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Polymer Science:

A Comprehensive Reference

VOLUME 5

POLYCONDENSATION

Editors-in-Chief

K. Matyjaszewski

M. Möller

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POLYMER SCIENCE: A COMPREHENSIVE REFERENCE

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POLYCONDENSATION

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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.

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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

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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.

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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 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 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 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.

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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.

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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.

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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

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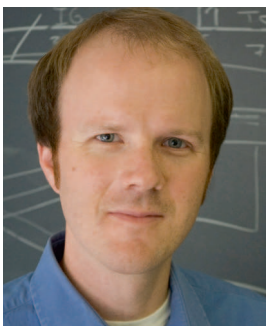
world's largest prize for invention for being 'one of history's most prolific inventors in medicine'. In 1989, Dr. Langer was elected to the Institute of Medicine of the National Academy of Sciences, and in 1992, he was elected to both the National Academy of Engineering and the National Academy of Sciences. 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 water–polymer 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

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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

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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 high-resolution 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

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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

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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.

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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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5.01 Introduction and Overview

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5.01.1 Introduction 1
5.01.2 Overview 1

5.01.1 Introduction

Polycondensates play a key role in our modern life. They substantially contribute to the quality, comfort, safety, and health of the global society. They are indispensable to cope with the diverse societal and technological challenges of the twenty-first century including energy, information, and transportation. Polycondensates will assure continuous progress, support innovative breakthroughs, and be essential for enduring sustainable economic growth.

The synthetic methodology of polycondensation allows for a broader variation of monomer and polymer structures than any other synthetic polymerization approach. Thereby, polycondensates have enlarged substantially the performance spectrum of polymers and contributed significantly to the success story of polymers and will continue to do so in the future.

The importance of polycondensates is best illustrated by the pyramid of thermoplastic polymers shown in Figure 1. Commodity polymers are based on vinyl monomers and account for more than 90% (by weight) of thermoplastic materials. However, one major drawback of commodity polymers is, in general, the thermal and mechanical properties. For example, their continuous service temperature is relatively low and limits their range of applications. Polycondensates paved the way to engineering plastics and high-performance polymers. They feature unique and outstanding mechanical and thermal properties such as high Young's modulus, tensile strength, dimensional stability, and heat resistance. As a result, numerous commercial polymers are polycondensates.

The development of the annual number of publications including patents containing the term 'polycondensation' is shown in Figure 2. It demonstrates the ongoing progress in the field of polycondensates. Certainly, the peak in research, development, and innovation was between 1960 and 1970. In spite of the fact that other polymerization methods got more and more popular during the last decade, the number of publications and patents is still continuously increasing. It is interesting to note that the number of patents is increasing faster than the number of publications demonstrating the ongoing industrial relevance and innovation potential of polycondensates.

This volume reflects recent developments of polycondensates and addresses challenges in polycondensation chemistry including materials aspects. The volume is structured into three sections: (1) fundamental principles and opportunities (Chapters 5.02 and 5.03), (2) modern synthetic approaches (Chapters 5.04–5.13), and (3) chemistry and technology of selected classes of polycondensates (Chapters 5.14–5.26).

It is obvious that this volume cannot cover all classes of the various types of polycondensates, which also should have deserved a chapter in this volume. Often excellent specialized books already exist. Also information on polyurethanes or polysiloxanes, for example, can be found in Volume 10 of *Polymer Science: A Comprehensive Reference* (Chapter 10.24 or Chapter 10.25).

5.01.2 Overview

Conventional polycondensation proceeds in a step-growth manner. Commonly, polycondensates feature – depending on the extent of the reaction – comparable broad polydispersity indices. According to the Carothers equation, a stoichiometric balance of monomers for high-molecular-weight polycondensates is of crucial importance. These basics, fundamental principles, and opportunities of step-growth polymerization are comprehensively reviewed in Chapter 5.02 by Musan Zhang, Stephen M. June, and Timothy E. Long. Special emphasis is also given on more complex polymer architectures, such as block copolymers, graft copolymers, dendrimers, branched and hyperbranched copolymers, and cyclic polymers.

Commercial polycondensates are based on industrially well-established monomers originating from oil-based feedstock. From an industrial point of view, the finite oil resources demand toward renewable resources suitable as raw material source for syntheses of these monomers is of critical importance. Therefore, Chapter 5.03 by Andreas Fuessl, Motonori Yamamoto, and Arnold Schneller gives an overview on primary intermediates from renewable resources and discusses opportunities in bio-based polymers.

Modern synthetic approaches to various types of polycondensates, polymer transformations, and supramolecular polymers, which often utilize condensation and addition chemistry, are covered in Chapters 5.04–5.13. In the past years, new approaches have been directed to exploit the general principles of polycondensation in a different manner. Using different reactivities of the functional groups of nonsymmetric monomers made a precise synthesis of sequential polycondensates possible. In Chapter 5.04, Ken-ichi Fukukawa and Mitsuru Ueda demonstrate that this can be accomplished to control the polymer microstructure and to tailor polymer properties. In Chapter 5.05, Kunio Kimura reports on nonstoichiometric polycondensation yielding high-molecular-weight polycondensates under stoichiometrically imbalanced conditions. In Chapter 5.06, Tsutomu Yokozawa outlines polycondensates with narrow molecular weight distribution that can be obtained utilizing a chain-growth condensation polymerization approach.

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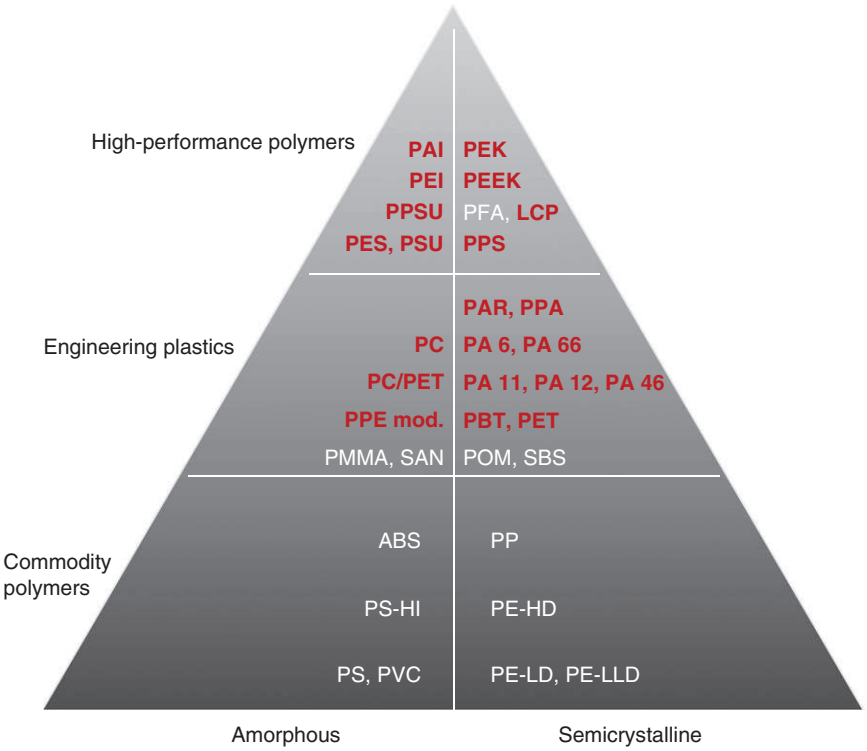

Figure 1 The polymer performance pyramid divided into commodity polymers, engineering plastics, and high-performance polymers with prominent examples; red-labeled denote to polycondensates. PS (HI), polystyrene (high impact); PVC, polyvinyl chloride; PE (LD, LLD, and HD), polyethylene (low density, linear low density, and high density); ABS, acrylonitrile-butadiene-styrene copolymer; PP, polypropylene; PMMA, poly(methyl methacrylate); SAN, styrene-acrylonitrile copolymer; POM, poly(oxymethylene); PA, polyamide; PC, polycarbonate; PPE, poly(phenylene ether); PBT, poly(butylene terephthalate); PET, poly(ethylene terephthalate); SBS, styrene-butadiene-styrene block copolymer; PAR, polyaramide; PPA, polyphthalamide; PES, poly(ether sulfone); PSU, polysulfone; PPS, poly(phenylene sulfide); PPSU, polyphenyl sulfone; PFA, perfluoroalkoxy copolymer; LCP, liquid crystalline polymer; PEI, polyether imide; PEEK, poly(ether ether ketone); PAI, poly(amide imide); PEK, poly(ether ketone).

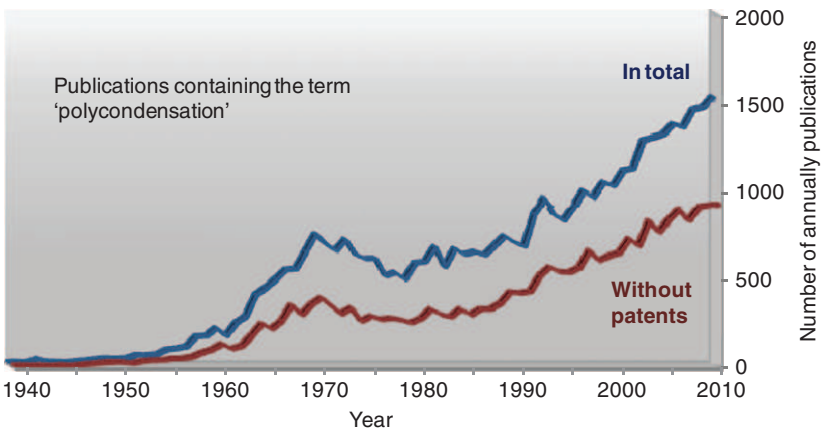

Figure 2 Development of publications and patents per year containing the term 'polycondensation' from the 1940 to 2010 (according to SciFinder).

A special type of polycondensation is the oxidative coupling polymerization. Recent progress in this field is summarized in Chapter 5.07 by Hideyuki Higashimura. Examples for the synthesis of poly(phenylene oxide)s, polyphenols, poly(phenylene sulfide)s, polyanilines, polypyrroles, polythiophenes, and polyphenylenes are discussed. Another broad approach to synthesize aromatic polymers is metal-catalyzed coupling reactions described in Chapter 5.08 by C. Daniel Varnado Jr. and Christopher W. Bielawski. Here, Kumada, Negishi, Stille, Suzuki, Heck, Sonogashira, and other coupling reactions are reviewed. Acyclic diene metathesis (ADMET) polymerization of linear diolefins is also a step-growth polycondensation method forming carbon–carbon bonds. This topic is reviewed in Chapter 5.09 by Erik B. Berda and Kenneth B. Wagener. High-molecular-weight polymers are achievable by removing the byproduct ethylene and, thus, ADMET provides an efficient route to polyolefins with precise distribution of functional groups, either within or pendant to the polymer backbone.

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For a long time, *in vitro* enzymatic catalysis has been successfully introduced in organic synthesis. Enzymatic polymerization is reviewed in Chapter 5.10 by Shiro Kobayashi. Enzymatic polymerization is defined as the *in vitro* polymerization of artificial substrate monomers catalyzed by an isolated enzyme via nonbiosynthetic pathways. Intriguingly, enzymatic polymerization is a highly selective method with respect to enantio-, regio-, and chemoselectivities and can be conducted under mild reaction conditions.

The basic principles of nonlinear polycondensates are covered in Chapter 5.11 by Mitsutoshi Jikei. Critical conversion for gelation, which causes the formation of insoluble polymers, is discussed on the basis of the Flory and Stockmayer theory. Furthermore, statistical consideration and typical examples for the preparation of soluble hyperbranched polymers are given.

Postpolymerization modification also referred to as polymer analogous reactions, represent a very versatile synthetic method for the synthesis of functional polymers and often utilize condensation, addition, substitution, or elemination reactions. Peter J. Roth, Kerstin T. Wiss, and Patrick Theato present these synthetic approaches to modify and functionalize polymers enabling novel (multi)functional polymers in Chapter 5.12.

A promising approach and ongoing challenge in macromolecular science exploits the formation of macromolecules by molecular self-assembly utilizing intermolecular interactions instead of the formation of covalent bonds. In Chapter 5.13, Andreas Winter, Martin D. Hager, and Ulrich S. Schubert review supramolecular polymers based on metal-to-ligand coordination, ionic interaction, or hydrogen bond formation. A variety of supramolecular polymers as well as potential applications are discussed.

The chemistry and technology of selected classes of polycondensates are reviewed in Chapters 5.14–5.26. Polyesters are probably the most important class of polycondensates. In Chapter 5.14, S. Richard Turner and Yanchun Liu review the state of the art of chemistry and technology of polyesters. Synthetic aspects, for example, solution, interfacially, and melt-phase processes are presented. Moreover, processing and uses of semicrystalline and amorphous polyesters are described. An overview on different polyester classes and on the industrially most important poly(alkyl arylester)s, such as poly(ethylene terephthalate) (PET), poly(cyclohexane-1,4-dimethylene terephthalate) (PCT), and poly(butylene terephthalate) (PBT) is given. In Chapter 5.15, Seema Agarwal reports on the different synthetic routes toward (bio)degradable polyesters. Polyesters allow for various degradation reactions such as hydrolysis, oxidative cleavage, and enzymatic attack. This opened the way to biodegradable polyesters featuring promising applications in various medical and nonmedical fields such as agriculture, medicine, pharmacy, and biomedical materials. In Chapter 5.16, Kazuhiko Takeuchi reviews synthetic approaches, properties, and future perspectives of semiaromatic and aliphatic polycarbonates. Polycarbonates are a prominent example of a successfully widespread used engineering plastic.

Aromatic polyethers, poly(ether ketone)s, polysulfones, and polysulfides belong to the class of high-performance polymers. High-performance polymers are characterized by their advantages over other polymers especially in applications, where greater thermal and oxidative stabilities, better solvent resistance, lower flammability, and higher strength are required. In Chapter 5.17, Ruilan Guo and James E. McGrath review on the history and recent advances in the syntheses, reactions, physical and chemical properties, and applications of these high-performance polymers.

Polyamides are another important class of engineering plastics. In Chapter 5.18, Ruud Rulkens and Cor Koning present a comprehensive overview of the chemistry and technology of polyamides. The thermal and mechanical properties of hydrolytically prepared fully aliphatic and semiaromatic commercial polyamides and their beneficial properties are discussed. In Chapter 5.19, Yukihiro Abe and Kazuyuki Yabuki report on various lyotropic polycondensates and fiber technology. For example, polyaramides are fully aromatic polyamides and feature exceptional high strength and heat resistance.

Aromatic polyimides have been well known as an important class of high-performance polymers. Recent development of these polymers involving their synthesis and properties are introduced by Guey-Sheng Liou and Hung-Ju Yen in Chapter 5.20. Their outstanding properties such as high thermal stability and exceptional mechanical properties with electrical and chemical resistances render them as suitable high-performance materials with applications in aerospace industries and as material for membranes for fuel-cell applications and gas or solvent separation. In Chapter 5.21 on *High Performance Heterocyclic Polymers* Alexandre L. Rusanov and Ludmila G. Komarova cover in detail synthetic procedures of other aromatic heterocyclic polymers, such as polyoxadiazoles, polythiadiazoles, and polytriazoles, polybenzaoles, polybenzimidiazols, and polybenzoazoles.

Polycondensation chemistry is also used to prepare high-performance polymers for (opto)electronic applications. In Chapter 5.22, Junji Sakamoto, A. Dieter Schlüter, and Matthias Rehahn review the recent progress in this field. The synthesis of polyarylenes, such as polyphenylenes, polyfluorenes, and poly(phenylene vinylene)s is discussed. From the synthesis point of view, Suzuki-Miyaura cross-coupling reactions – referred to as Suzuki polycondensation – proved to be the most effective and widely applicative metal-catalyzed polycondensation method. Another class of functional polycondensates is metal-containing macromolecules. Recent developments in the field of coordination and organometallic macromolecules are reviewed by Alaa S. Abd-El-Aziz and Sibel Sezgin Dalgakiran in Chapter 5.23. They can be regarded as polycondensates utilizing metal centers with different geometries and are described with respect to their structural differences, such as star-shaped molecules, various metal-containing dendrimers, and a combination of neutral and cationic metal complexes. Similar dendrimers can be considered as hyperbranched macromolecules with a perfectly defined and highly functionalized repetitive structure. In this volume, a large variety of phosphorus-containing dendritic architectures are reported by Anne-Marie Caminade and Jean-Pierre Majoral in Chapter 5.24. More information in the area of dendrimers is also discussed in *Polymer Science: A Comprehensive Reference* (Chapter 6.04).

Polycondensation chemistry is also used to prepare highly crosslinked polymers. Epoxy and phenol-formaldehyde resins

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have been well known as one of the most important classes of thermoset plastics. In Chapter 5.25, Tsutomu Takeichi, Takehiro Kawauchi, and Nobuyuki Furukawa report on development regarding these types of thermosets including their synthesis and properties. In the final chapter of this volume (Chapter 5.26), Theo Dingemans reports on the chemistry, properties, and selection criteria of all-aromatic high-temperature thermosets, which combine the outstanding properties of high-performance polymers with processability.

Acknowledgments

Both volume editors would like to express their sincere gratitude to the chapter authors for their valuable contributions, positive collaborations, and their engagement in this project. HWS would like to especially thank Dr. Klaus Kreger and Christine Scharf (University of Bayreuth) for their ongoing support in the course of preparing and finalizing this volume.

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Biographical Sketches

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5.02 Principles of Step-Growth Polymerization (Polycondensation and Polyaddition)

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5.02.1 Introduction and Historical Perspective

Since Wallace Carothers's early discoveries of polyesters and polyamides, with the many implications of the resulting Carothers's equation, the impact of engineering thermoplastics has continued to expand as new technologies demand high-performance macromolecular architectures. In his pioneering work from 1929, Carothers described a vision for polycondensation that expressed the requirement for reactive monomeric functional groups to form a new bond through the elimination of a small molecule or condensate.[1,2] The early work explored the reversible nature of polycondensation reactions and strategies to circumvent the strict requirements for successful step-growth polymerizations. Unlike conventional free-radical polymerization, early polycondensation polymers were reversible and susceptible to hydrolysis, which was an obstacle for obtaining high molecular weight polymers. In addition, Carothers acknowledged various types of polymer topologies through the alteration of monomer functionality.[2]

Eighty years after Carothers's early work, step-growth polymerization has emerged as a commercially viable approach for designing tailored polymers for a variety of applications. Although early interests in step-growth polymers were directed toward alternatives to vinyl-based polymers for commercial purposes, the unique advantages of step-growth polymers became increasingly apparent. For example, properties such as toughness, stiffness, and thermal stability were markedly improved compared to early free-radical derived polymers.[3] The versatility of these polymers advanced step-growth polymers into new industries, and this theme of expanding relevance to a variety of applications is still readily apparent today. This chapter outlines many synthetic methods for step-growth polymers and transitions to rapidly evolving applications in other disciplines. For example, step-growth polymers

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play an important role in biomedical applications due to their tunability and ability to modify mechanical, thermal, and drug delivery properties compared to conventional small-molecule drugs. It is remarkable that in a little over 50 years, step-growth polymerization has truly emerged as an interdisciplinary field of study.

The application of step-growth polymers could not have achieved such significance without an understanding of the synthetic principles that enable controlled and predictable morphological and mechanical properties of polymers. One unique advantage of step-growth polymerization is the ability to tailor the monomer choice, which directly affects the polymer backbone unlike many conventional free-radical polymers that have a nonfunctional hydrocarbon backbone. The development of novel monomers reenergized research interests and provided a new molecular handle to combine, centered on the fundamental understanding of structure–property–morphology relationships to improve and tailor polymer performance. The ability to design the polymer backbone allows for control of mechanical, thermal, and flexibility of the polymer chain. In addition, multifunctional monomers can be designed to create diverse polymer topology. The understanding of polymer chemical composition and topology promotes morphology control, which relates to various desirable polymer properties such as enhanced mechanical and thermal properties. Polymer research has engaged in an increasing interest toward creating sophisticated, versatile, and multifunctional polymers, which offer 'smart' capabilities such as dynamic assembly, stimuli-responsive, self-healing, and remendable properties.

In addition to creating polymers with tailored physical properties, polymer scientists are becoming increasingly aware of their contribution and responsibility to ameliorate environmental issues. Because step-growth polymers have expanded into various disciplines, global issues, such as diminishing natural resources, human disease, energy crisis, water purification, and climate change, have all been unavoidable concerns which polymer chemists and engineers have been trying to solve. Thus, many of the research efforts have been redirected to some of the first polycondensation polymers that Wallace Carothers studied in 1929, that is, polyesters.[4,5] The revival of polyester synthesis interest stems mainly from the need to transition away from petroleum-derived monomers and toward renewable resources. In addition, green chemistry promotes research in novel synthetic approaches such as enzyme catalysis, solvent-free, and no by-product polymerizations. The hydrolytically labile ester linkage allows polyesters to find applications not only in recyclable packaging, but also in biodegradable drug delivery devices and biomaterials.

This chapter focuses on the recent advances in the field of step-growth polymers and describes the basic principles first outlined by Wallace Carothers. Various polymer architectures are achieved through step-growth polymerization, and several examples of traditional classes of polycondensation and polyaddition polymers with novel applications will be reviewed. Applications of new chemistries, such as ionene synthesis, click chemistry, and Michael addition, expand the class of step-growth polymerizations. Finally, this chapter will explore synthetic strategies, such as enzyme-catalyzed and living polycondensation polymerization, that have been developed to circumvent challenges present in step-growth polymerization. Future directions for step-growth polymers feature new synthetic approaches that demonstrate the remarkable progress and discovery in step-growth polymerization since the time of Wallace Carothers.

5.02.2 Structure–Property Relationships in Step-Growth Polymers

The mechanisms and kinetics of polymerization often classify polymerization reactions into two specific subsets: chain-growth polymerization and step-growth polymerization. This chapter focuses exclusively on step-growth polymerization, while chain-growth polymerization will be reviewed elsewhere in this anthology. The tuning of monomer composition, molecular weight, and polydispersity dictate the final properties of the resulting polymer. Further tailoring of polymer architectures and topologies such as block copolymers, crosslinked networks, and hyperbranched polymers define the thermal and mechanical properties for specific applications.

5.02.2.1 Synthetic Principles

Step-growth polymerization involves the reaction of two reactive functional groups to form a new single functional group. For example, an addition–elimination reaction between two monomers, a dicarboxylic acid and a diol, creates a dimer of the two monomers chemically linked through a new ester bond and elimination of the condensate, water. Stepwise reaction of the dimers with subsequent monomers or dimers produces trimers and tetramers, respectively. Because of the sequence of monomer addition, monomers within the reaction are rapidly consumed during the initial stages of the reaction. However, high molecular weight is not initially obtained. The production or absence of a by-product condensate further defines two subclasses of polymers: polycondensation and polyaddition. Polycondensation produces polymers through the elimination of a small-molecule by-product such as hydrochloric acid, water, methanol, acetic acid, and others. Thus, synthesis of step-growth polymers using this approach depends largely on the removal of the condensate in order to drive equilibrium-based polymerization processes toward high molecular weight polymers. On the other hand, polyaddition proceeds without the formation of by-products. Typically, polyaddition requires highly reactive end groups or catalysts to synthesize polymers. Traditional examples of polyaddition polymers are polyurethanes (PUs) and epoxide curing; however, novel click polymers and ionenes are emerging as new modern classes of polyaddition step-growth polymers.

Due to high conversion of monomer requirement for sufficient molecular weight, synthesis of polymers using step-growth polymerization demands reactions that are quantitative. For this reason, synthetic considerations are required to achieve linear high molecular weight linear polymers:

1. high monomer conversion (> 99.9%);
2. difunctional monomers ($f = 2$);
3. monomer stoichiometry of A:B = 1:1;
4. elimination of side reactions such as degradation or cyclization;
5. accessibility of end groups;
6. high monomer purity.

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These conditions are required to achieve high molecular weight linear polymers. However, synthetic techniques have been developed to bypass stringent 1:1 monomer stoichiometry requirements. These details will be discussed later in this chapter, for example, interfacial polymerization.

Variations of monomer functionality as well as monomer composition afford polymers with tailored performance. Unlike chain-growth polymerization which contains a hydrocarbon polymer backbone, step-growth polymers incorporate the added advantage of a tailorable polymer backbone composition. Design of novel step-growth polymers often involves the synthesis of novel monomers. Typical limitations of commercial step-growth polymerization arise from the lack of available monomers and the cost of manufacturing the appropriate monomers for desired polymer properties.

As mentioned previously, step-growth polymerization demands specific reaction considerations to ensure high molecular weight polymers. The reactivity of end groups becomes critical to achieve high molecular weight for optimal properties. In addition to the reactivity of the end group, the concentration and accessibility of the end groups also affect the reaction rate. The species within the polymerization will transition from high monomer and end group concentrations to oligomers and lower concentrations of end groups. This change in reactive species will inherently alter the kinetics of polymerization. Changes in reaction polarity, volume, and viscosity ultimately impact the reaction.[6] As the polymerization reaches high conversions, the viscosity will increase dramatically and limit the mobility of the polymer end groups, and thus their statistical likelihood of reactions.

Some step-growth polymerizations proceed through an equilibrium reaction. The forward reaction promotes the growth of the polymer chain, and the reverse reaction encourages depolymerization. As the reaction toward polymers occurs, there is an inherent equilibrium-driven reverse reaction. Depending on the reaction, the removal of the condensate can drive the reaction forward. In addition, long reaction times are often required because high extent of conversion is necessary for high molecular weight polymers. Thus, many step-growth reactions require the aid of catalysts.

One of the fundamental problems facing polymer chemists today and throughout history is to understand and predict how structural changes will impact the physical, mechanical, chemical, and thermal properties of polymers. This is no simple task due to different aspects of a polymer's structure which play a significant role in deciding its ultimate properties. For example, polymers comprised of identical repeating unit will display dramatic differences in properties based on its molecular weight, topology, morphology, and thermal history. As expected, differences in chemical structure determine polymer properties. For example, nylon-6,6 exhibits dramatically different properties than the polyester formed from reacting 1,6-hexane diol with adipic acid. The only structural difference exists in the linkages between the repeating units, amides in the case of polyamides and esters in the case of polyesters. This minor structural difference contributes to significant variations in the physical properties of the two polymers. Understanding these differences and intelligently utilizing these molecular properties to design polymers with tailorable bulk properties is a challenge that the polymer chemistry community continues to address. Many recent advances in understanding of structure–property relationships within step-growth polymers will be discussed herein, but many unsolved challenges remain.

