl ₄	PA	86
$[W(CO)_4(dppe)] - ZrCl_4$	PA	86
$[WCl_2(CO)_3(PPh_3)_2] - ZrCl_4$	PA	86
$[(CO)_{A}W(\mu-CI)_{2}W(SnCl_{2})(CO)_{2}]$	PA (MW = 8300). <i>t</i> -BuC≡CH	87
$[(CO)_4W(\mu-CI)_2W(GeCl_2)(CO)_2]$	PA	88
[WCl(GeCl ₂)(CO) ₂ (CH ₂ CN) ₂]	PA	88
$[WX_{\circ}(CO)_{\circ}(CH_{\circ}CN)]$ $(X = CL = CH_{\circ}CN \cdot X = LL = CH_{\circ}CN \cdot PPh_{\circ}$	PA (36–43%)	89
$(V \Delta (00))(01300)(2)(V - 0), 2 - 01300, X - 1, 2 - 01300, 1133, 010, 2 - 01300, 1133, 010, 2 - 01300, 1133, 010, 2 - 01300, 1133, 010, 2 - 01300, 1133, 010, 2 - 01300, 1133, 010, 2 - 01300, 1133, 010, 2 - 01300, 1133, 010, 2 - 01300, 1133, 010, 2 - 01300, 1133, 010, 2 - 01300, 1133, 010, 2 - 01300, 1133, 010, 2 - 01300, 1133, 010, 2 - 01300, 1133, 010, 2 - 01300, 1133, 010, 2 - 01300, 1133, 010, 2 - 01300, 1133, 010, 2 - 01300, 1133, 010, 010, 010, 010, 010, 0$		00
$[WBr_{o}(CO)(CH_{o}CN)(n^{2}-HC=CPh)_{o}]$	PA (25%)	89
[WCl(SnCl)(0[300](1] -10=0[1])2]	τη (4970) τρυζ	00
	$C_{\text{DUU}=\text{UP}}(30\%, 10\%, = 23000)$	90
$U[VV_2\Pi(UU)_{10}]$ (U = E(4 V, F 14F)	OUPUIVITIET OF PA ATTU PTIO≡UIVIE, ETC.	91
$[(UU)_5W]_2[\mu-UH(U_6H_4-p-K)]$ (K = H, Me, UIMe)	∠-butyne, t-bub≡0H	92
$(UU)_9W_2[\mu-GH(G_6H_4-p-K)]$ (K = H, Me, OMe)	2-Butyne, t-BuC≡CH	92
$[W_3(\mu^{-}-U)(\mu^{-}UH)_2(\mu^{-}CI)_2(U)(\eta^{-}-PhC=CPh)_5]$	PA (MW = 8300), <i>t</i> -BuC≡CH	8/
$[W_2 Cl_6(tht)_3]$ (includes isomer $\mathcal{C}_{2\nu}$ and $\mathcal{C}_s)$	Acetylene, 2-butyne, 3-butyne, propargyl chloride, t-BuC=CH (60%, M_w = 56 000)	72

Catalyst	Monomer ^a	References
$Na_4[W_2Cl_8(THF)_x]$	PA (97%, M_n = 28 200), <i>n</i> -BuC=CH, <i>t</i> -BuC=CH, Me ₃ SiC=CH, ArC=CH internal alkynes	93
[Bu_N]_a[W_a(u=Cl)_aCl_a]	PA (30% M < 2000)	94
$Na[W_2(\mu-Cl)_3Cl_4(THF)_2]$	PA (98%, $M_{\rm W}$ = 159 000) and its derivatives (42–96%)	94
Rh catalyst		
$Rh_2(PF_3)_8$	PA, <i>t</i> -BuC=CH	95
$[Rh(LL)(chel)]X (LL = cod, nbd; chel = bipy, etc.; X = PF_6, ClO_4,$	PA (up to 96%, high <i>cis</i> content)	96,97
BPh ₄)		
[Rh(cod) ₂]BF ₄	PA derivatives (>85%)	98
[(NN'N)Rh(cod)]	PA (24%)	99
$[Rh(cod)Cl_2]L$ (L = tmeda, teda)	PA (up to 91%, high <i>cis</i> content)	96
[(cod)RhCl(H ₂ NCH ₂ CH ₂ CH ₂ NH ₂)]Cl	PA (>95%, MW = 6600), PA derivatives	100
$(cod)RhCl(Ph_2PC_6H_4-m-SO_3Na)$	PA	100
trans-[Rh(CO)(Ph ₂ PC ₆ H ₄ -3-CO ₂ H)(μ-NCMe=CHCMe=N)] ₂	PA	100
(Ph ₂ PC ₆ H ₄ -1-COO)Rh(CO)(NHMe=CHCMe=N)	PA	100
(Ph ₂ PC ₆ H ₄ -2-COO)Rh(CO)(indazole)	PA	100
trans-[Rh(CO)(Ph ₂ PC ₆ H ₄ -2-CHO)(μ-NCMe=CHCMe=N)] ₂	PA	100
$[Rh(cod)(SC_6X_5)_2]$ (X = H, F)	PA (X = F; 50%, MW \sim 35 000)	101
$Rh(cod)(SC_6F_5)(PPh_3)$	PA (41%)	101
$[Rh(diene)L_2]PF_6$ (diene = cod, nbd; L = dbn, dbu)	PA (42–53%, <i>M</i> _w = 200 000–1 750 000)	102
RhCl(diene)L (diene = cod, nbd)	PA (∼80%, <i>M</i> _w = ∼1 400 000)	102
[Rh(cod)Cl] ₂ (pda)	PA (39%, <i>M</i> _w = 7300)	103
Rh(cod)(mid)Cl	PA (75%, <i>M</i> _w = 12 500)	103
Rh(cod)(L)Cl (L = NH ₃ , <i>t</i> -BuNH ₂ , piperidine)	PA (57–72%, <i>M</i> _w = 6500–23 000)	103
Rh(cod)(bbpmt)	PA (64%, <i>M</i> _w = 11 000)	103
[RhCl(cod)] ₂ (µ ² -PCHP)	PA	104
RhH(PCP)(μ-Cl) ₂ Rh(cod)	PA	104
RhCl(PCP)(μ^2 -Cl) ₂ Rh(cod)	PA	104
[RhF(cod)(PPh ₃)]	PA (preliminary experiment)	105
[Rh(CF ₃)(cod)(PPh ₃)]	PA (preliminary experiment)	105
$[(cod)Rh{CH_3CO^-=CHCOO(CH_2)_2OCO(CH_3)=CH_2}]$	PA (>82%, $M_{ m w}$ = 11 000 \sim 16 000), PA derivatives	106
RhTp(cod) and its analogs	PA (quant), PA derivatives	107,108
RhBp(cod)	PA (100%, <i>M</i> _w = 66 000, MWD = 1.7)	107,108
$[(cod)Rh(LL)]ClO_4$ (LL = dppf, FcNP, FcNN)	PA (up to 94%, <i>M</i> _w = 145 000)	109
[(diene)Rh(N-O)] (diene = nbd, cod)	PA (97%, M_n = 93 000) and its derivatives, propargylamide	110
[(diene)Rh(N-N)] (diene = nbd, cod)	PA (93%, $M_n = 62000$) and its derivatives, propargylamide	110
(cod)RhCl(ŋ'-NNN)	PA (quant, $M_{\rm w}$ = 5060)	111
$[(cod)Rh(\eta^3-NNN)]X (X = OTf_4^-, [(cod)RhCl_2]^-)$	PA (up to 94.4%, <i>M</i> _w = 8620)	111
[(cod)RhX(bmin)] (X = Cl, Br, I)	PA (up to 75%, $M_{\rm w} \le 90000$)	112
$[(cod)Rh(\mu-3-phenylpyrazolyl)]_2$	PA (quant, $M_w = 100000$, MWD = 4.6)	113
(POP)[Rh(cod)] ₂	PA	114
Rh(nbd) · apo-Fr	PA ($M_{\rm n}$ = 13.1 ± 1.5 × 10 ³ , $M_{\rm w}/M_{\rm n}$ = 2.6 ± 0.3	115
IVI CALAIYST		140
NIGI2-NABH4	Acetylene, I-alkyne, propargyl alconol, etc.	110
NI(CU) ₄	Propiolic acid ester (oligomerization)	117
Cp ₂ NI	PA (29–50%, MW = 1600, IN DUIK polymerization), PA derivatives	118, 119
Cp₂Ni–LiB (B = Me. Ph. C≡CPh)	DPA (74%), PA (58%, $M_{\rm w}$ = 1100)	120
$Ni(cod)_2$ -CF ₂ CO ₂ CH ₂ CH ₂ CH ₂ CH ₂	PA (65% $M_{\rm W}$ = 12 000). PA derivatives	121
$[CDNi]_2(PhC=CH)$	PA (53%)	104
[CpNi(CO)] ₂	PA (40%)	104
CpNi(NO)	PA (23%)	104
CpNi(GeBr ₃)(CO)	PA (26%)	104
CpNi[P(<i>n</i> -Bu) ₃]I	PA (56%)	104
$CpNi[L]CI (L = P(OMe)_3, PPh_3)$	PA (38% and 52%, respectively)	104
Ni(CH ₃ CN) ₆ (BF ₄) ₂ -Et ₂ AICI	PA (65%, $M_{\rm p}$ = 5000)	122
$(1-R-Indenyl)Ni(PPh_3)(OTf)$ (R = Et, <i>i</i> -Pr, Bz)	PA (5%, $M_{\rm p} = 4400$)	123
(1-R,2-R'-Indenyl)Ni(PPh ₃)(thienyl) (R, R' = H. alkvl. Ph)	$PA(M_w = 50\ 000 - 75\ 000)$	124
$[(\eta^3:\eta^1-\text{Indenyl}(CH_2)_2\text{NMe}_2)\text{Ni}(PR_3)]X-MAO (R = Ph, Me. Cv)$	PA $(M_w = 34500 - 57700)$	125
$(1-\text{Me-indenyl})\text{Ni}(\text{PR}_3)(\text{C=CPh})-\text{MAO}(\text{R}=\text{Ph},\text{Cv})$	PA (59% and 32%, respectively)	126
$(1-Me-indenvl)Ni(PR_3)CI-MAO (R = Ph, Cy)$	PA (30% and 35%, respectively), 1- or 3-hexyne ($M_{\rm W}$ < 2400)	86

Catalyst	<i>Monomer^a</i>	References
CpNiCI(NHC)-MAO	PA (50%, M _w = 13 600, 1200 (bimodal))	127
CpNiX(NHC')–MAO	PA (up to 60%, <i>M</i> _w < 1600)	127
Pd catalyst		
$[Pd(CH_3CN)_4](BF_4)_2$	PA (30%, M_n = 9000), propiolic acid ester (90%, M_n = 3000)	128
[(dppf)Pd(CH ₃ CN) ₂](OTf) ₂	PA (90%, <i>M</i> _n = 18 800)	129
[(dippf)Pd(CH ₃ CN) ₂](OTf) ₂	PA (49%, <i>M</i> _n = 4300)	129
[Pd(<i>NN'O</i>)Cl]	PA (totally 55%, M_w = 1300–1400 (main peak))	130
$[Pd(\eta^{1},\eta^{2}-5-OMe-C_{8}H_{12})(N,O)]BF_{4}$	PA (<9%)	131
PdCl ₂	Propargyl alcohol, propiolic acid, propiolic acid ester (${\sim}90\%$)	132, 133
(PPh ₃) ₂ PdCl ₂	Propiolic acid ester (\sim 80%), propargyl alcohol	133
$[Pd(C \equiv CCH_2OH)_2(PPh_3)_2]$	Propargyl alcohol (90%)	134–136
Pt catalyst		
cis- and trans-PtCl ₂ (PPh ₃) ₂	PA (MW < 2000)	137
trans-PtHCI(PPh ₃) ₂	PA (MW < 2000)	137
Pt(PPh ₃) ₂	PA (MW < 2000)	137
$(PPh_3)_2Pt(\eta^2-HC=CPh)$	PA (MW < 2000)	137
cis-Pt(C=CPh) ₂ (PPh ₃) ₂	PA (MW = 6400)	137
$trans-Pt(C \equiv CPh)_2(PPh_3)_2$	PA (MW = 7200)	137
$[Pt(CO)_4][Sb_2F_{11}]$ in CO atom.	$PA(M_w = 3000 - 4300)$	138
cis- and trans-PtCl ₂ (PPh ₃) ₂	PA (MW < 2000)	137
trans-PtHCI(PPh ₃) ₂	PA (MW < 2000)	137
$PT(PPn_3)_2$	PA (MW < 2000)	137
$(PPn_3)_2 PI(\eta^HU=UPn)$	PA (MW < 2000)	137
	$PA(M_{W} = 5000 - 4500)$	130
Other transition metal catalysts		100
Rup(L)(L')G(L, L' = P, N, U donors)	$PA (98\%, M_n = 7000, PDI = 1.48)$	139
$Et_2NUU_2KUH(UU)(PUy_3)_2$	PA (IOW yield \sim 15–20%)	140
$(P\Pi \cup \exists U)_2 K U (\cup U) (P \cup Y_3)_2$	PA (IOW VIEID \sim 15–20%) Propiolic acid (74% 44 – 4000), propergyl clochol (65%	140
	Proproduble), and $(74\%, M_{\rm H} = 4000)$, propargyr alconor (65%,	141
$(m^{6}-C)(mono)$ PuCL (RMIM)	$\frac{115010010}{1000}$, etc. PA (conv 65% M - 300) and its derivatives	1/10
	PA terminal acetylene	1/12
Be(CO)_Br	PA terminal acetylene	143
(Mesitylene)Cr(CO)	PA (MW – 12 000)	140
[Cn*Cr(u-Cl)Me]	2-Butyne	145
$Fe(CH_2CH_2CO_2)_2 = AIFt_2$	PA	146
$Fe(naph)-Al(i-Bu)_3$	1-Butyne, 1-hexyne, 1-dodecyne	147
$Fe(prp)_3 - AIEt_3$	Internal alkyne	148, 149
Fe(chc) ₃ -AlEt ₃	Internal alkyne	148, 149
Fe(sal) ₃ -AlEt ₃	PA	150
$Co(oxin)_2 - AIEt_3$	PA	150
$Co(sal)_2 - AIEt_3$	PA	150
Ni(saldxm) ₂ -AlEt ₃	PA	150
VO(sal) ₂ –AlEt ₃	PA	150
VO(saldim) ₂ -AIEt ₃	PA	150
V(acac) ₃ –AIEt ₃	PA	151
Ti(edbp)Cl ₂ –AlEt ₃	PA (conversion = 96%, selectivity = 98%, M_n = 2200)	152
$II(OBu)_4$ -AlEt ₃	PA	151
$IIGI_3$ (or $IIGI_4$)-AIEt _n GI _{3-n}	Internal alkyne, mainly cyclic trimerization	153
SC naphthenate-AIK ₃ (K = Et, <i>I</i> -BU)	1-Hexane, etc.	154
NU(F ₂₀₄) ₃ -Fe(acac)-AI(FBU) ₃	$PA \ (CONVERSION = 47\%, \ IV_{W} = 8700000)$	155

^aThe values in parentheses are the yield of polymer, conversion, average molecular weight of polymer, and other properties.

PA, phenylacetylene; PDI, polydispersity index; dpma, di-*N*,*N*-(pyrrolyl-a-methyl)-*N*-methylamine; tht, tetrahydrothiophene; bipy, 2,2'-bipyridyl, NN'N, *N*-benzyl-*N*-(2-pyridylmethyl)-*N*-(2-pyrrolatomethyl)amine; tmeda, *N*,*N*,*N*',*N*'-tetramethylethylendiamine; teda, triethylendiamine; dbn, 1,5-diazabicyclo[4.3.0]non-5-en; dbu, 1,8-diazabicyclo[5.4.0]undec-7-en; pda, *o-phenylenediamine*; Cp, cyclopentadienyl; mid, *N*-methylimidazole; bbpmt, bis(4-*t*-Bu)-2-pyridylethylthiolate; Tp, hydridotris(pyrazolyl)borate; Bp, bis(pyrazolyl)borate; dppf, 1,1'-bis (diphenylphosphino)ferrocene; FcNP, 1-diphenylphosphino-2-(*N*,*N*-dimethylamino)methylferrocene; FcNN, 1,6-diferrocenyl-2,5-diazabexane; *NN'O*, 2-acetylpyridine or 2-formylpyridine benzoylhydrazones; *N*,*O*, 2,6-(*i*-Pr)₂(C₆H₃)N=C(Ph)-C(Ph)=O or 2-benzoylpyridine; dippf, 1,1'-bis(diisopropylphosphino)ferrocene; Cy, cyclohexyl; Cp*, pentamethylcyclopentadienyl; naph, naphthenate; acac, acetylacetonate; oxin, 8-hydroxyquinoline; sal, salicylaldehyde; saldxm, salicylaldoxime; saldim, salicylaldehydeimine; edbpH2, 2,2'-ethylidenebis(4,6-di-*tert*-butylphenol); N-O, 2-((phenylimino)methyl)phenoxy; N-N, *N*,*N*'(propane-1,3-diylidene)dianiline; NNN, 1,4-diisopropyl-1,4,7-triazacyclononane; bmin, 1-butyl-3-methyl imidazol-2-ylidene; POP, 2,6-bis(phosphanylmethyl)phenolate; apo-Fr, apo-ferritin; NHC, 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene. NHC', 1,3-dimesitylimidazol-2-ylidene; BMIM, 1-(*n*-butyl)-3-methyllimidazol-2-ylidene.



Figure 1 Metal carbene catalysts

the side chain.^{169,170} These polymers have high MWs $(\sim 1 \times 10^6)$.

In addition to group 6 transition metal catalysts, bulky aryloxo ligands can also replace the chlorine ligand(s) of NbCl₅ to form Nb(dmp)_nCl_{n-5}(solvent) (5, n = 1-2), which in the presence of cocatalysts such as EtMgBr or Et₃Al has the unique ability to polymerize terminal acetylenes such as *tert*-butylacetylene and PA.⁵³ Such an exceptional ability of the 5–cocatalyst system originates from the presence of bulky aryloxo groups, which have the same effect as that of bulkiness of the monomer. Ta carbene (6) induces living polymerization of 2-butyne (Figure 2) (*see* Section 3.31.2.6).¹⁷¹

3.27.2.3 Rh Catalysts

Rh catalysts are now recognized as one of the most powerful tools for the polymerization of monosubstituted acetylenes because of their high activity and high tolerance to polar functional groups. They can polymerize a relatively wide range of nonpolar and polar monomers such as PAs, propiolic acid esters, N-propargylamides, and other acetylenic compounds involving amino, hydroxy, azo, and radical groups. It should be noted that Rh catalysts generally achieve high stereoregularity (head-to-tail and *cis*-transoidal) of the polymer, particularly when applied to the polymerization of PA-type monomers. The mechanism of polymerization is considered as the insertion type, which has been elucidated by nuclear magnetic resonance (NMR) spectroscopic studies with one of the Rh catalysts.^{172,173} Some of the Rh catalysts can achieve living polymerization of certain acetylenic monomers. The only defect of Rh catalysts is that they are usually inapplicable to the polymerization of disubstituted acetylenes. Only one exception has been reported and is described below.