5.02.2.2 Molecular Weight Control

Molecular weight is arguably the single most important polymer parameter. Low molecular weight polymers have lower tensile strength, impact strength, toughness, and mechanical strength than their high molecular weight (> 5000-10 000 g mol^{-1}) counterparts. As such, an understanding and control of molecular weight is crucial in the synthesis and development of step-growth polymers. Fortunately, a theoretical approach exists for predicting molecular weight for linear step-growth polymerizations as a function of conversions.[7]

Let us consider the extent of conversion at some time, t, within the polymerization. For a 1:1 stoichiometric ratio of two difunctional monomers A–A and B–B, there is on average one unreacted A functionality and one unreacted B functionality per oligomeric (or polymeric) species.[7–10] The reaction of one A functional group with one B functional group forms one repeating unit. Thus, a polymer formed of the monomers A–A and B–B would have a repeating unit of –(–A–A–B–B–)–.[7–10] The total number of repeating units within a polymer is equal to one-half the total number of monomer units (assuming 1:1 stoichiometry). The number-average degree of polymerization (DP), $\bar{X}_n$, which relates to the average number of structural units from the reactive monomers, is equal to twice the number of repeating units per polymer molecule. It is important to note that this is different from chain-growth polymerization. In an A–A and B–B system, the formation of a repeat unit requires the conversion of two A functionalities and two B functionalities. Therefore, there are two resulting A–B functional groups per repeat unit. Restated, $\bar{X}_n$ is equal to the number of structural units per polymer chain. $\bar{X}_n$ is also signified as $\bar{P}$ or $\overline{DP}$.[7–10]

In order to further understand $\bar{X}_n$, one should first examine the mechanism of step-growth polymerization. Unlike chain-growth polymerization, step-growth reactions do not necessarily proceed through consecutive monomer addition. Instead, two monomers react to form a dimer, which may react with another monomer dimer to form a trimer or tetramer, respectively. Therefore, monomers are quickly consumed during the initial stages of polymerization. Ultimately, any oligomeric or polymeric chains may react with other oligomeric or polymeric species in the reaction. In contrast, the propagating polymer chains in chain-growth polymerizations react with single monomers until the propagating radical is terminated. In chain-growth polymerizations, high molecular weight polymers may be achieved even when monomer conversion is less than 100%. However, the DP of a step-growth polymerization relates directly to monomer conversion. In order to calculate $\bar{X}_n$ at a given time during the reaction, the concentration of polymeric or oligomeric molecules and the initial monomer concentration must be known. The concentration of unreacted monomer at t, $[M]_t$, is

$$[M]_t = [M]_0 - [M]_0 p = [M]_0(1-p) \qquad [1]$$

where $[M]_0$ is the initial concentration of monomer and p is the extent of functional group conversion at time t. Because the number of molecules in the system is directly proportional to the concentration of molecules, one can express the DP as

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$$\bar{X}_n = \frac{N_0}{N} = \frac{[M]_0}{[M]} \quad [2]$$

where N_0 is the initial number of monomer molecules and N is the number of oligomeric or polymeric molecules present in the system.[7–10] Rearrangement of eqn [1] yields the 'Carothers's equation'[7] or

$$\bar{X}_n = \frac{1}{(1-p)} \quad [3]$$

A careful examination of eqn [3] demonstrates the importance of high conversion in step-growth polymerization. Without high conversion, high DPs and subsequently high molecular weight are impossible to obtain. In the synthesis of small organic molecules, a reaction conversion of 90% is considered excellent. However, 90% conversion ($p = 0.9$) in a step-growth polymerization limits the DP of the final product to only 10 repeating units per polymer chain. As mentioned previously, a polymer's physical and mechanical properties are directly related to molecular weight, and therefore a polymer with only 10 repeating units is unlikely to possess desirable mechanical properties. **Figure 1** shows $\bar{X}_n$ as a function of p. From this plot, high DPs are only attained when conversion reaches approximately 98% or higher.[7–10]

Although knowledge of $\bar{X}_n$ is helpful, different polymer structures may have identical DPs and display different molecular weights because of different repeat unit molecular weights. Therefore, the number-average molecular weight ($\overline{M}_n$) of a polymer may be calculated as

$$\overline{M}_n = M_0\bar{X}_n + M_{EG} = \frac{M_0}{(1-p)} + M_{EG} \quad [4]$$

where $\bar{X}_n$ is the DP, M_0 is one-half the molecular weight of the repeat unit, and M_{EG} is the molecular weight of the end groups.[7–10] For sufficiently high molecular weight polymers, M_{EG} is considered negligible, and thus $\bar{M}_n$ simplifies to

$$\overline{M}_n = M_0\bar{X}_n = \frac{M_0}{(1-p)} \quad [5]$$

However, it is important to note the significance of end group molecular weights for oligomeric species.

Utilizing eqn [5], it is possible to predict the number-average molecular weight based on the percent conversion of monomer functionality, the molecular weight of the repeating unit, and the assumption of 1:1 stoichiometry. As in eqn [2], if a polymer is derived from two difunctional monomers, A–A and B–B, then the DP should be equal to the initial number of monomer molecules divided by the number of oligomeric or polymeric molecules present in the system. However, in eqn [2], there are an equal number of A–A molecules as B–B molecules. Therefore, if the stoichiometry is not 1:1, the number of available reactive functional groups becomes significant in determining the polymer molecular weight. N_0 is the average number of A–A monomers and B–B monomers, and therefore,

$$N_0 = \frac{N_A + N_B}{2} = \frac{N_A}{2}\left(1 + \frac{1}{r}\right) = \frac{N_A}{2}\left(\frac{1+r}{r}\right) \quad [6]$$

where N_A and N_B are equal to the number of A–A monomers and B–B monomers, respectively, and r is equal to N_A/N_B. B–B monomer is defined as the monomer in excess, and r will always be less than or equal to 1. The total number of molecules after reaction yields

$$N = \frac{1}{2}[N_A(1-p) + N_B(1-rp)] = \frac{N_A}{2}\left[(1-p) + \frac{(1-rp)}{r}\right] \quad [7]$$

Rearranging eqn [7] and substituting into eqn [2] we arrive at the number-average chain length or DP:

$$\bar{X}_n = \frac{N_0}{N} = \frac{1+r}{1+r-2rp} \quad [8]$$

Assuming 100% conversion, this equation simplifies to

$$\bar{X}_n = \frac{1+r}{1-r} \quad [9]$$

Ensuring a 1:1 stoichiometry is crucial to obtain a high molecular weight polymer. A 10% deficiency in monomer A–A would result in a maximum DP of 19. **Figure 2** illustrates the degree of conversion as a function of r. High DPs and high molecular weights are only achieved when the stoichiometric deficiency of A–A is less than 2%.[7–10]

Although stringent 1:1 stoichiometric conditions must be taken to synthesize high molecular weight step-growth polymers, the statistical effect of stoichiometry on molecular weight provides one major advantage: molecular weight control. As discussed previously, desirable mechanical, impact, and viscoelastic properties rely heavily on generating a high molecular

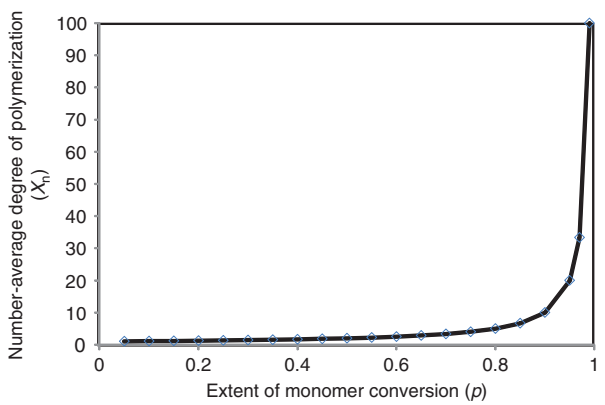

Figure 1 DP ($\bar{X}_n$) as a function of extent of conversion (p) or monomer consumption assuming 1:1 stoichiometry of functional groups.[10]

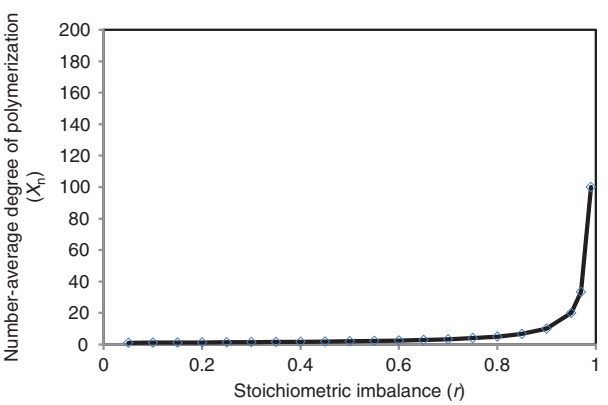

Figure 2 Number-average DP (X_n) as a function of stoichiometric imbalance, r.

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weight polymer. However, high molecular weight polymers also encounter synthetic challenges such as high melt viscosity. Above a certain molecular weight, the melt viscosity increases exponentially with molecular weight; this effect imparts difficulties in processing and fabrication of polymers. Therefore, the ability to control and limit molecular weight proves exceptionally useful when trying to tailor mechanical properties.[9]

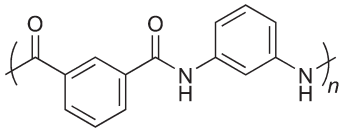
The synthesis of segmented block copolymers takes advantage of molecular weight control. Segmented block copolymers using step-growth polymerization often require the initial synthesis of a lower molecular weight difunctional oligomer. These lower molecular weight oligomers may be referred to as macromonomers or prepolymers. Utilizing a controlled stoichiometric excess of one monomer allows for accurate target of a specific molecular weight and ensures the presence of reactive end groups containing the same functionality as the monomer used in excess. The functionalized prepolymer may subsequently be reacted with complementary monomers to obtain segmented block copolymers. This synthetic route is commonly used in PUs, polyesters, and polysulfones.[9]

As mentioned previously, molecular weight may be the single most important variable when attempting to understand structure–property relationships within polymers. Thus, the ability to control molecular weight within a step-growth polymer is critical. Utilizing the techniques discussed herein, stoichiometric control or monitoring the extent of conversion of a polymerization can control the molecular weight in step-growth polymerization. With these abilities, the beginning of polymer property control has been established.[7–10]

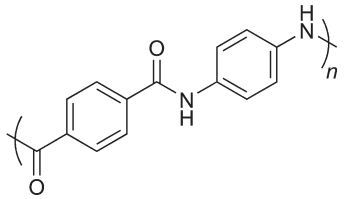
5.02.2.3 Aliphatic versus Aromatic Polymers

The selection of appropriate monomers will inherently affect the thermal, mechanical, and morphological properties of the polymer through differences in intermolecular interactions. Aromatic monomers are generally more thermally stable than aliphatic monomers, and this translates into the stability of the final polymer. In fact, aromatic polyamides are considered high-performance polymers with thermal stability greater than 500 °C. The choice of aliphatic versus aromatic also largely affects polymer morphology. The aliphatic polyamide poly (hexamethylene adipamide) (nylon-6,6) is a semicrystalline polymer with a melting temperature of 265 °C and is approximately 50% crystalline. This high melting temperature contributes to the high tensile strength and modulus desired for fiber formation. The melting temperature of fully aromatic poly(*p*-phenylene terephthalate) (PPPT) is higher than the degradation temperature of the polymer.

Aromatic polyamides such as poly(*m*-phenylene isophthalamide) (PMPI) and PPPT have significantly different thermal and mechanical properties simply from altering the regioisomers (**Figure 3**). Aromatic polyamides exhibit greater melting temperatures compared to aliphatic polyamides and therefore, require higher reaction temperatures. PPPT polymer chains have rodlike extended features through the highly regular *para*-substitutions and often form liquid crystalline solutions.[3,9] Solutions of PPPT are directly spun into fibers with high polymer chain orientation to produce excellent moduli values. In fact, PPPTs, commonly known under the trade name *Kevlar*®, are used in bullet-proof vests. However, PMPI, which is *meta*-substituted, have *meta*-linked 'kinks' within the polymer chain to disrupt the linearity of the chain conformations and does not form rodlike polymer chains. Thus, the mechanical properties of this aramid diminish compared to PPPT. PMPI, commonly called Nomex®, is often used as fire-resistant protective clothing.



Poly(*m*-phenylene isophthalamide) (PMPI) (Nomex®)



Poly(*p*-phenylene terephthalate) (PPPT) (Kevlar®)

Figure 3 Commercially significant aromatic polyamides.

5.02.2.4 Influences of Intermolecular Interactions

Monomer selection greatly determines the polymer properties; however, the underlying contributor of these properties arises from the intermolecular interactions of the polymer chains. Secondary interactions, such as van der Waals, hydrogen-bonding, and electrostatic interactions, promote ordering of the polymer chains, enable physical crosslinking, and enhance mechanical properties. These interactions, although relatively weak compared to covalent bonds, also have strong implications in the morphology of the polymer. **Table 1** summarizes these secondary interactions and their relative energy of dissociation. Intermolecular interactions are directly associated with the relative distance between the corresponding units involved in the interaction.

Table 1 Comparison of various secondary interactions and their associated dissociation energy[11]

Intermolecular interaction	*Dissociation energy (kJ mol^{-1})*	*Distance relationship*	*Polymer examples*
Dipole–dipole	2	$1/r^6$	Polyethylene
Hydrogen bonding	20	–	Polyamides, polyurethanes
Ion–dipole	15	$1/r^2$	
Ion–ion	250	$1/r$	Ionenes

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The distance of between the intermolecular interactions of the polymer bonding strongly influences dipole–dipole, hydrogen-bonding, and metal–ion interactions. In addition, the functionality of the interaction is predetermined. For example, hydrogen bonds require close proximity of two or three monomer units with hydrogen-accepting and hydrogen-donating groups. In contrast, ion–ion interactions create multifunctional physical crosslinks. These ion–ion crosslinks have profound implications on the chain mobility and greatly affect the thermal, morphological, and conductive properties of step-growth polymers.

Hydrogen-bonding interactions play a large role in the mechanical and thermal properties of polymers. This powerful interaction has been the basis for the outstanding properties seen in polyamides and PUs. In fact, a comparison of nylon-6 and polyethylene illustrates the influence of hydrogen-bonding interactions in polymers. High-density polyethylene, entirely comprised of hydrocarbons, has a melting temperature of 125 – 135 °C. However, incorporating an amide functional group between hexamethylene units increases the melting temperature to 235 °C for nylon-6. The difference between the melting temperatures results from the interchain hydrogen-bonding interaction within the polyamide crystallites.[12,13]

Meijer *et al.* investigated the role of hydrogen bonding and the effect of solvent polarity on the formation of hydrogen-bonding helical supramolecular structure in dilute solution and translated this relationship to the solid state with polymers.[14] The hydrogen bonding of benzene-1,3,5-tricarboxamides (BTAs) with alkyl side chains in nonpolar solvent, methylcyclohexane, favored the formation of self-assembling threefold helices even in dilute solutions. The addition of small amounts of polar solvent, *tert*-butyl ether, stabilized the formation of helices in solution. Spectroscopic techniques such as infrared spectroscopy and circular dichroism indicated that the solvent polarity significantly influenced the gain or loss of hydrogen-bonding units in solution. Figure 4 illustrates the transition of the hydrogen-bonding helical structures from dilute solution to solid-state microstructures.

Polymers with BTA telechelic functionality and varying backbone polarity further revealed the effects of hydrogen bonding on the solid-state structures. BTA-functionalized to nonpolar telechelic polymers indicated nanorod-like structures and phase segregation. However, if the polymer backbone polarity increased, the nanorod and phase segregations were essentially lost. These effects were similar to the hydrogen-bonding structures of monomeric BTA under polar and nonpolar dilute solutions. Under aprotic conditions, the polymer chains favored hydrogen-bonded helical conformations. In this case, the solid-state properties translated into extended nanorod structures. As the solution increased in polarity, telechelic groups tended to maintain their monomeric state and dissociate rather than associate with each other through hydrogen bonding. The solid-state properties reflected this morphology change through a loss of nanorod structure. In addition to solution properties and polarities, the researchers also investigated various types of polymers including polycaprolactone (PCL) and hydrocarbon-containing polymers. The results suggested that solution polarity and polymer polarity dictate the solid-state morphology of the polymers. More polar polymer chains such as PCL resulted in a less ordered solid-state microstructure.

5.02.2.5 Polymer Architecture

After molecular weight, the second most important parameter of a polymer in regard to mechanical, thermal, rheological, and impact properties is the architecture of the polymer. Polymer architecture, also referred to as topology, significantly impacts the physical properties of a polymer.[8–10] For a polymer with a given molecular weight and a constant repeating unit, the properties are extremely different between a linear versus a branched or hyperbranched topology. Furthermore, a cyclic polysulfone will have considerably different qualities than a linear polymer of the same molecular weight. Within this chapter, we will review seven different types of major polymer architectures: linear homopolymers, block copolymers, graft copolymers, dendrimers, branched and hyperbranched copolymers, and cyclic polymers (Figure 5).

5.02.2.5.1 Linear homopolymers

Most of the original step-growth polymers such as simple polyesters or polyamides are linear polymers. A polymer is considered to be linear if there are two end groups and no branch points.[8–10] In the absence of side reactions, including cyclic formation, the reaction products of two difunctional monomers A–A and B–B will produce a linear polymer. Step-growth polymerizations produce mainly linear polymers, although other topologies result from the intentional incorporation of branch and graft points or undesirable side reactions such as cyclization.

Above a certain molecular weight of a polymer, polymer chains may become entangled. Below this molecular weight, the chains are not sufficiently long enough to entangle. This molecular weight is called the critical molecular weight or M_c. Above M_c, entanglements result in what may be considered

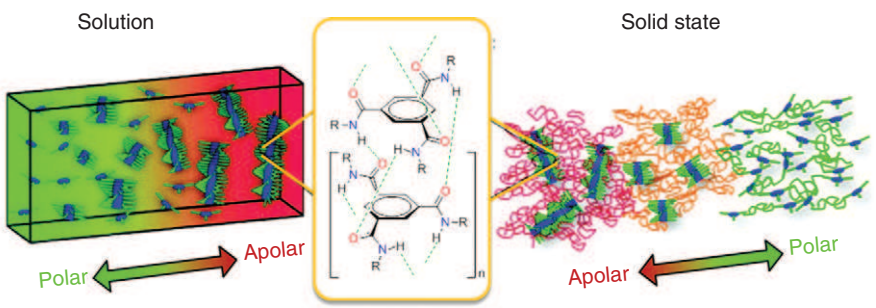

Figure 4 Translation of hydrogen-bonded polymers from solution to solid-state supramolecular morphology. Reprinted with permission from Mes, T.; Smulders, M. M. J.; Palmans, A. R. A.; Meijer, E. W. *Macromolecules* **2010**, *43* (4), 1981–1991.[14] Copyright (2010) American Chemical Society.

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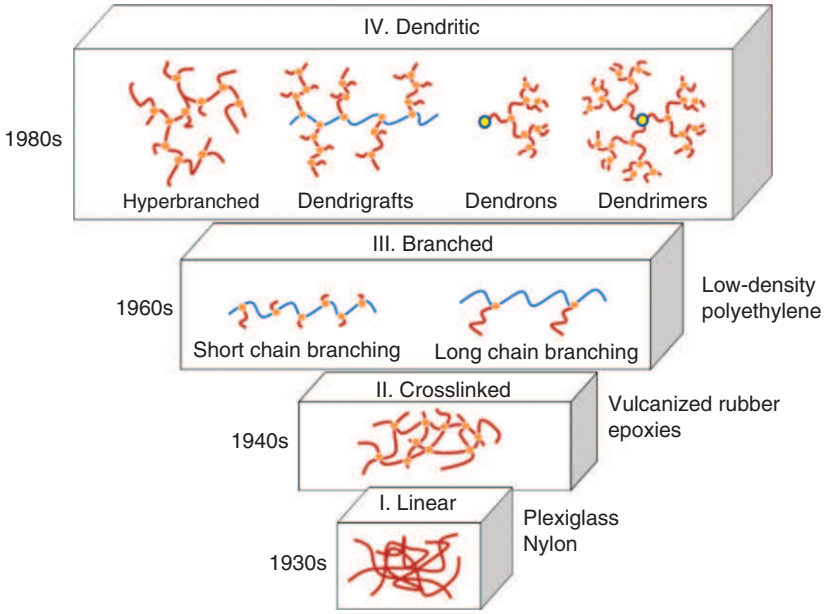

Figure 5 Chronological representation of major macromolecular architectures including linear polymers, crosslinked networks, branched polymers, and dendritic structures.[15]

'physical' crosslinks. Unlike covalent crosslinks, these physical crosslinks are transient and may unentangle at long time scales, which allow the polymer chains to reptate. Increasing the temperature also promotes chain mobility and facilitates polymer chain reputation and consequently unentanglement.[8–10] Incorporation of physical crosslinks also affects linear polymer mechanical properties. Noncovalent interactions including hydrogen-bonding and electrostatic interactions encourage physical crosslink formations such as crystallizations. Crystallites function as temporary crosslinks similar to chain entanglements, leading to enhanced mechanical properties. In nylon-6,6, these crystallites are formed due to the regular placement of amide functional groups. The hydrogen-donating amide N–H group hydrogen bonds to the hydrogen-acceptor amide carbonyl group on an adjacent chain and allows adjacent chains to organize. Unlike covalent crosslinks, the hydrogen-bonded crystallites generated temporarily reversible crosslinks at elevated temperatures and allowed for melt processing of polyamides, but still yielded high mechanical strength.[8–10]

5.02.2.5.2 Block copolymers

Block copolymers contain polymer segments comprised of different repeating units covalently linked together in a polymer chain.[8–10] For example, a block copolymer of A and B monomers may have the structure AAAAAAAAAAA–BBBBBBBBBBBBBB. This type of block copolymer is typically referred to as a 'diblock' copolymer. However, there are many different topologies which are considered block copolymers. Triblock copolymers have three blocks – one central block flanked by two blocks containing a different repeating unit, for example, AAAAAAAAAABBBBBBBBBBBBBAAAAAAAAAA. Segmented block copolymers are comprised of many alternating small blocks of two or more different types of repeating unit. Graft or brush block copolymers have one long main chain of one repeating unit and several smaller blocks of a second repeating unit branching off the polymer backbone. Figure 6 illustrates several of these different major block copolymer architectures.

In step-growth polymerization with difunctional monomers, block copolymers are synthesized using one B–B monomer and two monomers with 'A' functionality: A–A and A′–A′. Due to the difunctional nature of A–A and B–B step-growth polymerizations, it is difficult to synthesize a true diblock copolymer with difunctional monomers. In order to synthesize diblock copolymers by step-growth chemistry, there are a few synthetic techniques generally utilized. One method involves the utilization of A–B-type monomers such as 6-amino hexanoic acid. After reaching a desired percent conversion for a targeted molecular weight (using Carothers's equation to target a specific molecular weight), a selective end-capping agent must be utilized to remove one of the functionalities (A or B). At this point, each oligomeric or polymeric chain contains one functionality (B or A, respectively). A second A–B-type monomer may be subsequently added to couple with the initial oligomer to yield the diblock copolymer. A similar method may be utilized to synthesize triblock copolymers. The reaction between an excess of one difunctional monomer A–A with a different difunctional monomer B–B results in polymeric chains with A end groups. The subsequent addition of A–B-type monomers produces the two outer blocks. Both of these methods are difficult to regulate and involve several steps.

Linear multiblock copolymers are also known as 'segmented' block copolymers. Block copolymers feature many advantages, because they incorporate the thermal and mechanical properties of the individual blocks much like polymer blends. Because block copolymers are polymer

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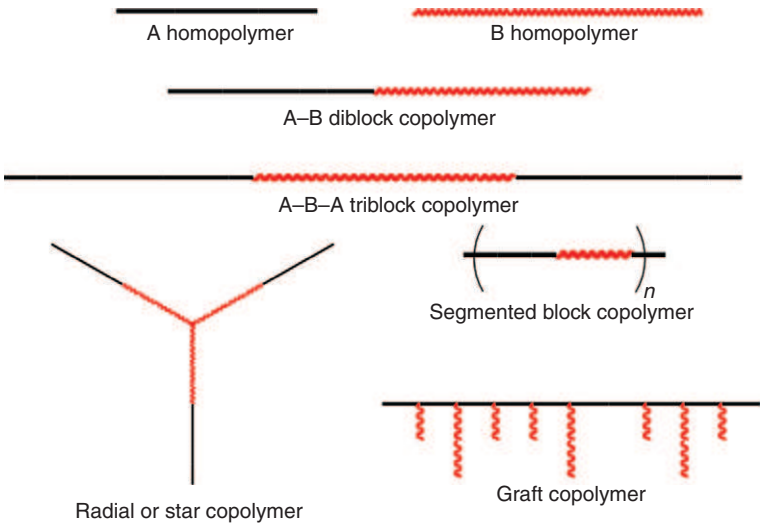

Figure 6 Various architectures for block copolymers.

blocks with individual and different repeating units covalently linked together, the phase separation behavior and morphology are dramatically different from polymer blends if the constitutive blocks are immiscible. The melt morphology of well-defined block copolymers with narrow polydispersities relates to the volume fraction of block copolymers.[16–18] Solution-casting techniques introduce other factors such as solvent selectivity and solution concentrations that also influence the polymer bulk morphology.[19] The morphology of the copolymers plays an important role for applications such as high-performance thermoplastic elastomers, fuel cell membranes, and water purification membranes. Thermoplastic elastomers are most notably known for their application in high-performance thermoplastic elastomers. These elastomeric materials contain low-modulus polymer segments with typically low-T_g covalently linked to high-modulus polymer segments. Due to the incompatibility of these polymer blocks, microphase separation occurs to impart the extraordinary tensile properties seen in elastomers such as high tensile strain, high reversible elongation, and low strain hysteresis.

One method to synthesize segmented block copolymers involves the reaction between difunctional oligomers. For example, in order to synthesize a segmented poly(siloxane imide), a poly(dimethyl siloxane) (PDMS) prepolymer was endcapped with an aminopropyl functionality. This macromonomer was reacted with another diamine and a dianhydride. The portions of the polymer that resulted from the reaction of the other diamine and the dianhydride would be considered the 'polyimide block', whereas the siloxane segment would be the 'siloxane block'.[20–23] Another synthetic technique to produce multiblock copolymers commonly used in PU synthesis utilizes polyether polyols such as poly(ethylene glycol) (PEG) or poly(propylene glycol) (PPG) as low glass transition temperature (T_g) soft segment blocks. In this case, PEG or PPG diols are reacted with an excess of diisocyanate to form a 'prepolymer' which is then subsequently reacted with a 'chain extender' such as hexane diol or butane diol (BD) to form high molecular weight polymer.

The ability to combine properties of the constitutive blocks affords tunable desired thermal and mechanical properties. The primary advantage arises from the immiscibility of the polymer blocks due to the thermodynamics of phase mixing. In the same way that a blend of PDMS homopolymer and polyimide homopolymer would eventually phase separate, copolymers comprised of PDMS segments covalently linked to polyimide segments also phase separate. This morphological consequence is a function of block composition and dictates many of the thermal and mechanical properties of the final block copolymer. At temperatures between the low- and high-T_g blocks, also known as the service temperature window, high-T_g blocks function as physical crosslinks and the low-T_g blocks act as flexible units allowing for elastomeric properties. Due to the thermally labile physical crosslinks, thermoplastic elastomers, unlike chemically crosslinked thermosets, are melt-processible at temperatures above the highest thermal transition.[8–10]

5.02.2.5.3 Graft copolymers

Graft or 'brush' copolymers are copolymers where a long polymer main chain contains many shorter chains stemming from the backbone. Graft copolymers are distinguished from other types of branched copolymers, because the branch points occur off the main backbone chain. In many cases, graft copolymers are synthesized in a two-step process beginning with a polymer backbone with a reactive functional group C (grafting from). Typically, a difunctional monomer A–A is reacted with a complementary difunctional B–B. One or both of the monomers also contain a third functionality C, which is either protected or nonreactive with functional groups A and B. Once the backbone polymer is synthesized, an oligomer, which includes one end group that is reactive with functionality C, is added and forms the brush polymer. Alternatively, two more difunctional monomers C–C and D–D (neither of which should react with the end groups of the backbone polymer) are added in stoichiometric ratios such that the brush blocks are the desired molecular weight (using Carothers's equation).

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An alternative and less utilized method called 'grafting to' is to synthesize the brush section first. After synthesis of the brush, the brush block is endcapped on one end with a difunctional monomer.[15,24,25] This difunctional monomer is reacted with a complementary difunctional monomer to form the backbone chain. However, this method is rarely utilized because conversion of the difunctional endcapped brush block is typically low due to steric hindrance. This problem is further exacerbated when the reaction proceeds past the initial dimer and trimer phases into coupling of oligomers to form high-order polymers. At this point, the steric hindrance impedes the rate of reaction to essentially zero.

5.02.2.5.4 Dendrimers

Dendrimers are another form of branched polymers that have stimulated significant attention from the scientific community in the last few decades.[15,26–29] Dendrimers are highly branched monodispersed polymers that emerge from a single core. There are two major methodologies for the synthesis of dendrimers: divergent and convergent.[15,26,27,30] In a divergent synthesis, the core is a di-, tri-, or more functional monomer (which we will refer to as A_2, A_3, etc.). Subsequently, another monomer, typically difunctional with the core functionality and monofunctional with a complementary functionality such as A_2B, is reacted with the core. In order to control conversion and maintain monodispersity, the A functionalities are chemically protected with a protection group. The first reaction step is referred to as a generation 1 or G_1 dendrimer. After deprotection of G_1, addition of more A_2B monomers affords another generation. After each subsequent generation, rigorous separations and purifications are necessary to ensure monodispersity and complete conversion of the previous generation. The divergent approach enables a high degree of dendrimer growth control; however, the additional generations increase steric hindrance and lead to lengthy branch conversion with each generation.

In a typical convergent synthesis, the separate dendrons, or arms of the dendrimer, are synthesized separately and combined with the inner core to make the final dendrimer. In this case, the dendrons can be functionalized and the core linker can be protected and subsequently deprotected and reacted with the core. Alternatively, the dendron ends can be functionalized and protected, then deprotected after final dendrimer assembly. This method is advantageous, because dendrons are smaller than dendrimers and provide simpler isolation and purification steps leading to a facile synthesis of higher order dendrimers. However, steric constraints impart difficulty for the focal points to react with the core. A large excess of the high-generation dendrons can overcome this synthetic challenge; however, this approach is synthetically wasteful and therefore can be very expensive.