Dinuclear Rh complexes, $[(nbd)RhCl]_2$ (7) and $[(cod)RhCl]_2$ (8, cod = 1,5-cyclooctadiene) (Figure 3),²³ and zwitterionic Rh complexes, $(nbd)Rh^+BPh_4^-$ (9),¹⁷⁴ have been frequently employed for the polymerization of PAs. Catalyst 7 is usually more active than 8 because the strongly coordinating nbd ligand stabilizes the active species. Catalyst 7 is very stable under air and



Figure 3 Conventional Rh catalysts.

moisture, which facilitates the experimental procedure. The most widely applied catalyst is a binary catalyst composed of 7 and excess Et_3N ,^{23,175,176} which gives excellent yields of stereoregular poly(PA)s with high MW ($M_n > 10^5$). Et₃N expedites the formation of Rh single-site species, [(nbd)RhCl(NEt₃)], via the cleavage of bridging Rh-Cl bonds and the coordination of triethylamine, which could easily shift to the true active species.¹⁷⁵ Combinations of 7 with suitable organometallics such as n-BuLi, Et₃Al, and alkali metal amide greatly accelerate the polymerization of PA.^{177,178} Living polymerization of PAs is feasible by using a well-characterized Rh complex, (nbd) $(PhC \equiv C)Rh(PPh_3)_2$ (10), in conjunction with $4-(N_1)_2$ N-dimethylamino)pyridine (DMAP).^{172,173,179,180} An extension of this system is a multicomponent catalyst, [(nbd)RhOMe]2-PPh3-DMAP.¹⁸¹ A ternary Rh catalyst system, [(nbd)RhCl]2-LiC(Ph)=CPh₂-PPh₃,^{182,183} induces the living polymerization of PAs. In the latter case, the initiating species is a vinylrhodium (11a and 11b), which was isolated and well characterized by X-ray analysis.¹⁸⁴ Further details on the living polymerization are provided in Section 3.31.2.6.



Figure 2 Nb and Ta catalysts bearing alkoxy groups.



Figure 4 New Rh catalysts bearing the strongly π -acidic diene, namely, tfb.

Recently, Masuda's group demonstrated that rhodium catalysts that contain a strongly π -acidic diene, namely, tetrafluorobenzobarrelene (tfb), show higher catalytic activity and turnover frequency (TOF) than their nbd analogs (Figure 4). For instance, [(tfb)RhCl]₂ (12) achieves complete consumption of monosubstituted acetylenes in a shorter reaction time than [(nbd)RhCl]₂ (1), indicating higher TOF with 12.¹⁸⁵ Complex 12 can be derivatized to other tfb-Rh catalysts, such as [(tfb)Rh{C(Ph)=CPh₂}(PPh₃)] (13) and [(tfb)Rh $(\eta^6-Ph)BPh_3$] (14). Catalyst 13 polymerizes PA in a living fashion to afford polymer with the most narrow MWD (i.e., polydispersity index 1.03) reported thus far.¹⁸⁶ Catalyst 14 shows higher activity than conventional 9.187 Optically pure dimethyl-introduced zwitterionic complexes 14-(R,R)-tfbMe₂ and 14-(S,S)-tfbMe2 (Figure 5) are effective for the helixsense-selective polymerization of a certain monosubstituted acetylene monomer (see Section 3.27.3.3).¹⁸⁸ Complex 14 is converted into a cationic derivative, [(tfb)Rh(PPh₃)₂][BPh₄] (15), by the reaction of 14 with PPh_3 , which also induces the living polymerization of PA in the presence of amines.¹⁸⁹

A few reports have suggested that rhodium catalysts that have a variety of bidentate ligands are composed of two different types of coordination sites (Figure 6). Xue *et al.*¹⁹⁰ have demonstrated the catalytic activity of a neutral Rh catalyst bearing a phosphinosulfoimido ligand, [(nbd)Rh (Ph₂PCH₂CH₂NTs)] (16, Ts = SO₂C₆H₄-*p*-Me), in the polymerization of PA. Jiménez *et al.*¹⁹¹ investigated a series of cationic



Figure 6 The Rh catalysts bearing P-L-type bidentate ligands.

Rh catalysts coordinated by hemilabile $Ph_2P(CH_2)_nZ$ -type bidentate ligands (17, n = 2 or 3; Z = OMe, NMe_2 , SMe) that polymerize PA and its derivatives efficiently. Using NMR spectroscopy, they were able to directly observe the initiating species in the polymerization of PA using a catalyst containing the phosphinoamino ligand. A phenylethynyl Rh species is formed in the reaction of 17 (with diene = cod; n = 3; $Z = NMe_2$) with PA, along with the formation of an ammonium moiety derived from the bidentate ligand and an acetylenic terminal proton of PA. Prior to this, it had been revealed that Rh acetylide-type complexes form in the reaction of certain complexes with acetylenic monomers.^{181,192} This is the first case demonstrating that the reaction forming Rh acetylide is driven by the formation of ammonium salt. Complex 17 with diene = tfb, n = 3, and $Z = NMe_2$ can achieve quasi-living



Figure 5 Optically active Rh catalysts.

polymerization of PA in the presence of DMAP. This work also contributed to further studies on branched poly(PA) formed with the same catalyst, as reported by Angoy *et al.*¹⁹³

The Rh-catalyzed polymerization proceeds in various solvents such as benzene, tetrahydrofuran (THF), ethanol, and triethylamine.^{23,175} Among the solvents, ethanol and triethylamine are favorable for PAs from the viewpoint of both polymerization rate and polymer MW. Polymerization of PAs is feasible even in aqueous media by using water-soluble catalysts. For example, $[(cod)Rh(mid)_2][PF_6]$ (mid = N-methylimidazole) provides cis-transoidal poly(PA) (cis 98%) in high vield (98%).¹⁰³ (cod)Rh(O₃SC₆H₄-p-CH₃)(H₂O) and (nbd)Rh $(O_3SC_6H_4-p-CH_3)(H_2O)$ also work as water-soluble catalysts. A water-soluble cationic bipyridine ligand enables the recovery and reuse of the conventional catalyst 8, which polymerizes PA in aqueous conditions under air.¹⁹⁴ Polymerization of PA in compressed (liquid or supercritical) CO₂ has been studied using a rhodium catalyst, [(nbd)Rh(acac)] (acac = acetylacetone).¹⁹⁵ A higher polymerization rate is obtained in CO₂ than in conventional organic solvents such as THF and hexane. Recently, ionic liquids have been examined as media for Rh-catalyzed polymerization of PA.¹⁹⁶

Recently, a few heterogeneous Rh catalysts have been reported. Kopaczyńska *et al.*¹⁹⁷ demonstrated that rhodium nanoparticles stabilized by polyvinylpyrrolidone exhibit catalytic activity in the polymerization of PA. The stereochemistry of the polymer produced with this catalyst is purely *cis*-transoidal. The progress in polymerization can be monitored by atomic force microscopy (AFM) and transmission electron microscopy (TEM). This report includes the first detection of a spectacular helical poly(PA) using AFM imaging. Son and co-workers¹⁹⁸ reported that the nanoparticles composed of the (benzoquinone)Rh(cod) complex and aluminum compounds catalyze the polymerization of PA. The catalyst nanoparticles can be recovered by centrifugation, and the recovered nanoparticles show almost the same activity.

3.27.2.4 Group 10 Metal Catalysts

Group 10 transition metal catalysts based on Ni and Pd are a relatively new class of catalysts for the polymerization of substituted acetylenes. Therefore, the number of reports on these catalysts is still limited. Some of the earlier reports stated that group 10 catalysts rather induce cyclic and linear oligomerizations of acetylene monomers.

The polymerization of N,N-dimethylpropargylamine and ethynylpropargylsilane with Ni(NCS)₂PPh₃¹⁹⁹ and [Pd $(C=CR)_2(PPh_3)_2$ (R = SiMe₃, CH₂OH, CH₂NMe₂),²⁰⁰ respectively, provides insoluble metal-coordinated conjugated polymers. 2-, 3-, and 4-Nitrophenyl propargyl ethers polymerize with PdCl₂ in dimethylformamide (DMF) giving soluble brown polymers, which show broad MWD with peak tops at 4×10^3 and $1 \times 10^{5,201}$ [Pd(C=CC₆H₄C=CH)₂(PPh₃)₂] is a more active catalyst for the polymerization of polar substituted acetylenes such as propargyl alcohol and propargyl esters. The corresponding polymers formed in moderate to good yields (66-81%) and had relatively high MW $(M_w > 1.5 \times 10^4)$.²⁰² A Ni analog, [Ni(C=CC₆H₄C=CH)₂(PPh₃)₂], gives polymers in much lower yield (less than 20%). In both cases, the poly (propargyl alcohol) and poly(propargyl ester)s formed are completely soluble in polar and nonpolar organic solvents. 3-Diethylaminophenyl propargyl ether affords a low-MW $(M_{\rm p} \sim 4 \times 10^3)$ soluble polymer. Poly(cyanoacetylene) has been prepared from the corresponding monomer using a variety of Pd and Ni catalysts such as (Ph₃P)₂PdCl₂ and $(Ph_3P)_2NiCl_2$ ²⁰³ The polymers formed have M_w of around 1×10^4 , and always contain catalyst metals as shown by elemental analysis. The catalyst system Ni(cod)2-CF3COO(allyl) polymerizes PA to give a polymer of $M_{\rm n}$ 12000 in good vield.²⁰⁴ Cyclopentadienylnickel complexes produce a mixture of polymers ($M_{\rm n} \sim 3 \times 10^3$), linear oligomers, and cyclic oligomers.¹²¹

Li *et al.*¹²⁹ reported the first well-characterized palladium catalysts such as [(diphosphine)PdCl(Me)] (diphosphine = 1,1'bis(diphenylphosphino)ferrocene (dppf), etc.) for the polymerization of PA. Active cationic species are formed by the reaction with silver triflate in the presence of CH₃CN, which polymerize PA via the insertion mechanism, judging from the presence of a methyl group in the polymer obtained (Scheme 3). Shiotsuki *et al.*²⁰⁵ applied this chemistry to the synthesis of end-functionalized poly(PA), in which an analogous series of Pd complexes, [(dppf)PdBr(R)], with AgOTf catalyze the polymerization of PA and a variety of 'R' groups of the catalysts are introduced at the end of the polymer formed.

Darkwa's group investigated a series of new Pd catalysts, 18–22, as listed in Figure 7. These Pd catalysts oligomerize or polymerize PA to from poly(PA) in moderate to high yields.



Active initiating species





Figure 7 Novel Pd catalysts bearing pyrazole/pyrazolyl ligands.

A series of catalysts (18) in conjunction with silver triflate show moderate activity in the oligomerization of PA.²⁰⁶ Catalysts 19–22 also require activation with silver triflate in the polymerization of PA. The effect of substituents (R) on the pyrazole/pyrazolyl ligands is significant, and it was observed that bulkier groups are more favorable for high monomer conversions.²⁰⁷

3.27.2.5 Group 8 Metal Catalysts

Among group 8 transition metal catalysts, iron-based Ziegler-type catalysts such as $Fe(acac)_3-Et_3Al$ (1:3) have been well known from the early stage of the catalyst investigation. They are readily prepared *in situ* to polymerize sterically unhindered terminal acetylenes such as *n*-alkyl acetylenes, *sec*-alkyl acetylenes, and PAs.^{22,24} The poly(PA) formed has red color and *cis*-cisoidal structure, and is insoluble and crystalline.

Well-defined Ru carbene catalysts, which are well known as very active catalysts for olefin metathesis reactions, have been elucidated to polymerize un- and substituted acetylenes such as α , ω -diynes, propiolic acid esters, and DPAs. Grubbs 1st, 2nd-, and 3rd- (23–25, respectively, Figure 8) generation catalysts polymerize unsubstituted acetylene.²⁰⁸ Catalyst 27, modified from Grubbs–Hoveyda Ru carbene catalyst (26) by varying the electronic nature and by steric placement of the ligand, achieves living cyclopolymerization of an α , ω -diyne.^{209,210} It is noteworthy that Grubbs–Hoveyda Ru carbene (26) can also polymerize monosubstituted acetylenes and DPAs, even in the presence of polar functional groups such as ester, amide, and carbonate in a DPA monomer.²¹¹ It has been difficult to achieve polymerization by using early transition metal catalysts including group 5 and 6 metals and Rh catalysts.

Grubbs first-generation catalyst (23), Grubbs–Hoveyda Ru carbene catalyst (26), and a series of Ru carbene complexes listed in Figure 9 catalyze the polymerization of *o*-substituted PAs such as represented by (*o*-isopropoxy)phenylacetylene.²¹² In particular, the Grubbs–Hoveyda catalyst 26 results in the highest yield (72%) of the corresponding polymer among all polymers of simple acetylenic compounds subjected to Ru-catalyzed polymerization. The substituents at the *ortho*position of PA-type monomers are assumed to serve as supportive ligands that maintain and prolong the life of unstable propagating carbene species.

3.27.2.6 Living Polymerization

It is quite important to precisely control the detailed structure and MW of polymers, because they affect specific properties and functions of the polymers. These objectives can be achieved using transition metal catalysts by designing the catalyst systems by choosing metals, ligands, and cocatalysts. As for the category of π -conjugated polymers, a limited number of examples for living polymerization have been reported. The polymerization of substituted acetylenes is one of the successful examples. It affords the tailor-made conjugated macromolecules such as end-functionalized polymers, block copolymers, star-shaped polymers. Table 4 shows typical examples of the living polymerization of substituted acetylenes. The kind of monomers undergoing living polymerization is specified by the type of catalyst. Thus appropriate catalysts must be selected in order to synthesize well-defined polymers from the individual monomers (Figure 10).

3.27.2.6.1 Living polymerization by metal halide-based metathesis catalysts

In this category, the most convenient living catalysts are group 6 transition metal chloride or oxychloride, generally expressed as MO_nCl_m -cocatalyst-ROH (M = Mo or W; n = 0 or 1; m = 5 or 4).^{22,169} While quantitative initiation efficiency is not achievable, they have the advantage of accessibility. As the first example of living polymerization of acetylene monomers, $MoCl_5$ -n-Bu₄Sn-EtOH was reported in case of 1-chloro-1-octyne as a monomer.²¹³ The poly(1-chloro-1-octyne) formed has narrow MWD ($M_m/M_n < 1.2$), and the living nature was confirmed by the linear dependence of MW on monomer conversion and by the successful initiation of the polymerization of second-charged monomers with the living prepolymer.

A molybdenum oxychloride-based catalyst system, $MoOCl_4-n$ -Bu_4Sn-EtOH, is more active than that based on $MoCl_5$.²¹⁴ In the polymerization of 1-chloro-1-octyne by the oxychloride-based catalyst, the propagation rate is increased and MWD of the polymer formed is smaller. This ternary



Figure 8 Ruthenium carbene catalysts for the polymerization of monosubstituted acetylenic monomers.



Figure 9 Bimetallic ruthenium carbene catalysts for the polymerization of *o*-substituted PA derivatives.

catalyst also induces living polymerization of ortho-substituted PAs bearing bulky groups such as CF₃, SiMe₃, and GeMe₃.²¹⁵⁻²¹⁷ The bulky ortho-substituents are essential to achieve excellent living polymerization. Actually in the case of using (o-methylphenyl)acetylene, a sterically smaller monomer, the living nature is slightly lower.²²¹ This would be because ortho-substituents preclude chain transfer and termination. It is noteworthy that a PA derivative, (4-n-Bu-2,3,5,6-tetrafluorophenyl)acetylene, which has two medium-sized ortho-substituents, also yields a polymer with low polydispersity.²¹⁸ MoOCl₄-n-Bu₄Sn-EtOH catalyst also induces the polymerization of the following disubstituted acetylenes in a living fashion: internal alkynes (e.g., 2-nonyne, 3-nonyne),²²² 1-chloro-2-phenylacetylene,²²³ and diethyl di-2-butynyl malonate $[(EtO_2C)_2C(CH_2C=CMe)_2]^{.224}$ Stereospecific living polymerization of tert-butylacetylene is possible with MoOCl₄-*n*-Bu₄Sn-EtOH, which gives a polymer with narrow MWD.²¹⁹ The *cis* content reaches 97% at low temperature (-30 °C). *Cis* content decreases when polymerization is conducted with MoOCl₄ or MoOCl₄–*n*-Bu₄Sn. A detailed NMR study of the stereoregularity of poly(*tert*-butylacetylene) showed that the cis content depends on the rate of Lewis acid-catalyzed isomerization from the *cis* to the *trans* form.²²⁵

A variety of cocatalysts such as Et_3Al ,^{226,227} Et_2Zn ,²²⁸ and *n*-BuLi^{229,230} can be used instead of *n*-Bu₄Sn. It is of interest that the addition of the third component, the protic additive, affects the initiation efficiency and block copolymerization behavior except in the case of *n*-BuLi. Initiation efficiency decreases in the order of *n*-Bu₄Sn > $Et_3Al > Et_2Zn > n$ -BuLi. Consequently, extremely high-MW polymers (>10⁵) with very narrow MWD (<1.03) are attainable by using MoOCl₄–*n*-BuLi.²²⁹ Tungsten-based multicomponent catalysts, WOCl₄–*n*-BuLi, and WOCl₄–EtMgBr,

Monomer	Catalyst ^a	Cocatalyst ^a	$M_{\rm w}/M_{\rm n}$	References
CIC≡C- <i>n</i> -C ₆ H ₁₃	28	Bu₄Sn/EtOH	1.13	213, 214
HC≡CC ₆ H ₄ - <i>o</i> -CF ₃	28	Bu₄Sn/EtOH	1.06	215
HC≡CC ₆ H ₄ - <i>o</i> -SiMe ₃	28	Bu₄Sn/EtOH	1.07	216
HC≡CC ₆ H ₄ - <i>o</i> -GeMe ₃	28	Bu₄Sn/EtOH	1.08	217
HC≡CC ₆ F ₄ - <i>p</i> -Bu	28	Bu₄Sn/EtOH	1.16	218
HC≡C- <i>t</i> -Bu ^b	28	Bu₄Sn/EtOH	1.12	219
MeC=CMe	6		1.03	171
$(HC \equiv CCH_2)_2C(CO_2Et)_2$	4a		~ 1.20	166–168
HC≡CC ₆ H ₄ - <i>o</i> -SiMe ₃	4h′		1.05	164
HC≡CPh ^c	10	DMAP	1.15	172, 173, 179
HC≡CPh ^c	29	PPh ₃ /DMAP	1.11	181
HC≡CPh ^c	7	PPh ₃ /LiC(Ph)=CPh ₂	1.14	182, 183
HC≡CPh ^c	11a		1.05	184
HC≡CPh ^c	13		1.03	186
HC≡CPh ^c	15	[/] PrNH ₂	1.09	189, 220
HC≡CPh ^c	17a	DMAP	1.20	191

Table 4	Living po	lymerization	of substituted	acetylenes
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^aSee Figure 10.

^bStereoregular (*cis* 97%) and living polymer is formed. ^cStereoregular (all-*cis*) and living polymers are formed.

have been proved to achieve controlled polymerizations of *o*-CF₃-PA, *o*-Me₃Si-PA, (4-*n*-Bu-2,3,5,6-tetrafluorophenyl) acetylene, 3-decyne, and 5-dodecyne.^{231,232}

With a half-metallocene ternary catalyst, CpMoCl₄cocatalysts–EtOH, *ortho*-substituted PAs polymerize in a living fashion, where the cocatalyst is EtMgBr, Et₃Al, and *n*-BuLi. CpMoCl₄ is more resistant to air and moisture than MoOCl₄ owing to the steric and electronic effect of Cp ligand, while the activity of CpMoCl₄-based catalysts is slightly lower and the initiation efficiency is still low (up to 13.1%).

3.27.2.6.2 Living polymerization by single-component metal carbene catalysts

In the polymerization of acetylene compounds by the metathesis mechanism, an ideal initiator composed of transition metals has a carbene ligand, which promisingly achieves precisely controlled polymerization.

A Ta vinylalkylidene complex (6), confirmed by a single-crystal X-ray analysis, was revealed to polymerize 2-butyne in living polymerization.¹⁷⁰ The initiation efficiency is quantitative, and the living end can be end-capped with aromatic aldehydes. As polymers from symmetric acetylenes are generally insoluble, soluble poly (2-butyne) is accessible if the degree of polymerization is suppressed below 200. The NMR analysis of living oligomers of 2-butyne clearly indicates that both *cis* and *trans* structures exist in the main chain.

A number of Mo carbene catalysts, bearing various modified ligands, have been reported and proven to elegantly induce living polymerization of acetylene monomers (Figure 11). The first example is the cyclopolymerization of 1,6-heptadiynes catalyzed by Mo carbenes 4a-c.^{166,167} Mo carbenes ligated by bulky imido and alkoxy groups are quite effective. In this catalyst system, the initiation efficiency of catalysts and polymerization behavior can be improved by detailed modification of the ligands as well as polymerization conditions. Consequently, a disubstituted alkylidene complex 4d gives a

relatively narrow MWD of 1.17. This would be because the initiation rate is accelerated by the modification to be close to the propagation rate. The ability of these Mo carbenes to tolerate polar functional groups permits living polymerization of functionalized monomers containing ester, sulfonic ester, and siloxy groups. End-capping of the polymers is readily accomplished using aromatic aldehydes including *p*-*N*, *N*-dimethylaminobenzaldehyde and *p*-cyanobenzaldehyde. Cyclopolymerization of 1,6-heptadiynes with **4a–d** offers polymers having both five- and six-membered cyclic structures. In contrast, **4e** and **4f**, which have bulky carboxylate ligands, produce polymers bearing only six-membered rings.¹⁶⁸

PAs bearing substituted groups on their phenyl ring have been adopted in the Mo carbene-initiated polymerization. Well-defined polymers are readily obtained with Mo carbenes 4g-i.^{164,165} Isolation of 4g-i cannot be accomplished without the addition of an appropriate base because of their instability. As in the case of metal halide-induced living polymerizations, bulky ring substituents at the *ortho*-position of monomers are required for controlled polymerization. The most characteristic feature of these polymerization systems is that all the steps including initiation and propagation can be readily monitored by an NMR technique. Eventually it was found that the alkylidene groups of 4 selectively undergo α -addition onto *o*-Me₃Si-PA, whereas the selectivity of α -addition decreases with the decrease in the bulkiness of *ortho*-substituents.

Metal-containing monomers, such as ferrocenylacetylene and ruthenocenylacetylene, have been subjected to living polymerization with Mo carbene 4j, which has bulky alkoxy ligands.²³³ Living polymers are inaccessible with 4g–i, which are suitable for *ortho*-substituted PAs. Due to the poor solubility of metal-containing polymers, the degree of polymerization must be restricted below ~40 in order to produce soluble polymers. Similar metallocene-containing monomers, HC=CC₆H₄-*o*-Fc (Fc = ferrocenyl), HC=CC₆H₄-*p*-CH=CHFc, HC=CC₆H₄-*p*-N=NFc, and HC=CC₆H₄-*p*-C=CFc, polymerize in a living manner in the presence of 4j.^{234,235}



Figure 10 Catalysts for living polymerization of substituted acetylenes.

3.27.2.6.3 Stereospecific living polymerization by Rh catalysts

Among a number of transition metal catalysts for polymerization of acetylenes, Rh catalysts can be classified as the most excellent one in terms of both stereospecificity and living nature. Rh-catalyzed living polymerization was first accomplished in 1994.¹⁷⁷ A well-characterized catalyst (9) in conjunction with DMAP demonstrated its excellent ability to offer a quantitative yield of poly(PA)s with narrow MWD. The single-crystal X-ray analysis of 9 confirmed the presence of

4a:
$$R^1 = C_6H_3 - 2, 6 - i Pr_2$$
, $R^2 = OCMe(CF_3)_2$, $R^3 = CMe_2Ph$, $R^4 = H$
4b: $R^1 = C_6H_3 - 2, 6 - i Pr_2$, $R^2 = OC(CF_3)_3$, $R^3 = CMe_2Ph$, $R^4 = H$
4c: $R^1 = 1 - Adm$, $R^2 = OCMe(CF_3)_2$, $R^3 = CMe_2Ph$, $R^4 = H$
4d: $R^1 = C_6H_3 - 2, 6 - i Pr_2$, $R^2 = OCMe(CF_3)_2$, $R^3 = Ph$, $R^4 = H$
4d: $R^1 = C_6H_3 - 2, 6 - i Pr_2$, $R^2 = OCMe(CF_3)_2$, $R^3 = Ph$, $R^4 = H$
4g: $R^1 = C_6H_4 - 2 - i - Bu$, $R^2 = O_2CPh_3$, $R^3 = CMe_2Ph$, $R^4 = H$
4g: $R^1 = 1 - Adm$, $R^2 = OCH(CF_3)_2$, $R^3 = CMe_2Ph$, $R^4 = H$
4i: $R^1 = 1 - Adm$, $R^2 = OCH(CF_3)_2$, $R^3 = CMe_2Ph$, $R^4 = H$
4i: $R^1 = 1 - Adm$, $R^2 = OCH(CF_3)_2$, $R^3 = Ph$, $R^4 = Me$
4j: $R^1 = 1 - Adm$, $R^2 = OCH(CF_3)_2$, $R^3 = Ph$, $R^4 = Me$
4k: $R^1 = C_6H_3 - 2, 6 - Me$, $R^2 = OCH(CF_3)_2$, $R^3 = CMe_2Ph$, $R^4 = H$

Figure 11 Mo carbene catalysts for living polymerization of substituted acetylenes.

phenylethynyl ligand coordinating through an σ -bond between a Rh metal center and a terminal ethynyl carbon atom. It is considered that in the initiation step of polymerization, the monomer molecule inserts into this σ -bond, and then Rh–H species would be formed via the elimination of 1,4-diphenyl-1,3-butadiene, which is actually detected experimentally.¹⁸⁰ The presence of DMAP is essential to control the polymerization process. In the absence of DMAP, the polydispersity index of the polymer formed increases to 1.3, and the gel permeation chromatography (GPC) profile gives a small new peak whose MW is twice that of the major product. The high stability of the propagation centers allows the isolation of poly(PA) having active propagation sites, which can sequentially polymerize different monomers to give precisely controlled block copolymers.

One striking feature of stereoregular polyacetylenes is their simple NMR spectral patterns, which facilitate elucidation of the polymerization mechanism as well as the polymer structure. A copolymer of PA with partly ¹³C-labeled PA (Ph¹³C=¹³CH) shows two doublet carbon signals with $J_{13C-13C}$ of 72 Hz, indicating the presence of ¹³C=¹³C bond in the polymer backbone.¹⁸⁰ This is a clear indication of the insertion mechanism instead of the metathesis pathway.

A further developed system, [(nbd)Rh(OMe)]₂–Ph₃P– DMAP, has enabled the enhancement of initiation efficiency to 70% from 35%.¹⁷² The polymerization with [(nbd)Rh (OMe)]₂–Ph₃P–DMAP is 3–4 times faster than that with 9. The isolation of [(nbd)RhOMe]₂ is unnecessary; a simple mixture of commercially available [(nbd)RhCl]₂, Ph₃P, NaOMe, and DMAP induces the living polymerization of PA without broadening the polydispersity.

A next-generation isolable catalyst is a rhodium vinyl complex (11a, 11b, and 13),^{183,186} one member of which is fully characterized by X-ray analysis.¹⁸³ Catalysts 11a and 11b give living polymers derived from PA and its *para*-substituted analogues. Living polymerization is possible even in the presence of water.²³⁶ The *in situ* formation of an analog of 11, [(nbd)Rh {C(Ph)=CPh₂}(PPh₃)], by a combination of [(nbd)RhCl]₂ (7), LiC(Ph)=CPh₂, and Ph₃P also induces living polymerization with quantitative initiation efficiency.^{182,183} A feature of this polymerization system is the ability to introduce functional groups at the initiation terminal. For example, living poly(PA) bearing a terminal hydroxy group is readily obtained using a three-component catalyst, $[(nbd)RhCl]_2$, LiCPh=C(Ph)(C₆H₄-*p*-OSiMe₂-*t*-Bu), and Ph₃P, followed by desilylation of the polymer formed. Polymerization of β -propiolactone with the terminal phenoxide anion of this polymer gives a new block copolymer of PA with β -propiolactone.²³⁷

As shown above, the tfb-coordinating Rh catalysts generally display higher activity in the polymerization of PAs than nbd analogs. Vinyl-Rh catalyst 13 polymerizes PA in a living fashion to afford polymer with the most narrow MWD (i.e., polydispersity index 1.03) reported thus far.¹⁸⁶ The other tfb-coordinating Rh cationic catalyst (15) also accomplishes the living polymerization of PA in the presence of excess ¹PrNH₂, in which an MWD of 1.09 is achieved.¹⁸⁹ The other tfb–Rh cationic complex, 17a, bearing a bidentate Ph₂PCH₂CH₂CH₂NMe₂ with BF₄ as a counteranion also displays quasi-living nature in the polymerization of PA, in which the MWD reaches 1.20.¹⁹¹

3.27.3 Monosubstituted Acetylene Polymers

Table 5 lists representative examples of polymerization of monosubstituted acetylenes, catalysts, and MWs of the polymers formed. Mo, W, and Rh catalysts, all of which involve transition metals, are particularly effective. Whereas Mo and W catalysts are sensitive to polar groups in the monomers, Rh catalysts are tolerant to such groups. Mo and W catalysts are effective toward sterically crowded monomers, while Rh catalysts are rather restricted to a particular type of monomers including propargyl esters, N-propargylamides, alkyl propiolates, and PAs. Fe and Pd complexes are also useful in some cases. It is noted that not only sterically unhindered monomers but also very crowded ones afford high-MW polymers with W and Mo catalysts. An overview of typical monosubstituted acetylene monomers such as aliphatic acetylenes, ring-substituted PAs, and other arylacetylenes is presented below.

3.27.3.1 Aliphatic Monosubstituted Acetylene Polymers

Aliphatic terminal acetylenes with *prim*- and *sec*-alkyl groups provide orange to yellow, high-MW polymers, when

Table 5 Polymerization of monosubstituted acetylenes (HC=C-R)

Monomer (R)	Catalyst	<i>M</i> _n (×10 ³)	References
Propargyl alcohol			
-{-CH ₂ OH	Pd(PPh) ₃ (C=CC ₆ H ₄ C=CH) ₂ Pd(PPh ₃) ₂ (C=CCH ₂ OH) ₂ [(cod)RhCll ₂	33 (<i>M</i> _w) 53 6	202 238 134
-{-СН(СН ₃)ОН	(nbd)Rh ⁺ BPh ₄ ⁻	21	239
Propargyl ether			
-{-{CH20-	WCI ₆	10	240
$R' = -\xi - O - C_8 H_{17}$ $-\xi - O - C - (CH_2)_m - CH_3$			
m=3−9 -ξ·CH₂O-√−−NO₂	MoCI ₅ -EtAICI ₂	480	241
-{-{-CH20-	[(nbd)RhCl] ₂	31	242
OCH_3 - $\xi CH_2O \xrightarrow{O}_{N-N} OC_8H_{17}$	[(nbd)RhCl] ₂ -Et ₃ N	26.7	243, 244
Propargyl ester			
O −ξ·CH₂O−Č−R′	$Pd(PPh)_3(C=CC_6H_4C=CH)_2$	15-21 (<i>M</i> _w)	202
$R'=CH_3,C_6H_5$			
O -{{∙CH₂O−C−R′	(nbd)Rh ⁺ BPh ₄ ⁻	4.9–40	245
$R' = CH_3, C_5H_{11}, CHBrCH_3, C_6H_5, C(C_6H_5)_3$			
$\begin{array}{ccc} & O & CH_3 \\ -\frac{1}{2} \cdot CH_2 O - \overset{C}{C} - \overset{C}{C} + \overset{C}{CH_2} \cdot CH_2 \cdot Br \\ & H & \overset{m}{C_6} H_5 \end{array}$	(nbd)Rh⁺BPh4 ⁻	16	246

OR′ OR′ -{}-CH₂O−CNHCO₂C(CH₃)₃	(nbd)Rh⁺BPh₄ ⁻	21–22	247
$R' = H, CH_3$	(nbd)Rh⁺BPh₄ [−]	47	248
-{-CH ₂ O-C-N-O		10.00	0.40
-{-{-{-{	(NDO)KU, BLU ⁴	10-30	249
О -{{-Сн(Сн ₃)О-С-R'	(nbd)Rh⁺BPh₄ ⁻	24–81	250
$R' = -\xi - CH_3, -\xi - C_5H_{11} -\xi - C(CH_3)_3 -\xi$			
О -ξ-CH(CH₃)O−C −R′	(nbd)Rh⁺BPh₄ [−]	93–141	251
$R' = -\xi - \bigvee_{N_{O}}^{N_{O}} \cdot -\xi - \bigg_{N_{O}}^{N_{O}} \cdot -\xi - \bigg_{N_{O}}^{N_{O}} \cdot -$			
$-\frac{2}{2} CH(CH_3)O - C - C + CH_2 C + CH_3 - Br + CH_3 -	(nbd)Rh⁺BPh₄ ⁻	26–136	252

Monomer (R)	Catalyst	<i>M</i> _n (×10 ³)	References
$\begin{array}{c} O CH_3 \\ H_3 \\ -\frac{1}{2} \cdot CH(CH_3)O - C - C + CH_2 \cdot CH + Br \\ CH_3 C_6H_5 \end{array}$	(nbd)Rh⁺BPh₄ [−]	33–71	253
Propargyl carbonate			
-{-{	$[(nbd)RhCl]_2-Et_3N$	19	254
0-Propargyl carbamate			
Ο H -ξ-CH₂O-C-N CO₂H	(nbd)Rh⁺BPh₄ [−]	4.8	255
Р′ О Н Р′ -ξ-СНО-С−N−С−R‴ Н	(nbd)Rh⁺BPh₄ [−]	13–191	256
$R' = H, CH_3, R'' = C_5H_{11}, CO_2C_3H_7$			
Propargylamine			
-ξ-CH ₂ N(CH ₃) ₂	$Pd(PPh_3)_2[C=\!\!CCH_2N(CH_3)_2]_2$	15	238
-ξ-CH ₂ N -ξ-CH ₂ N -ξ -ξ'-CH ₂ N -ξ'-CH ₂ N -ζ'-CH ₂ N -ξ'-CH ₂	[(nbd)RhCl]₂–Et₃N MoCl₅–Bu₄Sn	47–240 18–53	257
-ξ-CH ₂ N	MoCl ₅ , WCl ₆	Insoluble	258

-{-E-CH2N	[(nbd)RhCl]₂–Et₃N MoCl₅–Ph₄Sn	9.1 148	259
C(CH ₃) ₃			
N-Propargylamide			
H O -{-{	(nbd)Rh⁺BPh₄ ⁻	6.5–2.6	260, 261
m = 0-7			
H O -{-{CH ₂ -N-C-R'	Ph Ph	5.0–44	262
$R' = CH(CH_3)_2, CH_2CH(CH_3)_2, C_5H_{11}$	P(4-FC ₆ H ₅) ₃		
H O H O - ξ -CH ₂ -N-C-C ₄ H ₉ / - ξ -CH ₂ -N-C-C ₈ H ₁₇	(nbd)Rh⁺BPh₄ ⁻	10–20	263
H O -{-{CH ₂ -N-C-R'	(nbd)Rh⁺BPh₄ ⁻	18–25	264
R'= 2			
H O	(nbd)Rh⁺BPh₄ [−]	15–57	265
$R' = CH_3, C_2H_5, C_3H_7$			
H O - - {-CH ₂ -N-C-CH(C ₂ H ₅)C ₄ H ₉	$(nbd)Rh^+BPh_4^-$	18	266

Table 5	(Continued)
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Monomer (R)	Catalyst	<i>M</i> _n (×10 ³)	References
H O -{-{CH ₂ -N-C-R'	(nbd)Rh⁺BPh₄ [−]	19–32	267, 268
· <u></u> ² / ₂ ····································			
H O -{{-CH ₂ -N-C-R'	$(nbd)Rh^+BPh_4^-$ $(nbd)Rh^+BPh_4^-$ (emulsion polymerization)	12–15 10	269 270
H O -§-CH ₂ -N-C-R'	(nbd)Rh⁺BPh₄ [−]	15–20	271
$R' = -\xi \xrightarrow{O} / -\xi \xrightarrow{O'} or $			