A cartoon structure of a dendritic polymer is shown in Figure 7. This cartoon outlines the core (black), G_1 (red), G_2 (blue), G_3 (green), and G_4 (brown). The cartoon also demonstrates the repeating nature of dendrimers. Each end point of each generation splits into two subsequent end points in the next generation. The number of end groups, N_{EG}, of a dendrimer can be expressed as

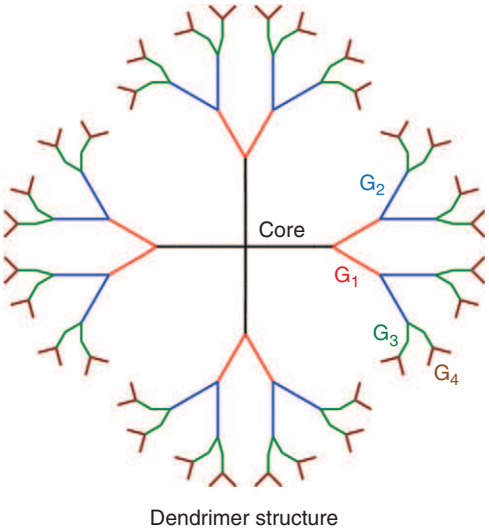

Figure 7 Cartoon depicting dendrimer structures in which black represents the core, and red, blue, green, and brown represent the first, second, third, and fourth generations, respectively.

$$N_{EG} = x2^n \quad [10]$$

In this equation, x is the number of branches off the core, and n is the number of generations. Therefore, a G_1 dendrimer with four branch points contains eight end groups. The corresponding G_4 dendrimer would produce 64 end groups. When considering the number of end groups of a dendrimer, the synthesis of higher generation dendrimers or dendrons remains a synthetic challenge due to steric crowding of the end groups. As mentioned previously, all end groups of the prior generations must be successfully deprotected to ensure that the reaction proceeds to 100% conversion. Often, an excess of the A_2B monomer will drive the previous generation to adequate conversion. However, this method presents its own difficulties, because rigorous purification and deprotection are required after synthesis of every generation.

There are several different types of dendritic structures, such as dendrimers, dendrons, dendronic surfaces, dendriplexs, and dendrigrafts. Figure 8 shows cartoon representations of these dendritic structures as well as others. Dendrimers were discovered in the late 1970s independently by two groups: Buhlier *et al.*[31] in Germany and Tomalia *et al.*[32] at Dow Chemical in Midland, MI. Tomalia *et al.* coined the term 'dendrimer' in 1985 in an article outlining the synthesis of the poly(amidoamine) (PAMAM) dendrimer series.[32] By the mid-1990s, dendrimers elicited a significant amount of attention in the literature, with tens of thousands of papers, patents, and lectures given on the topic since their early exploration in the early 1980s.[15]

Dendrimers are used for a plethora of applications.[15,26,30] The functions of dendrimers have been well reviewed elsewhere,[15,26,27,30] and thus will only be discussed briefly herein. Dendrimers have been used in polymer blends and in polymer gels to obtain different mechanical properties than their nondendritic counterparts, such as fast cure coatings and highly gelled surfaces. Dendrimers containing transition metal complexes have been utilized in photochemistry for light harvesting

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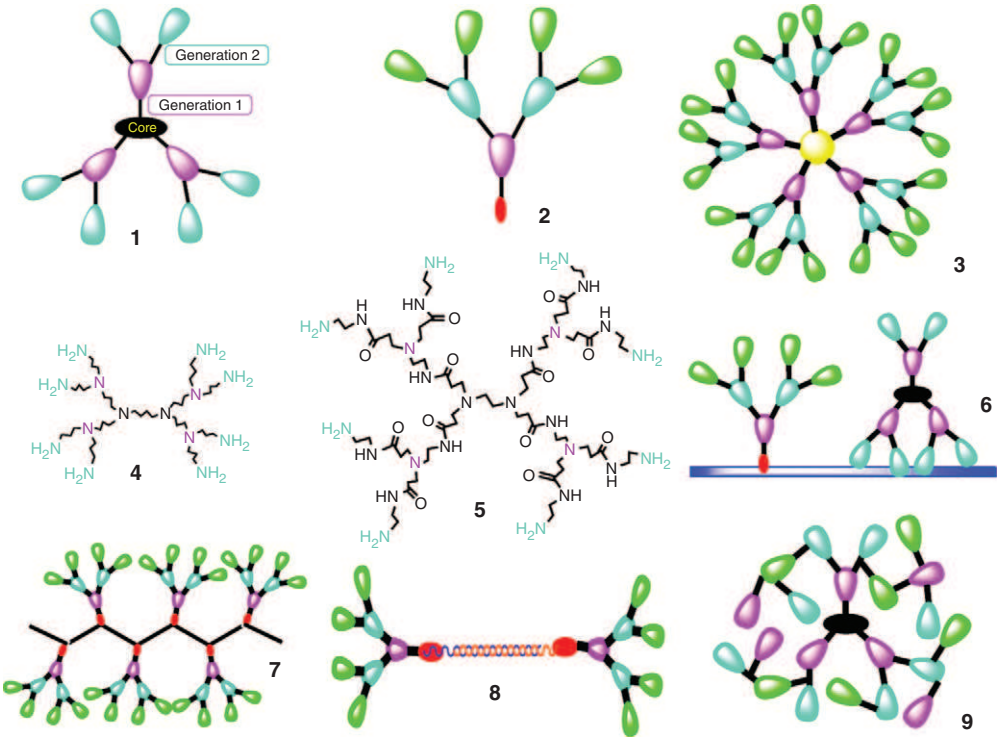

Figure 8 Cartoon representing several dendritic structures including (1) dendrimer, (2) dendron, (3) dendritic nanoparticle, (4) polypropylene imine (PPI) dendrimer, (5) poly(amidoamine) PAMAM dendrimer, (6) dendronic and dendritic surface, (7) dendronized polymer, (8) dendriplex, and (9) dendrigraft. Reprinted with permission from Astruc, D.; Boisselier, E.; Ornelas, C. *Chem. Rev.* **2010**, *110* (4), 1857–1959.[26] Copyright (2010) American Chemical Society.

and subsequent energy transfer.[33,34] The dendrimers convert the wavelength of absorbed UV light and retransmit it as IR or visible light and facilitate charge separation. Functionalized dendrimers have been utilized in supramolecular assembly.[35,36] Dendrimers have also been widely used in catalysis. In particular, they have seen used as catalysts for separation, recycling, and organocatalysis.[37–39] Some of the most prominent and promising applications of dendrimers are those for biomedical applications. In particular dendrimers have seen significant use in drug delivery such as drug encapsulation, dendrimer-drug conjugates, drug nanocarriers, anticancer agents, and gene delivery agents.[40–42] Other biomedical applications include photodynamic therapy, medical theranostics, and biosensors.[43–45] Acknowledging this wide array of applications, perhaps some of the synthetic challenges of dendrimers are overshadowed by their advantages, and it is expected that dendrimers and dendritic structures will continue to play a significant role in materials and biomaterials science.

5.02.2.5.5 Branching and hyperbranching

Dendrimers may be the best known type of polymer with multiple branch points, but other branched polymers have also obtained significant amounts of notoriety in the literature.[15,46–51] Branched polymers, though not as well controlled in molecular weight or polydispersity as dendrimers, still have significant applications. These multibranched polymers are further classified as branched or hyperbranched polymers depending on the number of branch points. Unlike dendrimers, these can be synthesized in a one-pot reaction without any need for stepwise synthesis and purification. The products are often polydispersed and do not have a homogenous extent of branching per unit. However, compared to dendrimers, these branched polymers are more typical step-growth polymers and obey step-growth kinetics and Carothers's equations. **Figure 9** demonstrates a cartoon stick representation of a hyperbranched polymer.

Because hyperbranched polymers are not as controlled or symmetric as dendrimers, they have not seen as much utility as dendrimers in nanotechnology or medicine. However, branched polymers afford many of the same advantages because they possess a large number of functional end groups per polymeric chain. This allows hyperbranched polymers to be very useful for applications like coatings and resins, since they are synthetically simple and cost effective enough to be utilized in large-scale applications. In many of these applications, it is less critical that the structure be 'perfect' like that of a dendrimer and much more important that the synthetic process be simple and inexpensive.

Hyperbranched polymers are synthesized using monomers that have two or more of one functional group and one of the second functional group (e.g., AB_2). However, a similar method can be utilized to form branched polymers combining A–A difunctional, B–B difunctional, and a small amount of AB_x-functionalized monomers. This method requires caution, because too much of the AB_x branching agent is likely to lead to cyclizations and eventual crosslinking. In addition, AB_x monomers are often difficult to isolate due to undesired

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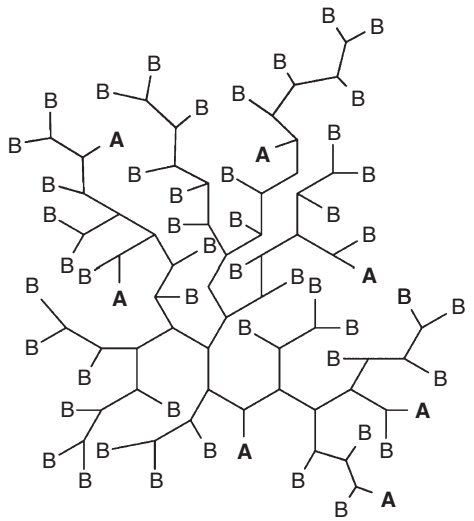

Figure 9 Cartoon depicting a polymer hyperbranched structure.[50]

self-reactions, thus A_2 monomers and one B_3 monomer are employed to synthesize hyperbranched polymers. To prevent side reactions, the A_2 monomer is added slowly to the reaction vessel which already contains the B_3 monomer thereby limiting the cyclization side reaction during the initial stages of the reaction.[48–50,52–55]

Figure 10 represents a cartoon scheme of hyperbranched polymers synthesis by two routes. In particular, the route on the left leaves behind one focal point or type A functionality per hyperbranched polymer molecule. Alternatively, the route on the right eliminates any residual unreacted A functionality. The addition of a small amount of using any di-, tri-, or higher order functionalized B monomer, B_x, such that all focal points are reacted, ensures no remaining A functional groups. Both of the synthetic schemes remove the potential for cyclization or cross-linking, because the A functionality is never present more than once per monomeric unit.[49,50]

As mentioned above, the primary applications for hyperbranched polymers include large-scale commercial resins or coatings. For these applications, the ability to incorporate a large number of functional end groups per polymer molecule is exceptionally useful. For example, if every B functionality in **Figure 10** was an epoxide unit and the hyperbranched polymer was utilized in an epoxy resin, the rate of gelation would be higher and the kinetics of the cure would relate to the concentration of epoxide functional groups allowing epoxide-functionalized hyperbranched polymers to find application in 'quick cure' epoxy resins. Hyperbranched polymers have also found some utilization as additives in linear polymers to improve the rheological and flow properties of these polymers.[56–58] Furthermore, they have demonstrated utility as additives to modify the thermal properties and modulus properties of polymers. Hyperbranched polymers offer significantly

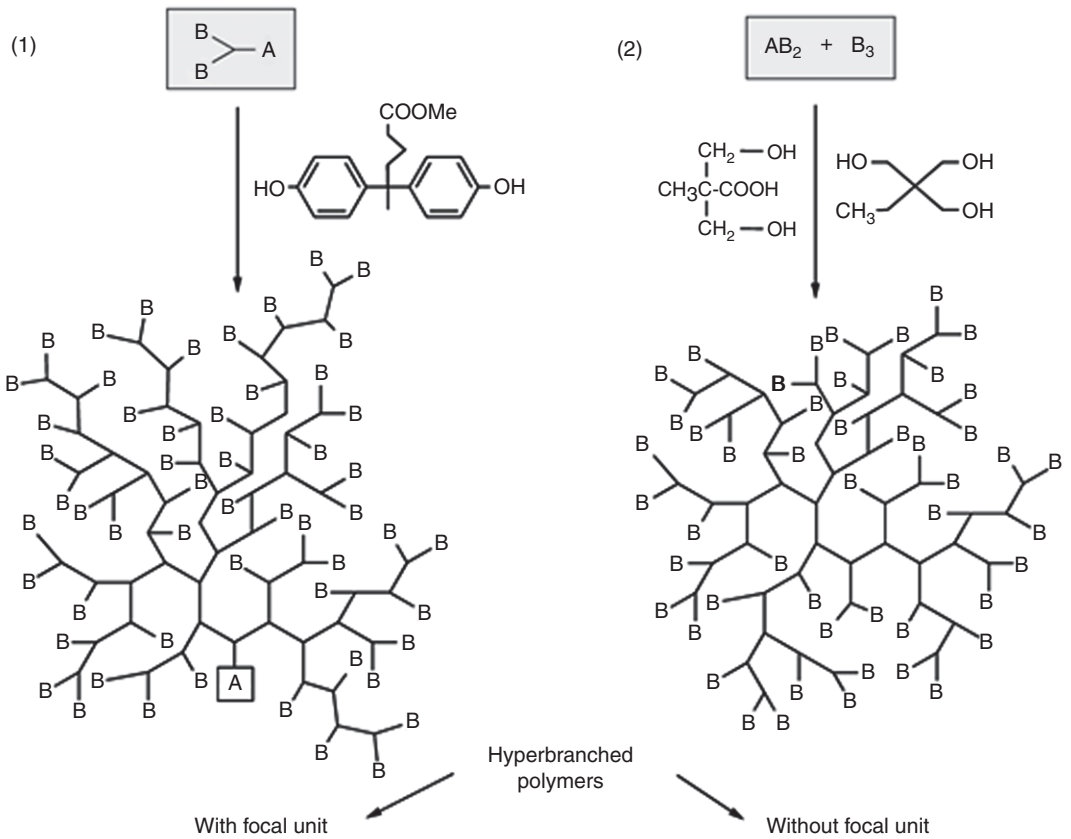

Figure 10 Synthesis of hyperbranched polymers using two methods: (1) utilization of an AB_2 monomer; this approach will always leave one unreacted 'A' functionality or 'focal point' per macromolecule; and (2) utilization of an AB_2 monomer with a B_3 monomer (no unreacted 'A' functionality or 'focal point'). Reprinted with permission from Voit, B. I.; Lederer, A. *Chem. Rev.* **2009**, *109* (11), 5924–5973.[50] Copyright (2009) American Chemical Society.

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lower solution and melt viscosity than linear polymers of similar molecular weight and tend to be exceptionally soluble. In spite of these advantages, hyperbranched polymers show limited utility compared to the standard linear high-performance step-growth polymer applications and typically do not form free-standing films. This is due to the lack of chain entanglements, and therefore films of hyperbranched polymers tend to be brittle and fragile. In spite of this disadvantage, it is clear that hyperbranched polymers impart some significant advantages in materials science.[49,50]

5.02.2.5.6 Cyclic polymers

In step-growth polymerization, the need for caution has arisen with many synthetic techniques involving step-growth polymerization to avoid cyclization and crosslinking. However, a fair amount of literature aims to elucidate the deliberate synthesis of cyclic polymers and their presence in virtually all step-growth polymerization reactions.[59–61] Even standard difunctional $A_2 + B_2$ linear polycondensations all at some point reach a molecular weight at which it is possible for the remaining A functionality on one end group to self-react with the unreacted B functionality on the other end group of the polymer chain. When this occurs a cyclic polymer is formed, and the chain is effectively terminated resulting in a lower polydispersity and lower molecular weight.

Cyclization is especially prevalent at lower monomer concentrations in solution. At low concentrations, an oligomeric end group is statistically less likely to encounter a complementary end group from another growing oligomer and increasingly likely to simply find its own chain end and form the macrocycle. Examples of cyclic structures are shown in Figure 11. However, this reaction is increasingly likely with AB_2, $A_2 + B_3$, and other standard monomer schemes for creating branched and hyperbranched polymers. In fact, hyperbranched polymers at high conversions often have a cyclic or multicyclic core and a hyperbranched exterior. Kricheldorf *et al.* investigated and reviewed the intentional synthesis and study of cycles and multicycles within polymers in branched, hyperbranched, and linear step-growth polymerizations.[59–61] A complete understanding of cyclic polymers and their presence within linear and branched polymer syntheses has yet to be finalized, and the practical applications thus far of cyclic polymers and cyclic residues within linear polymerizations have not been established. However, as all step-growth polymerizations have the potential for cyclization, it is certain that research in this area will remain, and the interest in cyclic polymers will continue to grow.

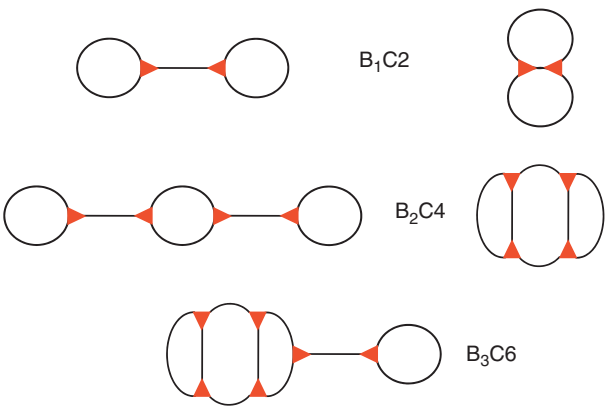

Figure 11 Cartoon demonstrating some examples of cyclic polymer structures based on monomer functionality, where B stands for 'bridge' units and C stands for 'cyclic structures'.[61]

Based on the discussion of polymer architecture included herein, it is evident that polymer architecture and topology are both important factors to consider when attempting to understand and to control final polymer properties. For a given type of step-growth polymer, simple modifications of the polymer architecture invoke drastically different properties. A thorough understanding of the effects of topology and architecture on polymer properties may lead to dramatically enhanced property control. The specific polymer topology is often engineered to provide properties for a specific application. These structures may be carefully controlled through precise synthetic techniques and an applied understanding of how step-growth polymer parameters, such as monomer composition, functionality, and end group accessibility, translate into differences in polymer architecture.

5.02.3 Synthesis of Step-Growth Polymers

Step-growth polymerization occurs in 'steps' to form new chemical bonds as described earlier in this chapter. There are two types of step-growth polymerization processes: polycondensation and polyaddition. Both classes of polymerizations proceed in the same fashion of monomer to dimer to tetramer and high molecular weight polymer. The differences in the two classes of step-growth polymers as well as examples of these polymers are described in the following sections.

5.02.3.1 Polycondensation Polymers

Polycondensation polymers are a class of step-growth polymers in which the formation of a new functional group results in the elimination of a small-molecule by-product. Classical examples of polycondensation polymers include polyesters, polyamides, polyimides, and poly(arylene ethers) (PAEs). These polymers utilize organic reactions such as addition–elimination chemistry to afford polymers with specific functional linkages. The resulting polymer linkages provide properties such as hydrolyzability, hydrogen-bonding interactions, and dipolar interactions. Careful monomer selection and polymer topology further tailor the mechanical properties of these polymers. The immense amount of established research demonstrates the expanding impact of polycondensation polymers in commercial industry.

5.02.3.1.1 Polyesters

Within the last 20 years, the number of polyester plant industries in Europe, USA, and Japan have grown and promoted the growth of polyester production to an estimated 3 billion pounds a year.[62] Because of the substantial growth of polyester plants now developing in China, it was estimated that in 2010, polyester production will surpass 100 billion pounds a year. China, itself, contributed 80% of the new polyester plants recently developed.[62] In the field of synthetic fibers, polyesters

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Table 2 Growth of polymer fibers from 1996 to 2000[62]

Fibers	Production (per 10^8 kg) 1996	1998	2000	Percent increase from 1999
Polyester				6.2
Thread	60.1	93.4	98.0	
Staple fiber	50.8	68.9	73.4	
Polyamide				6.4
Thread	29	30.8	32.6	
Staple fiber	5.4	4.5	4.5	
Polypropylene (thread and staple fiber)	18.1	24.5	25.4[a]	5
Polyacrylic	21.8	21.8	22.7	5.6
Cellulose	27.2	23.6	24.5	0.4
Other (elastomeric, aramid, carbon, etc.)	0.9	1.8	1.8[b]	–
Total	215.0	269.4	283.9	3.5

[a]Including 10.0–13.6 × 10^8 kg of polypropylene fibers.[62]
[b]Including 5.4 × 10^7 kg of aramid and carbon fibers.[62]

dominated the total amount of polymer-based fibers within the last decade. Table 2 summarizes the contribution of common polymers in the fiber industry.[62] Interestingly, polyester fibers contributed to nearly 60% of all fiber production in 2000. This trend emphasized the importance of this polymer within economically important fiber production. PET fibers afforded approximately 45% of all PET produced. Because of chain stiffness and crystallinity, PET fibers demonstrated excellent tensile properties, solvent resistance, toughness, and fatigue resistance. Solid-state resins accounts for the second largest application of PET. The demand for cheap packaging and bottles has become the main contributor for the demand for PET development.

Polyesters, most notably poly(ethylene terephthalate) (PET), also assume an important role in the food packaging industry. The large-scale production of PET provided the packaging industry with cheaper production costs. PET films are often bi-axially stretched in order to induce crystallization. Interestingly, these films are optically clear although the film is nearly 50% crystalline.[3] In addition, these polymers possess mechanical properties capable of withstanding the large pressures of carbonated drinks. It is estimated that the polyester food packaging industry constitutes a significant amount of the overall polymeric applications. As these industries continue to expand, the demand for affordable and more environmentally friendly polyesters with tailored properties will stimulate and influence the future research within this growing field.

One method that enables simple modification of polyester properties relates to the monomer selection. The discovery of new monomers promotes the continuing growth of applications for this field. Polyesters have emerged as an economically important commercial commodity and have found utility in a variety of applications including fibers, thermoplastic elastomers, coatings, and high-performance polymers due to their outstanding mechanical and thermal properties.[3] Polyesters are polymers with ester linkages within the backbone. These ester linkages are hydrolytically unstable, and this attribute has launched a growing field of biodegradable polyester research from recyclable polymers for packaging to drug delivery vehicles with degradable and controllable drug delivery.[63–65] In addition to their degradation properties, polyesters also employ monomers derived from renewable resources. Over the years, polyesters continue to possess desirable advantages such as tunable properties for the packaging and fiber industries.

There is current interest within the industry to limit its dependency on nonrenewable petroleum-derived monomers, and research is directed toward monomers derived from renewable resources. The research often involves new catalysts or simple methods to transform plant-based starches to useful diols. Typically, the cost of monomer becomes the limiting factor in polyester synthesis, and often a consideration between properties and cost of production becomes crucial for commercial polyesters. For example, exchanging ethylene glycol (EG) for longer glycols such as 1,4-BD increases crystallization rate and allows for faster production; however, the cost of production for PET is much less compared to poly(butylene terephthalate) (PBT).[3]

Another recent interest centers around cardo-monomers for their application in novel aromatic polyesters.[66] Cardo-monomers are monomers that contain looped or cyclic structures. Research literature suggested introducing these bulky groups into polyesters will increase free volume, chain stiffness, and solubility. Successful high molecular weight cardo-monomer-containing polyester employed phase transfer-catalyzed interfacial polycondensation. Addition of the bulky group from the cardo-diol substantially increased both the T_gs ranging from 207 to 287 °C.[66] Although the properties of the polyesters showed promise for thermoplastics, the challenging synthesis of the cardo-diol limits its application in the field.

Scheme 1 illustrates the main mechanistic pathway in which polyester synthesis proceeds. Typically, a strong nucleophile such as an alcohol attacks an activated carbonyl such as a carboxylic acid or acyl halide to form the tetrahedral intermediate. Upon elimination of the condensate X–Y, the new ester linkage is formed. The entire reaction proceeds through an equilibrium mechanism. Various leaving groups and nucleophiles are summarized within Scheme 1 as well. The reaction conditions as well as the cost of monomer dictate the choice of monomer.

Understanding the principles of the equilibrium addition–elimination reaction for polyesterification becomes crucial to attain high molecular weight polymers. According to Scheme 1, the forward reaction produces an ester functional group and a condensate by-product. Conversely, the reverse reaction hydrolyzes the ester bond when the condensate or simply water is present and translates to depolymerization. Because the species within step-growth reactions are dynamic throughout the extent of the reaction, the equilibrium favors the reverse reaction or depolymerization as the polymerization proceeds forward due to higher concentration of the condensate.[2,67] In order to address this concern, many polyester syntheses are conducted in the melt phase at elevated temperatures well above the boiling point of the by-product or condensate and removal of the condensate drives the reaction toward polymerization.

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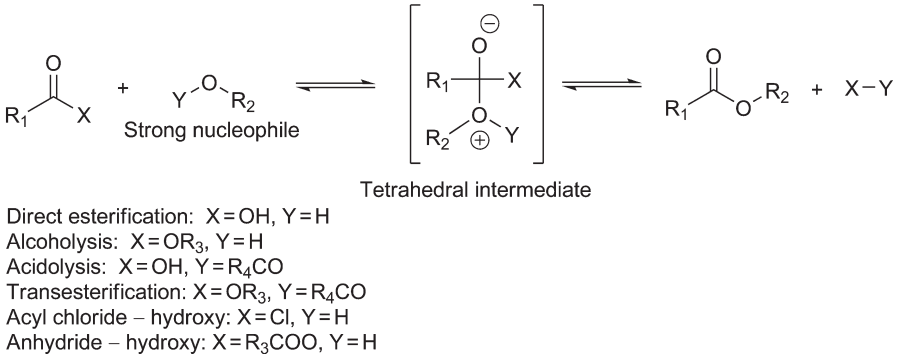

Scheme 1 Equilibrium addition–elimination mechanism for polyesterification reactions.[3]

Melt polymerization represents a common synthetic approach for many step-growth polymers such as polyesters. Temperature ranges for bulk polymerization must be at least 10–20 °C above the melting point of the polymer. However, because many bulk polymerization occurs at high temperatures 150-350 °C, careful consideration must be paid in order to limit the effects of side reaction such as thermooxidation.[68] Bulk reactions are therefore conducted under an inert atmosphere. As the reaction proceeds from monomer to oligomer to polymer, the role of chain entanglement begins to dominate the melt reaction through the form of higher melt viscosity. The following equation describes the relationship between melt viscosity (n_o) and molecular weight (M) using a power relationship that was first described by Fox and Flory in 1951:[69]

$$n_0 \propto M^{3,4}$$

This equation suggests that a gradual increase in molecular weight results in a large increase in melt viscosity.

The melt viscosity plays a direct role in the molecular weight control of any step-growth bulk polymerization. A common misconception in melt step-growth polymerization is that the kinetics of step-growth polymerization within the melt decreases with time due to the change in reactivity of end groups.[1,2,7] In reality, the reactivity of the end groups does not change with polymerization extent, because reactivity of functional groups is directly related to the collision position, energy, and frequency of the reactive groups. The more accurate reason for the differences in step-growth polymerization kinetics is attributed to the dynamics of the reactive species. As the reaction proceeds from monomers to oligomers to polymers, the rate of diffusion for each of these species changes dramatically. Monomers will diffuse through the melt much faster than oligomers or polymers due to chain entanglements. For this reason, the accessibility of the oligomers and polymer end groups will be less than that of the monomer, and thus reaction kinetics during step-growth polymerization will not remain constant.

In addition to melt viscosity effects, the removal of the condensate and low molecular weight by-products also becomes essential for accelerating the reaction and increasing molecular weight. Various techniques ameliorate these issues such as purging the system with nitrogen gas to facilitate removal of the condensate. In addition, vigorous stirring will also promote diffusion of the reactive end groups and removal of the condensate. High vacuum is applied to the final stages of bulk polymerizations to attain high molecular weight. Because of the reaction mechanism of step-growth polymerization, high molecular weight of polycondensation polymers will not occur until high conversion of polymerization occurs.

Due to these reasons, step-growth reactions require long reaction times and catalysts to increase reaction rates. For example, synthesis of polyesters with aromatic carboxylic acids and glycols utilizes metal glycolates through high ligand exchanges.[70] The rate constant of the reaction depends much on the pK_a of the carboxylic acid as well as on the sterics and the electronic contributions of the aromatic ring. Typical polyester polycondensation catalyst employed are metal alkylates such as tin, antimony, and titanium. These catalysts are sensitive to hydroxyl or carboxylic acid groups.[3] Metal alkylates form metal alcoholate complexes to facilitate ligand exchange. In contrast, Lewis acid catalysts, such as zinc or manganese, coordinate with the carbonyl oxygen of the ester to increase the nucleophilicity of the carbonyl compound.