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Monomer (R)	Catalyst	<i>M</i> _n (×10 ³)	References
$-\frac{H}{\xi} - CH_2 - N - C$	(nbd)Rh⁺BPh4 [−]	13	288
Н О -{{-CH2-N-C-R'	(nbd)Rh⁺BPh4 [−]	11–21	289
$R' = \bigvee_{CO_2CH_2C_6H_5}^{2^5} \bigvee_{CO_2CH_2C_6H_5}^{NHCO_2C(CH_3)_3} \bigvee_{CO_2CH_2C_6H_5}^{2^5} \bigvee_{CO_2CH_2C_6H_$			
$H O$ $I = -\xi - CH_2 - N - C \sum_{i=1}^{N} NHCO_2C(CH_3)_3$	$(nbd)Rh^+BPh_4^-$	7.0–11	290, 291
$(CH_2)_m$ HCO_2CH_2			
$-\xi - CH_2 - N - C $ $(CH_2)_m$ $NHCO_2C(CH_3)_3$			
<i>m</i> =3, 4			
$-\frac{H}{2} - \frac{H}{N} - H$	(nbd)Rh⁺BPh₄ [−]	8.1–9.3	292
$R' = CH_3, CH_2CH_2CO_2CH_2C_6H_5$			

+ $O+$ $+$ $+$ $+$ $+$ $+$ $+$ $+$ $+$ $+$	(nbd)Rh⁺BPh₄ [−]	9.6–25	293
(CH ₂) _m CO ₂ -			
<i>m</i> =1,2			
	(nbd)Rh⁺BPh₄ ⁻	12	294
CO ₂ CH ₂ C ₆ H ₅			
	[(nbd)RhCl] ₂ -Et ₃ N	8–87	295
$R' = CH_3, CH(CH_3)_2, CH_2CH(CH_3)_2, CH_2C_6H_5, C_6H_5$			
$H O \qquad $	$(nbd)Rh^+BPh_4^-$	17–24	296
$-\xi$ -CH ₂ -N-C O F O F O F O F O F O F O F O F O F O			
$R' = CH_3, C_6H_5$			
$R'' = C(CH_3)_3, -\xi - C(CH_3)_3$			
Ċ(CH ₃) ₃			

Monomer (R)	Catalyst	<i>M</i> _n (×10 ³)	References
-§-CH ₂ -N-C - ¹ / _R ,	[(nbd)RhCl] ₂ Et ₃ N	10–210	297
$ \begin{array}{l} {\sf R}' = {\sf CH}_3, {\sf CH}_2{\sf C}_6{\sf H}_5 \\ {\sf R}'' = {\sf C}_2{\sf H}_5, {\sf C}_4{\sf H}_9, {\sf C}({\sf CH}_3)_3, {\sf CH}_2{\sf C}_6{\sf H}_5, {\sf CH}({\sf C}_6{\sf H}_5)_2, \\ {\sf C}({\sf C}_6{\sf H}_5)_3, {\sf CH}_2{\sf CH}_2{\sf C}6{\sf H}_5, {\sf 1}, {\sf 4}\text{-}{\sf C}_6{\sf H}_4\text{-}{\sf C}_6{\sf H}_{13} \end{array} $			
H O -{}-CH ₂ -N-C -	(nbd)Rh⁺BPh₄ ⁻	14	298
$-\xi - CH_2 - N - C - N - N - N - N - N - N - N - N$	[(nbd)RhCl] ₂ —Et ₃ N	7–44	299
$R' = CH_3, CH_2C_6H_5, C_6H_5$ $R'' = H, C_6H_{13}$			
	[(nbd)RhCl] ₂	8	251
$-\xi$ -CH ₂ -N-C N-O	(nbd)Rh⁺BPh₄ ⁻	Insoluble	248
$-\xi - CH_2 - N - C - N - C - N - O$	(nbd)Rh⁺BPh₄ [−]	1.5–3.7	249

H O -{{-CH ₂ -N-C-OR'	[(nbd)RhCl] ₂	52	254
H O -{-CH2-N-C-OR'	[(nbd)RhCl] ₂	24–52	300
N-Propargylurea			
H O H I II I -{{-C-N-R'	(nbd)Rh⁺BPh₄ ⁻	25–38	301
$R'=-\xi^{-}C_{2}H_{5}-\xi^{-}\hspace{-1.5cm}-\xi^{-}}$			
	(nbd)Rh⁺BPh₄ ⁻ (nbd)Rh⁺BPh₄ ⁻ (emulsion polymerization)	13 14	302 303
H O - ξ -CH ₂ -N-C-N			
-§-CH ₂ -N-C-N	(nbd)Rh⁺BPh₄ [−]	14	303
H O H N C - N N N	(nbd)Rh ⁺ BPh ₄ ⁻ (emulsion polymerization)	56	274

Monomer (R)	Catalyst	<i>M</i> _n (×10 ³)	References
H O -ξ-CH ₂ -N-C-N	(nbd)Rh⁺BPh₄ ⁻	0.4	304
N-Propargy/phosphonamidate /	(nbd)Rh⁺BPh₄ [−]	5.6–12	305–307
$ \begin{array}{c} H & O \\ I & II \\ -\xi - CH_2 - N - P - O \\ R' \\ R' \end{array} $			
$R' = CH_3, C_2H_5, C_3H_7, C_6H_5$			
N-PropargyIsulfamide			
$-\frac{H}{\xi} - CH_2 - N - S - R'$	(nbd)Rh⁺BPh₄ ⁻	3–15	308
$R'_{=} -\xi - (CH_2)_x H$ $x = 2-4, 8$			
$-\xi - (CH_2)_y H y = 0 - 3$			
-\$-			
-{-{-{	(nbd)Rh ⁺ BPh ₄ ⁻ (emulsion polymerization)	16	303

Other monosubstituted alkylacetylene derivatives



Table 5	(Continued)
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Monomer (R)	Catalyst	<i>M</i> _n (×10 ³)	References
-ξ-(CH ₂) _m O-С-О- m=2-5	(nbd)Rh⁺BPh₄ [−]	6.4–28	315
H O -{{- CH ₂ CH ₂ -N-C-R'	$[(nbd)RhCl]_2$ -Et ₃ N, (nbd)Rh ⁺ BPh ₄ ⁻	9–22	314, 316, 317
R'= 32			
H O H -{-{−}CH₂CH₂CH₂-N−C	$(nbd)Rh^+BPh_4^-$	11	314
$\begin{array}{c} O\\ H\\ P(OC_2H_5)_2\\ I\\ -\xi\text{-}CH_2CHCO_2C_2H_5 \end{array}$	WCI ₆ EtAICI ₂	9	318
÷ ⊖ -ξ·CH₂PPh₄ BPh₄	MoCl ₅ –Ph ₄ Sn	12	319
$(C_2H_5)_2N$ - $\{-(CH_2)_3-C-0-(N(C_2H_5)_2)$	(nbd)Rh⁺BPh₄ ⁻	14.2 (<i>M</i> _w)	320

-§-(CH ₂) ₈ -C-O-C-R'	(nbd)Rh⁺BPh₄ ⁻	16–22	321
$R' = -\frac{\xi}{\xi} \cdot (CH_2)_3 - \frac{H}{\xi} - \frac{O}{\xi} - CH_2 - \frac{H}{\xi} - \frac{O}{\xi} - CH_2 - $			
	[(nbd)RhCl] ₂ Et ₃ N	15	322
-{{-(CH ₂) ₈ -C-O-(CH ₂) ₂ -N			
$-\xi - (CH_2)_8 - C - N - SC_8H_{17}$	(nbd)Rh⁺BPh₄ [−]	16	323
Propiolate $-\xi$ -C-O(CH ₂) ₆ -O-C-U-OC ₇ H ₁₅	[(nbd)RhCl] ₂	354 (<i>M</i> _w)	324

Monomer (R)	Catalyst	<i>M</i> _n (×10 ³)	References
	[(nbd)RhCl] ₂ MoOCl ₄ Bu ₄ Sn [(nbd)RhCl] ₂	250 18 110	325 326
$ \begin{array}{c} O \\ -\xi \cdot C - O \end{array} $	[(nbd)RhCl]₂ MoOCl₄–Bu₄Sn	21–80 5.1–130	327 328
О -{-{-С-ОС ₆ H ₁₃		20–43	211
Propiolamide			
О Н -§-С-N-R'	(CH ₃) ₃ COK (PhCN) ₂ PdCl ₂	1.9–10 1–3	329 330
$H = C_4 \Pi_9$, $C(C \Pi_3)_3$, $C_8 \Pi_{17}$, (S)-CH(CH ₃)C ₆ H ₅ , C ₆ H ₅			
Propiolonitrile			
-ξ-CN	$(Ph_3P)_2NiCl_2$	9	203
Enylacetylene			
-§-	$[(nbd)RhCl]_2-Et_3N$	24	331
Ethynylacetylene			
-§	WCI ₆ –Ph ₃ Bi	4	332

Phenylacetylene derivatives





 $\mathsf{R}\!=\!\mathsf{H},\,\mathsf{CH}_2\mathsf{CH}(\mathsf{CH}_3)_2,\,\mathsf{CH}_2\mathsf{CH}_2\mathsf{CO}_2\mathsf{C}_8\mathsf{H}_{17},$

CH₂CH₂CO₂-





R′=H, C(CH₃)₃, Si(CH₃)₃, F

See Section 3.27.2

$\label{eq:cac} \begin{array}{l} \mbox{Fe}(acac)_3-Et_3Al \\ [(nbd)RhCl]_2-Et_3N \\ MOCl_5-Bu_4Sn \\ WCl_6-Ph_4Sn \end{array}$	39-higher than the exclusion limit 240-higher than the exclusion limit 4.4-14 3.5-7.4	333
[(nbd)RhCl] ₂ Et ₃ N	116	334
(nbd)Rh ⁺ BPh ₄ ⁻	16–55	335





3–205

187

Monomer (R)	Catalyst	<i>M</i> _n (×10 ³)	References
-§-	Various Ru carbene complexes	-39	212
$ \begin{array}{l} {\sf R}' = {\sf OCH}({\sf CH}_3)_2, \ {\sf CO}_2{\sf C}_2{\sf H}_5, \ {\sf F}, \ {\sf CF}_3, \ {\sf Si}({\sf CH}_3)_3, \\ (S){\rm -}{\sf CO}_2{\sf CH}_2{\sf CH}({\sf CH}_3){\sf C}_2{\sf H}_5, \\ (S){\rm -}{\sf OCH}_2{\sf CH}({\sf CH}_3){\sf C}_2{\sf H}_5 \end{array} $			
H ₃ C -ξ-C(CH ₃) ₃	$W(CO)_6$ - CCI_4 - h_V	1400	336
H ₃ C	[(nbd)RhCl] ₂	2500 (<i>M</i> _w)	337
-ξ-(CH ₃) ₃	[(nbd)RhCl] ₂	2100 (<i>M</i> _w)	338
-ξ	WOCl ₄	19	339
-ई-	[(nbd)RhCl] ₂	1160	340
−ξ-⟨−−OR′ − −ξ-⟨−−OC _m H _{2m+1}	[(nbd)RhCl] ₂ –(<i>S</i>)- or (<i>R</i>)- <i>N</i> , <i>N</i> -dimethylphenylethylamine	204–869 (<i>M</i> _w)	341





Monomer (R)	Catalyst	<i>M</i> _n (×10 ³)	References
$-\xi \cdot X \longrightarrow O + O + O + O + O + O + O + O + O + O$	[(cod)RhCl]₂–(<i>S</i>)- or (<i>R</i>)-phenylethylamine, (nbd)Rh⁺BPh₄ [−] –(<i>S</i>)- or (<i>R</i>)- phenylethylamine–Cul	22–800 (<i>M</i> _w)	346, 347
-§-{-}-0	[(nbd)RhCl] ₂ Et ₃ N	72	348
$-\xi$ OH C_mH_{2m+1}	[(nbd)RhCl] ₂ Et ₃ N	57–81	349, 350
$-\xi$ OH C_mH_{2m+1} $m=4, 10, 11$			
$-\xi - (CH_2O)_2 - R'$	[(nbd)RhCl] ₂	2–273 (<i>M</i> _w)	351
R'=H, (CH ₂) ₂ OH, (CH ₂) ₂ OSO ₂ CH ₃ ,			
$(CH_2)_2OSO_2$ CH_3			
(CH ₂) ₂ OSi(CH ₃) ₃ , (CH ₂) ₂ Cl			



Monomer (R)	Catalyst	<i>M</i> _n (×10 ³)	References
	(nbd)Rh⁺BPh₄ ⁻	10–35	355
<i>m</i> =1−3 −ξ-√OR′	(nbd)Rh⁺BPh4 [−]	174–1430 (<i>M</i> _w)	356
$R' = \frac{AcO}{AcO} \frac{OAc}{AcO} \frac{AcO}{AcO} \frac{OAc}{AcO} \frac{AcO}{AcO} \frac{\xi}{\xi}$			
$\begin{bmatrix} O \\ ACO $			
$-\xi$ $O(CH_2)_{10}$ $C-N$ SH CdS nanorod	[(cod)RhCl] ₂	-	357
$-\xi$ $O(CH_2)_m$ $m=3, 6, 8$	[(nbd)RhCl] ₂ –Et ₃ N	94–148	358




$-\xi \xrightarrow{CH_3}_{I} \xrightarrow{O}_{CH_3} \xrightarrow{O}_{I} \xrightarrow{O}_{CH_3} \xrightarrow{O}_{I} \xrightarrow{O}} \xrightarrow{O}_{I} \xrightarrow{O}_{I} \xrightarrow{O}_{I} \xrightarrow{O}_{I} \xrightarrow{O}_{I}} \xrightarrow{O}_{I} \xrightarrow{O}_{I} \xrightarrow{O}_{I} \xrightarrow{O}} \xrightarrow{O} \xrightarrow{O}_{I} \xrightarrow{O} \xrightarrow{O} \xrightarrow{O}_{I} \xrightarrow{O} \xrightarrow{O} \xrightarrow{O}} \xrightarrow{O} \xrightarrow$	[(nbd)RhCl] ₂ -KN(SiCH ₃) ₃	1135–5700	367
	[(nbd)RhCl] ₂	48	368
-{-{K'	[(nbd)RhCl] ₂	-	369
$R' = NH_2, N(CH_3)_2, CH_2NH_2, CH_2N[CH(CH_3)_2]_2$			
-{-\NH_2	$PdCl_2$, $PtCl_2$, $RuCl_3$, (nbd) $PdCl_2$	-	370
$-\xi$ $N(C_4H_9)_2$	[(nbd)RhCl] ₂ -Et ₃ N	>1000	371
$-\xi \xrightarrow{N_3} R' = \underbrace{\gamma_2} \xrightarrow{OH} OH \xrightarrow{\gamma_2} C_5 H_{11}$ NHR' (R)-, (S)- (R)-, (S)-	[(nbd)RhCl] ₂ Et ₃ N	160	372
-§-\N	[(nbd)RhCl] ₂ Et ₃ N	974 84 (<i>M</i> _w)	373 374

Monomer (R)	Catalyst	<i>M</i> _n (×10 ³)	References
	[(nbd)RhCI] ₂ Et ₃ N	76	375
	[(nbd)RhCl] ₂ Et ₃ N	12 (<i>M</i> _w)	374
-§-{\	[(nbd)RhCl] ₂ Et ₃ N WCl ₆ Bu ₄ Sn	Insoluble 104	376
$-\xi$ m, p - m, p - m-, p - m-, p - m-, p - m-, p - m-, p - m-, p - m-	[(nbd)RhCl] ₂ Et ₃ N	1.9–115	377

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$-\xi$ $-\xi$ $-\xi$ $-\xi$ $-\xi$ $-\xi$ $-\xi$ $-\xi$	[(nbd)RhCl]₂–Et₃N WCl ₆ –Bu₄Sn	212–240 3–44	378
$-\frac{1}{2}$	[(nbd)RhCl]₂–Et₃N WCl ₆ –Bu₄Sn	9–74 30–94	379
$-\xi - \underbrace{N \bigoplus}_{CI} \bigcirc \underbrace{\bigoplus}_{Br} \bigcirc N - (CH_2)_5 CH_3$	None	-	380
$= \frac{1}{2} - $	[(nbd)RhCl] ₂ Et ₃ N	6.4–1280 (<i>M</i> _w)	381
$-\xi = \sqrt{\frac{0}{N-N}} - OC_m H_{2m+1}$	[(nbd)RhCl] ₂ Et ₃ N	25.4–29.3	382, 244
m = 4, 8, 10 $m = 4, 8, 10$ $m = 4, 8, 10$ $m = 4, 8, 10$	Schrock carbene	-	383

Monomer (R)	Catalyst	<i>M</i> _n (×10 ³)	References
	[(nbd)RhCl] ₂ Et ₃ N Schrock carbene	110 5.2–6.8	384
-{-{-}-{-}-{-}-{-}-{-}			
-{- N N R'	[(nbd)RhCl]2Et ₃ N	16–104	385
$R' = OC_4H_9, CO_2C_6H_{13}$			
$-\xi$ N	[(nbd)RhCl] ₂ Et ₃ N	76 (<i>M</i> _w)	386
-§-{	$\label{eq:cod} $$ [(cod)RhOCH_3]_2$ \\ $$ Mo[OC(Me)(CF_3)_2]_{=}N(2,6-i-Pr_2C_6H_3)$ \\ $$ =CHCMe_2Ph$ \\ $$ EHCMe_2Ph$ \\ $$ CHCMe_2Ph$ \\ $$ The expected of th$	15–100 9	387 388
$R' = H, CH_3, t-Bu, F, Br, CN, NO_2, N(CH_3)_2, C \equiv CSi(CH_3)_3$			
	[(nbd)RhCl] ₂ Et ₃ N	227–594	389
<i>m</i> - or <i>p</i> -, $R' = H$, $C(CH_3)_3$			
-{-NO2	[(cod)RhCl] ₂ [(nbd)RhCl] ₂	16 2	390 391
$-\xi - V = -$	[(nbd)RhCl] ₂	320–760	392
$R' = -\xi$			

$-\xi - K' - C - N - C - OCH_3$ CH ₂ CH(CH ₃) ₂	[(nbd)RhCl] ₂	20–1240 (<i>M</i> _w)	393
$R' = -, -O(CH_2)_{10}-$			
	$ \{ Mo[OC(Me)(CF_3)_2]_2 = N(2,6-Me_2C_6H_3) \\ = CHCMe_2Ph \} $	11–19	234
<i>o</i> - or <i>p</i> - X = –, –CH=CH–, –N=N–			
-§-	[(nbd)RhCl] ₂ Et ₃ N	6–20	394
$R' = OC_4H_9, OC_{10}H_{21}, OC_{16}H_{33}, NO_2$			
	[(nbd)RhCl] ₂ Et ₃ N	530 (<i>M</i> _w)	395
-ξ-\N	[(nbd)RhCl] ₂ Et ₃ N	18	374
(C ₂ H ₅) ₂ N	(nbd)Rh ⁺ BPh ₄ ⁻	53.1 (<i>M</i> _w)	320
-§-N(C ₂ H ₅) ₂			
-{	[(nbd)RhCl] ₂ -Et ₃ N	-	396

Monomer (R)	Catalyst	<i>M</i> _n (×10 ³)	References
	WCI ₆ –Et ₃ SiH	122–469 (<i>M</i> _w)	397
$R' = H, CH_3, CH(CH_3)_2$			
-{-{	$[(\text{cod})\text{Rh}(\mu\text{-OMe})]_2$	31–43	398, 399
-{-{-}-{-}{-}			
(H ₃ C) ₃ Si	$[(nbd)RhCl]_2-Et_3N$	340	400
Si(CH ₃) ₃			

(H₃C)₃Si

-Si(CH₃)₃



Monomer (R)	Catalyst	<i>M</i> _n (×10 ³)	References
H NHCO ₂ C(CH ₃) ₃	(nbd)Rh⁺BPh₄ [−] , [(nbd)RhCl] ₂ –Et ₃ N	14–29	405
$ \begin{array}{c} & & & \\ & & & \\ & & & \\ & & & \\ -\xi - & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & &$	(nbd)Rh⁺BPh4 ⁻ , [Rh(cod)Cl]2	11–113	323
$R'=H, -\xi - C - CH_3$			
$-\xi \xrightarrow{H O H O C_2H_5}_{N-C-N} \xrightarrow{OC_2H_5}_{N-C}$	(nbd)Rh⁺BPh₄ [−]	150–360	406, 407
$R' = CH_3, CH_2CH(CH_3)_2, CH(CH_3)C_2H_5, CH_2C_6H_5, CH_2CO_2C_2H_5, CH_2CO_2C_2H_5, CH_2CO_2C_2H_5$			
-ई-С-он	Heat Hydrolysis of the ester precursor	n.d. -	408 409–411
-ξО С-осн ₃	(nbd)Rh ⁺ BPh ₄ ⁻	218	174
$-\xi$ C	[(nbd)RhCl] ₂	-	409

$-\xi$ $-\xi$ C $-O\left(CH_2CH_2O\right)$ CH_3	[(nbd)RhCl] ₂ Et ₃ N	5.4–47	412
$-\xi - C - O - CH_2CH_2OCH_2CH_2CH_2CH_2Si - CH_3 - CH_3 - C_4H_9 $	[(nbd)RhCl] ₂ -Et ₃ N	207–349	413
	[(nbd)RhCl] ₂ Et ₃ N	161–776	414
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			
-ξ-([(nbd)RhCl] ₂ Et ₃ N	122	415
$-\xi - \underbrace{ \begin{array}{c} O \\ H \\ - \end{array} } \underbrace{ \begin{array}{c} C \end{array} } \underbrace{ \begin{array}{c} C \\ - \end{array} } \underbrace{ \begin{array}{c} C \end{array} } \underbrace{ \begin{array}{c} C \end{array} } \underbrace{ \begin{array}{c} C \end{array} } \\ \\ \end{array} } \underbrace{ \begin{array}{c} C \end{array} } \underbrace{ \begin{array}{c} C \end{array} } \underbrace{ \begin{array}{c} C \end{array} } \underbrace{ \end{array} } \\ \\ \\ \end{array} } \underbrace{ \begin{array}{c} C \end{array} } \underbrace{ \begin{array}{c} C \end{array} } \underbrace{ \end{array} } \underbrace{ \begin{array}{c} C \end{array} } \\ \\ \end{array} } \underbrace{ \begin{array}{c} C \end{array} } \underbrace{ \end{array} } \\ \\ \\ \end{array} } \underbrace{ \begin{array}{c} C \end{array} } \underbrace{ \end{array} } \underbrace{ \begin{array}{c} C \end{array} } \underbrace{ \end{array} } \\ \\ \end{array} } \underbrace{ \begin{array}{c} C \end{array} } \\ \\ \\ \end{array} \end{array} } \underbrace{ \begin{array}{c} C \end{array} } \underbrace{ \end{array} } \\ \\ \end{array} \\ \end{array} \\ \end{array} \\ \\ \end{array} \end{array} } \underbrace{ \begin{array}{c} C \end{array} } \underbrace{ \end{array} } \\ \\ \end{array} $ } \begin{array}{c} C \end{array} \\ \\ \end{array} \\	[(nbd)RhCl] ₂ Et ₃ N	1300	416
$-\xi$ C $-O$ $(CH_2)_4$ $-O$ C F_e F_e	[(nbd)RhCl] ₂ Et ₃ N	647	361
$-\xi - \int_{-\frac{1}{2}}^{0} - O(CH_2)_m O - \int_{-\frac{1}{2}}^{0} - CN$ $m = 6, 12$	[(nbd)RhCl] ₂ Et ₃ N	27–158 (<i>M</i> _w)	417

Monomer (R)	Catalyst	<i>M</i> _n (×10 ³)	References
-§	(nbd)Rh⁺BPh₄ [−]	Insoluble	418
$R' = OC_5H_{11}, -\xi O-C - OC_5H_{11}$			
-§-	(nbd)Rh⁺BPh₄ [_]	169	360
$-\xi - \sum_{m=2,8}^{O} \sum_{n=1}^{N-N-N} \sum_{n=1}^{N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-$	[(nbd)RhCI] ₂ Et ₃ N	64–71 (<i>M</i> _w)	419
NO ₂			
	[(nbd)RhCl] ₂ Et ₃ N	285	322
$-\xi$ O $N-C_3H_7$ O			

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Monomer (R)	Catalyst	<i>M</i> _n (×10 ³)	References
$-\xi$ CO_2CH_3	[(nbd)RhCl] ₂	1201 (<i>M</i> _w)	423
$-\xi - \underbrace{ \begin{array}{c} O & H \\ H & H \\ C & -N \\ C & C \\ C & H_3 \end{array} }_{(R)^-, (S)^-, (R/S)^-} CO_2 C_{10} H_{21} \\ C & C	[(nbd)RhCl] ₂ -Et ₃ N	465–774 (<i>M</i> _w)	424–427
$-\xi$ CO_2CH_3 \dot{E} $CH(CH_3)_2$	[(nbd)RhCl] ₂ [(nbd)RhCl] ₂ Et ₃ N	370 (<i>M</i> _w) 371 (<i>M</i> _w)	428 429, 430
$-\xi$ CO_2CH_3 (R)-, (S)-	[(nbd)RhCl] ₂	-	431
$-\xi \xrightarrow{O} \stackrel{H}{\underset{i}{\overset{H}{\underset{i}{\overset{i}{\underset{i}{\overset{i}{\underset{i}{\underset{i}{\overset{i}{\underset{i}{\underset$	(nbd)Rh⁺BPh₄ [−]	280	432
$-\xi$ $-\xi$ C-N C-N C-N C-N $CO_2C_2H_5$ $CH_2CH_2CO_2C_2H_5$ $CH_2CH_2CO_2C_2H_5$ $CH_2CH_2CO_2C_2H_5$	[(nbd)RhCl]2–Et3N	415–674	433



Monomer (R)	Catalyst	<i>M</i> _n (×10 ³)	References
$-\xi \xrightarrow{O}_{H} \xrightarrow{O}_{O} \xrightarrow{O}_{NH_{4}} \xrightarrow{O}_{H}$	[Rh(cod) ₂]BF ₄	-	440
$-\xi \xrightarrow{O}_{I} \xrightarrow{H}_{I} \xrightarrow{CO_2C_2H_5} \xrightarrow{CO_2C_2H_5} \xrightarrow{CO_2C_2H_5}$	(nbd)Rh ⁺ BPh₄ [−]	190	441
$-\xi \xrightarrow{O}_{I} \xrightarrow{H}_{I} \xrightarrow{CO_2C_2H_5}_{H'} \xrightarrow{CO_2C_2H_5}_{H'}$	(nbd)Rh ⁺ BPh₄ [−]	35–250	442
$R' = CH_3, CH_2CH(CH_3)_2, CH(CH_3)C_2H_5, CH_2C_6H_5, CH_2CO_2C_2H_5, CH_2CO_2C_2H_5, CH_2CO_2C_2H_5$			
Other monosubstituted arylacetylene derivatives			
-\$-\$-	WCl ₆ -Ph ₃ Bi	46	443
$r^{s^{2}}$	WCl ₆ Ph ₄ Sn	9–37	444





Monomer (R)	Catalyst	<i>M</i> _n (×10 ³)	References
-Si	NbCl5Ph4Sn	69 (<i>M</i> _w)	313
-§-N	WCl ₆ -Bu ₄ Sn [(nbd)RhCl] ₂ -Et ₃ N	9.3 Insoluble	452
$-\frac{3}{R'} \xrightarrow{2} R'$ R' $2 - \text{ or } 3 - R'$	Rh(C=CPh)(nbd)(PPh ₃) ₂	800–1150	453
$H = -\frac{1}{2} \cdot C_{13} H_{27}$ $\frac{1}{2} \cdot C_{8} H_{17}$	[(nbd)RhCl] ₂	160	454

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Monomer (R)	Catalyst	<i>M</i> _n (×10 ³)	References
0 N-C-O-R' 2- or 3-	(nbd)Rh⁺BPh₄ ⁻	12–92	457
R' =			
H_3C $-\xi \ll CN$ N CN CN	[(nbd)RhCl] ₂	3	458
S S S S	[(nbd)RhCl] ₂ Et ₃ N	12	459
$-\xi \longrightarrow M = Fe \text{ or } Ru$	Mo[OC(Me)(CF ₃) ₂] ₂ =N(2,6-Me ₂ C ₆ H ₃) =CHCMe ₂ Ph (nbd)Rh ⁺ BPh ₄ ⁻	15–16	233 460

polymerized with iron alkanoate-organoaluminum catalysts. On the other hand, tert-alkylacetylenes, which are sterically very crowded, can be polymerized by Mo and W catalysts, and the MWs of the polymers reach several hundred thousands. Many examples of polymerizations of heteroatom-containing acetylenes have been reported. The heteroatoms include Si, halogens, O, S, and N. Especially, Si and F endow the polymers with unique properties and functions, and they are unlikely to deactivate polymerization catalysts. Hence the synthesis of Siand F-containing polyacetylenes has been examined extensively. For instance, (trimethylsilyl)acetylene is polymerizable with W catalysts, but the polymer product is partly insoluble in any solvent. (Perfluoroalkyl)acetylenes yield white polymers soluble in only fluorine-containing solvents. Recently, many monomers containing ether, ester, amide, carbamate, and sulfamide groups have successfully been polymerized by using Rh catalysts, mostly [(nbd)RhCl]₂ and (nbd)Rh⁺BPh₄⁻. While Rh catalysts can polymerize monomers having OH group, COOH group terminates the Rh-catalyzed polymerization. Late transition metals such as Ru, Rh, and Pd are not oxophilic and so they will be useful as catalysts for the polymerization of highly polar monomers. If highly active Ru and Pd catalysts are developed, they will be very useful.

3.27.3.2 Aromatic Monosubstituted Acetylene Polymers

The polymerization of PA and its ring-substituted derivatives is extensively studied due to the high polymerizabilities. The typical catalysts include W, Rh, and Fe catalysts. W catalysts produce an auburn polymer having *trans*-rich structure; WCl₆-Ph₄Sn is highly active, while W(CO)₆-CCl₄-hv is useful to achieve high MW ($M_n \sim 1 \times 10^5$). The polymerization by Rh catalysts proceeds in alcohols and amines to form a yellow polymer. A feature of Rh catalysts is high tolerance to polar groups, and hence they are useful for various PAs with functional groups. Another feature of Rh catalysts is that they give poly(PA) whose MW reaches up to around one million. When Fe(acac)₃-Et₃Al is used, the poly(PA) formed is insoluble in any solvent and has *cis*-cisoidal structure.

An interesting trend has been observed so far in the polymerization of ortho-substituted PAs by W and Mo catalysts: PA itself does not produce very high-MW polymer with W and Mo catalysts (MW < 10^5). On the other hand, PAs having bulky CF₃ and Me₃Si groups at the ortho-position provide polymers whose MW is as high as about one million and in high yields. Thus, the steric effect of the ortho-substituents greatly affects the polymerizability of PAs and the MW of the polymer formed, while the electronic effect hardly influences them. For a similar steric reason, (p-t-butyl-o,o-dimethylphenyl)acetylene, an orthodimethyl-substituted PA, also polymerizes into high-MW polymer with W and Mo catalysts. Unlike W and Mo catalysts, Rh catalysts are not suitable for ortho-substituted PAs because Rh catalysts are rather sensitive to the steric effect. Instead, Rh catalysts are suitable for various PAs having polar groups (e.g., ether, ester, amine, carbazole, imine, nitrile, azobenzene, nitro groups) at the *para*-position, resulting in the formation of high-MW poly(PA)s. Many such examples are given in Table 5.

Various polymers have been prepared from monosubstituted acetylenes having condensed aromatic rings instead of phenyl group. Such condensed aromatic rings include naphthyl, anthryl, phenanthryl, fluorenyl, pyrenyl, and so on. These monomers polymerize with W, Mo, and Rh catalysts, where the polymer yield usually decreases in the order of W>Mo>Rh. The *cis* content of the polymers increases in the order of W<Mo<Rh, and the polymer solubility decreases in this order. Both 1- and 2-naphthylacetylenes polymerize in high yields with W catalysts. 9-Anthrylacetylene polymerizes with W catalysts into a polymer insoluble in any solvent. However, if a long *n*-hexoxycarbonyl group is introduced at the 10 position, the polymer formed becomes soluble. This polymer has dark purple color. 1- and 2-Anthrylacetylens are sterically less hindered and the polymers formed are solvent soluble. These polymers having condensed aromatic rings are generally deeply colored (dark brown to dark purple) and show third-order nonlinear optical properties.

Examples of polyacetylenes whose main chain is directly bonded to heteroaromatic rings (e.g., silole, carbazole, imidazole, tetrathiafulvalene, ferrocene) are increasing. Such polymers are usually obtained by one of W, Mo, and Rh catalysts. The polymers formed are expected to display interesting (opto)electronic properties such as electrochromism, cyclic voltammetry, and electroluminescence.

3.27.3.3 Helical Polymers of Monosubstituted Acetylenes

The helix is the most common regulated higher order structure of macromolecules. Many sophisticated functions and intricate biological activities of biomacromolecules largely depend on their well-ordered helical structures. Since the discovery of helical structure of isotactic polypropylene,⁴⁶¹ various types of helical polymers have been synthesized. 43,462-464 Among them, conjugated helical polymers such as polyisocyanides,⁴⁶⁵ polysilanes,^{466–468} and polyacetylenes are intensively studied because of their unique functions based on the helical structures as well as conjugated main chains. Helical polymers of monosubstituted acetylenes were first synthesized with an Fe catalyst.⁴⁶⁹ After the development of Rh(I) complexes^{96,174,470} and [Rh(nbd)Cl]2-triethylamine471 as catalysts for PA polymerization, they are most commonly used for stereospecific polymerization of monosubstituted acetylenes due to their high tolerance toward various polar functional groups.²³

Propargyl alcohol is the most simple acetylene monomer that has a hydroxy group; it undergoes polymerization with Pd and Rh catalysts.^{134,202,238} 1-Methylpropargyl alcohol is a chiral derivative of propargyl alcohol and has various applications in the field of organic chemistry; for example, it has been utilized for the regioselective carbometalation with Grignard reagents affording 2-substituted allylic alcohols,472 in the synthesis of 2-substituted indoles via Sonogashira coupling cyclization,⁴⁷³ as a precursor of chiral allenylzinc and indium reagents,⁴⁷⁴ and in the synthesis of phosphinoyl 1,3-diene.⁴⁷⁵ The polymerization of methylpropargyl alcohol and the ester derivatives was first reported in 2007.²³⁹ The polymers obtained form helices, and the helical conformation of the polymer having ester groups is thermally more stable than that of the polymer containing hydroxy groups.²⁵⁰ The remarkable ability of such a small chiral moiety to induce helicity is most likely due to the location of the chiral group adjacent to the main chain. In other words, the presence of a chiral group in close proximity to the main chain has enough of an effect to induce a helix that is stabilized by steric repulsion between the side chains.



Figure 12 Possible conformations of tightly (top) and loosely (bottom) twisted helical *cis*-stereoregular poly(*N*-propargylamide) $[-CH=C(CH_2NHCOH)-]_n$, which accompany helically arranged intramolecular hydrogen-bonding strands (dotted lines) formed between the amide groups at the *i*th and (*i*+3)th units (top) and the *i*th and (*i*+2)th units (bottom). Methine and methylene hydrogen atoms are omitted for clarity.

Chiral N-propargylamides polymerize with Rh catalysts to give cis-stereoregular polymers with moderate MWs.²⁶⁴ The polymers show large specific rotations and intense circular dichroism (CD) signals in the absorption region of the main-chain chromophore, indicating that they adopt helical conformations. The amide I absorption peaks in the solution state infrared (IR) spectra of the polymers appear around 1640 cm⁻¹ irrespective of the concentration, which are low compared to those of the monomers. These data lead to a conclusion that intramolecular hydrogen bonds are constructed between the pendent amide groups of the polymers as shown in Figure 12. Poly(N-propargylamide)s undergo helix-helix transition upon temperature change.268 All the copolymers exhibit no optical activity at certain temperatures, which depends on the copolymer composition. The thermodynamic parameters of helix transition also depend on solvent.

The helical sense of copolymers of *N*-propargylbenzamides is tunable by varying the content of either chiral bulky monomer and achiral nonbulky monomer, or chiral nonbulky monomer and achiral bulky monomer.²⁸⁰ The smaller the pendent group of the achiral monomer is, the more easily the preferential helical sense changes with the copolymer composition. The free energy differences between the plus and minus helical states as well as the excess free energy of the helix reversal of those chiral-achiral random copolymers are estimated by applying the modified Ising model.

The secondary structure of poly(*N*-alkynylamide)s is influenced by the position of the chiral center and amide group.³¹⁴ The position of the chiral center mainly affects the helical pitch, which becomes short when the chiral center is positioned away from the main chain. The stability of the helical structure is also influenced by the position of the amide group. Based on the molecular orbital study, it is concluded that poly(*N*-propargylamide)s with right-handed helical structure display a plus Cotton effect around 390 nm. This is also confirmed by the exciton chirality method using porphyrin as a chromophore.²⁹⁶

The copolymer obtained from D-alanine-derived *N*-propargylamide and L-valine-derived monomer undergoes

helix-helix transition upon temperature change.^{283,284} This phenomenon results from chiral competition between the structurally different enantiomeric amino acid-derived units. The helix-forming abilities of the two units differ depending on the temperature.