The side reactions within bulk polymerizations must be considered. Short chain oligomers contribute to nearly 2–3% of the polymer produced. Cyclic oligomers are often dependent on the monomers chosen. Cyclization occurs at any time of the polymerization process because step-growth polymerization allows for reaction of any accessible end group.[61] The reaction temperature strongly influences cyclization reactions, and, as a result, the decrease in end group concentrations severely affects the polymer molecular weight.[70] Other side reactions which may occur at elevated temperature include the etherification of EG to form diethylene glycol or dioxane by-products through dehydration. In many cases, simple modifications in catalyst choice from metal acids such as zinc, lead, and manganese acetates can prevent side reactions such as etherification.[70] Other side reactions occur via chain scission due to thermal degradation of the ester bond. Scheme 2 below represents an example of polyester chain scission to produce the alkene-terminated oligomer which is subject to nucleophilic attack by the carboxylic acid. This side reaction causes defects within the polymer. Elimination of acetaldehyde also occurs and influences packaging applications. Substantial yellowing of the polymer also results as a consequence of thermal or oxidative degradation. Selecting an appropriate catalyst, removing oxygen from the reaction, providing an inert atmosphere, and reducing reaction temperatures are practical approaches to avoid side reactions.

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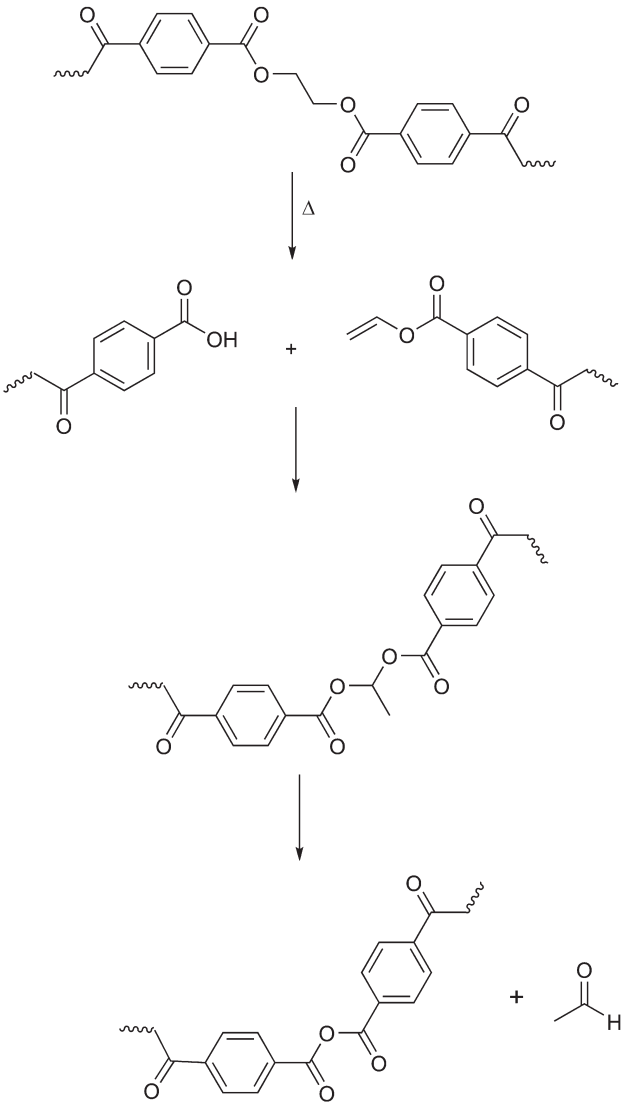

Scheme 2 Thermal degradation of PET through chain scission and anhydride formation.

Economically significant polyesters have principally focused on aliphatic–aromatic polyesters derived from diols with alkylene oxide units and diesters with terephthalate or isophthalate units. PET dominates the commercial plastics application in fibers, molding resins, and film formation for packaging applications. Early development and commercialization of PET encountered difficulties, because the terephthalic acid (TA) used could not be obtained in high purity. However, this obstacle was solved through the use of the diester monomer, dimethyl terephthalate (DMT). PET possessed several advantages. Melt polymerization eliminated the use of volatile solvents, greatly reduced production costs, and simplified purification steps. In addition, the ability to drive the reaction to high conversions through distillation of the diol monomer to facilitate polymerization and transesterification circumvented the strict requirement of 1:1 monomer stoichiometry in conventional step-growth polymerization. Thus, the 1:1 stoichiometry so vital for attaining high molecular weight polymers was not a necessity and an excess of diol monomer is commonly used to increase the formation of EG-endcapped DMT. However, the removal of excess EG at the second stage using reduced pressure essentially approaches 1:1 stoichiometry.

Synthesis of PET occurs through two stages with the aid of metal acetate catalysts such as calcium, manganese, cobalt, and zinc. The first stage occurs at 190–195 °C, below the boiling point of EG, 197 °C, and above the melting point of DMT, 140–142 °C. At this point, the high reaction temperature facilitates methanol distillation and drives the reaction forward. Bis (2-hydroxyethyl)terephthalate and oligomers are formed during this initial stage. In the second stage, a stepwise increase in reaction temperature from 190 to 280 °C and reduced pressure during the last hour of the reaction increase the reaction rate and continue polymerization through transesterification and removal of EG. The final temperature of 280 °C maintains melt homogeneity. As the reaction proceeds, the molecular weight of PET increases, and crystallization occurs within the melt if the reaction temperature is not above the melting temperature of PET, 265 °C. Melt heterogeneity results in large polydispersities, because polymeric chains within crystals are inaccessible for ester interchange. Catalysts are employed to facilitate the reaction. Metal acetates catalyze the first stage of the reaction, and antimony(III) oxide is often added during the second stage of the reaction to continue condensation.

In addition to melt polymerization, polyesters can be synthesized through interfacial condensation. One advantage of this method is that 1:1 stoichiometry is not required to acquire high molecular weight, because polymerization occurs at the solvent interface. In addition, polymerization occurs rapidly and is only limited to the diffusion of monomers at the solvent interface. Synthesis of polyesters using this approach occurs through a reaction between an acyl halide and glycol in two immiscible solvents. Each solvent contains one of the reactive monomers and polymers can be isolated as a film or a filament through drawing the polymer from the interface. Interfacial polymerization can be quite advantageous for polymers which are unstable at high temperatures and has been used for the synthesis of polyesters, polyamides, PUs, and polysulfonamides.[71] However, the use of solvent, monomer expense, and acidic by-product are often undesirable in large-scale production of polymers.

5.02.3.1.2 Polyamides

Polyamides contain amide functional groups within the polymer backbone. The unique properties of polyamides arise from the hydrogen-bonding capabilities of the amide functional group. These strong intermolecular interactions afford high melting and thermally stable polymers with excellent mechanical properties. Scheme 3 below illustrates the synthesis of polyamides through two methods: direct amidation and self-amidation. Direct amidation utilizes two difunctional monomers, A–A and B–B, to form the new amide bond. Self-amidation uses AB-type monomers often from amino acid derivatives. Again, stoichiometric balance of the functional group in a 1:1 stoichiometry is a requirement for the synthesis of high molecular weight polymerization. In direct amidation, careful control of monomer stoichiometry is a necessity. For self-amidation, the bifunctional monomer achieves 1:1 stoichiometry. In both cases, however, monomer purity is required. Careful consideration must be taken to prevent side reactions which may limit the molecular weights of polyamides. Side

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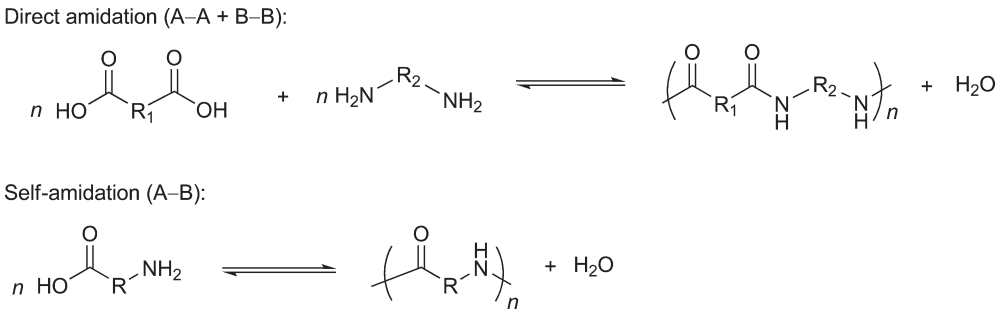

Scheme 3 Synthesis of polyamides through direct amidation or self-amidation of an amino acid.

reactions such as oligomeric cyclization occur with diamines containing less than four methylene units. Decarboxylation is also a concern for lower diacid monomers. In addition, pressurized systems prevent the escape of volatile cyclic oligomers.

Many polyamides employ the salt solution method. Nylon-6,6 can be polymerized using this approach without addition of a catalyst. The salt solution method proceeds in three stages. In the first stage, the reaction between hexamethylene diamine and adipic acid forms the salt in solution. Conveniently, this method is quite exothermic, and the reaction proceeds through the precipitation of the salt from solution. On the industrial scale, a watery salt slurry was used directly for the second stage of the polymerization process. This method also provides the added advantage of a 1:1 stoichiometry inherent in AA–BB-type monomers arising from the carboxylate and protonated amine during salt formation.

In the second stage, the salt further reacts under pressure and heat to form the prepolymer. Polymerization occurs under pressure, because the volatilization of hexamethylene diamine, which boils at 205 °C, will result in a loss of this monomer in the reaction and cause a stoichiometric imbalance of the functional groups. This stage can be achieved through an autoclaving procedure and stepwise increase in temperature from 210 to 290 °C. The prepolymer formed during this event will typically be semicrystalline; however, further reaction is needed to remove the condensate, water, and drive the reaction forward. As the reaction continues and the polyamide chains grow, the melt viscosity increases, and melt polymerization becomes difficult.

Because of the high melting temperatures of polyamides, prepolymers are typically reacted within melt extruders where solid-state polymerization occurs at atmospheric pressure and 290 °C. Further orientation of polymer chains through processing techniques induces higher degrees of crystallinity. Although one could imagine applying melt reaction conditions used in polyester synthesis to polyamide polymerization, such as elevating temperatures and reducing pressure to drive the reaction forward, several concerns prevent this polymerization technique, and solid-state polymerization at atmospheric pressures are employed instead. At high reaction temperatures and reduced pressures, aliphatic polyamides undergo side reactions that cause branching and substantial coloring of the polymer.

Control of polymer architecture allows for design of applications including drug delivery, molecular imaging, electroactive devices, and membrane technology. The growing field of polymer drug delivery takes advantage of the ability to design and regulate the delivery of drugs through controlled and predictable manners. Another advantage of polyamides arises from their similarity to naturally occurring polymers, namely, polypeptides. Incorporation of amino acids as bio-based monomers has become increasingly popular in the field of biomedicine due to their inherent biocompatibility and extensive monomer selection.

Wathier *et al.* described the synthesis of dendritic macromolecules from peptide monomers.[72] The advantages of the high surface functionalization and branching density from dendrimers were needed for sufficient crosslinking reactions for forming wound-healing hydrogels. Dendrimers derived from lysine and cysteine with varying branch density were synthesized and crosslinked with poly(ethylene glycol dialdehyde) to form thiazolidine linkages. This reaction occurred quickly and spontaneously at relatively neutral pH (7.4) upon mixing the two solutions. Dynamic mechanical analysis (DMA) revealed an increase in modulus with increasing dendron density. Due to the mild conditions and fast *in situ* crosslinking of the hydrogel, this technique of crosslinking peptide-derived dendrons through the formation of thiazolidine linkages affords a facile and safe method for wound-healing sutures (Figure 12).

In contrast to the linear aliphatic polyamides described above, there have been interests in the synthesis of aromatic polyamides (aramid). Garcia *et al.* recently reviewed the advances in aramid research.[73] The significant properties which arise from the stiffness of the polymer chains and high directionality from the anisotropic liquid crystalline solution pioneered the technologies for engineering commercial aramids. These properties provided excellent high thermal and mechanical properties that give rise to their outstanding tensile, mechanical, and flame-resistant properties.[73] Many aromatic polyamides can be directly spun into fibers from the polymer solution due to the

Figure 12 Peptide dendritic monomers derived from amino acids produced a fast curing hydrogel for sealant-repaired corneal incisions. Reprinted with permission from Wathier, M.; Jung, P. J.; Camahan, M. A.; *et al. J. Am. Chem. Soc.* **2004**, *126* (40), 12744–12745.[72] Copyright (2004) American Chemical Society.

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alignment of the stiff polymer chains from the extended chain conformations in solution. Recent advances in aramid technologies have allowed aromatic polyamides to find application in membrane technologies and electroactive and optically active devices. Further developments in the area of aromatic polyamides aim to advance these high-performance polymers and improve their outstanding mechanical properties.

There are currently two main methods for synthesizing aramids: low-temperature solution methods and high-temperature solution methods. Later developments in the synthesis of PPPT replaced hexamethylphosphoramide (HMPA) with polar solvents such as *N*-methyl-2-pyrrolidone (NMP), *N*,*N*-dimethylformamide (DMF), and *N*,*N*-dimethylacetamide (DMAC) with calcium chloride to aid in disrupting the strong hydrogen bonds. Under the principles of step-growth polymerization, the requirement for extremely high monomer purity remains an obstacle in polyaramide synthesis. Molecular weight considerations are confronted during the synthesis of polyaramides. Polydispersity of approximately 2.0 results from low molecular weight aramide oligomers. The polydispersity reaches close to 3.0 when high molecular weight polymer is attained.

Research interests in aromatic polyamides currently focus on creating synthetic methods to attain soluble polyaramides. Due to the high degree of crystallinity, polyaramides are difficult to melt-extrude or redissolve for solution casting which limits their versatility in applications. Therefore, incorporating new monomers, which increase chain flexibility, disrupts chain regularity, decreases the hydrogen-bonding intermolecular interactions, and increases polymer solubility in solvents such as DMF, NMP, and dimethyl sulfoxide (DMSO). Typical polymerization of polyaramides utilizes the acyl chloride method due to the reduced basicity of aromatic diamines.

5.02.3.1.3 Polyimides

Incorporation of heterocyclic and aromatic units within the polymer backbone provided excellent thermal stability and mechanical properties. Aramids and PET were two types of aromatic polymers that displayed desirable properties with high melting temperatures. These polymers were synthesized using aromatic monomers, and high molecular weight polymers were difficult to reprocess due to thermal degradation and high processing temperatures. The main demand for aromatic or heterocyclic polymers with low processing temperatures stemmed from the aerospace industry which required adhesive or polymer–composite formulations with high thermal stability and optimal mechanical properties under harsh environments.[3,74,75] Polyimides currently find application in a variety of technologies. In addition to high-performance resins, structural foams, and molecular composites, polyimides are utilized in electronics and microelectronic devices. Polyimides elicited interest in membrane technologies specifically for gas separation and fuel cell applications. Because of their ease of processing, the ability to acquire high thermal stability, and naturally high free-volume properties, the field of polyimide research continues to expand even today.

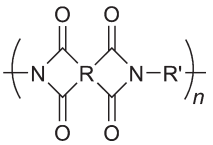
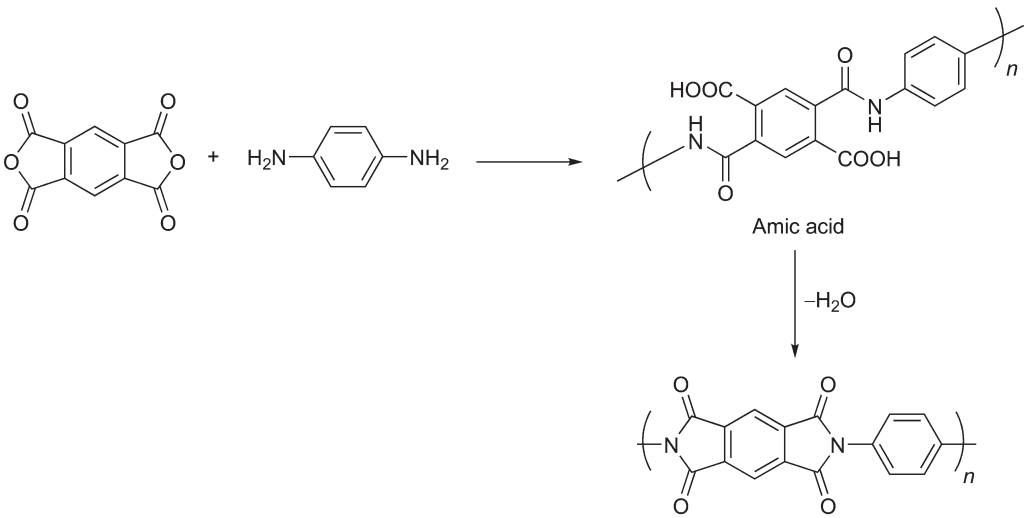


Figure 13 General structure for polyimides.

Polyimides were the first known polycondensation polymers in which the aromatic or heterocyclic units were formed during polymerization. Cyclization of the monomers was the method of incorporating cyclic groups into the polymer backbone rather than the addition of aromatic or cyclic monomers. Figure 13 illustrates a general formula for the structure of polyimides where 'R' groups are aromatic or aliphatic units. A demand for low processing temperatures and high thermal stability launched the first investigation involving endcapped low molecular weight oligomers with maleimide.[75,76] Because of the low molecular weight, these oligomers had low melting and flow temperatures which allowed them to be easily processed.

Scheme 4 illustrates the synthesis of polyimides between a dianhydride and a diamine. The anhydride ring-opening



Scheme 4 General reaction between dianhydrides and diamines to form the polyimide through an amic acid intermediate followed by dehydration and cyclization of the amic acid. Note that there are several isomeric possibilities during the amic acid stage leading to increased solubility. However, these isomers are essentially eliminated during the cyclization.

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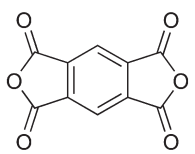
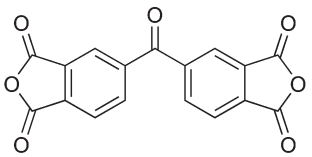
reaction results in the intermediate amic acid structure. Due to the various isomers achieved in the amic acid form, the polymer remains soluble and processible. Upon reaction between the carboxylic acid and amide to eliminate water and create the cyclic imide functional group, the polymer loses these structural isomers, and the polymer becomes insoluble. A list of common aliphatic and aromatic dianhydride and diamines are shown in Figures 14 and 15. The high melting temperature of the resulting polymer further complicates the synthesis of aromatic polyimides. Thus, aromatic polyimides are commonly synthesized in polar aprotic solvents such as DMF, DMAC, and NMP at low reaction temperatures to acquire the amic acid. The amic acid form of the polymer is still processible and soluble in solvent; however, the aromatic polyimide is insoluble. Further heating of the polymer cyclodehydrates the amic acid to form the imide bond.

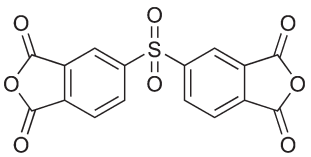
Similar to many step-growth polymerizations, polyimide synthesis also follows a nucleophilic addition–elimination mechanism in which each reaction step is in equilibrium. Thus, the forward reaction encourages the formation of the polymer, and the reverse reaction favors depolymerization. Polyimide syntheses are condensation reactions, and the



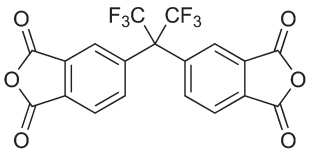
Pyromellitic dianhydride (PMDA)



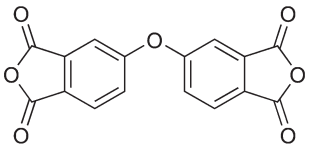
3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA)



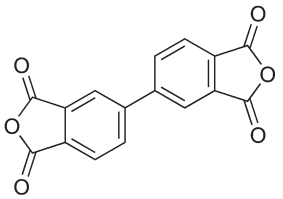
3,3',4,4'-Diphenylsulfonetetracarboxylic dianhydride (DSDA)



2,2'-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA)

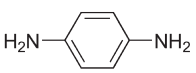


4,4'-Oxydiphthalic anhydride (ODPA)

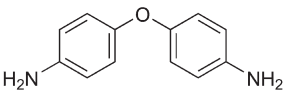


3,3',4,4'-Biphenyltetracarboxylic dianhydride (BPDA)

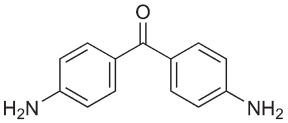
Figure 14 Chemical structures of commonly used dianhydrides for polyimide synthesis.



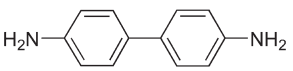
Benzene-1,4-diamine



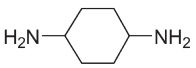
4,4'-Oxydianiline



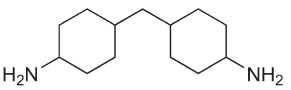
Bis(4-aminophenyl)methanone



Benzidine



Cyclohexane-1,4-diamine



4,4'-Methylenedicyclohexanamine

Figure 15 Chemical structures of common diamines used in polyimide synthesis.

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condensate, water, must be removed from the reaction during the cyclization step to prevent undesirable low molecular weight polymer. In addition, the reaction in solution is further complicated, and imide bond formation actually requires two mechanistic steps. The first step involves the ring opening of the dianhydride through a nucleophilic substitution reaction and elimination of the carboxylic acid. In this case, the carboxylic acid equates to the condensate which is covalently attached to the polymer to form the amic acid. Therefore, this equilibrium process cannot be driven through the elimination of the condensate. However, this first step is conveniently exothermic due to ring opening, and the reaction temperature controls the kinetics. Increasing the temperature will favor lower molecular weight polyimides while cooling the reaction favors higher molecular weight polymers.

Because the reaction is in equilibrium, reaction conditions such as monomer reactivity, solvent polarity, and temperature strongly influence polyimide synthesis.[77] Reaction rates increase as the basicity of the diamines increases. However, if the basicity of the diamines is adequate, lowering the temperature of the reaction will not greatly affect the reaction kinetics.[78,79] In addition to reaction temperature and monomer reactivity, solvent polarity also played a large role in the reaction kinetics.[80,81] Polar aprotic solvents increase reaction rates due to hydrogen-bonding polymer–solvent complexations and stabilization of the amic acid. In the second step, tertiary alkyl amines or aromatic pyridines catalyze the thermal imidization.

During the synthesis of polyimides, dry conditions must be obtained to eliminate possible side reactions, such as hydrolysis of the dianhydride to form the dicarboxylic acid. In addition, water enhances the reverse reaction through hydrolysis of the amic acid to produce the dicarboxylic acid and the amine. Interestingly, the polydispersity of the polyamic acid increases, reaches a maximum, and slowly decreases with time due to the reverse reaction.[75] This effect can be seen directly with the increase and subsequent decrease in solution viscosity. Another complication that arises during the polyimide synthesis is the phase separation reaction during thermal imidization condensation second step. Phase separation of the polyimide from the poly(amic acid) prevents a homogenous polymerization.

Melt polymerization and solution polymerization of polyimides have been described.[3,9,75] Melt polymerization of tetracarboxylic acid and diamines occurs much in the same way as polyamides through an initial low molecular weight salt formation from low heating at 110 to 138 °C.[77] Upon an increase in temperature to 250-300 °C for several hours, the reaction condenses water and the imide functional group is formed. The main drawback for this approach centers on the requirement for the reaction temperature to be above the highest thermal transition temperature of the polyimide. The nucleophilicity of the diamines also plays a large role in the melt polymerization of polyimides. Aromatic diamines are not basic enough to form the salt with carboxylic acid. Thus, only aliphatic diamines containing at least seven methylene units are used to form high molecular weight polyimides. The addition of flexible ether linkages incorporated through the dianhydride monomer reduced polyimide melting temperatures.

Polyimides find application in electronic devices and membrane technologies. Fasel *et al.* recently described the condensation reaction of subnanometer-thick linear and crosslinked polyimide films through thermal annealing of 4,4′-diamino-*p*-terphenyl (DAPT) or 2,4,6-tris(4-aminophenyl)-1,3,5-triazine (TAPT), with 3,4,9,10-perylenetetracarboxylic-dianhydride (PTCDA) on Au (111) crystals (**Figure 16a**).[82] Interestingly, the researchers found that monomer deposition formed planar, organized supramolecular monolayers upon the substrate. **Figure 16b** shows the organization of the hydrogen-bonded DATP-PTCDA suprastructure using scanning tunneling microscopy (STM). Upon thermal annealing at 267 °C, the reaction formed imprinted parallel polyimide strands, which were preorganized through the hydrogen bonding of the monomers as seen in **Figure 16c**.

Further investigation using STM with triamine monomers indicated a porous network structure rather than parallel polymer strands. The authors concluded ultrathin polyimide films were deposited onto Au(111) substrates to form preorganized suprastructures through the hydrogen-bonding interaction between the dianhydride and diamines. Upon thermal annealing, STM images revealed ordered polyimide strands when diamines (DATP) and dianhydrides (PTCDA) were reacted due to the preorganization of the monomers. Reaction of the triamine (TAPT) with the dianhydride (PTCDA) displayed a different porous network structure after thermal imidization. This method proved promising as a facile and controllable approach to synthesize thin polyimide films containing specific morphological structures.

Polyimide graft copolymers were also explored for developing nanoporous films. One example depicted in **Figure 17** highlights a poly(amic ester) backbone with poly(propylene oxide) (PPO) grafts. This polymer represents one of the few examples in the literature of the second synthetic route discussed in the graft copolymer section of this chapter toward graft copolymers. In this case, two mono-hydroxy endcapped PPO macromonomers were reacted with a dianhydride to form the corresponding bis-isophthalic acid ester. This acid ester was then converted to the corresponding acyl chloride and subsequently reacted with an aromatic diamine to form the poly (amic acid) backbone containing PPO grafts. This reaction was successful despite the steric hindrance due to the flexibility of PPO and the high reaction rate of amines with acyl chlorides. Upon heating, the PPO blocks condensed away to form the polyimide and regenerated the macromonomer. The PPO blocks and the poly(amic ester) backbone phase separated during film formation to form nanoporous polyimide films.[24]

Another example of potential polyimide utilization within the field of electronics and microelectronics is segmented poly (siloxane imide) adhesives functionalized with photo-cleavable units in the main chain. Long and co-workers detailed the synthesis of cyclobutane diimide-containing poly(siloxane imides).[22] The cyclobutane diimide functionality enabled photo-cleavage of the polymer upon UV irradiation. The incorporation of the PDMS segment within the polyimide backbone allowed for microphase separation and elastomeric properties. **Figure 18** is an atomic force microscopy (AFM) phase image of this poly (siloxane imide) demonstrating this microphase separation.[22] In this image, the hard segments are the lighter portions, and the soft segments are the darker portions.