The copolymerization of D-alanine-derived *N*-propargylamide, L-valine-derived *N*-propargylamide, and pyrene-based monomer gives helical copolymers carrying pyrene.²⁸⁵ The secondary structure of the copolymer is tunable by the composition of the optically active amino acid units and solvent, which makes it possible to control the direction of the pyrene groups in the side chain. The interaction between the pyrene groups is small when the copolymer takes a helical structure. The pyrene groups are regularly positioned in the polymer side chain. The copolymer emits weak fluorescence, because the population of excimer is small. On the other hand, the pyrene groups get close when the copolymer takes a random structure. In this case, the copolymer emits strong fluorescence based on the excimer.

Propiolates having various chiral alkyl substituents undergo polymerization with $[(nbd)RhCl]_2$ to give highly *cis*stereoregular polymers.³²⁷ The polymers display large specific rotations and intense CD signals, indicating that they exist in helical conformations with predominantly one-handed screw sense. The Mark–Houwink–Sakurada plots of the stereoregular *cis*-transoidal poly(propiolate)s clearly indicate the stiff main chain, that is, the slope of the plot of poly(hexyl propiolate) is 1.2, which is comparable to that of poly(hexyl isocyanate).³²⁶ The stiffness of poly(propiolate)s originates from the helical conformation with a large helical domain size.

A wide variety of poly(PA) derivatives adopt helical conformations. Achiral poly(PA)s having carboxylic groups and crown ether moieties predominantly induce one-handed helical structures by the addition of optically active compounds such as esters and the ammonium salts of amino acids.⁴³ Helixsense-selective polymerization is achieved using optically active amines as cocatalysts to yield poly(PA)s substituted by bis (hydroxymethyl) groups with biased helix sense, 341,476,477 wherein intramolecular hydrogen bonding between the hydroxy groups stabilizes the helical structure. Anion recognition systems are constructed based on the interaction between urea-substituted⁴⁰⁶ and sulfonylamide-substituted⁴⁴¹ polymers. Alanine-derived helical poly(PA) furnishes the twisting cables, spiral ribbons, spherical vesicles, and helical nanotubes.423 N-Methylvaline-derived polymer catalyzes the asymmetric reduction of aromatic ketimines.⁴⁰⁴ The color and helical structures of hydroxy-containing poly(PA) films are tuned by exposure to organic solvent vapor and heat.^{349,350}

3.27.3.4 Photoelectronically Functional Polyacetylenes

The luminescent property is one of the most important functions of conjugated polymers. The photo- and electroluminescence of substituted polyacetylenes have been energetically studied. Although the homopolymer of 9-anthrylacetylene obtained with W catalyst is insoluble,⁴⁴³ the polymer from 1-naphthylacetylene is a soluble dark purple polymer having an absorption maximum at 580 nm. The polymer exhibits the largest third-order nonlinear optical susceptibility among the polymers from monosubstituted acetylenes.⁴⁴⁵ Poly(anthrylacetylene)s bearing oligooxyethylene units exhibit blue

emission (emission maximum 470 nm) upon photoexcitation at 380 nm.⁴⁴⁷ They show a fairly large ionic conductivity $(4.1 \times 10^{-5} \text{ S cm}^{-1})$ at 80 °C upon doping with Li(CF₃SO₂)₂N.

Polymers from terminal acetylenes strongly emit luminescence upon photoexcitation.⁴⁷⁸ Higher photoluminescent efficiency is observed for polyacetylenes having biphenyl moieties, which emit strong deep-blue light at 380 nm. This unexpected strong emission seems to originate from the ordering of the pendent mesogens that enhance the main-chain conjugation of the polymers.

N-Carbazolylacetylene also polymerizes with W catalysts, giving a polymer with a high degree of main-chain conjugation and a large third-order susceptibility.⁴⁵² Carbazole-containing W-based polyacetylenes exhibit UV–vis absorption apparently at a longer wavelength than the Mo- or Rh-based counterparts. They show photoconductivity and electroluminescence.^{259,377,378}

3.27.4 Disubstituted Acetylene Polymers

3.27.4.1 Polymerization of Disubstituted Acetylenes

In general, disubstituted acetylenes are sterically more crowded than their monosubstituted counterparts and, consequently, their effective polymerization catalysts are restricted virtually to group 5 and 6 transition metal catalysts; Rh and other late transition metal catalysts are hardly effective. Among disubstituted acetylenes, those with less steric hindrance (e.g., linear internal alkynes) polymerize with Mo and W catalysts but tend to yield cyclotrimers with Nb and Ta catalysts. On the other hand, sterically crowded disubstituted acetylenes (e.g., TMSP, DPA and its ring-substituted derivatives) do not or hardly polymerize with Mo or W catalysts, but they do polymerize with Nb and Ta catalysts successfully. The polymers from disubstituted acetylenes having two identical groups or two groups of similar sizes are generally insoluble in any solvent. Most polymers from disubstituted acetylenes are colorless, although some aromatic polymers are colored yellow. Table 6 lists typical examples of the polymerization of disubstituted acetylenes.

3.27.4.1.1 Aliphatic acetylenes and monoarylacetylenes

2-Alkynes (e.g., 2-octyne), which are sterically not very crowded, polymerize with Mo catalysts to give polymers with MWs over one million. For these monomers, W and Nb catalysts are less effective, and Ta catalysts yield only cyclotrimers. Symmetrical dialkylacetylenes (e.g., 4-octyne) are slightly more crowded, and consequently Nb, Ta, and W catalysts exhibit high activity, while Mo catalysts are hardly active. Since 1-phenyl-1-alkynes (e.g., 1-phenyl-1-propyne) possess even larger steric effects, Nb and Ta catalysts produce polymers having MW equal to $1 \times 10^5 - 1 \times 10^6$. By contrast, W catalysts are inactive.

3.27.4.1.2 Heteroatom-containing acetylenes

TMSP, a sterically highly crowded Si-containing acetylene, polymerizes with Nb and Ta catalysts, but does not with Mo or W catalysts. TaCl₅ and NbCl₅ alone can polymerize this monomer, and addition of cocatalysts such as *n*-Bu₄Sn accelerates polymerization and/or increases the MW of the polymer. The MW of the polymer obtained with TaCl₅–Ph₃Bi reaches

four million, which is among the highest for all the substituted polyacetylenes. 1-Trimethylgermyl-1-propyne polymerizes in a similar way to TMSP. The monomers in which one of the methyl groups on the Si of TMSP is replaced by the *n*-hexyl and phenyl groups are polymerizable, while those that have ethyl or higher alkyl groups in the place of the methyl group bonded to the acetylenic carbon are not polymerizable because of steric hindrance.

Mo catalysts are uniquely effective in the polymerization of S-containing disubstituted acetylenes. Although there is a possibility that S as well as O in the monomer deactivates group 5 and 6 transition metal catalysts, the basicity of S is weakened by the conjugation with the triple bond, resulting in the lower coordinating ability to the propagating species. Cl-containing monomers afford high-MW polymers. For instance, the polymerization of 1-chloro-1-octyne, 1-chloro-2-phenylacetylene, 1-chloro-2-β-naphthylacetylene is catalyzed and bv $MoCl_5-n-Bu_4Sn$ and $Mo(CO)_6-CCl_4-hv$ to give polymers whose MW reaches around 10⁶ at the maximum. It appears that the electron-withdrawing chlorine atom plays a certain role in the inertness of these monomers to Nb, Ta, and W catalysts.

3.27.4.1.3 Diphenylacetylenes and analogues

DPA itself forms a polymer in the presence of $TaCl_5-n-Bu_4Sn$. TaCl₅ alone is ineffective as catalyst for this monomer, indicating that the presence of cocatalysts such as $n-Bu_4Sn$ and Et_3SiH is indispensable for the formation of active species in the polymerization of this monomer. The polymer formed possesses a very high thermal stability, but is insoluble in any solvent. Regarding polymer solubility, there is a tendency that polyacetylenes having two identical alkyl groups in the repeating unit are insoluble in any solvent, whereas polyacetylenes having methyl and a long alkyl group are soluble in various solvents. By analogy, one can hypothesize that *para-* or *meta-*substituted DPAs will provide soluble polymers.

In fact, soluble, high-MW polymers have been obtained from many DPAs with bulky ring substituents. For instance, 1-phenyl-2-[(*p*-trimethylsilyl)phenyl]acetylene polymerizes with TaCl₅-cocatalyst in high yield. The polymer thus obtained is totally soluble in toluene and chloroform, and its MW is as high as about two million. In contrast, TaCl₅ alone and NbCl₅-cocatalyst are ineffective toward this monomer unlike TMSP. The DPAs with *m*-Me₃Si, *m*-Me₃Ge, *p*-*t*-Bu, and *p*-*n*-Bu groups polymerize similarly, leading to totally soluble, high-MW polymers. Poly(DPA)s having spherical ring substituents such as Me₃Si, Me₃Ge, and *t*-Bu groups show high gas permeability as an interesting function, which will be discussed in Section 3.27.4.3.1.

3.27.4.2 Reactions of Disubstituted Acetylene Polymers

Since only Ta and Nb catalysts, which are not tolerant to polar groups, are available for the polymerization of disubstituted acetylenes, it is generally difficult to synthesize disubstituted acetylene polymers having protic and/or highly polar substituents such as hydroxy, carboxy, and sulfonic acid groups. In order to obtain polar group-containing polymers of disubstituted acetylenes, recently polymer reactions have been employed. Polymer reactions have proved useful also in the preparation of poly(DPA) membrane, namely, while the

Table 6 Synthesis of polymers from disubstituted acetylenes

Mono	mer		Catalyst	$M_{ m w}~(imes 10^3)$	References
(a) Ali	iphatic acetylenes (R ¹	C≡CR ²)			
1 2 3 4 5 6	R ¹ =Me <i>n</i> -Pr Me Me Me Me	$R^2 = n \cdot Pr$ $n \cdot Pr$ $SiMe_3$ $SiMe_3$ $SiMe_3$ $SiMe_2 - n \cdot C_6H_{13}$	MoCl ₅ NbCl ₅ TaCl5 NbCl5 TaCl5-Ph3Bi TaCl5-Ph3Bi	1100 Insoluble 730 220 4000 1400	479 480 481, 482 481,482 483 484
7	CH ₃	—Si(CH ₃) ₂ CH ₃ ,	TaCl₅-Ph ₃ Bi	80 (<i>M</i> _n)	485
8	CH ₃	-Ge(CH ₃) ₃	TaCl ₅	1400	486, 487
9	CH ₃	-CO ₂ (CH ₂) ₆ O ₂ C	MoCl ₅ -Ph ₄ Sn	11	324
10 11 12 13	Me MeS -SPh Cl	-S- <i>n</i> -Bu <i>n</i> -C ₆ H ₁₃ - <i>n</i> -C ₁₂ H ₂₅ <i>n</i> -C ₆ H ₁₃	MoCl₅–Ph₃SiH MoCl₅–Ph₃SiH MoCl₅–Ph₄Sn MoCl₅– <i>n</i> -Bu₄Sn	180 130 25 1100	488 489 490 491
(b) M	onoarylacetylenes (R ¹	C=CR ²)			
14 15	R ¹ =Me <i>n</i> -C ₆ H ₁₃	R ² =Ph Ph	TaCl₅− <i>n</i> -Bu₄Sn TaCl₅− <i>n</i> -Bu₄Sn	1500 1100	492 493
16	<i>п</i> -С ₅ Н ₁₁	-§-	TaCl₅− <i>n</i> -Bu₄Sn	7.5 (<i>M</i> _n)	494
17	Me		NbCl₅–Et₃SiH	350	495
18 19 20	Me Cl Cl	-C ₆ H₄- <i>p</i> -Adamantyl Ph -C ₆ H₄- <i>p</i> -Adamantyl	TaCl₅– <i>n</i> -Bu₄Sn MoCl₅– <i>n</i> -Bu₄Sn MoCl₅– <i>n</i> -Bu₄Sn	1000 690 110 (<i>M</i> n)	496 497 496
21	CI		$MoCl_5$ — Et_3SiH	270	498
22 23	CI Br	$-C_6H_4$ - p -SiMe ₃ Ph	Mo(CO) ₆ −CCl₄−hv MoCl₅− <i>n</i> -Bu₄Sn	940 ∼20 (<i>M</i> n)	499 500
24	Ph	$(CH_2)_9O-Si$ Ph Ph Ph Ph Ph	WCl ₆ −Ph₄Sn	33	313
25	Ph	$-CO_2(CH_2)_6O_2C$ $ O(CH_2)_6CH_3$	MoCl₅-Ph₄Sn	239	324
26	Ph	-co ₂	WCI ₆ −Ph₄Sn	13	501
27	Ph	$-CO_2(CH_2)_2O$ $-CC$ $-CH_2O$ $-CC$ Me	MoCl₅–Ph₄Sn	61	502

References

 $M_{\rm w}~(imes 10^3)$

Catalyst

Table 6 (Continued) Monomer 28 Ph O</t

28	Ph	-(CH ₂) ₉ O-C-C-(CH ₂) ₄ CH ₃	WCl ₆ −Ph₄Sn	62 (<i>M_n</i>)	503
29	-S <i>-n-</i> Bu	Ph	WCl ₆ –Ph ₃ SiH	10	490
(c) Dia	rylacetylenes (R¹C≡CR	²)			
30 31 32 33	R ¹ =Ph Ph Ph Ph	$R^2=Ph$ - C_6H_4 - p - t - Bu - C_6H_4 - p - n - Bu - C_6H_4 - p - A damantyl	TaCl₅– <i>n</i> -Bu₄Sn TaCl₅– <i>n</i> -Bu₄Sn TaCl₅– <i>n</i> -Bu₄Sn TaCl₅– <i>n</i> -Bu₄Sn	Insoluble 3600 1100 2200	493 504 504 496
34	Ph	\checkmark	TaCl₅− <i>n</i> -Bu₄Sn	590	505
		-§			
35	Ph	\prec	TaCl₅- <i>n</i> -Bu₄Sn	1000	506
		-{			
36	Ph		TaCl₅- <i>n</i> -Bu₄Sn	>6000	507
		-&			
37	Ph Ph	$-C_6H_4$ - p -SiMe ₃	TaCl ₅ - <i>n</i> -Bu ₄ Sn	2200	508–510
30 39	Ph	$-C_6H_4-p$ -SiPh ₃	TaCl ₅ – <i>n</i> -Bu ₄ Sn	1900	509
40	Ph	-C ₆ H ₄ - <i>p</i> -SiMe ₂ - <i>i</i> -Pr	TaCl₅– <i>n</i> -Bu₄Sn	1600	512
41	Ph	<i>p</i> -C ₆ H ₄ Si(CH ₃) ₂ CH ₂ ····	TaCl₅− <i>n</i> -Bu₄Sn	>100	513
42	Ph	-C ₆ H ₄ - <i>m</i> -Ge(CH ₃) ₃	TaCl ₅ –9-borabicyclo [3.3.1]nonane (9-BBN)	1000	514
43	-C ₆ H ₄ - <i>p</i> -SiMe ₃	β-Naphthyl	TaCl ₅ – <i>n</i> -Bu ₄ Sn	3400	515
44	-C ₆ H ₄ - <i>p</i> -SiMe ₃		TaCl₅− <i>n</i> -Bu₄Sn	3400	516
45	-C ₆ H ₄ - <i>p</i> -SiMe ₃		TaCl₅– <i>n</i> -Bu₄Sn	700	516
46	Ph	-C ₆ H ₄ - <i>p</i> -OSiMe ₂ - <i>t</i> -Bu	TaCl₅− <i>n</i> -Bu₄Sn	4000	517
47	Ph	-}-0	WCl ₆ Ph ₄ Sn	12	518
48	Ph	-§-()-0-()	WCl ₆ −Ph₄Sn	22	519
49 50	Ph Ph	-C ₆ H ₄ - <i>p</i> -OPh <i>i-</i> Pr.	TaCl ₅ – <i>n</i> -Bu₄Sn WCl ₆ –Ph₄Sn	1700 30	520 501
		-C6H ₄ -p-CO ₂			
		Me			

Table 6 (Continued)

Mono	omer		Catalyst	$M_{ m w}~(imes 10^3)$	References
51 52 53 54	Ph Ph -C ₆ H ₄ - <i>p</i> -SiMe ₃ -C ₆ H ₄ - <i>p</i> -SiMe ₃	$-C_{6}H_{4}-\rho-N-Carbazolyl-C_{6}H_{4}-\rho-NPh_{2}-C_{6}H_{4}-\rho-NPh_{2}-C_{6}H_{3}-m,\rho-F_{2}$	TaCl₅– <i>n</i> -Bu₄Sn TaCl₅– <i>n</i> -Bu₄Sn TaCl₅– <i>n</i> -Bu₄Sn TaCl₅– <i>n</i> -Bu₄Sn	190 570 520 1100	521 522 522 523
55	-C ₆ H ₃ - <i>m,p</i> -F ₂	-§-	TaCl₅− <i>n</i> -Bu₄Sn	670	494, 505
56	-C ₆ H ₃ - <i>m,p</i> -F ₂	-{-{-}	TaCl₅− <i>n</i> -Bu₄Sn	1100	506
57	-C ₆ H ₂ - <i>m</i> ,m, <i>p</i> -F ₃		TaCl₅− <i>n</i> -Bu₄Sn	1230	524
58	-C ₆ H ₂ - <i>m</i> ,m, <i>p</i> -F ₃	-C ₆ H ₄ - <i>p</i> -SiMe ₂ - <i>n</i> -C ₅ H ₁₁	WCl ₆ −Ph₄Sn	10	518
59	Ph	-§-(CI CI	TaCl₅– <i>n</i> -Bu₄Sn	4900	507
60	Ph	Fe Fe	TaCl₅− <i>n</i> -Bu₄Sn	Insoluble	525
61	Ph	Fe Fe	TaCl₅− <i>n</i> -Bu₄Sn	530	525

preparation of poly(DPA) membrane by solution casting is impossible because of its insolubility, desilylation of silyl-containing poly(DPA) membranes to poly(DPA) membranes has been developed. Examples of such polymer reactions are illustrated in **Scheme 4** and discussed below.

Poly(DPA) is, thermally, the most stable substituted polyacetylene, but it is insoluble in any solvent, and hence it is impossible to fabricate a membrane from it by solution casting. In order to prepare this polymer membrane, desilylation of poly[1-phenyl-2-*p*-(trimethylsilyl)phenylacetylene] (PTMSDPA) membrane has been examined by use of trifluoroacetic acid as catalyst in hexane.^{510,526} The desilylation reaction proceeds to completion, as evidenced by IR spectroscopy and the anticipated weight decrease (eqn [a] in **Scheme 4**). As expected, the poly (DPA) membrane produced is insoluble in any solvent and possesses high thermal stability. This polymer shows fairly high gas permeability irrespective of the absence of any spherical substituent, as described below. The pinanylsilyl-containing poly(DPA) in eqn [b] is soluble, membrane-forming, and CD- active, indicating helical structure. The desilylation of this polymer proceeds similarly to give a poly(DPA) membrane. Quite interestingly, the polymer formed maintains helical structure in the membrane form, according to CD spectroscopy. Applying the same desilylation reaction, various poly(diarylacetylene)s including poly(1- β -naphthyl-2-phenylacetylene),⁵¹⁵ poly[1-(2-fluorenyl)-2-phenylacetylene],⁵¹⁶ and poly[1-(2-phenanthryl)-2-phenylacetylene]⁵¹⁶ have been prepared.

Disubstituted acetylenes with hydroxy groups do not polymerize because Ta and Nb catalysts are deactivated by polar groups such as hydroxy groups. In contrast, a protected monomer, that is, 1-phenyl-2-*p*-(*t*-butyldimethylsiloxy)phenylacetylene, polymerizes to give a high-MW polymer.⁵¹⁷ This polymer is soluble in common organic solvents and provides a free-standing membrane. Desilylation of a poly[1-phenyl-2*p*-(*t*-butyldimethylsiloxy)phenylacetylene] membrane yields a poly(DPA) that has free hydroxy groups (eqn [d] in Scheme 4). This is the first example of a poly(DPA) carrying a highly polar group. Unlike the starting polymer, poly(1-phenyl-2*p*-hydroxyphenylacetylene) is insoluble in nonpolar solvents such as toluene and chloroform but partly soluble in methanol.

PTMSDPA and its copolymers with 1-phenyl-2-(4-*t*-butyl-phenyl)acetylene undergo sulfonation in the presence of a mixture of acetic anhydride and sulfuric acid in chloroform solution⁵²⁷ (eqn [e] in **Scheme 4**). The degree of sulfonation for PTMSDPA is evaluated to be 1.55 per repeating unit and the

highest, while the values of the copolymers are 0.57–0.85. The acid treatment leads to simultaneous complete desilylation according to IR spectroscopy. The sulfonated product shows quite different solubility properties from those of PTMSDPA; that is, it is totally soluble in acetone, methanol, and dimethyl sulfoxide (DMSO). Thermal decomposition temperature (5% weight loss) of the sulfonated polymer is over 300 °C,



Scheme 4 (Continued)



Scheme 4 Reactions of polymers from disubstituted acetylenes.

indicating good thermal stability. A patent has also appeared about sulfonation of poly(DPA) derivatives.⁵²⁸

Polymer reaction approaches provide a variety of polar disubstituted acetylene polymers. For example, the azide–alkyne click reactions are useful to attach a number of polar functional groups (FGs) including various azobenzene moieties to the pendants of poly(1-phenyl-5-chloro-1-pentyne) (eqn [f] in **Scheme** 4).⁵²⁹ Nucleophilic substitutions of the same starting polymer result in the formation of imidazole-functionalized disubstituted acetylene polymer (eqn [g]).⁵³⁰ The degree of incorporation of imidazole moiety is about 65%, and the polymer product is nearly insoluble in THF, chloroform, and DMF, but exhibits good solubility in ethanol. Hydrolysis reaction of poly[1-(*m*-methoxycarbonylphenyl)-1-octyne] yields a carboxy-functionalized disubstituted acetylene polymer, poly[1-(*m*-carboxyphenyl)-1-octyne] (eqn [h]).⁵³¹ Hydrazine-catalyzed deprotection of poly(1-phenyl-11-*N*-benzimide-1-undecyne) affords the corresponding polyamine, which can be further ionized with hydrobromic acid to give a polyelectrolyte ammonium salt (eqn [i]).⁵³²

Cylindrical polymer brushes composed of a poly(DPA) main chain and poly(oxyethylene) side chains have been prepared by the so-called graft-from method. For example, 1-(*p*-trimethylsilylphenyl)-2-(*m*-methylphenyl)acetylene is at first polymerized into a high-MW polymer ($M_w = 2 \times 10^6$), then the *m*-methyl group is converted into the chloromethyl

group, and finally oligo-oxyethylene chains ($m = \sim 8$) are incorporated by substituting the chlorine atom (eqn [j]).⁵³³ The degree of polyethylene glycol (PEG) substitution is estimated to be about 0.25 on the basis of the methyl group. Another example utilizes atom transfer radical polymerization (ATRP) of PEG-carrying methyl methacrylate initiated from bromine-containing poly(DPA).⁵³⁴

3.27.4.3 Functions of Disubstituted Acetylene Polymers

3.27.4.3.1 Gas-permeable polyacetylenes

Polymers from disubstituted acetylenes have been most intensively examined as gas-permeable materials aiming at practical application.^{24,32,35,535} These studies are motivated by the extremely high gas permeability of PTMSP (Figure 13),^{24,481} which is the most permeable material available among all polymers. The oxygen permeability coefficient (P_{O2}) of TMSP ranges from 4000 to 9000 barrers, which is about 10 times larger than that of poly(dimethylsiloxane). In addition to its high permeability, the ability of PTMSP to yield a free-standing film and its gas permeation mechanism, the latter of which is different from that of poly(dimethylsiloxane), have attracted much attention among membrane scientists. PTMSDPA (Figure 13) is a typical, highly gas-permeable poly(DPA) and shows high thermal stability compared to PTMSP.



Figure 13 Structures of PTMSP and PTMSDPA.

The P_{O2} values and oxygen/nitrogen selectivities (P_{O2}/P_{N2}) (25 °C) of about 100 substituted polyacetylenes have been measured so far.^{24,32,35} Among these substituted polyacetylenes, many of the polymers with large PO2 values contain spherical substituents, such as t-Bu, Me₃Si, and Me₃Ge groups. By contrast, a majority of the less-permeable polyacetylenes possess long *n*-alkyl groups. When the phenyl group is the main substituent, the gas permeability of the resulting polyacetylenes is usually considerably lower. For comparison, the values (P_{02}/P_{N2}) of commercially available Pop oxygen-permeable polymer membranes at 25 °C are as follows:^{536–538} poly(dimethylsiloxane), 600 barrers (2.0); poly(4-methyl-1-pentene), 32 barrers (2.1); natural rubber, 23 barrers (2.3); poly(oxy-2,6-dimethylphenylene), 15 barrers (5). In general, substituted polyacetylenes are very permeable to gases, which is attributable to their high free volume, which is presumably derived from their low cohesive energy structure. stiff main chain, and spherical substituents.

Table 7 shows oxygen permeability data of PTMSP and related polymers. The triethylsilyl analogue of PTMSP exhibits lower oxygen permeability than does PTMSP, although the bulkier triethylsilyl group appears to be effective in generating molecular-scale voids. In a similar manner, substitution of one methyl group on the silicon atom in PTMSP by longer alkyl groups lowers oxygen permeability. The oxygen permeability of poly(1-trimethylgermyl-1-propyne) is comparable to that of PTMSP. The *tert*-butyl derivative of PTMSP is not available because of too large steric hindrance. Poly(4-methyl-2-pentyne), the isopropyl analog of PTMSP, has been obtained and shows fairly high oxygen permeability. Incorporation of alkylene and phenylene spacers into PTMSP reduces oxygen permeability.

PTMSP, which has long been known as the most gas-permeable polymer, is still being investigated with respect to various aspects of its permeation of gases and liquids. The research subjects include the following: membranes based on PTMSP for liquid–liquid separation;⁵⁴³ the effect of direct-current discharge treatment on the surface properties of a PTMSP membrane;⁵⁴⁴ cross-linking and stabilization of nanoparticle-filled PTMSP nanocomposite membranes for gas

	5 -				
	+C= R ¹	=c) R ²	P ₀₂		
No.	R^1	R ²	Barrer ^a	P ₀₂ /P _{N2}	References
1	Me	SiMe ₃	$4\times10^39\times10^3$	1.8	24, 539
2	Me	SiEt ₃	860	2.0	484, 540
3	Me	SiMe ₂ Et	500	2.2	539–541
4	Me	SiMeEt ₂	440	2.1	540
5	Me	-SiMe ₂ - <i>i</i> -C ₃ H ₇	460	2.7	539, 540
6	Me	-SiMe ₂ -n-C ₃ H ₇	100	2.8	541
7	Me	GeMe ₃	7800		486, 487
8	Me	<i>i</i> -Pr	2700	2.0	542
9	Me	-(CH ₂) ₃ SiMe ₃	130	2.4	540
10	Me	-C ₆ H ₄ - <i>p</i> -SiMe ₃	240	2.4	539, 540

Table 7Oxygen permeability coefficients (P_{02}) and P_{02}/P_{N2} of PTMSP and itsanalogs

^a1 barrer = $1 \times 10^{-10} \text{ cm}^3$ (STP) cm⁻¹ cm⁻² s⁻¹ cmHg⁻¹

separations;⁵⁴⁵ cross-linking PTMSP and its effect on physical stability;⁵⁴⁶ gas transport properties of MgO-filled PTMSP nanocomposites;⁵⁴⁷ bromination of PTMSP with different microstructures and properties of bromine-containing polymers;⁵⁴⁸ desilylation of substituted polyacetylenes by nanoparticles;⁵⁴⁹ pure and mixed gas CH₄ and *n*-C₄H₁₀ permeability and diffusivity in PTMSP;⁵⁵⁰ gas transport properties of PTMSP and ethylcellulose filled with trimethylsilylsaccharides of different MWs and the impact on fractional free volume (FFV) and chain mobility;⁵⁵¹ Fourier transform IR spectroscopy study of PTMSP aging;⁵⁵² effect of fumed silica nanoparticles on the gas permeation properties of substituted polyacetylene membranes;⁵⁵³ and free volume and interstitial mesopores in silica-filled PTMSP nanocomposites.⁵⁵⁴

Table 8 shows oxygen permeability data of poly(DPA)s. Ring-substituted poly(DPA) derivatives are thermally very stable ($T_0 > 400$ °C) and possess film-forming ability. The ease in modifying ring substituents provides an opportunity to tune the permeability as well as the solubility and second-order conformation of the polymer. The permeability of poly(DPA)s depends significantly on the shape of the ring substituents.^{32,35} Specifically, those with bulky ring substituents such as *t*-Bu, Me₃Si, and Me₃Ge groups (Nos. 1, 3–5 in **Table 8**) exhibit very large P_{O2} values of up to 1000–1500 barrers, which is about one-fourth that of PTMSP and approximately twice as large as that of poly(dimethylsiloxane).

While poly(DPA) is insoluble in any solvent, its derivatives with bulky ring substituents are usually soluble in common solvents such as toluene and chloroform and give membranes by solution casting. A poly(DPA) membrane has been prepared by the desilylation of a PTMSDPA membrane that was catalyzed by trifluoroacetic acid.^{510,526} The prepared polymer membrane displays high thermal stability, insolubility in any solvent, and high gas permeability (e.g., an oxygen permeability of 910 barrers at 25 °C; No. 2 in **Table 8**). The high gas permeability of poly(DPA) seems to be due to the generation of molecular-scale voids. In a similar way, poly(DPA)s that contain various silyl groups, such as Me₂*i*-PrSi, Et₃Si, and Me₂*n*-C₈H₁₇Si groups, are soluble in common solvents, and poly(DPA) membranes can be obtained by desilylation of these membranes.⁵²⁶ The P_{O2} values (120–3300 barrers) of the poly(DPA)s are fairly varied from one another despite having the same structure. When the bulkier silyl groups are removed, the oxygen permeability tends to increase to a larger extent.

Poly(DPA)s with silyl groups and fluorine atoms are highly gas-permeable.⁵²³ The FFV of poly[1-(4-fluoro)phenyl-2-*p*-(trimethylsilyl)phenylacetylene] is 0.28 and appreciably large (e.g., PTMSDPA has an FFV of 0.26^{555}). The P_{O2} of poly[1-(4-fluoro)phenyl-2-*p*-(trimethylsilyl)phenylacetylene] is as high as 2900 barrers, which is about twice that of PTMSDPA. The incorporation of fluorine atoms into PTMSDPA generally enhances gas permeability (Nos. 1, 6, 8 in Table 8). Desilylation of these polymers does not change oxygen permeability very much, despite the disappearance of the spherical trimethylsilyl group (Nos. 2, 7, 9 in Table 8).

DPA monomers containing a substituted biphenyl group have been synthesized and then polymerized with $TaCl_5-n$ -Bu₄Sn catalyst to produce the corresponding poly

	$+ \begin{array}{c} C = C \\ R^1 & R^2 \end{array}$		P ₀₂			
No.	R ¹	R^2	Barrer ^a	P ₀₂ /P _{N2}	References	
1 2 3 4 5 6 7 8 9 10 11	Ph Ph Ph Ph C ₆ H ₄ - <i>p</i> -SiMe ₃ Ph C ₆ H ₄ - <i>p</i> -SiMe ₃ Ph Ph	$\begin{array}{l} -C_{6}H_{4}\text{-}p\text{-}SiMe_{3} \\ Ph \\ -C_{6}H_{4}\text{-}m\text{-}SiMe_{3} \\ -C_{6}H_{4}\text{-}m\text{-}GeMe_{3} \\ -C_{6}H_{4}\text{-}p\text{-}f\text{-}C_{6}H_{4}\text{-}p\text{-}F \\ -C_{6}H_{4}\text{-}p\text{-}F \\ -C_{6}H_{4}\text{-}p\text{-}F \\ -C_{6}H_{3}\text{-}m,p\text{-}F_{2} \\ -C_{6}H_{3}\text{-}m,p\text{-}F_{2} \\ -C_{6}H_{4}\text{-}p\text{-}OSiMe_{2}\text{-}t\text{-}Bu \\ -C_{6}H_{4}\text{-}p\text{-}OH \end{array}$	1100–1550 910 1200 1100 2900 3000 3600 3800 160 8.0	2.1 2.2 2.0 2.2 1.5 1.4 1.5 1.3 3.2 3.3	35, 509 510, 526 509, 523 514 504 523 523 523 523 523 517 517	
12	Ph	-ۇ-	1100	2.1	507	
13	Ph	-ۇ- CI	1400	1.9	507	

Table 8 Oxygen permeability coefficients (P_{02}) and P_{02}/P_{N2} of poly(diphenylacetylene)s

^a1 barrer = 1×10^{-10} cm³(STP) cm cm⁻² s⁻¹ cmHg⁻¹

(DPA)s.⁵⁰⁷ The polymers formed are soluble in common organic solvents such as cyclohexane, toluene, and chloroform, and have high thermal stability over 400 °C according to TGA. These polymer membranes, especially those with twisted biphenyl groups, exhibit high gas permeability; for example, their P_{O2} values range from 130 to 1400 barrers. The membranes that have two methyl or chlorine atoms in the biphenyl group show fairly high gas permeability (P_{O2} 1100 and 1400 barrers, respectively), most likely because the twisted biphenyl structure is useful in generating molecular-scale voids (Nos. 12, 13 in Table 8).

Hydroxy group-containing poly(DPA)s show interesting CO₂ permeation behavior (Table 9), as explained below.⁵¹⁷ The P_{O2} value of poly[1-phenyl-2-*p*-(*t*-butyldimethylsiloxy) phenylacetylene] (poly(p-SiODPA)) at 25 °C is 160 barrers, which is relatively small among those of poly(DPA) derivatives. The permeability of poly(p-SiODPA) to other gases is also relatively low. The permeability of poly[1-phenyl-2-m-(*t*-butyldimethylsiloxy)phenylacetylene] (poly(*m*-SiODPA)) to all gases is somewhat higher than that of poly(p-SiODPA). The PO2 values of desilylated polymers poly(1-phenyl-2-p-hydroxyphenylacetylene) (poly(p-HODPA)) and poly(1phenyl-2-m-hydroxyphenylacetylene) (poly(m-HODPA)) are 8.0 and 15 barrers, respectively, which demonstrate significant decreases of gas permeability after desilylation, probably owing to the decrease of FFV. In general, polymers bearing hydroxy groups such as poly(vinyl alcohol) ($P_{O2} = 0.00665$ barrers) commonly exhibit very low gas permeability and can be utilized as gas barrier membranes.538,540 When this is taken into account, the relatively high gas permeability of poly (p-HODPA) and poly(m-HODPA) suggests fairly sparse structures, as are common for sterically crowded substituted polyacetylenes. The separation factors of CO₂ and methane $(P_{\rm CO2}/P_{\rm CH4})$ and of CO₂ and nitrogen $(P_{\rm CO2}/P_{\rm N2})$ of poly (p-HODPA) and poly(m-HODPA) are 14-48 and appreciably large, 556,557 indicating that the separation performance for CO₂ is remarkably improved upon desilylation. It is especially noteworthy that the P_{CO2}/P_{CH4} value of poly(*p*-HODPA) is located above the Robeson's upper bound.⁵⁵⁸ The methane permeability, P_{CH4}, remarkably decreases compared to P_{CO2} upon desilylation, which is reasonable because methane is nonpolar and fairly bulky.

 $\label{eq:poly1-aryl-2-p-(trimethylsilyl)phenylacetylene]s (aryl = naphthyl, ^{515} fluorenyl, ^{516} phenanthryl ^{516}) are soluble in common solvents, and afford free-standing membranes. These$

Si-containing polymer membranes are desilylated to yield the membranes of poly(1-aryl-2-phenylacetylene)s. Both the starting and the desilylated polymers show very high thermal stability and high gas permeability. For instance, the T_0 and P_{O2} values of poly(1- β -naphthyl-2-phenylacetylene) are 470 °C and 4300 barrers, respectively (No. 2 in Table 10).

Diarylacetylenes having fluorenyl groups and other substituents (trimethylsilyl, *t*-butyl, bromine, fluorine) also polymerize with TaCl₅–*n*-Bu₄Sn, forming high-MW polymers (M_w 10⁵–10⁶) in about 10–60% yields.⁵⁰⁵ These polymers are soluble in common organic solvents, and give tough free-standing membranes by solution casting. These polymer membranes show quite high gas permeability; for example, the P_{O2} value of the polymer that contains 9,9-dimethylfluorenyl and phenyl groups is as large as 4800 barrers (No. 3 in **Table 10**). The polymer membrane that possesses two fluorine atoms at the *meta*- and *para*-positions of the phenyl ring displays the highest oxygen permeability (P_{O2} 6600 barrers) among this type of polymers.