In addition to relevance in the electronics field, polyimides are gaining attention in the area of fuel cell applications. Watanabe *et al.* recently demonstrated durable aliphatic and aromatic polyimide ionomers were suitable for electrolyte membranes.[83] Synthesis of sulfonated polyimides produced highly conductive clear ductile polymer films ($0.18\,S\,cm^{-1}$)

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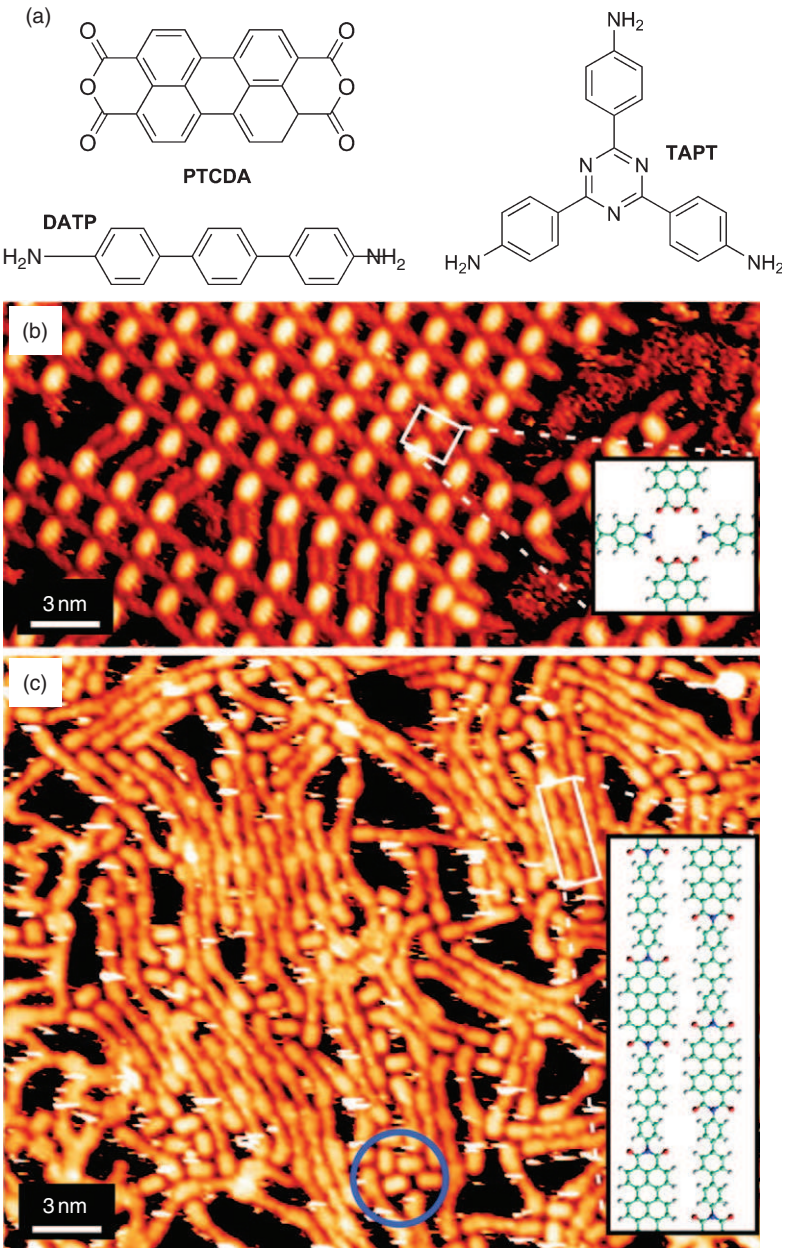

Figure 16 Subnanometer ultrathin polyimide films on Au(111) substrates. (a) Monomers used in polyimide formation. (b) Hydrogen-bonded planar sheets of monomers prior to annealing. White boxed area indicates the hydrogen-bonded structure between the PTCDA and DATP. (c) Polyimide ultrathin film through the annealing of the hydrogen-bonded monomers. Blue circled area highlights unreacted DATP and PTCDA monomers. White boxed area shows parallel polyimide strands after thermal imidization. Reprinted with permission from Treier, M.; Richardson, N. V.; Fasel, R. *J. Am. Chem. Soc.* **2008**, *130* (43), 14054–14055.[82] Copyright (2008) American Chemical Society.

which surpassed Nafion®, the standard benchmark for fuel cell membranes, at 140 °C and 100% relative humidity. These sulfonated polyimide ionomers possessed excellent thermal and oxidative stability. Furthermore, scanning transmission electron microscopy (STEM) images revealed spherical ionic clusters whose size, distribution, and microphase separation could be controlled through the degree of polyimide branching. Small, homogenous, and well-distributed ionic domains are thought to increase proton transport and conductivity for fuel cell applications.

5.02.3.1.4 Poly(arylene ethers)

PAEs are high-performance polymers that have arylene–ether linkages in the polymer backbone. These polymers have found extensive application due to their thermal stability, enhanced mechanical properties, and excellent resistance to hydrolysis and oxidation.[3,74,84] In addition, multiple organic synthetic methods have allowed this class of aromatic polymers to be expanded and explored to fine-tune not only the composition of the polymer but also cost-effective methods that eliminate or reduce side reactions. Properties of PAEs are in part attributed

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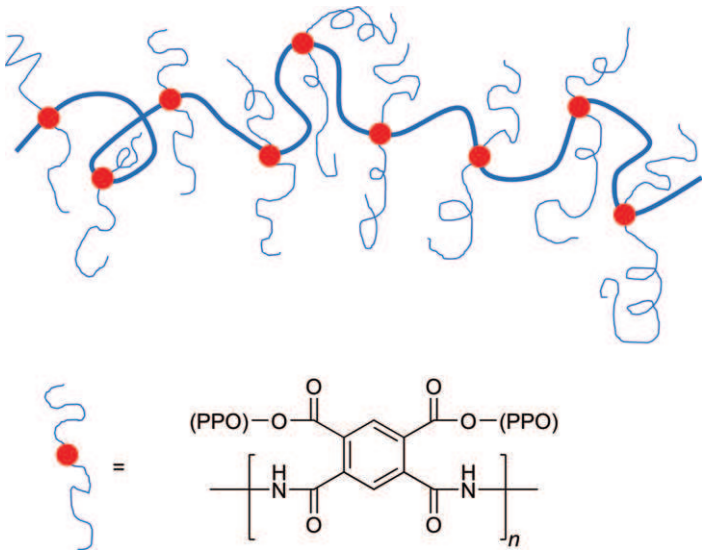

Figure 17 Poly(amic ester)-*graft*-propylene oxide. Condensation of the amic ester into the imide releases the PPO block.[24]

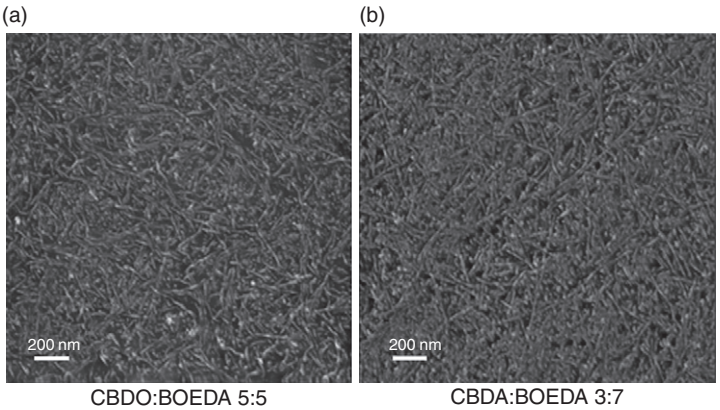

Figure 18 Atomic force microscopy (AFM) phase images of microphase-separated segmented block poly(siloxane imide) demonstrating 'hard segments' (lighter portion) and 'soft segments' (darker portion). June, S. M.; Suga, T.; Heath, W. H.; Long, T. E.; Qin, L.; Puligadda, R. Journal of Adhesion **2010,** *86* (10), 1012–1028.[22] Reprinted by permission of the Taylor & Francis Ltd.

to the aromatic ether linkage which gives rise to chain flexibility. This flexible linkage affords desirable secondary transitions such as benzene ring flips to occur which impart desirable impact properties.

The versatility of PAEs originates from the multiple synthetic methods available for creating these polymers. The three major divisions of organic synthetic reactions are highlighted below, and their advantages and disadvantages will be discussed:

1. electrophilic aromatic substitution,
2. nucleophilic aromatic substitution, and
3. metal-catalyzed coupling reactions.

Electrophilic aromatic substitution reactions for the synthesis of PAEs are typically Friedel–Craft reactions. This reaction can occur in bulk or in solution with the aid of a metal catalyst such as $FeCl_3$, $AlCl_3$, and $AlBr_3$.[74,85] Reaction of an activated arenesulfonyl halide with benzene creates the poly(sulfone). Replacing benzene with diphenyl ether can easily incorporate ether linkages into the polymer backbone to synthesize poly (ether sulfones).This method will generate an acid by-product. Alternatively, the reaction between diphenyl ether and terephthaloyl chloride also generates poly(arylene ether ketones).

Both bulk and solution polymerizations are possible with the Friedel–Craft reaction. The bulk reaction entails creating low molecular polymer in the melt. Subsequent heating of the ground polymer at 230–250 °C facilitates the removal of the acid while reducing possible radical side reactions on the sulfonyl chloride.[10] Unfortunately, this synthetic approach causes some side reactions and crosslinking which lead to an irregular polymer backbone. Lowering the temperature of the second heating stage and using limited amounts of catalyst (0.1–4 wt.%) reduce the possibility of side reactions.[86] Polymerization can also occur in solution using $AlCl_3$ and methylene chloride as the solvent. However, the main drawbacks of this approach include purification of the catalyst and low molecular weight due to insolubility of the polymer.

The main approach for synthesizing PAEs is through the nucleophilic aromatic substitution of an activated aryl halide. This synthetic route occurs in solution and requires higher

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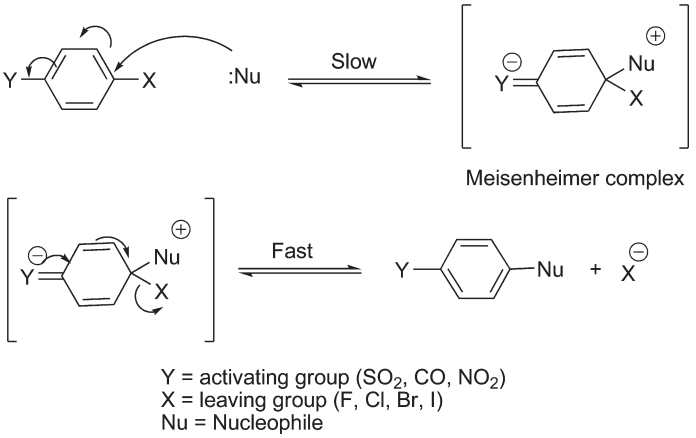

Scheme 5 Nucleophilic aromatic substitution mechanism commonly used to synthesize poly(arylene ether sulfones) or poly(arylene ether ketones).

temperatures than the electrophilic aromatic substitution reaction. However, side reactions are less likely to occur, and the reaction is more tolerable of other functional groups. Scheme 5 illustrates the nucleophilic aromatic substitution mechanism, and there are several features which distinguish this reaction. The first step reaction in which the nucleophile adds to the electropositive carbon is the rate-limiting step. The electronegative halide creates a partially electropositive charge on the carbon through induction and causes the nucleophile to preferentially add at that site.

Because this step is rate determining, the strength of the nucleophile and the electronegativity of the halide substituent dictate the rate of the reaction. Thus, the rate of the reaction follows this trend for the halide leaving group: F >> Cl > Br > I. Addition of the nucleophile to the activated arene to generate the Meisenheimer complex, a resonance-stabilized intermediate, was supported through the isolation of the salt and examination of the influence of the electron-withdrawing group on the reaction rate. Therefore, electron-withdrawing groups such as NO_2, SO_2, and CO encourage and stabilize this first step. The fast and second step involves the rearomatization of the benzene ring and the removal of the leaving group.

Other approaches utilizing metal-coupling reactions have also been explored. The Ullman reaction is a common method for synthesizing PAEs between diphenol and aromatic halide using a copper catalyst. This synthetic route affords greater variability of polymer composition, because activating groups are not needed. The main drawbacks include purification and removal of the copper catalyst and the need for expensive brominated catalysts. Other metal-coupling reactions have also been investigated including the reaction with nickel catalyst and halogenated aromatic compounds.[74,84,85,87] Less expensive aromatic chlorides and milder reaction conditions are advantages of this approach.

PAEs have recently been explored for their fuel cell application, because the aromatic groups can be subjected to ionization to generate the charged species.[85] McGrath *et al.* recently investigated the effect of polymer block length on the bulk morphology of poly(arylene ether sulfones) for proton exchange membranes.[87] TEM micrographs illustrated the effects of charge placement on the morphology of the sulfonated poly(arylene ether sulfones).[87] Randomly sulfonated copolymers showed lack of long-range microphase separation. Transmission electron microscopy of the sulfonated PAES systems demonstrated both ionic interactions and block length impacted the polymer bulk morphology. As the block length increased, the extent of microphase separation became more regular, and the interlamellar spacing also increased with block length.

5.02.3.2 Polyaddition

The second class of step-growth polymers is polyaddition polymers. Polyaddition polymers do not form small-molecule by-products, and polymer examples of this class includes PUs and epoxy resins. New classes of step-growth reactions are expanding this class of step-growth polymers and will be described in later sections of this chapter.

5.02.3.2.1 Polyurethanes

PUs are polymers with carbamate linkages within the backbone. PUs were developed in the 1930s by Otto Bayer *et al.* at I. G. Farbenindustrie at Leverkusen, Germany, and quickly became a main competitor for nylon and polyamides.[88,89] Since then, the applications of PUs have expanded to encompass coatings, shoe soles, foams, and thermoplastic elastomers. Within the past decade, PUs have also reached the biomedical industry and now have found application in implants, soft tissue replacement, angioplasty balloons, drug delivery, and biocompatible tissue scaffolds.[90] The unique ability to control the chemical structure as well as in fine-tuning polymer chain stiffness, flexibility, and morphology enables this class of step-growth polymers to acquire desirable properties for a variety of applications.

There are many approaches for forming the carbamate linkage; the standard method includes the nucleophilic addition reaction between a diol and diisocyanate. Conveniently, this reaction does not produce a condensate by-product and thus falls into the category of polyaddition step-growth polymers. Polymerization occurs readily without removal of the reaction condensate. The isocyanate functional group has the ability to form different types of linkages including urethane, urea, and amide bonds which further increase this monomer's versatility in polymer synthesis. The reaction between an isocyanate and carboxylic acid gives rise to the amide linkage and carbon dioxide. Formation of polymer foams often takes advantage of this by-product to create voids within the polymer.

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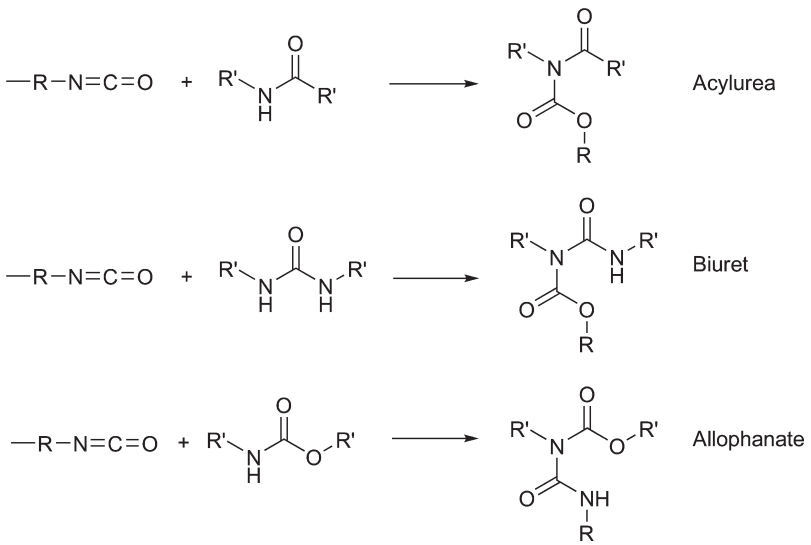
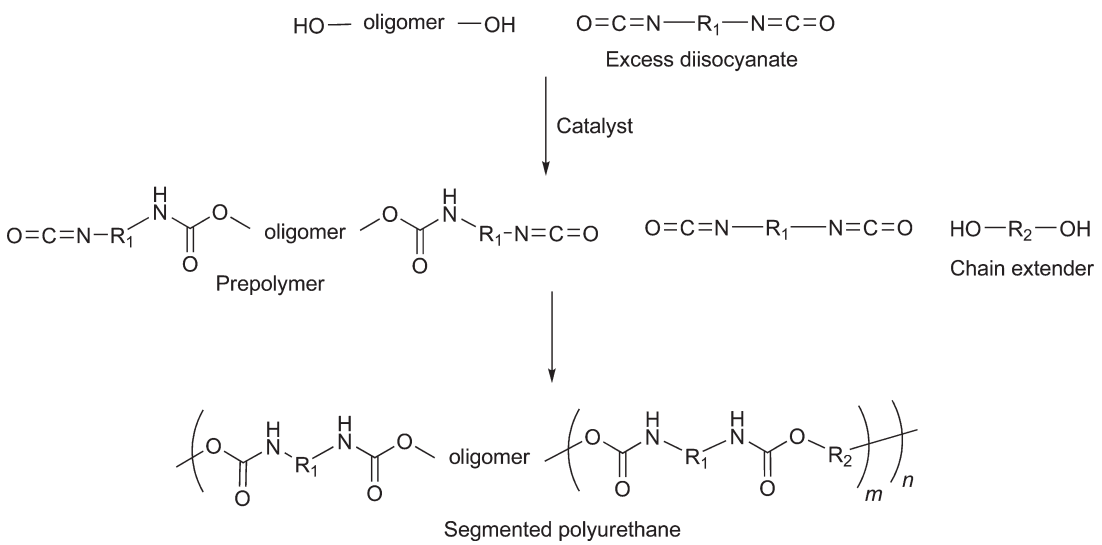


Scheme 6 Possible side reactions from excess isocyanates during PU polymerization leading to branching or crosslinking.

One concern with the synthesis of PUs is the possibility of crosslinking or hyperbranching side reactions. Careful control of monomer stoichiometry and reaction temperature can eliminate side reactions. These reactions occur through the additional reaction of the urethane or urea nitrogen to unreacted isocyanates. Scheme 6 illustrates possible side reactions that occur from the nucleophilic nitrogen of the urethane linkage.

The outstanding properties of PUs can be attributed to the hydrogen bonding between the urethane and urea groups. This intermolecular interaction also contributes to the crystallinity; however, the hydrogen-bonding interaction in urethane linkages is weaker than in urea and amide groups.[91–93] The hydrogen-bonding unit within the hard segment block gives rise to the high T_g and the microphase separation behavior typically seen in segmented PUs. The degree of hydrogen bonding and morphology of the segmented PUs depend largely on the choice of chain extender. Many thermoplastic elastomers take advantage of strong hydrogen-bonding intermolecular interaction to impart exceptional elastomeric properties such as high strain and low mechanical hysteresis.

Segmented block copolymers of PUs have also remained one of the main types of PUs. Segmented PUs are synthesized with chain extenders or without chain extenders. Scheme 7 illustrates a conventional two-step approach utilizing the prepolymer method for synthesizing segmented block PUs. Soft segment blocks including polyether polyols are often reacted with excess diisocyanate. The isocyanate-functionalized soft segment block is called the prepolymer. Soft segment blocks should have low T_g below −50 °C.[93] Other soft segment block polyols include polyesters, polybutadiene, PCL, and polycarbonate.[3] Subsequent addition of a diol chain extender will react with the prepolymer and excess diisocyanate to produce



Scheme 7 Synthetic scheme for the preparation of segmented PUs using a prepolymer method.

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a hard segment block with a higher density of urethane linkages. Hard segment block properties are tailored through the diisocyanate and can form highly crystalline domains.

The block structure allows for microphase separation to create physical crosslinks due to the incompatibility of the polymer blocks, which can be further facilitated through hard segment crystallization in the case of PU. Monomer stoichiometry and the soft segment molecular weight define the hard segment content. The careful choice of hard block and soft block composition, and hence thermal transitions for the corresponding block, determines the application and processing window. The flexible soft segment block attributes to the high elongations typically seen in PU elastomers, and the hard segment block provides mechanical stability and acts as physical crosslinks.

Figure 19 represents a list of commonly used diisocyanates and their chemical structure. There are many synthetic routes that are taken to synthesize diisocyanates including Curtis, Hoffman, and Lossen rearrangements. Hoffman and Lossen rearrangements are commonly used to synthesize aliphatic diisocyanates.[89] Aromatic diisocyanate monomers produce mechanically tougher polymers. Aromatic diisocyanates are more reactive, thermally and hydrolytically stable, and less volatile than their aliphatic counterparts; however, they are generally less UV stable and can cause yellowing of the polymer. Selection of aliphatic diisocyanates, such as 4,4′-dicyclohexylmethane diisocyanate (HMDI), also has the added complexity of mixed stereoisomers which can play a large role in the thermal and mechanical properties of the polymer. Reactivity of diisocyanates with other functional groups also differs. Reactions of amines with diisocyanates are faster and more reactive than hydroxyl groups, water, and carboxyl groups. In addition, steric hindrance of these functional groups also directly affects the reaction kinetics.

PU synthesis typically employs tertiary amines or organotin compounds to increase the reaction rates and facilitate the linear polymerization rather than branching and crosslinking side reactions or reactions with water. The reaction kinetics of PU synthesis directly relate to the basicity and steric hindrance of the tertiary amines. For example, triethylene diamine with a pK_a of 8.2 is more basic than triethylene amine whose pK_a is 10.8, and the relative reaction rate of butanol to phenyl isocyanate is 3.3:0.9 with triethylene diamines and triethylene amine, respectively.[89] Although the reaction rate for the nucleophilic addition reaction increases with amine basicity, the side reactions which produce crosslinked or hyperbranched structures as illustrated in Scheme 6 can also increase as well. Careful control of the catalyst choice and reaction temperatures can lower the probability of branching or crosslinking side reactions.

Unlike conventional ABA triblocks which generally have block molecular weights ranging from 30 000 to 100 000 g mol^{-1} depending on the polymerization method, segmented block copolymers have alternating block lengths with molecular weights between 1000 and 5000 g mol^{-1}.[93] Moreover, the molecular weight, composition, and weight content of ABA immiscible triblocks often form unique long-range morphological features such as spherical, cylindrical, biocontinuous gyroids, and biocontinuous lamellar.[94] Specifically, it is the microphase separation of the immiscible blocks which attributes to useful elastomeric and mechanical properties.[84] The correlation between the molecular weight of these blocks and the influence on morphology has been heavily studied within the past decade.[94–99] In contrast to the well-defined block copolymers often synthesized using living polymerization techniques, segmented block copolymers, such as PUs, do not have well-defined block structures but a distribution of block length. This characteristic leads to the loss of long-range microphase separation; however, phase separation can still be seen.

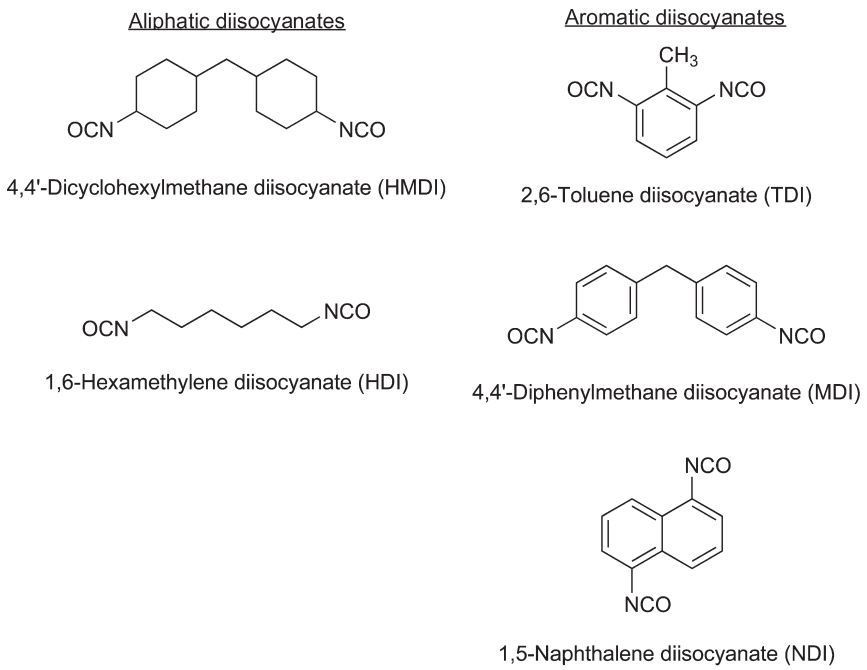

Figure 19 List of commonly used aliphatic and aromatic diisocyanates for PU synthesis.

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Synthesis of segmented thermoplastic copolymers using step-growth polymerization finds wider applications due to the ability to tailor the polymer backbone through monomer choice. Thus, hard segment and soft segment block compositions can be easily modified which translates to better control of the elastomeric properties. Studies on nonchain-extended PU systems showed differences in microphase separation behavior compared to polyureas due to differences in the degree of hydrogen bonding. Wilkes, Yilgor, and others investigated the effects of diisocyanate symmetry on the morphological behavior of poly(ether-urethanes).[100–102] The synthetic method used in the experiment involved stoichiometrically reacting 1000 g mol^{-1} poly(tetramethylene oxide) (1K PTMO) polyols with various symmetrical (4,4′-diphenylmethane diisocyanate (MDI), toluene diisocyanate (TDI), HMDI) and unsymmetrical (HMDI, TDI, and MDI) diisocyanates to afford high molecular weight polymer.

Atomic force microscopy investigated the impact of diisocyanates symmetry on the microphase separation of poly (ether-urethanes) and poly(ether-ureas). Symmetrical diisocyanates such as PPDI, HDI, and CHDI improved polymer mechanical properties and microphase separation.[93] Unsymmetrical diisocyanates produced low-T_g, structurally inadequate polymer films and lacked microphase separation when investigated with AFM. The results demonstrated the importance and influence of diisocyanate symmetry on the polymer morphology and the mechanical properties of the poly(ether-urethanes). In contrast, poly(ether-ureas), which have bidentate hydrogen-bonding capabilities, indicated no influence of diisocyanate symmetry on the microphase separation. However, the symmetry of the diisocyanate, which most likely affected the hard segment crystallinity, affected the morphology and structure of the phases.[93]

In addition to the symmetry of the diisocyanate, segmented PUs are also complicated through a variety of factors which influence the morphology and phase separation such as chemical composition of the blocks, molecular weight, crystallizability of the hard segment, and thermal history.[93] High molecular weight prepolymers increase the microphase separation of the segmented block copolymer, while prepolymers with high polydispersities will encourage phase mixing.[93] One of the most important factors, which determine the morphologies and the properties of segmented PUs, depends on the choice of isocyanate. The symmetry of the isocyanate and the extent of electrostatic strength can regulate the crystallinity of the hard segment.

Although the study from Yilgor *et al.*[93] examined the influence of diisocyanate symmetry and hydrogen-bonding capabilities on the morphology of the segmented PU, the effects of molecular weight on morphological structure was not investigated. The specific relationship between molecular weights of segmented block and polymer morphology poses more complications mainly due to the difficulties of controlling block molecular weights in prepolymer methods. Although the molecular weight of the prepolymer used in many segmented PU synthesis is often known, the effective molecular weight of the hard segment block is difficult to elucidate. One method to bypass this obstacle is to react two prepolymers with known molecular weights such as polyols and an α,ω-difunctionally terminated oligomer, preferably with isocyanate groups. This approach avoids the use of chain extenders and allows for a systematic study of the influence of block molecular weight on polymer morphology.

Recently, Meijer *et al.* investigated the crystal structures of linear aliphatic PUs containing 5–10 methylene units using transmission electron microscopy (TEM) and X-ray and electron diffraction analysis.[103] Hydrogen bonding of the PUs produced crystals with lamellar crystal thicknesses between 5 and 10 nm. Further investigations showed that these hydrogen-bonded crystal lattices were formed through fully extended chain conformations in an ordered triclinic lattice. Furthermore, the hydrogen bonds were set between antiparallel chains very similar in fashion to aliphatic linear polyamides.

One of the more interesting polymer properties that have elicited much attention is the special shape memory characteristics that have been found in many thermoplastic-segmented PUs.[104–108] Shape memory polymers (SMPs) are generally polymer networks that have the ability to hold a certain physical shape after deformation and return to the original physical state after being exposed to an external stimulus such as temperature, light, and pH. Many shape memory polyurethanes (SMPUs) have already been reported,[105, 107–110] and research is increasing the understanding in this area to better tailor the switching properties. In many cases, the composition of the various segments in the segmented PUs contributes to a thermal transition which allows for the shape memory and shape recovery processes to exist. Typically, a *switching* segment and a *permanent* segment are established with the desired thermal transition temperature. The *switching* segment allows the polymer to morph and change its overall physical shape at the transition temperature, T_{trans}, and the *permanent* segments act as physical anchors whose thermal transition is generally above T_{trans} and retains the original primary shape. Upon heating the sample above T_{trans}, the flexible switching segment acquires more chain mobility to establish a new physical shape. Reheating the deformed polymer above T_{trans} entropically drives the polymer chain to convert back to the random-coil conformation.

Segmented PUs have been recently explored for shape memory applications since the block copolymers are able to form physical networks through microphase separation and crystallization of hard segment. In addition, the syntheses of segmented PUs have been well defined and various types of soft segment precursors, diisocyanate monomer choice, and chain extenders allow for tailored polymer designs, specifically for shape memory properties. In order for shape memory properties to be useful in smart material applications, the reversibility and memory of the polymer shape must occur quickly and preferably with little hysteresis such that the properties of the polymer following repetitive physical deformation remain unchanged throughout deformation.