Acetylenic monomers containing indan and other groups also provide polymers with the TaCl₅–n-Bu₄Sn catalyst.⁵⁰⁶ Most of the polymers formed are soluble in common organic solvents, and afford free-standing membranes by solution casting. Despite the absence of bulky spherical groups, polymethylated indan-containing polymer membranes show extremely high gas permeability. For instance, the P_{O2} value of the polymer bearing 1,1,3,3-tetramethylindan and phenyl groups can reach 14 400 barrers. In particular, the P_{O2} values of polymers having 1,1,3,3-tetramethylindan and either p-fluorophenyl or p,m-difluorophenyl groups reach 17 900 and 18 700 barrers, respectively (Nos. 11, 12 in Table 10), which are clearly larger than that of PTMSP.

PTMSDPA, a disubstituted acetylene-based glassy polymer, exhibits higher permeabilities to organic vapors than to permanent gases due to its rigid polyacetylene backbone and bulky side groups.⁵⁵⁹ The gas permeability and desilylation effect of poly(DPA)s that have trimethylsilyl and alkyl groups have been studied.⁵⁶⁰ Sulfonic acid groups have been introduced into poly(DPA)s to yield ionic and hydrophilic polyacetylenes.^{527,528} The degree of sulfonation usually ranges from 0.5 to 1.5 per repeating unit, and free-standing membranes can be obtained from the sulfonated polymers. Application of the membranes as proton-conducting fuel cell membranes has been examined.⁵²⁸ These membranes can also be used as CO₂ separation membrane materials.⁵²⁷ The sulfonated polymers

 Table 9
 Gas permeability coefficients (P) of siloxy- and hydroxy-containing poly(diphenylacetylene)s

	P (barrer ^a)							
Polymer	H ₂	CO2	02	N ₂	CH₄	P <i>O</i> 2/P <i>N</i> 2	Р <i>СО2</i> /Р <i>СН</i> 4	P <i>CO</i> 2/P <i>N</i> 2
Poly(<i>p</i> -SiODPA) ^b Poly(<i>m</i> -SiODPA) ^b Poly(<i>p</i> -HODPA) ^c Poly(<i>m</i> -HODPA) ^c	330 380 56 86	810 880 110 130	160 190 8.0 15	50 67 2.4 5.1	160 170 2.3 9.6	3.2 2.8 3.3 2.9	5.1 5.2 47.8 13.5	16.2 13.1 45.8 25.5

 a1 barrer = 1 × 10⁻¹⁰ cm³(STP) cm cm⁻² s⁻¹ cmHg⁻¹.

^bMethanol-conditioned.

^cHexane-conditioned.

P-values measured at 25 °C.

	$(c=c+c+R^1 R^2)$		P ₀₂		
No.	R ¹	R^2	Barrer ^a	P ₀₂ /P _{N2}	References
1 2	C ₆ H₄- <i>p</i> -SiMe₃ Ph	β-Naphthyl β-Naphthyl	3 500 4 300	1.8 1.6	515 515
3	C ₆ H ₄ - <i>p</i> -SiMe ₃		1 650	1.7	516
4	Ph		2 150	1.7	516
5	C ₆ H ₄ - <i>p</i> -SiMe ₃		1 300	2.0	516
6	Ph		4 300	1.6	516
7	Ph		4800	1.5	505
8	C ₆ H₄- <i>p</i> -F	- <u>8</u> -	6200	1.3	505
9	C ₆ H ₃ - <i>m,p</i> -F ₂	- <u>s</u> -	6 600	1.3	505
10	Ph	- <u></u>	14 400	1.2	506
11	C ₆ H ₄ - <i>p</i> -F	-8	17 900	1.2	506
12	C ₆ H ₃ - <i>m,p</i> -F ₂	-8-	18700	1.1	506

Table 10 Oxygen permeability coefficients (P_{02}) and P_{02}/P_{N2} of poly(diarylacetylene)s

 a 1 barrer = 1 × 10⁻¹⁰ cm³(STP) cm cm⁻² s⁻¹ cmHg⁻¹.

exhibit high CO₂ permselectivity; for example, their CO₂/N₂ separation factors are over 31. The sulfonated poly(DPA) with the highest degree of sulfonation displays the highest CO_2/N_2 ratio of 75.

3.27.4.3.2 Photoelectronically functional polyacetylenes

With regard to photoelectronic functions, monosubstituted acetylene polymers have been studied more than disubstituted acetylene polymers, because they are generally more conjugated and colored due to their less sterically demanding structure. However, considering the higher stability of the disubstituted acetylene polymers, they may be more suited for practical applications.

3.27.4.3.2(i) Photoluminescence and electroluminescence

Many studies on the photoluminescence behavior of disubstituted acetylene polymers have been reported. Several recent studies are introduced here.

DPAs and 1-phenyl-1-alkynes show intense photo- and electroluminescences. A systematic investigation of the luminescence of poly(DPA)s has revealed that these polymers exhibit photoluminescence around 530 nm and electroluminescence around 550 nm. In a similar way, poly(1-phenyl-1-alkyne)s photochemically and electrochemically emit strong lights with spectral maxima located around 455 and 470 nm, respectively. Green and blue emissions are observed from electroluminescent devices using poly(DPA)s and poly(1-phenyl-1-alkyne)s, respectively, as emission layers.⁵⁶¹⁻⁵⁶⁴

The effect of alkyl chain length on the fluorescence of poly (DPA)s containing alkylsilane moieties (**30** in **Figure 14**) in their side chains has been studied.⁵⁶⁵ Longer alkyl groups in the side chains of the polymer lead to longer fluorescence lifetimes. A longer alkyl group is also shown to be more effective than a shorter alkyl group in aligning the polymer chain parallel to the shearing direction. New poly(DPA)s with alkoxy, silyl, and fluorine groups (e.g., **31**) have been synthesized using W and Ta catalysts.⁵¹⁸ The polymer solutions emit a strong, bluish-green light when photoexcited. Polymers containing electron-donating alkoxy groups show slightly longer

fluorescence maxima as compared to polymers with electron-withdrawing fluorine atoms.

Polymer 32 (Figure 14) has been synthesized and its photoluminescence has been studied.⁵⁶⁶ The ethynyl group of the DPA moiety polymerizes exclusively, resulting in a soluble polymer. The chloroform solution of the polymer shows a backbone emission centering at 522 nm, whereas the silole pendant is nonradiative at room temperature. Intramolecular rotations of the Ph groups on the silole moieties are responsible for the nonradiative decay of the silole chromophore. The intramolecular rotations, however, can be largely restricted through a cooling process of the polymer solution, which shows cooling-enhanced emission. Thus, the silole emission becomes dominant at lower temperatures. On the other hand, fluorescence energy transfer occurs from the main chain to the silole pendant in poly(1-phenyl-1-alkyne) (33),³¹³ that is, the blue light emitted from the skeleton excites the pendant, resulting in the emission of green light.

α-Naphthalene-containing poly(DPA)s with methylene spacers of different lengths (m = 4, 6, 8) (e.g., **34** in Figure 14) have been synthesized. Although the TaCl₅–n-Bu₄Sn catalyst results in insoluble products in low yields, the WCl₆–Ph₄Sn catalyst forms soluble polymers with high MWs (M_w up to 5.0×10^4) in satisfactory yields of up to 62%.⁵¹⁹ When the polymers are photoexcited in THF solution, the polymers emit strong green lights with high efficiencies (up to 98%). No significant shifts in the photoluminescence spectra are observed even though the polymers are cast into thin solid films, suggesting little involvement of aggregative or excimer emission. A multilayer electroluminescent device has been constructed that emits a green light of 520 nm with a maximum



Figure 14 Disubstituted acetylene polymers that show photoluminescence, electroluminescence, and related functions.

external quantum efficiency of 0.16%. The spectral stability is outstanding: no recognizable change is observed in the electroluminescence spectrum even when the device current is raised.

Novel fluorene-containing polymers, poly[1-pentyl-2-(9,9-dimethylfluoren-2-yl]acetylene] (**35** in Figure 14) and poly[1-(3,4-difluorophenyl]-2-(9,9-dimethylfluoren-2-yl]acetylene] (**36**), have been synthesized using TaCl₅–n-Bu₄Sn as the catalyst.⁴⁹⁴ These polymers show emission peaks from 402 to 590 nm. In addition, their electroluminescent properties have been studied in heterostructure light-emitting diodes (LEDs), using these polymers as an emitting layer. A device based on **36** exhibits an orange-red emission at 602 nm with a maximum luminescence of 923 cd m⁻² at 8 V. A device with indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene) (PEDOT)/a mixture of **35** and **36** (98:2 wt ratio)/Ca/Al shows near-white emission. Its maximum luminance and current efficiency are 450 cd m⁻² at 15 V and 1.3 cd A⁻¹, respectively.

For organic light-emitting diode (OLED) applications, novel poly(DPA)s (e.g., **37** in **Figure 14**), which exhibit air stability, better solubility in common organic solvents, and higher luminescence than polyacetylene, have been examined as emitters.⁵⁶⁷ The devices have a maximum brightness of 827 cd m^{-2} at 12 V and a maximum current efficiency of 0.78 cd A^{-1} at 9 V with a maximum luminescence at 536 nm.

Fluorine-containing poly(DPA), **37** in Figure 14, shows a large redshift in UV–vis absorption and photoluminescence emission and a very high luminescent efficiency as compared to its counterpart which lacks the two fluorine atoms.⁵²⁴ The device performance can be improved by using a light-emitting copolymer composed of **37** and a carbazole-bearing unit (**38**). An LED of ITO/PEDOT/**38**/Ca/Al displays a maximum luminescence of 4230 cd m⁻² at 14 V and a maximum current efficiency of **3.37** cd A⁻¹ at 7 V.

Nanohybridization of inorganic semiconductors with organic conjugated polymers is expected to lead to the creation of new hybrids with combined advantages of the two components, namely, the high charge mobility of the inorganics and the ready processability of the organics. Poly(DPA) containing ammonium bromide moieties (39 in Figure 14) and PbBr₂ provide a functional perovskite nanohybrid that shows a higher photoconductivity than its parent polymer 39 alone.⁵⁶⁸

3.27.4.3.2(ii) Sensing and patterning

Fluorescent substituted polyacetylenes can be used for sensors by virtue of their specific photoluminescence responses to interactions with analytes. When one equivalent of Cu^{2+} ion is added to a solution of 40 (Figure 15), the photoluminescence of the polymer reduces to half the original value.⁵³¹ The effect of Fe³⁺ is more remarkable; it completely quenches the emission. In contrast, the photoluminescence becomes stronger in the presence of Al^{3+} .

A sequential chemosensor based on imidazole-containing substituted polyacetylenes **41** has been developed. Among the different kinds of metal ions, only Cu²⁺ ion can completely and efficiently quench or turn off the strong fluorescence of **41** (Figure 15), with a detection limit as low as 1.48 ppm.⁵³⁰ The associated Stern–Volmer quenching constant is as high as $3.7 \times 10^5 \text{ M}^{-1}$, because of the high affinity of Cu²⁺ from other metallic ions. The Cu²⁺-quenched light emission of **41** can be turned on by the addition of CN⁻ ion, thus allowing the polymer to function as a unique dual-response sequential ionosensor for cyanide detection.

An imidazole-functionalized disubstituted acetylene polymer (42 in Figure 15) has been synthesized via a postfunctional strategy^{569,570} and evaluated as sensor for copper ions and α -amino acids by fluorescence quenching. Fluorescence quenching is observed at low Cu²⁺ (7.0 × 10⁻⁷ M⁻¹) concentration. The fluorescence intensity sharply decreases with an increase in Cu²⁺ concentration. The addition of α -amino acids to the solution of 42/Cu²⁺ complex enhances the fluorescence of 42, presumably due to the removal of copper ions from the complex by α -amino acids. Upon addition of glycine, the quenched fluorescence turns on immediately. The detection limit is as low as $6.0 \times 10^{-5} M^{-1}$.

The fluorescence quenching behavior of thin films of PTMSDPA (43 in Figure 15) has been investigated for the purpose of application of this polymer to mono- and multicolor fluorescence imaging.⁵⁷¹ When the film is exposed to 365-nm UV light with a power of 18.6 mW cm⁻² in air at room temperature, the fluorescence band with a maximum at 530 nm rapidly decreases, and then finely resolved fluorescent images are easily obtained using photomasks. After a prolonged irradiation time of 30 min, the film of 43 exhibits an IR absorption peak at 1650 cm⁻¹ due to the carbonyl group. Based on this, it has been presumed that the fluorescence quenching reaction is due to the small amount of diradical formed initially upon UV irradiation. The fluorescence of the film of 43 is little quenched under an irradiance less than 1.15 mW cm⁻² even for tens of minutes, whereas the fluorescence of a highly photosensitive dye, such as Nile red, is readily quenched because of the high polarity in the excited state. As a result, the Nile red-dispersed film of 43 provides multicolor fluorescent images upon an irradiance of 1.15 mW cm⁻². The exposed through the photomask portions appear yellowish-green similar to 43, whereas the protected portions are colored reddish-orange similar to Nile red.

UV irradiation of **44 (Figure 15)** readily initiates photopolymerization of its acrylic pendants.⁵⁷² Development of the exposed films gives well-defined photoresist patterns. The patterned lines glow under UV illumination, because the poly



Figure 15 Disubstituted acetylene polymers that show sensing, patterning, and related functions.

(DPA) main chain of 44 is highly emissive in a green color. Polymers from disubstituted acetylenes are usually resistant to thermolysis. Some of them, however, are sensitive to photooxidation, which quenches their photoluminescence. For example, UV irradiation of a film of 45 in air through a mask quenches the luminescence of the exposed region, while the unexposed area remains emissive in a blue color.⁵⁷³ A photoluminescence image is thus directly drawn without a developing process.

3.27.4.3.2(iii) Helical polyacetylenes

Helices represent a typical secondary structure of polymers, and in cases where one sense is predominant over the other sense, a chirality is generated. The first example of chiral disubstituted polyacetylene is a PTMSP-based one (46 in Figure 16), synthesized in good yields using TaCl₅–Ph₃Bi.⁴⁸⁵ The main chain of 46 is not well ordered, judging from the small specific rotation and CD signal. This is probably due to the less controlled geometrical structure (*cis* and *trans*) and low regioselectivity (head-to-tail and head-to-head) of the polymer. A silicon-containing helical polyacetylene is also synthesized by polymerization using M(CO)_xL_γ (M = Mo, W) as catalyst.⁵⁷⁴

Poly(DPA) having dimethyl-(-)-pinanylsilyl side groups (47 in Figure 16) exhibits a very large specific rotation ($[\alpha]_D > 2000^\circ$) and complicated but very intense CD signals.⁵¹³ The desilylation of a membrane of 47 provides a poly(DPA) membrane, which exhibits a large specific rotation ($[\alpha]_D$ +5590°) and intense CD signals in the 350–450 nm region, indicating that the main chain retains the helical conformation with a large excess helix sense irrespective of the absence of chiral pendent groups.⁵¹⁰

Helical polymers can be categorized as stable ones and thermodynamic ones. Stable helical polymers have the potential to be used as stationary phases for high-performance liquid chromatography (HPLC) enantioseparation and as chiral membranes for selective permeation. The racemates with different configurations may pass through the molecular voids in the chiral membranes at different permeation rates, resulting in separation of racemic mixtures. This possibility has been studied by using a chiral membrane of polymer 47 with a one-handed helical conformation.⁵⁷⁵ 2-Butanol is a small, not-so-polar molecule and direct separation of its racemates by using a chiral HPLC column is difficult. In the enantioselective permeation of racemic 2-butanol through the chiral membrane of 47, it was proven that the (*R*)-isomer

preferentially permeates through the chiral membrane in high selectivity ($\alpha^{R} = 9.24$) and enantiomeric excess (ee = 80.5%).

Optically active poly(DPA) derivatives, poly(4-((S)-2methoxyoctyloxy)diphenylacetylene) (48 in Figure 16), poly(4-((S)-2-triethylsiloxyoctyloxy)diphenylacetylene) (49), and poly(4-((S)-2-hydroxyoctyloxy)diphenylacetylene) (50), have been synthesized and their chiroptical and liquid crystalline properties have been examined.⁵⁷⁶ The mirror image of the CD spectra of 48 and 49 in dilute solution indicates that their polymer backbones adopt a helical conformation with opposite handedness. Polymer 50 prepared from 49 by deprotection of the triethylsilyl group shows the same helical handedness as in 49. All of these polymers have a lyotropic liquid crystalline property while thermotropic liquid crystalline behavior is observed in 48 and 50. The spin-cast films of 48-50 show strong bisignate CD signals centered at the absorption band of the polymer backbone, suggesting the formation of a chiral organization.

3.27.4.3.2(iv) Liquid crystalline polyacetylenes

Polymer **51** (Figure 17) is a poly(1-phenyl-1-alkyne) derivative containing a mesogenic pendant with a biphenyl core.²⁹ It displays a smectic A (SA) mesophase in the temperature range of 172–158 °C when cooled from its isotropic melt. Its cousin **52**, which has a phenylcyclohexyl core, exhibits a nematic (N) mesophase at much lower temperatures (90–108 °C), although it differs from **51** by only one ring in the mesogenic core (i.e., cyclohexyl in **52** vs. phenyl in **51**).

The liquid crystalline properties and optical anisotropy of poly[1-phenyl-2-*p*-(dimethyl-*n*-octadecylsilylphenyl)acetylene] (53 in Figure 17) have been investigated in detail.⁵⁷⁷ Polymer 53 exhibits unexpected smectic phase liquid crystallinity in highly concentrated aromatic organic solvents such as toluene. The two major absorption bands, located at 430 and 370 nm, are attributable to the π - π * transition parallel to the main chain and the localized π - π * transition with a charge transfer characteristic among mesogenic repeating units perpendicular to the main-chain axis, respectively. Polymer 53 exhibits highly polarized absorption and fluorescence bands in a sheared film. The main-chain axis of the polymer is aligned parallel to the shearing direction, whereas the long axis of the stilbene-like side group is perpendicular to the shearing direction.

A novel acetylene monomer containing a cyanoterphenyl group, namely, 1-[(4'-cyano-4-terphenyl)oxy]-3-octyne, has been polymerized with WCl₆-Ph₄Sn catalyst to yield a liquid crystalline aliphatic polyacetylene (54 in Figure 17).⁵⁷⁸ Polymer



Figure 16 Disubstituted acetylene polymers that take helical structures.



Figure 17 Disubstituted acetylene polymers that show liquid crystallinity.

54 exhibits a nematic phase, as observed under a polarizing optical microscope, and shows a strong emission at 411 nm.

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Alkyne Polymerization

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