Shape memory poly(ester-urethanes) have found much interest from biomedical applications due to their shape recovery properties and biodegradability from polyester blocks such as poly(lactic acid) and poly(ε-caprolactone). Wang *et al.* investigated the morphological consequences from deformation of poly(ester-urethanes) that have shape memory properties using Fourier transform infrared spectroscopy (FTIR).[111] Various other spectroscopic techniques have been employed to better understand the polymer microstructure transition that provides these shape memory and shape recovery properties including small-angle X-ray scattering (SAXS), wide-angle X-ray

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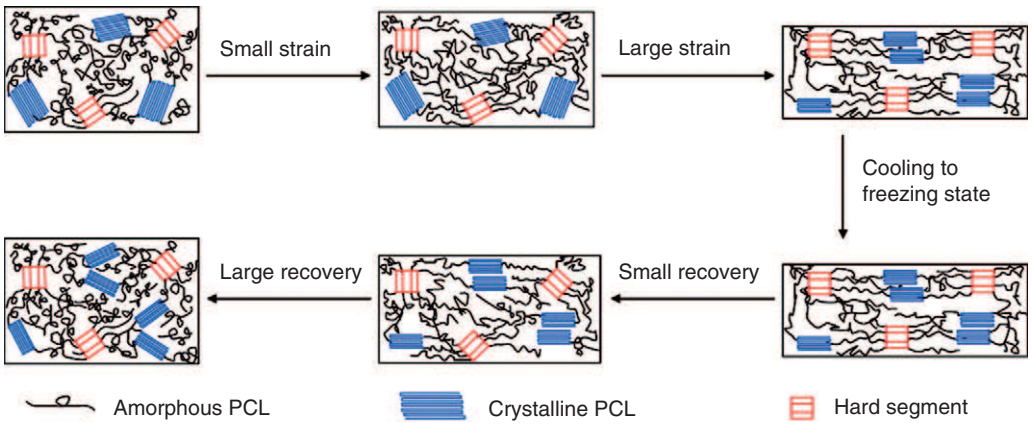


Figure 20 Schematic of the microstructure transition of shape memory poly(ester-urethanes) under strain deformation and shape recovery. Reprinted with permission from Wang, W.; Jin, Y.; Ping, P.; *et al. Macromolecules* **2010**, *43* (6), 2942–2947.[111] Copyright (2010) American Chemical Society.

diffraction (WAXD), DMA, and AFM. Figure 20 depicts a representative schematic of poly(ester-urethanes) undergoing small and large strain and the shape recovery process under a thermal stimulus. Using FTIR, the investigators concluded that the amorphous phase consisting of the soft segment PCL became more oriented under small induced strain. However, crystalline domains from the PCL as well as the hard segment urethane block remained largely unhindered. When larger strain is applied, the amorphous PCL becomes even more oriented and begins to undergo strain-induced crystallization while the original crystallites from the PCL and hard segment phase also begin to align. Most importantly, the hydrogen bonding from the hard segments is slightly weakened and rearranged to adopt a newly fixed microstructure. Shape recovery largely relies on the entropy of the system to recover a more random-coil conformation of the amorphous chains and relies on restoring the intermolecular hydrogen-bonding interactions that were weakened during strain deformation. The result confirmed others' work, which concludes that a recovery of the segmented PU to its original shape was largely dependent on the polymer microstructure.[110,112,113]

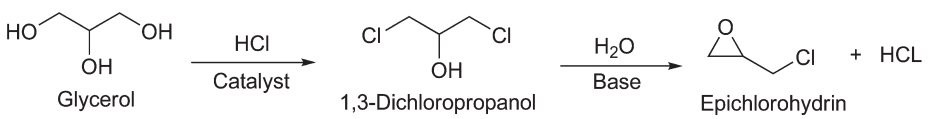
5.02.3.2.2 Epoxy resins

Epoxy resins are an important class of step-growth polymer which has allowed for a quick step technique to synthesize thermoset networks. Epoxy thermosets are reactions between an epoxy resin, a small molecule or prepolymer that is functionalized with epoxide end groups, and a hardener or crosslinking agent. The crosslinking agent has a functionality $f > 2$ to allow for oligomer formation, branching, and finally crosslinking.

One of the interesting factors about epoxy curing arises from the unique geometric structure of the epoxy ring. The development of epichlorohydrin facilitated the wide utility and application of this curing process to extend beyond small-molecule diepoxies and include epoxy-functionalized prepolymers. With the need to be more ecologically mindful, Scheme 8 highlights a green chemistry approach to synthesize epichlorohydrin from glycerol, a transesterification by-product from vegetable oil.

The epoxy ring itself is a heterocyclic three-membered planar ring.[114] Although the chemical compositions of the carbon and oxygen within the ring are sp^3-hybridized and should have characteristic 109.5° tetrahedral structures, the formation of the three-membered ring compresses the internal angles of the epoxy ring to nearly 60°. Thus, the hybridized orbitals of the carbon atoms are more similar to the trigonal planar sp^2 orbitals. Many previous literatures reviewed the effect of chemistry and hyperconjugation of the strained three-membered ring.[115,116] The compressed internal angle of the epoxide ring translates to a very large ring strain energy of approximately 113 kJ mol^{-1}. The release of ring strain contributes to the major driving force for the fast and efficient mode of curing used in thermosets.

The epoxy curing occurs through a complex process in which the dynamics and the polymer structure change during the curing chemistry. The reaction occurring between an epoxy resin and a hardener such as a diamine first occurs through the production of the small oligomers. Because the hardener has a functionality greater than 2, branching and eventual crosslinking will occur. During the branching stage, the polymer is still soluble in the reaction medium; however, as the reaction continues to cure, the reaction product will lose solubility or begin to swell in the reaction solvent and gelation takes place. Because the curing process is such a dynamic and complicated progression, properties of the polymers also change throughout the reaction.[117] In fact, the curing process directly influences the viscoelastic properties as the monomers and reactants transition from oligomers to branched and finally crosslinked networks. The choice of epoxy resin, hardener,



Scheme 8 Synthesis of epichlorohydrin from glycerol, a by-product of transesterification from vegetable oil, from Solvay Epicerol™ process.

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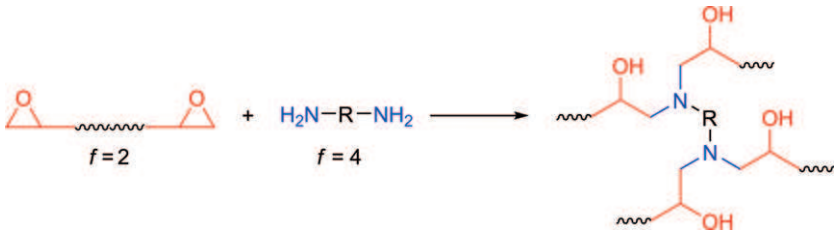

Scheme 9 General epoxy resin curing between a diepoxide (functionality (f) = 2) and diamine (f = 4).

and crosslink density directly influences the polymer storage modulus increase as the epoxy resin cures. Because the chain mobility of the polymer thermoset decreases with crosslinking, the T_g also begins to rise as the curing process occurs.

Scheme 9 represents a general epoxy resin curing reaction between a diepoxide and diamines. The reaction of the epoxide ring can occur between an electrophile or a nucleophile to generate the ring-opening reaction and the subsequent alcohol. In general, the primary and secondary alcohols can be produced, since in theory, both carbons of the epoxide ring are likely to react with the nucleophile or electrophile. However, the sterics of the reaction generally leads to the attack of the less sterically hindered carbon and subsequently the secondary alcohol as seen in Scheme 9. Common nucleophiles used in epoxy reactions are alcohols, amines, and carboxylic acids. Alkyl halides and isocyanates are possible electrophilic reactants with epoxides as well.

Epoxy curing has found vast utility in self-healing applications since the reaction occurs quickly and without any aid of catalysts. In many self-healing systems, microcapsules containing a reactant or catalyst are generated and blended into a binary polymer matrix. Upon stress or mechanical damage, the microcapsule will rupture and react with the surrounding matrix to repair the polymer damage. The curing agent or compound held within the microcapsule contains the same chemistry as the polymer matrix to repair the damage with the same polymer composition to maintain matrix homogeneity. Epoxide reactions offer advantages such as a fast cure which is often necessary for quick polymer repair.

Recently, Sottos and co-workers developed a method to prepare microcapsules containing reactive amines using interfacial polymerization rather than conventional emulsion techniques to create the walls of the microparticles.[118] These particles were intended for epoxy adhesive applications with potential self-healing properties. The capsules contained the very reactive diethylene triamine which was created using a water-in-oil emulsion method and stabilized in a nanoclay suspension with polyisobutylene (PIB). Upon removal of PIB, the particles were quickly reacted with TDI to create a polyurea wall. Careful addition of the TDI allowed for unaggregated microparticles with diameters averaging about $26 \pm 10\,\mu m$ (Figure 21). The amine-containing capsules were blended with epoxy resin and curing was performed upon added pressure to rupture the capsules.

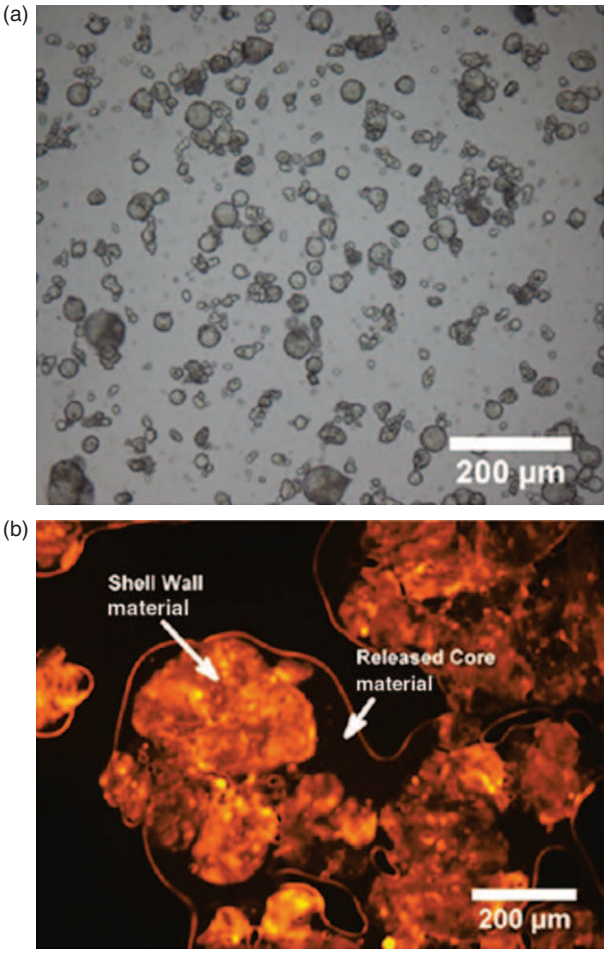

Figure 21 Micrographs of epoxy-cured polymer composites: (a) optical micrograph of amine-filled microcapsules in solution for self-healing epoxy composites; (b) fluorescence micrograph reflecting the response of microcapsules under applied pressure.[118] Reprinted with permission from Wang, W.; Jin, Y.; Ping, P.; *et al. Macromolecules* **2010**, *43* (6), 2942–2947.[111] Copyright (2010) American Chemical Society.

5.02.4 Future Direction for Step-Growth Polymers

Step-growth polymers have developed immensely since the early discoveries of polyesters and polyamides. The polymerization methods highlighted in the previous sections have played an important role in many commercial polymer developments. One of the main advantages of step-growth polymerization is the ability to incorporate functional monomers within the polymer main chain. Bio-derived monomers and enzyme catalysis are becoming popular to reduce our dependency on fossil fuels. The synthesis of novel monomers enables researchers to challenge the performance limits of current polymer products, and the re-emergence of traditional synthetic organic methods is

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being explored for new and exciting step-growth polymers. These innovations create opportunities to enable new applications and explore novel compositions.

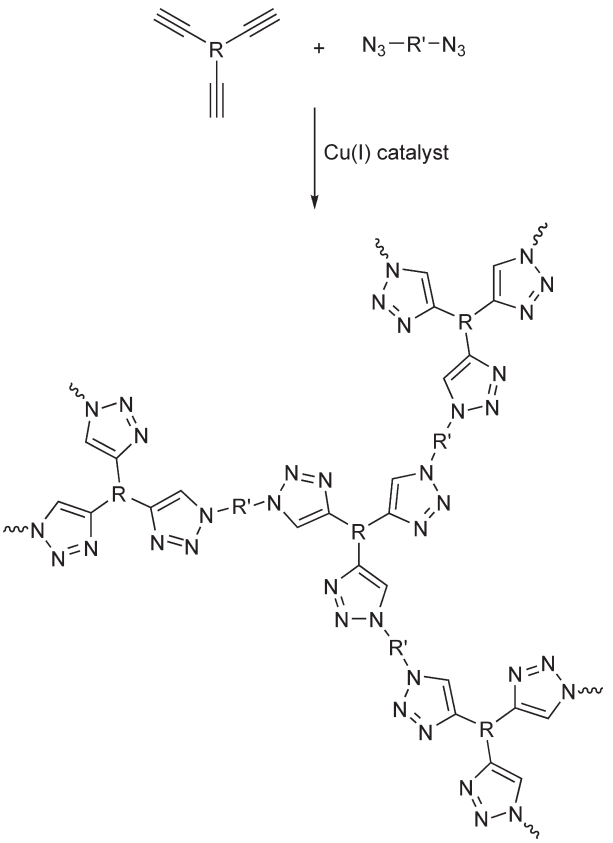
5.02.4.1 New Strategies for Step-Growth Polymers

In the previous sections, the discussion has primarily revolved around many of the 'classical' step-growth polymers and synthetic techniques. Some of the most exciting work performed in the last decade on polycondensations and polyadditions has been in nontraditional step-growth polymers. A recurring theme in these new synthetic techniques is to utilize high-yielding and highly specific organic reactions to synthesize novel step-growth polymerizations. In many cases, *orthogonal* reactions are elicited to improve the reaction efficiency and expand the available functional groups in a polymer system.[88,119,120] Orthogonal reactions are defined as 'a set of completely independent classes of protecting groups… [in which] each class of groups can be removed in any order and in the presence of all other classes'.[121] These highly specific reactions introduce an array of functional groups available for step-growth polymerizations that were previously unachievable. In many cases, these methods utilize functional groups that are not typically considered traditional step-growth functional groups. The principles of 'standard' step-growth polymerization methodologies, nevertheless, provide a foundation to discover new polymeric architectures using nontraditional step-growth polymerization.

5.02.4.1.1 Click chemistry

Click chemistry represents a practical, well-understood organic reaction to quantitatively synthesize step-growth polymers. Click chemistry was discovered by Huisgen in the 1950s; however, it was Sharpless who coined the term 'click' chemistry to define highly efficient synthetic reactions that were tolerant of various functional groups and occurred under mild synthetic conditions.[122–124] Since that time, click chemistry has experienced a synthetic renaissance especially in the polymer community. The efficiency of click reactions further allowed polymer chemistry to extend across interdisciplinary opportunities.

Although many reactions are termed 'click', the primary click reaction utilized in polymer chemistry involves the Huisgen copper-catalyzed coupling of a terminal alkyne with a terminal azide to exclusively form the 1,2,3-triazole unit (Scheme 10).[123,125–139] Click reactions proceed without the elimination of a small-molecule by-product and therefore this reaction is classified as a polyaddition polymerization. A major benefit of the click reaction is its reactant specificity and tolerance of other functional groups. Furthermore, the click reaction occurs with high conversions in virtually any solvent, including aqueous solvent systems, and at relatively low temperatures. These combined advantages enable click reactions particularly well suited for step-growth polymerizations of all varieties including linear, graft, hyperbranched, and dendritic polymers. Step-growth polymers synthesized by click chemistry are referred to as polytriazoles.[125] The predictability and regularity of this reaction are exceptionally convenient toward high-yield synthesis of stereoregular 1,4-disubstituted 1,2,3-triazoles. Ruthenium-catalyzed click chemistry, though not as prevalent in the literature, yields the stereoregular 1,5-disubstituted triazole.[88,125,140,141]



Scheme 10 Hyperbranched polytriazole synthesized by $A_2 + B_3$ step-growth polymerization.[125]

Since the inception of the copper-catalyzed click chemistry, click reactions have broadened the field of polymer science and remained a prominent method to achieve numerous polymer architectures. Researchers have utilized click chemistry to synthesize pendant and end group functional polymers. This allows for facile postpolymerization addition of subsequent functionality that may not be compatible with the polymerization reaction. Also, pendant-functionalized polymers and simple addition of terminally functionalized oligomers achieved graft block copolymers.[127] Block copolymers have also been described through click reactions of alkyne- and azide-functionalized oligomers.[127,138] Click reactions of multifunctional core monomers and monofunctionalized oligomeric arms afforded star copolymers. Click chemistry was also extensively investigated as conjugation reactions of polymers to various substrates such as fullerenes, nanotubes, and other nanomaterials.[120,127,142,143]

Despite the clear advantages of click chemistry for organic and polymer synthesis, click reactions have only recently been utilized for the direct polymerization of step-growth polymers. Voit *et al.* first attempted the click reaction of a hyperbranched polymer using an AB_2 monomer containing a bisazide and alkyne functionality.[144] Special care was taken to avoid premature polymerization of the monomers during synthesis, and unfortunately the only product was a rubbery, insoluble precipitate from the reaction.[144] An alternate synthetic route was to utilize click chemistry to synthesize hyperbranched polymers using $A_2 + B_3$ monomers.[140] This approach prevented autopolymerization of the monomers, and thin films were achieved

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through solution or spin casting the polymer directly from the reaction. The first successful synthesis of a soluble hyperbranched polytriazole was performed in 2008 by Shi *et al.*[145,146] Almost simultaneously, Tang and co-workers were also able to obtain soluble hyperbranched polytriazoles.[140]

Click chemistry has been heavily described in the literature as a suitable approach to synthesize dendrimers.[26,30,128,131,143] Dendrimers have shown extensive applications in the field of biomedical drug delivery due to their monodispersity, high terminal functionality, and ability to encapsulate or conjugate drugs, dyes, and diagnostic imaging agents. Sharpless and co-workers described the first synthesis of a two-step, convergent copper-catalyzed click dendrimers in 2004.[143] Click chemistry allowed for efficient synthesis of monofunctional azide dendronic arms, and subsequent reaction of the dendrons to a trialkyne afforded the dendrimer at high yields. Due to the nature of the click reaction and the absence of by-products, challenging purification of the dendrons, which is often a disadvantage in dendrimer synthesis, was alleviated. Click reactions of divergently synthesized dendrimers were also successful.[27] Divergent synthesis of dendrimers affords higher generation growth due to the avoidance of steric effects. Purity levels and yield of each dendrimer generation were > 95% and > 99%, respectively.

One of the advantages of click polymerization is the high reaction rates at relatively low temperatures. This is especially advantageous for the synthesis of polyesters. Some of the disadvantages of classical polyester synthesis are the extremely high reaction temperatures, long times, high vacuums, and precious metal catalysts required to achieve high molecular weight. Bisalkyne monomers containing ester functional groups were reacted with diazides to form polyesters containing triazole rings under mild conditions. The incorporation of the heterocyclic triazole ring effectively increased the thermal properties and represented the first series of high molecular weight click polyester.[136,147] The ability to synthesize polyesters under mild conditions using click chemistry introduces a new approach to incorporate novel monomers that were once not readily achieved through traditional polyester synthetic methods.

Some of the major disadvantages associated with copper-catalyzed click chemistry as a route for step-growth polymerization include poor solubility of the final product, necessity of a metal catalyst, and difficulty removing the catalyst upon polymerization. However, the convenience of this reaction, high reaction efficiency, lack of by-product, and ability to introduce heteroatoms within the backbone of a polymer main chain offer advantages that outweigh many of these disadvantages. Although click chemistry has been primarily used as a pendant or terminal functional group introduction to perform postpolymerization reactions, polytriazoles synthesized directly by step-growth polymerization of bisalkynes and diazides are becoming increasingly prominent in the literature and will remain as a viable approach to synthesize novel heterocyclic step-growth polymers.

5.02.4.1.2 Ionene synthesis

Ionenes are polymers containing quaternized nitrogens on the polymer backbone. Ion-containing polymers have received increased attention in the literature due to their potential role in recent developments for energy storage, transport, and generation of fuel cell membranes.[148–156] Ionenes have also found significant usage in water purification systems, antimicrobial membranes,[157] and other biomaterials for drug delivery and gene delivery agents.[158–161] Although the vast majority of ion-containing polymers are synthesized with pendant ionic groups, there are many advantages to incorporating ions in the polymer backbone. The synthetic approach for ionenes allows for precise control of charge placement and charge density within the polymer. Most ion-containing polymers, such as sulfonated polysulfones or polystyrenes or Nafion®-type polymers, do not have regular charge placement due to the noncontrolled nature in which they are synthesized.[162]

The reaction between a ditertiary amine and dialkyl halide, also termed the Menshutkin reaction, was first described in 1933 and still represents the primary synthetic method for ionenes.[163] The nomenclature of nonsegmented ionenes with simple aliphatic monomer structures without double bonds or aromatic groups in between is conventionally x,y-ammonium ionene where x is the number of methylene units in the diamine and y is the number of methylene units in the dihalide.[164] Solvent polarity and choice of halides heavily influenced the polymerization reaction rate.[165] Ionene chlorides were determined to proceed much slower than the ionene bromides due to leaving group effects. Sterically hindered dihalides also effectively decreased the reaction rate. Further investigations indicated the reaction occurred through a one-step bimolecular mechanism. Monomer selection readily achieved precise synthetic control over the charge placement and density within the polymer backbone. The choice of the dihalide is particularly important when considering polymer properties. More basic halides will typically result in lower thermal stability, because the primary degradation mechanisms of ionenes are the reverse Menshutkin reaction and the Hoffman elimination reaction. The Hoffman elimination reaction, in particular, is much faster with a more basic anion. Therefore, the larger, less basic anions, such as Br– and I–, are much more likely to result in more thermally stable polymers.[164]

To obtain regular charge placement, researchers have utilized a ditertiary amine with an alkyl dihalide of the same length. For example, *N,N,N′,N′*-tetramethylhexane-1,6-diamine polymerized with 1,6-dibromohexane produces a polyionene containing one quaternized nitrogen per six carbons in the backbone. To obtain more 'blocky' charge placement, simply varying the lengths of the ditertiary amine and the alkyl dihalide yields the desired charge placement.[164,166] For example, the polymerization of *N,N,N′,N′*-tetramethyldodecane-1,12-diamine with 1,2-dibromoethane produces a much more 'blocky' charge placement.[167–169] Expanding on this research, alkyl halide-functionalized PEG segments were reacted with 1,6-hexane diamine to yield ionenes with blocky charge placements.[170] In order to achieve segmented block ionenes that also contain hydrophobic segments and hydrophilic segments, utilization of blocky polyether diols, such as PEG-PPG block polyols, or incorporation of multiple diols, with varying hydrophobicities, such as PEG diols and PTMO diols, have also been synthesized.[164] Some interest does exist in branched and crosslinked ammonium ionenes, and although $A_2 + B_3$ monomer system could be utilized, most of the work in branched and crosslinked ionenes have revolved around functionalization with acrylate and allyl sites for subsequent crosslinking using free-radical techniques.[164]

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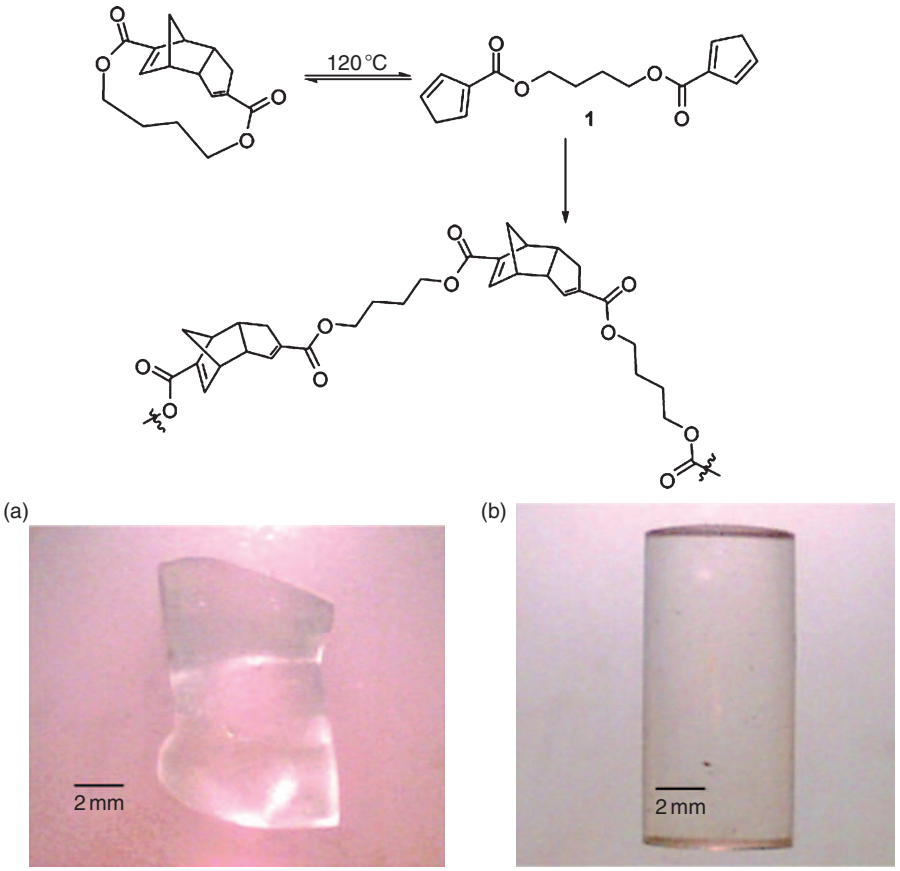
Obtaining reliable ionene molecular weights is challenging due to the high charge ratio in ammonium ionenes and propensity of charged polymers to aggregate in solution. It is crucial for measurement techniques such as size exclusion chromatography (SEC), light scattering, and intrinsic viscosity that the polymer chains in solution be nonassociating and nonaggregated. Therefore, the identification of solvent for SEC can be very difficult. Long and co-workers were able to perform absolute molecular weight characterization of 6,12- and 12,12-ammonium ionenes in 54/23/23 (v/v/v%) H_2O/MeOH/AcOH with 0.54 M NaOAc at Tf626y446-10.941 Td (SEC)Tj /T1_1 8.46Mand



Scheme 12 Diels–Alder as a synthetic method for the synthesis of healable materials and photographs of (a) polymer after compression testing and (b) the same sample after thermal remending, demonstrating shape memory. Reprinted with permission from Murphy, E. B.; Bolanos, E.; Schaffner-Hamann, C.; *et al. Macromolecules* **2008**, *41* (14), 5203–5209.[186] Copyright (2008) American Chemical Society.

by-products like many click reactions. Unlike the Huisgen click reaction which produces heterocyclic triazole rings, the Diels–Alder reaction proceeds mainly through new carbon–carbon bond formation. Similar to the azide–alkyne click coupling, Diels–Alder reactions of diene- or dienophile-functionalized polymers have found significant use for side chain coupling, star formation, or brush polymers. Moreover, Diels–Alder reactions are reversible and are susceptible to the 'retro-Diels–Alder' reverse reaction, which allows them to be explored for many self-healing and remendable materials (Scheme 12).[129,130,186,187]

The thermally induced Diels–Alder reaction occurs between a diene and an electron-deficient dienophile without the aid of catalysts. There have been some reports of Diels–Alder reaction as a route for step-growth polymerization in the literature. In fact, one of the first known reactions of cyclopentadiene was by the 'father of polymer science' H. Staudinger.[186,187] Staudinger was able to synthesize poly(cyclobutadiene) by the [2 + 4] cycloaddition reaction, but it was Alder and Stein who discovered the reaction mechanism. Since the early pioneering of Diels–Alder work, other researchers have incorporated this reaction into step-growth polymerizations. Wudl and co-workers were able to successfully synthesize Diels–Alder polymer networks.[186,187] Significant effort has also been devoted to the furan–maleimide coupling using A–B-type monomers. These compounds are relatively stable, because the Diels–Alder reaction did not occur until at least 80 °C.[137,184,185]

Diels–Alder reactions are thermally reversible reactions, and the temperature at which this occurs depends highly on the substituents. In some aspects, this thermal reversibility may be considered a disadvantage because it limits the thermal stability of the material. However, Wudl and co-workers have taken advantage of this property to synthesize thermally remendable single-component polymer networks.[186] Single-component self-healing and remendable systems avoid the use of heterogeneous polymer systems, which incorporate encapsulated catalyst or monomer components into the polymer matrix and reduce mechanical homogeneity. The cyclic monomer chosen for the single-component crosslinked system was based on dicyclopentadiene. The cyclic monomers underwent the retro-Diels–Alder reaction at 120 °C to yield the α,ω-bis (cyclopentadiene) and formed the Diels–Alder adduct with neighboring monomers. The remaining double bond after the Diels–Alder reaction allowed for trimer formation with cyclopentadiene units to generate mechanically robust and solvent-resistant crosslinked networks.

More importantly, the authors hypothesized when these polymer networks were subjected to a mechanical stress, only the most strained chemical bonds, the Diels–Alder bonds, were broken. Therefore, the Diels–Alder reaction may reoccur upon heating to enable thermal remending of the polymer networks. Scheme 12 represents the synthesis of Wudl's Diels–Alder-based polymer and images of a mechanically compressed

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sample before and after thermal remending. The images reflect the excellent shape memory properties of these novel polymer networks. Also, when performing fracture testing and subsequent heating, the deleterious point of fracture was almost completely removed, and the sample recovered as much as 60% of its initial strength.[186] The thermally reversible Diels–Alder reaction permitted the synthesis of thermally remendable polymer systems.

5.02.4.1.5 Polybenzimidazoles

Polybenzimidazoles (PBIs) are a class of polymers that are well known in the literature.[85,150] Although these polymers have only recently reached any level of commercial significance, they do incorporate desirable properties such as thermal stability and flame resistance for firefighter coats, space suits, and metal-working gloves. Commercial PBIs are synthesized in a two-step melt solid-state polymerization from 3,3′,4,4′-tetraaminobiphenyl and diphenyl isophthalate. This process produces only moderate molecular weights, and the polymers are typically only soluble in dipolar aprotic solvents with salt under high pressure.[150]

Recently, PBIs, have garnered interest in the fuel cell industries as potential proton exchange membranes. One of the primary disadvantages of typical proton exchange membranes such as Nafion® is the necessity to be hydrated in order to obtain high proton conductivity. Unfortunately, this eliminates their utility at temperatures above 80 °C, because the membranes tend to dry out, which lowers conductivity. In contrast, the tertiary nitrogens in the PBI imidazole rings are susceptible to protonation in acidic conditions and thus may be utilized for proton transfer. In order for this to occur, the polymer must first be doped with phosphoric acid to create an acidic-enough media to protonate the PBI and facilitate proton transfer.[150] Because the boiling point of phosphoric acid is significantly higher than water, PBI-based proton exchange membranes were able to operate at significantly higher temperatures, which significantly improved proton-transfer efficacy.[150,155,156]

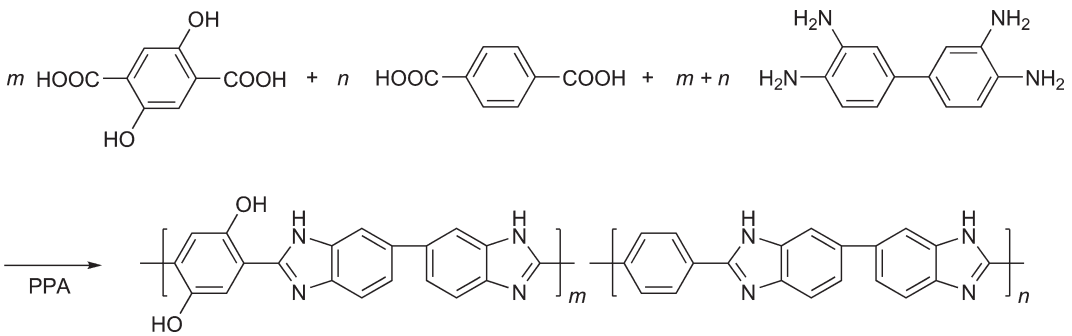
Unfortunately, PBIs can only be doped in phosphoric acid at relatively low loadings before mechanical properties start to significantly diminish. Furthermore, the methods used to load PBI membranes with high amounts of phosphoric acid were tedious and included several steps. These complications limited the usage of highly doped phosphoric acid-containing PBI membranes. To combat these challenges, Benicewicz and co-workers developed the synthesis of PBIs in polyphosphoric acid (PPA) via a sol–gel process. After film casting, the PPA was hydrolyzed to phosphoric acid. These highly conductive membranes contained high amounts of phosphoric acid, retained exceptional mechanical properties even at elevated temperatures, and proved to be efficient high-temperature proton exchange membranes for fuel cells.[155,156]

The Benicewicz group is currently synthesizing functionalized PBIs by this method and has recently published the synthesis of hydroxy-functionalized PBI membranes in PPA. The hydroxyl functionalization allows for reversible crosslinking when exposed to phosphoric acid, which leads to extremely durable films and membranes. In fact, flexible, free-standing, and tough films suitable for proton exchange membrane fuel cells were cast with loadings as low as 2.5% PBI in PPA. **Scheme 13** demonstrates the synthesis of these samples in PPA.[155,156] Although for many years the application of PBI seemed limited, they are emerging as potential proton exchange membranes. By utilizing new synthetic techniques, these materials may find increased commercial prominence in the years to come.

5.02.4.1.6 Polyesters for current and emerging technologies

Polyesters offer a rich and diverse structure–property window with a vast array of difunctional and multifunctional monomers of sufficient purity for quantitative conversions. Polyesters also suggest more recently a rapidly growing importance due to their inherent biodegradability and opportunities for bio-based carboxylic acid and hydroxyl monomers. Thus, one can envision continued research and commercial interests because of the decreased reliance on fossil fuels, opportunities for quantitative conversion to starting monomers, and biodegradation for lessened impact on our environment. In addition, tailored polyesters in the biomedical arena have enabled numerous therapeutic delivery systems that permit time-release drug delivery, gene delivery vectors, and biodegradable tissue scaffolds for regenerative medicine.[180,188–190] New discoveries within the polyester family have catalyzed many new technologies. Many macromolecular parameters are easily tuned using step-growth polymerization methodologies, including composition, molecular weight, molecular weight distribution, topology, sequence, and stereochemistry. Thus, polyester design enables a systematic investigation of structure–property relationships and carefully tailored properties for diverse performance, ranging from food packaging to biomedical devices.

There is rapidly growing interest in the identification of monomers derived from renewable resources with special attention on synthetic pathways based on the principles of green chemistry.[191] The transition from petrochemical-derived monomers to renewable resources reflects the awareness of



Scheme 13 Synthesis of a functionalized PBI in PPA for high-temperature proton exchange membrane fuel cell application.[156]

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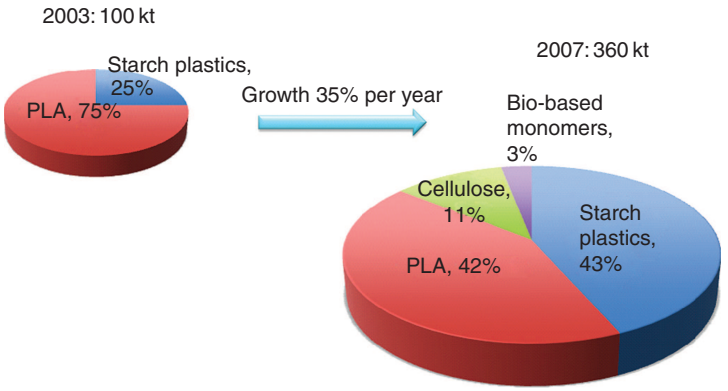
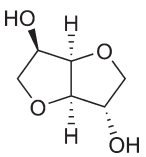
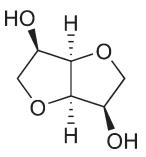
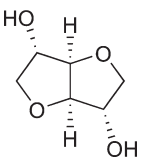


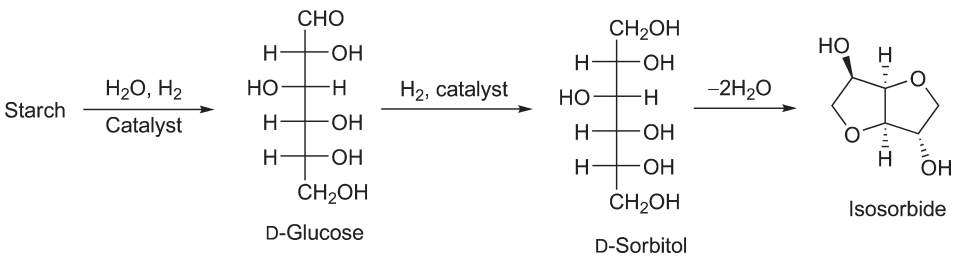
Figure 23 Growth of bio-based polymers derived from renewable resources from 2003 to 2007.[193]

consumers and industry on the importance of incorporating more sustainable chemistry commercial products. In fact, plastics production currently accounts for nearly 7% of worldwide oil and gas consumption.[190–192] Due to the rising concern pertaining to the limited amount of fossil fuels and the variability of fossil fuel costs, there is a renewed interest in utilizing renewable resources to produce high-performance polymers. Researchers are focused on the utility of biomass, plant-derived resources, to produce novel monomers. Figure 23 illustrates a 38% growth of bio-based polymers derived from renewable resources from 2003 to 2007. Industrial polymers derived from starch have nearly doubled in the contribution of all bio-based polymers in 2007.

The development of cyclic diols from cereal-based polysaccharides, 1,4:3,6-dianhydrohexitols, has also received attention due to their increased rigidity within the polymer backbone. Recently, a review from Pascault *et al.*[192] discussed the advantages of utilizing these monomers for polymer synthesis. Table 3 summarizes the three isomers of 1,4:3,6-dianhydrohexitol monomers: isosorbide, isomannide, and isoidide. Stereochemical variation of the hydroxyl group afforded differences in the monomer melting temperature, reaction kinetics, and polymer thermal properties. Scheme 14 describes the synthesis of 1,4:3,6-dianhydrohexitols. Initial enzymatic degradation of starch resulted in glucose or mannose, which was further catalytically reduced to sorbitol and mannitol. Subsequent dehydration and cyclization of sorbitol and mannitol produced the bicyclic diols, isosorbide and isomannide, respectively. Of the three isomers, isosorbide is the only one produced on a large industrial scale. A recurring requirement to afford high molecular weight step-growth polymers is the necessity for sufficient monomer purity. Limitations arising from monomer purity have been

Table 3 Stereoisomers of starch-modified monomers for polyesters derived from renewable resources. Specific stereoisomers of the monomers determine monomer melting temperatures and final polyester properties[192]

Chemical name	*Isosorbide 1,4:3,6-dianhydro-D-glucidol*	*Isomannide 1,4:3,6-dianhydro-D-mannitol*	*Isoidide 1,4:3,6-dianhydro-L-iditol*
Molecular structure			
Melting temperature	61 – 62 °C	81 – 85 °C	64 °C



Scheme 14 General synthetic strategy for the synthesis of isosorbide from starch.[192,194]

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the central obstacle preventing transition of sugar-based diols into large-scale commercial production. In particular, monomer degradation and deleterious side reaction during the monomer synthesis lead to discoloration of the resulting polymers as well as reduced molecular weight.

The ability to effectively increase polyester T_g and avoid petroleum-derived aromatic monomers reflects some of the main advantages for utilizing these cyclic diols. The kinked structure of isosorbide prevented crystallization; however, isosorbide, a rigid bicyclic diol, effectively stiffened the polymer main chain and increased T_g. The highest all-aliphatic isosorbide-containing polyester displayed the highest T_g of approximately 60 °C,[195] while terephthalate-containing isosorbide polyesters revealed a T_g near 190 °C.[196] Recently, more attention is directed toward entirely aliphatic polyesters due to their potential biodegradability.[182,197,198]

Kricheldorf *et al.* investigated all-aliphatic copolyesters derived from isosorbide, 1,4-cyclohexane dicarboxylic acid (CHDA), and succinic acid to develop biodegradable polyesters from renewable monomers.[199] These copolyesters indicated tunable high T_gs depending on the stereochemistry of the bicyclic diol. Homopolymers of CHDA and isosorbide revealed the highest T_g (146 °C) followed by isomannide (133 °C) and isoidide (115 °C).[199] Replacing the cyclic diacid with an aliphatic linear diacid, succinic acid, essentially lowered the T_g to 77 °C. Thus, the results concluded that isosorbide and its derivatives are suitable diols for the synthesis of polyesters with tunable glass transition temperatures.

Biodegradable poly(lactide)s (PLAs) have emerged in packaging applications as a solution to reduce waste production. Renewable lactide monomers are derived from corn or sugar feedstocks, processed to D-glucose, and finally fermented to result in the cyclic dimer, lactide.[193,198] Using various metal catalysts, lactide monomers undergo ring-opening polymerization to produce the linear aliphatic polyester. Degradation of PLA produces lactic acid, which further metabolizes into carbon dioxide and water. Recent work from the Hillmyer research group demonstrated successful ring-opening polymerization of lactide and menthide monomers from renewable feedstock yielding thermoplastic elastomers.[200–202]

In addition to polymers derived from starch, vegetable oil-derived polymers including triglycerides and fatty acids such as stearic, oleic, and linoleic acid have also been described.[192,203] Triglycerides are typically hydrolyzed to produce glycerol and a mixture of fatty acids. Furthermore, these potential monomers are naturally occurring, exhibited biocompatibility, and suggested potential impact in many biomedical applications. Due to the presence of unsaturated functionality in the mixture of fatty acid monomer, these monomers are suitable for many postreactions such as dimerization or epoxidation reactions. Similar to separation and purification difficulties for isomannides, by-product removal presents a challenge for the large-scale production and utilization of these triglyceride-based monomers for industrial applications. Typically, fractional distillations are often employed to separate the various components of the fatty acid products. Another challenge limiting the utilization of triglycerides in step-growth polymerization is the lack of perfect difunctionality in the monomer structure.[192] Many common fatty acid monomers only contain a single carboxylic acid site; however, ricinoleic acid, being an exception, is a naturally occurring difunctional fatty acid that is suitable for various polyester syntheses.

Current efforts have been strongly undertaken in the industry to provide a company built upon transformation of large-scale chemical production based on green chemistry principles. In 2004, the US Department of Energy compiled a list of the top 12 sugar-derived monomers that are able to compete against petrochemically derived monomers.[204] One industrial example that addressed this concern is the chemical company Segetis, whose efforts are highly dependent on expanding technology based entirely on renewable resources. Their technology centers on levulinic ester ketals, a primary bio-based precursor for various monomers. These initiatives further comment on the importance of sustainability in both the academic and industrial scale.

5.02.4.2 New Synthetic Approaches

5.02.4.2.1 Nonaqueous emulsion polymerization

Polymer nanoparticles find many applications in engineering and life sciences. Nanoparticles are of particular interest for the development of polymeric drug delivery vehicle, magnetic imaging devices, and biosensors.[205–208] Formation of nanoparticles typically employs emulsion polymerization which involves two immiscible solvent, organic and aqueous. However, due to the nature of the reaction conditions, most nanoparticles were synthetically restricted to free-radical polymerizations. The first reported step-growth nanoparticles utilized the 'Grubbs second generation' ruthenium catalysts to perform acyclic diene metathesis (ADMET) in an aqueous emulsion.[209] The ADMET polycondensation of *para*-divinylbenzenes produced conjugated nanoparticles. Fluorescent conjugated nanoparticles were also recently reported using the oxidative coupling Glaser reaction.[210] The Glaser coupling reaction conveniently avoided strict stoichiometric conditions to afford diethynyls from terminal monosubstituted alkynes. The application of emulsion polymerization has been limited for step-growth polymers since an aqueous condition would essentially compete with the equilibrium reaction and encourage hydrolytic depolymerization.

Encouragingly, Klapper *et al.* have developed a unique approach for the synthesis of polymer nanoparticles using oil-in-oil emulsions.[211] This particular method is desirable for many step-growth polymerizations in which traditional oil-in-water emulsion techniques would cause hydrolysis of the polymer. In addition, the group has investigated the nonaqueous emulsion techniques for a variety of step-growth polymers including polyamides, PUs, and polyesters, although this technique was not limited to step-growth polymerization. Synthesis of polar step-growth polymers such as polyesters and PUs using the oil-in-oil technique required a polar aprotic solvent such as DMF dispersed in cyclohexane or acetonitrile. For the first time, polyester nanoparticles were synthesized under mild conditions with regular and well-defined shape and size using oil-in-oil emulsion polymerization (**Figure 24**). First, acetonitrile in cyclohexane was combined with an amphiphilic block copolymer poly(isoprene-*b*-methyl methacrylate) (PI-PMMA) which served as the surfactant stabilizer in a traditional emulsion polymerization. The diol was dissolved in the DMF phase and emulsified into the cyclohexane phase as micelles. Dropwise addition of the dichloride and base, pyridine or triethyleneamine, allowed diffusion of the

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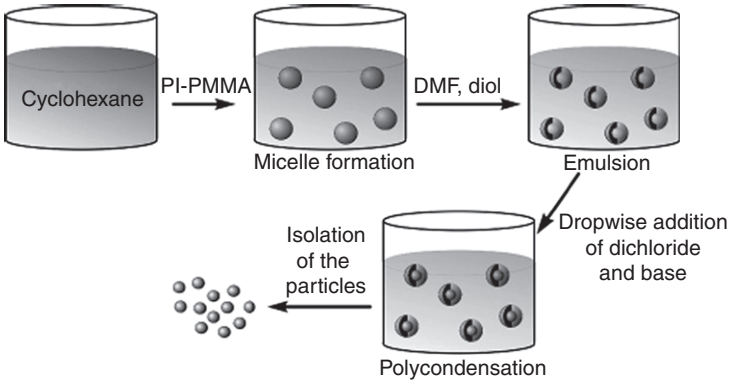

Figure 24 Nonaqueous emulsion polycondensation. Reprinted with permission from Klapper, M.; Nenov, S.; Haschick, R.; *et al. Acc. Chem. Res.* **2008**, *41* (9), 1190–1201.[211] Copyright (2008) American Chemical Society.

dichloride from the continuous cyclohexane phase into the dispersed micelles.

Figure 25 shows scanning electron micrograph (SEM) of polyester nanoparticles formed using this emulsion technique. Particle sizes were narrowly distributed and produced nanoscaled spherical beads of approximately 38 nm based on SEM. Weight-average molecular weights of the polyester beads were approximately 22 000 g mol^{-1} which was significantly higher than previously investigated emulsion techniques.[211] The summarized techniques reveal the complexities, challenges, and triumphs of emulsion polymerization for step-growth nanoparticles.

5.02.4.2.2 Lipase-catalyzed polymerization

The use of lipase-catalyzed coupling reactions in step-growth chemistry has also elicited much attention for their ecofriendly approach for polymer synthesis. Lipases facilitate many of the hydrolysis reactions of triglycerides into glycerol and fatty acids. In the category of polyesters, lipases have been utilized for ring-opening polymerization of cyclic monomers as well as condensation of hydroxyl and acid end groups.[212,213] Early work described the use of porcine pancreatic lipases (PPL) to synthesize polyesters through linear polycondensation of ω-hydroxyesters and ring-opening polymerization of ε-caprolactone.[214] Unfortunately, these enzyme-catalyzed polymerizations suggested low rates of propagation and required long reaction times. Further investigations revealed the rate of initiation was highly dependent on the choice of the nucleophilic initiator; however, kinetic studies of PPL-catalyzed PCL demonstrated controlled linear first-order kinetics independent of initiator concentration.[215] In addition, low molecular weights were attributed to the PPL-catalyzed hydrolysis reaction. Nevertheless, bio-derived renewable enzyme-catalyzed polymerizations offer distinct advantages for step-growth polymerization such as tolerance of aqueous mediums and high regio- and enantioselectivity.[216,217] Furthermore, the avoidance of transition metal catalysts enables this method to be potentially useful for synthesis of bioresorbable polyesters for biomedical applications.

Much of the work from Gross's research has focused on the use of a highly selective immobilized enzyme Novozyme-435, a *lipase B* enzyme from *Candida antartica* (CALB), to synthesize

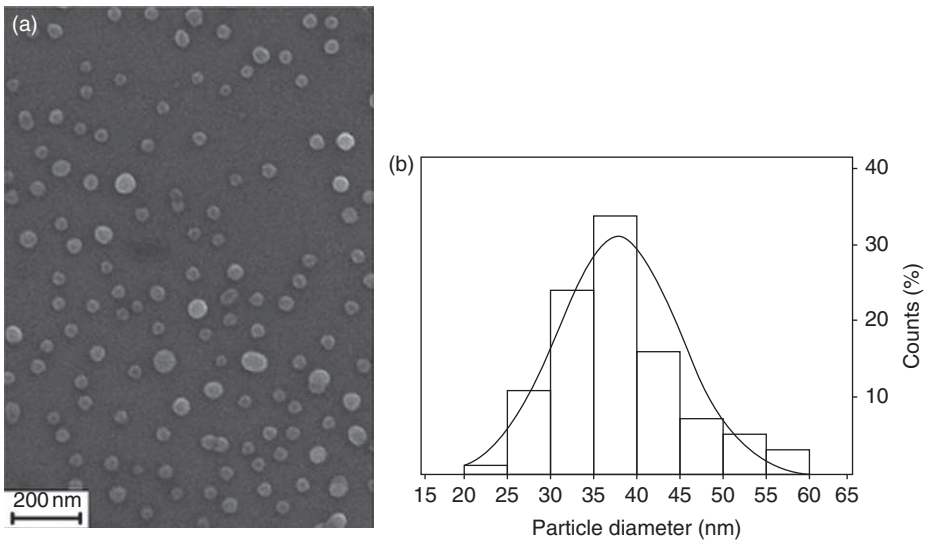

Figure 25 Size and shape of polyester nanoparticles synthesized using oil-in-oil emulsion polymerization: (a) SEM image and (b) particle distribution from SEM image. Polyester nanoparticles displayed an average particle size of 38 ± 7 nm. Reprinted with permission from Klapper, M.; Nenov, S.; Haschick, R.; *et al. Acc. Chem. Res.* **2008**, *41* (9), 1190–1201.[211] Copyright (2008) American Chemical Society.

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polyesters and polyester block copolymers.[218,219] The crystal structure of CALB was discovered in 2006, and it was hypothesized that the catalytic active center consists of three critical amino acids: serine (Ser105), histidine (His224), and aspartic acid (Asp187).[217] The three-dimensional structure of the active site assembled through a series of hydrogen-bonding interactions. Imidazole serves as a general base upon insertion of an ester substrate to promote acyl–enzyme intermediate formation and subsequent release of the alcohol by-product.[220] The acyl–enzyme intermediate allows for a nucleophilic attack of the carbonyl, and the imidazolium ring from histidine facilitates protonation and release of the newly formed ester.

Early work has demonstrated the effectiveness of CALB-catalyzed sorbitol- or octanediol-containing aliphatic polyester polymerization in the absence of solvent.[176,218,221] Further advances revealed the versatility of this enzyme to tailor macromolecular structure. Solvent-free cobalt crosslinking of a CALB-catalyzed copolymer containing unsaturated fatty acids illustrated a green approach to synthesize polymer coatings. Branched topologies were also achieved through lipase catalysis of ε-caprolactone and an AB_2 monomer, 2,2-bis(hydroxymethyl)butyric acid.[222] Another example of lipase-catalyzed hyperbranched polyesters utilized trimethylolpropane as the branch core and linear aliphatic diacids and diols.[223] Graft polymer brushes have also been described.[224] 2-Hydroxyethyl methacrylate or ω-hydroxyl-ω′-methacrylate-PEG served as initiators of the lipase-catalyzed ring-opening polymerization of ω-pentadecalactone. Subsequent free-radical polymerization of the resulting vinyl macromonomer afforded highly dense polymer properties with intriguing crystallization behavior.

The efforts of many enzyme-catalyzed polyester researches have centered on the formation of block copolyesters for potential bio-derived thermoplastic elastomers. Living or controlled polymerizations have been traditional synthetic approaches to afford well-controlled block copolymers. However, volatile solvents and transesterification of the polyester blocks have limited the versatility of this synthetic method. Ring-opening polymerization with an ω-hydroxy-terminated polybutadiene macroinitiator and subsequent free-radical polymerization of the macromonomer represent one method used to achieve a diblock structure.[225] Other examples of block copolymer synthesis have also been described in the literature.[205,226–228]

Lipase-catalyzed polymerization has proven to be an efficient method to synthesize polyesters based on the principles of green chemistry. Extensive research elucidated the kinetics and mechanisms of the polymerization and served as a platform that launched further investigations on the applicability of this approach to synthesize tailored macromolecular architectures. Although the body of research in lipase-catalyzed polymerizations is only in its infancy, the initial understanding and examples of polyester encourage its continuing exploration. This synthetic method reflects the interdisciplinary efforts of step-growth research to bridge together the fields of biochemistry, polymer chemistry, and life sciences; take advantage of nature's design; and respond to the growing challenges of sustainability.

5.02.5 Concluding Remarks

Although much of this chapter focused on traditional step-growth polymers, there is a renewed interest in discovering novel monomers, functionalities, and methods for future step-growth processes. As polymer scientists, the techniques and synthetic methods used to generate traditional step-growth polymers have developed significantly since Carothers early pioneering work. However, the principles of step-growth polymerization continue to serve as the inspiration for many new step-growth polymers. Step-growth polymers have proven to be especially useful in achieving a variety of macromolecular structures with tailored performance. In order to address future challenges in polymer science, we must tackle questions in an interdisciplinary manner. We must strive to reduce our dependency on petroleum feedstocks, and we need to design high-performance polymers with a keen attention to sustainability. Step-growth polymerization processes are excellent platforms to achieve these critical goals.

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5.03 Opportunities in Bio-Based Building Blocks for Polycondensates and Vinyl Polymers

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5.03.1 Introduction

Thermoplastic polymers are one of the major achievements that macromolecular science provided in the last century. Due to their high versatility in structures, processing, and properties, thermoplastic polymers are nowadays present and established in almost every application of our daily life. A substantial part of this success story was and still is the access to crude oil as an abundant and cheap source for monomers for plastics. This is reflected in Figure 1 in the form of the well-known polymer pyramid representing the broad commercial product portfolio of thermoplastics. According to a generally accepted convention, these polymers can be divided into three major groups: commodity polymers, engineering thermoplastics, and high performance polymers. Within each group, semicrystalline and amorphous polymers have been commercialized. Each subsegment comprises various polymer types – again an evidence for the broad diversity of fossil-based thermoplastic polymers.[1]

Within the last decade, this strong dependence of the polymer portfolio on oil availability has been increasingly scrutinized. The discussions about global warming and the finiteness of oil resources stimulated the general search for alternatives for fossil sources. One aspect thereof is the use of renewable resources as future raw material for plastics. A closer

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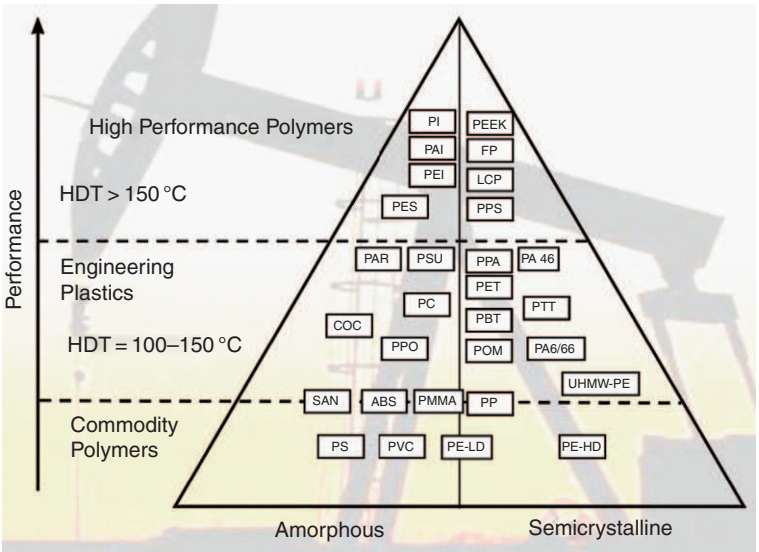

Figure 1 The polymer pyramid of thermoplastic polymers (see **Box 1** for explanation of abbreviations).

Box 1 Explanation of Abbreviations

Standard Polymers

PMMA	Polymethyl methacrylate
PE-HD	High-density polyethylene
PE-LD	Low-density polyethylene
PP	Polypropylene
PS	Polystyrene
PVC	Polyvinylchloride
SAN	Styrene acrylonitrile copolymer

Engineering Polymers

ABS	Acrylonitrile-butadiene-styrene-copolymer
COC	Cyclo-olefin copolymer
PA	Polyamide
PAI	Polyamide imide
PAR	Polyarylate
PBT	Polybutylene terephthalate
PC	Polycarbonate
PET	Polyethylene terephthalate
PTT	Polytrimethylene terephthalate
POM	Polyacetal
PPA	Polyphthalamide
PPO	Polyphenylene oxide
UHMVV-PE	Ultra high molecular weight polyethylene

High Performance Polymers

LCP	Liquid crystal polymer
FP	Fluoro polymers
PI	Polyimide
PEEK	Polyetherketone
PEI	Polyetherimide
PES	Polyethersulfone
PPS	Polyphenylenesulfide
PSU	Polysulfone

look reveals that biochemistry provides already many opportunities for bio-based solutions.

This review extends from those that have already reached the marketplace to those that are highly speculative and as yet far from realization. It also tries to give an answer to the question, is it possible to create a polymer pyramid based on renewable resources?

5.03.1.1 Definition and Scope of Biopolymers

For the definition and the scope of biopolymers, a different picture can be used (**Figure 2**). Based on environmental stability (durable or biodegradable) and origin (bio-based or fossil), four sectors can be identified:

Sector 1. Polymers that are bio-based (synonymously used: derived from renewable resources) and that are not biodegradable. They are used mainly for durable applications.

Sector 2. Bio-based and biodegradable polymers that can be converted by microorganisms such as fungi and bacteria into water, carbon dioxide, and biomass. They have to meet the criteria of scientifically recognized norms for biodegradability and compostability of plastics and plastic products. In Europe, this is the norm EN 13432/EN 14995, and in North America ASTM D6400.

Sector 3. Fossil-based polymers that are biodegradable and compostable after the biodegradation norms according to EN 13432/EN 14995 and ASTM D6400.

Sector 4: Fossil-based polymers that are not biodegradable or compostable. Note that this segment covers almost all of the thermoplastic polymers of **Figure 1** and accounts for roughly 99% of worldwide plastics today.

Consequently, the field of biopolymers include sectors 1, 2, and 3. This definition is in line with the European Bioplastics Association.[2]

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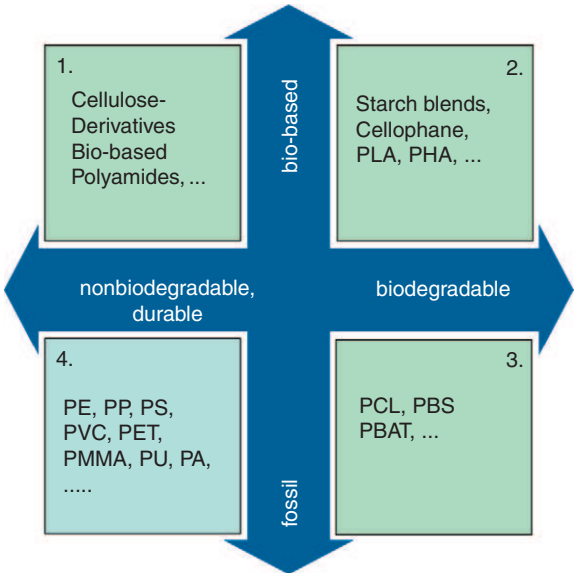


Figure 2 Classification of biopolymers (green, biopolymers; blue, fossil and durable).

A key learning from Figure 2 is that biodegradation is a function of the chemical structure of a polymer and does not depend on the origin of the source. Therefore, a bio-based polymer is not necessarily biodegradable, and – vice versa – there are also fossil-based polymers on the market that are biodegradable. Biodegradable polymers are usually used in short-life applications like packaging (bio-waste bags), agriculture (as mulch film), and forestry where the unique property, such as biodegradation, gives a clear advantage to the customer and the environment.[3]

5.03.1.2 Value Chain of Biopolymers

For a more sophisticated evaluation of the chances and potentials of biopolymers, it is crucial to compare biopolymers with conventional polymers in terms of performance and sustainability. Sustainability can be expressed by the life cycle analysis, a generally accepted tool for calculating the environmental impact of each step of the value chain (for a detailed discussion of the methodology, see Reference 4).

For the biopolymers, the analysis encompasses the view on the renewable source, the monomer, the polymer, and the final product that can be a compound with various additives or a blend of different polymers (Figure 3).

The focus of this review is on the chemistry of primary building blocks derived from renewable resources. The aim is to show the big variety that can be obtained from nature and the thermoplastic polymers synthesized therefrom. It is important to note that these building blocks can enter the existing downstream processes into higher refined products, but for the sake of clarity, the scope is limited on primary products.

The review is structured into four major parts. It starts with an extensive overview of the primary intermediates out of natural origin. The next three parts describe the opportunities in bio-based thermoplastic polymers that are divided according to the polymeric pyramid into commodity polymers, engineering plastics, and high performance polymers.

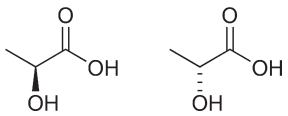
5.03.2 Monomers

Monomers from renewable resources can be obtained via two routes, by fermentation of building blocks from carbohydrates and by chemical processing of plant oils.

5.03.2.1 Monomers via Carbohydrate Fermentation

5.03.2.1.1 Lactic acid

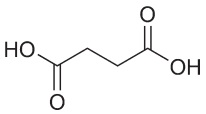
Lactic acid (2-hydroxypropionic acid) is one of the large-scale chemical that is produced via fermentation. The commonly used feedstocks are carbohydrates obtained from different sources like corn starch, sugarcane, or tapioca starch – depending on local availability. The carbohydrates are hydrolyzed into monosaccharides and then fermented under the absence of oxygen by microorganisms into lactic acid. Lactic acid is the building block for polylactic acid, but it is also used in a broad variety of food and cosmetic applications. Bio-based lactic acid is optically active, and the production of either L-(+)- or D-(–)-lactic acid can be directed with bioengineered microorganisms.[5]



5.03.2.1.2 Succinic acid

Succinic acid is a platform chemical with a global demand of ~30 000 tons yr^{-1}. It is used as an intermediate or building block for the synthesis of C4 chemicals (Figure 4), like 1,4-butanediol, tetrahydrofuran, and so on. Today, succinic acid is produced from *n*-butane via oxidation to maleic anhydride and hydrogenation into the final product.[6]

Succinic acid can also be produced via anaerobic fermentation, especially from sources like starch and different C5 and C6 sugars.[7]



A very prominent example is the microorganism *Basfia succiniciproducens*, which was extracted from a cow rumen.[8] The specific feature of the microorganism is the consumption of one molecule of carbon dioxide for the production of one molecule of succinic acid. This makes the bio-based succinic acid an ideal alternative to

Figure 3 Value chain of biopolymer products.

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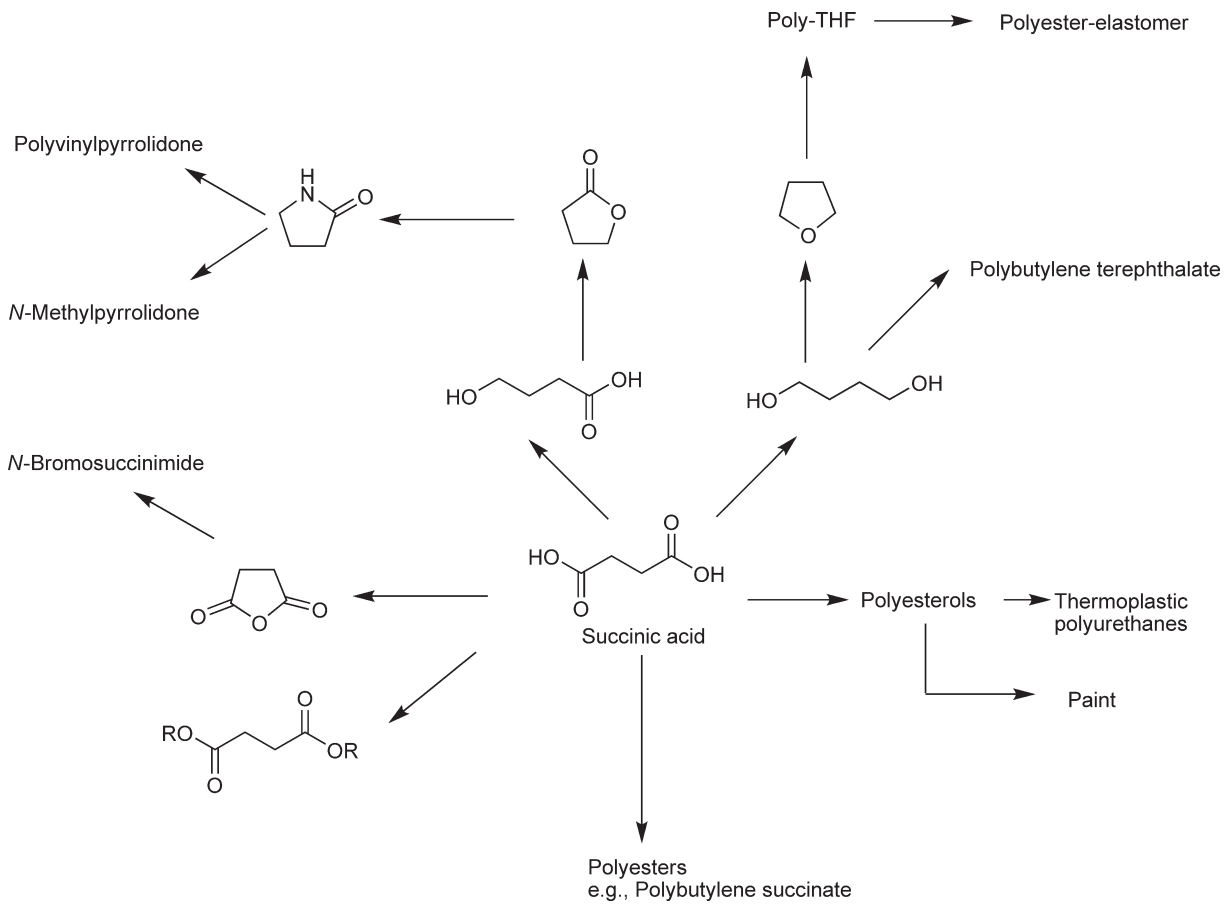

Figure 4 The succinic acid platform.

the fossil-based product either from an economic or sustainability aspect. With these advantages, this intermediate is an interesting building block for thermoplastic engineering plastics such as bio-based polyesters, polyamides, and polyesteramides.

5.03.2.1.3 Olefins

5.03.2.1.3(i) Ethylene and propylene

Polymers made from ethylene and propylene are prominent examples for the success story of plastics during the last 60 years, because of, *inter alia*, access to the inexpensive and abundant oil-based feedstock.[9]

Despite this favorable situation, industrial activities were initiated to produce these polymers also from renewable resources. The starting material is bioethanol, which is produced through fermentation from sugarcane or corn on a large scale; for example, in Brazil and in the United States, bioethanol is used as an alternative to oil-based fuel. Subsequent catalytic conversions lead to ethylene and propylene,[10] which are ready-to-use monomers for existing polymerization plants (drop-in) (**Figure 5**). A commercial product of Bio-PE is already on stream,[11] and the commercialization of a Bio-PP was announced.[12]

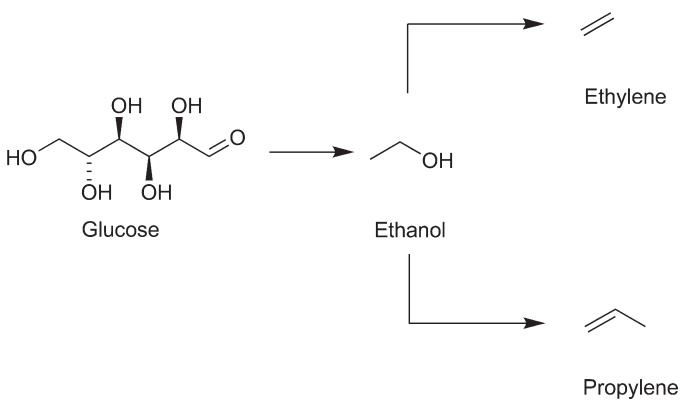

Figure 5 Synthesis of bioethanol from glucose.

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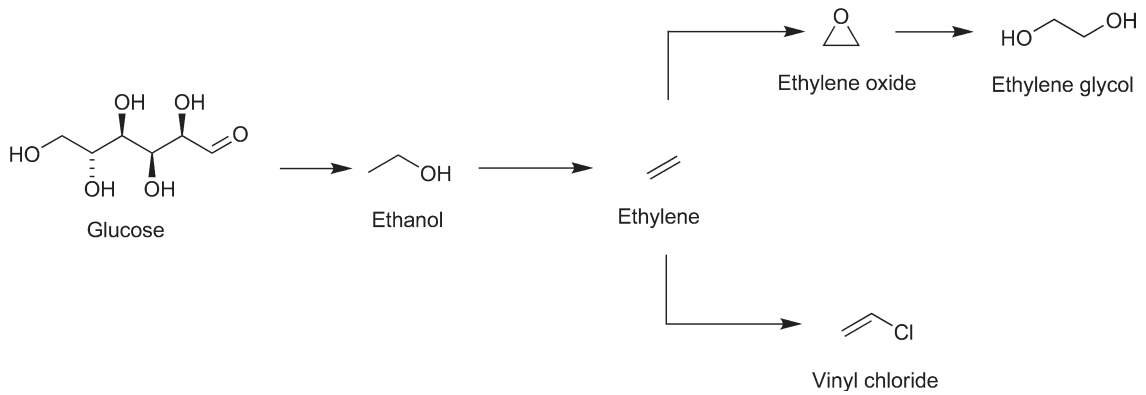

Figure 6 Schematic production of bioethylene and its derivatives.

With the availability of bio-based ethylene and propylene, the established value chains of ethylene and propylene can be entered with downstream products like vinyl chloride, acrylic acid, acrylic esters, acrylonitrile or ethylene glycols, and so on – made from renewable resources. Out of these opportunities, bio-based ethylene glycol is already available,[13] and the production of vinyl chloride from sugarcane was already announced in December 2007 (Figure 6).[14] So far, bio-based polyvinylchloride has not been seen in the market.

5.03.2.1.3(ii) Butadiene and isoprene

1,3-Butadiene and isoprene are important building blocks for the production of synthetic rubbers. Production of bio-based 1,3-butadiene from fermentatively produced butanol through dehydrogenation is reported.[15] Also a report on the fermentative production of isoprene was published recently.[16]

5.03.2.1.4 Adipic acid, hexamethylene diamine, and ε-caprolactam

Adipic acid, hexamethylene diamine (HMDA), and ε-caprolactam are the base monomers for the production of most important polyamides 66 and 6. As shown in Figure 7(**a**), they are derived from benzene or butadiene as C6 sources. Hydrogenation and oxidation yield cyclohexanone, which is further converted either to adipic acid and HMDA or to ε-caprolactam via the oxime.[17] These routes are very well established in industry and are running with high efficiencies.

The synthesis of these monomers from renewable resources has attracted much attention in academia and industry. Several routes are suggested, all starting from carbohydrates, such as glucose (Figure 7(**b**)).

5.03.2.1.4(i) Adipic acid

Fermentative production of adipic acid from glucose was first published by Frost and Draths.[18] Bioengineered microorganisms that are capable of producing adipic acid were recently announced by Genomatica.[19] A new chemical route, the catalytic conversion of glucose to adipic acid via glucaric acid, was reported by Rennovia as shown in Figure 8.[20]

As shown in Figure 9, adipic acid is a C6 platform chemical and can be converted by chemical process into adipodinitrile through amidation and dehydration. Adipodinitrile is the starting material for the production of HMDA[21] and aminocapronitrile[22] that can be converted into ε-caprolactam.[23]

Starting from renewable adipic acid, it is possible to produce, for example, bio-based polyamides 66 and 6 (*see* Chapter 4.02).

5.03.2.1.4(ii) Hexamethylene diamine and ε-caprolactam

Alternatively, HMDA and ε-caprolactam can also be produced from bio-based propylene or butadiene

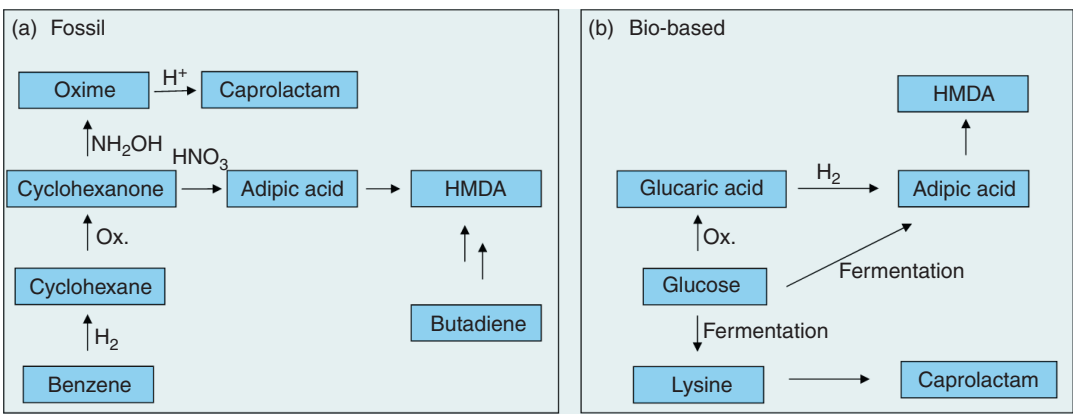

Figure 7 Fossil vs. bio-based route of adipic acid, hexamethylene diamine, and ε-caprolactam.

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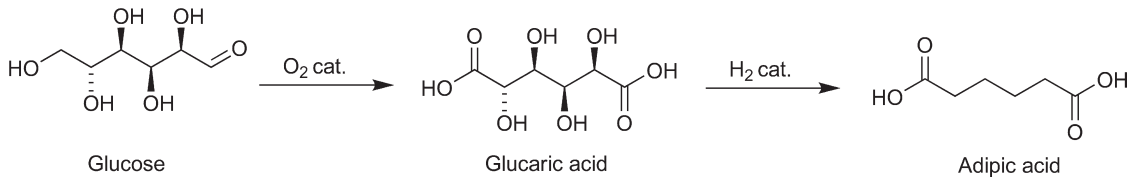

Figure 8 Adipic acid derived from glucose.

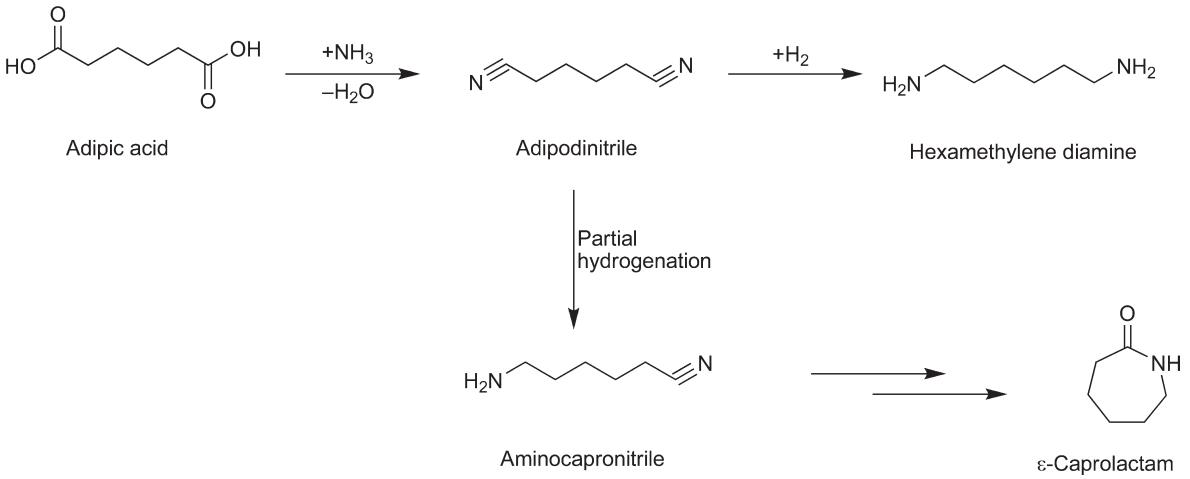

Figure 9 Adipic acid as a C6 platform chemical.

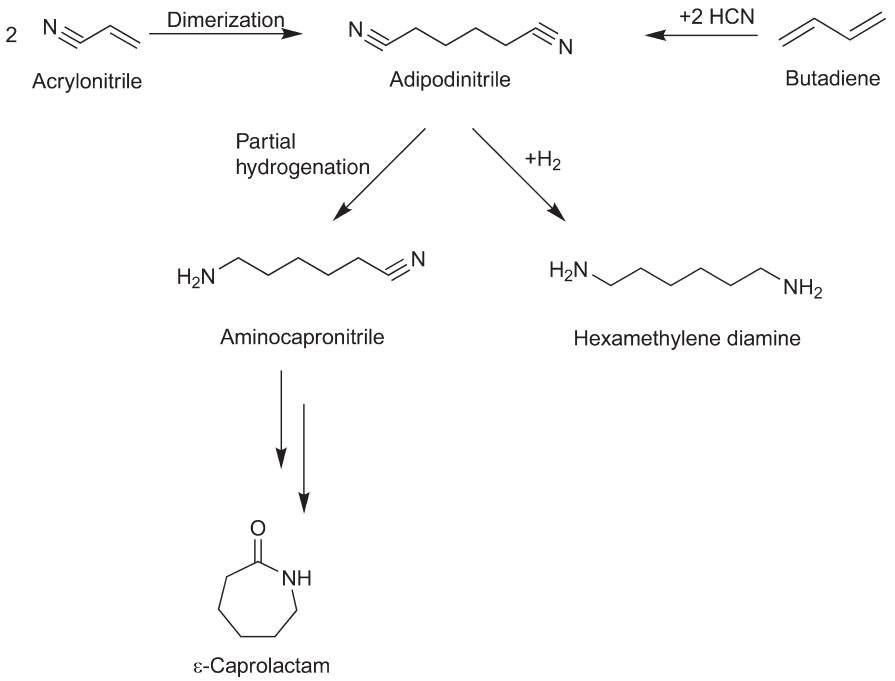

Figure 10 Alternative route for bio-based hexamethylene diamine and ε-caprolactam.

(*see* Section 5.03.2.1.3).[17,24] Starting from bio-based acrylonitrile or bio-based butadiene, adipodinitrile can be obtained. As already described above, adipodinitrile is used as the starting building block for HMDA and ε-caprolactam (Figure 10).[23]

Another route taking advantage of nature's synthetic performance starts from the amino acid lysine. Lysine is produced commercially on large scale through fermentation and is used mainly for feed.[25] ε-Caprolactam is accessible via the cyclization of lysine to a caprolactam derivative followed by a deamination step (Figure 11).[26] The deamination reaction works so far only with stoichiometric amounts of hydroxylamine-*O*-sulfonic acid.[27] This prevents an industrial-scale production of this route. Possibly, a biocatalytical/enzymatical conversion of this deamination step is more promising, as shown in Figure 12.[28]

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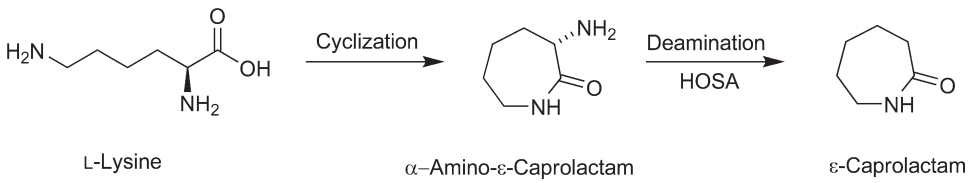

Figure 11 ε-Caprolactam derived from L-lysine.

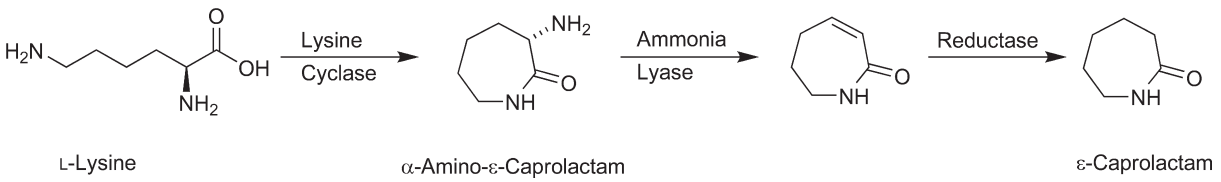

Figure 12 Biocatalytical/enzymatical conversion of L-lysine to ε-caprolactam.

5.03.2.1.5 Pentamethylene diamine and tetramethylene diamine

Pentamethylene diamine (1,5-diaminopentane) can be produced from L-lysine by decarboxylation *in vivo*[29] or enzymatically *in vitro* using lysine decarboxylase (**Figure 13**).[30]

The synthesis of tetramethylene diamine *in vivo* through decarboxylation of ornithine has reported as well.[31]

5.03.2.1.6 Terephthalic acid

Terephthalic acid is a very versatile and widely used monomer for almost all industrial polycondensate polymers. It is produced on large scale (ca. 34 million tons per annum) by air oxidation of *p*-xylene. Production of *p*-xylene from biomass has been reported. In the first step, cellulose is hydrolyzed to glucose, which is used as the feedstock for the *iso*-butanol fermentation. *Iso*-butene is then synthesized through a dehydration step from *iso*-butanol. After a dimerization step from *iso*-butene into *iso*-octene, *p*-xylene is obtained via a catalytic conversion step. A similar process from fermentative bioethanol via 1-butanol has been reported as well (**Figure 14**).[32]

Production of terephthalic acid from furan dicarboxylic acid (FDCA) and ethylene has also been reported.[33]

5.03.2.1.7 Furan dicarboxylic acid

The synthesis of 2,5-FDCA from renewable raw material via 5-hydroxymethylfurfural has been described.[34] 2,5-FDCA is supposed to have similar properties to terephthalic acid and isophthalic acid as a component in polyesters and polyamides (**Figure 15**).[35]

5.03.2.1.8 Isosorbide

Isosorbide can be obtained from starch through hydrolysis to glucose, hydrogenation to sorbitol, and dehydration to the final building block.[36] Isosorbide can be used as a diol comonomer for the synthesis of polyesters and polycarbonates.[37] Modification of isosorbide to diaminoisosorbide that can be used for the synthesis of polyamides has also reported (**Figure 16**).[38]

5.03.2.2 Monomers via Chemical Processing of Plant Oils

5.03.2.2.1 Olefins

Besides the synthesis of ethylene and propylene from bioethanol (*see* Section 5.03.2.1.3), these monomers are, in principle, also accessible through thermal cracking of hydrocarbons produced by Fischer–Tropsch synthesis from CO and H_2 derived from biopolymers or vegetable oils like Canola oil or modified plant oil using cracking catalysts.[39] Such a process is part of the biorefinery

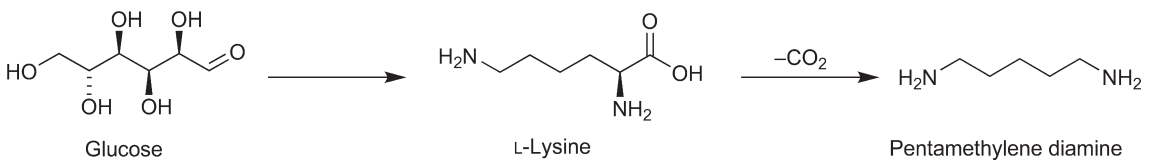

Figure 13 Pentamethylene diamine from L-lysine.

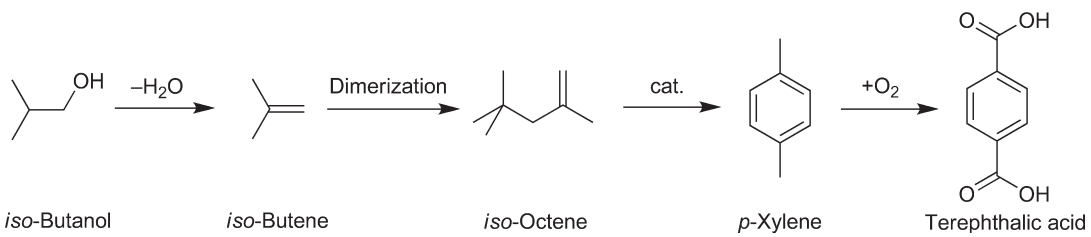

Figure 14 From bio-based *iso*-butanol to terephthalic acid.

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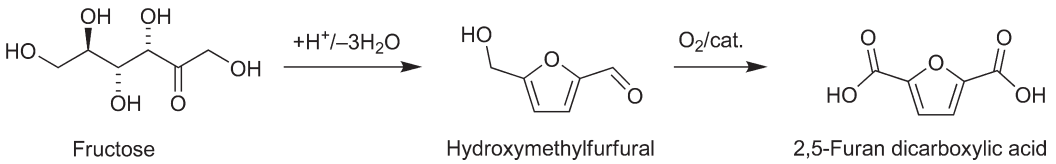

Figure 15 Synthesis of 2,5-furan dicarboxylic acid starting from fructose.

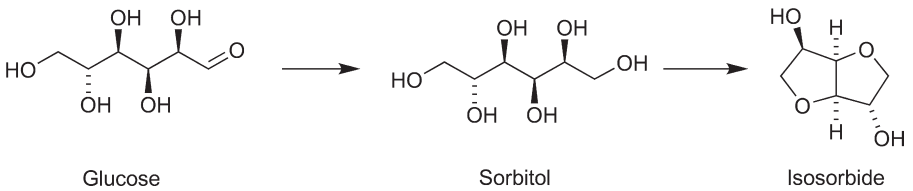

Figure 16 Synthesis of isosorbide from sorbitol.

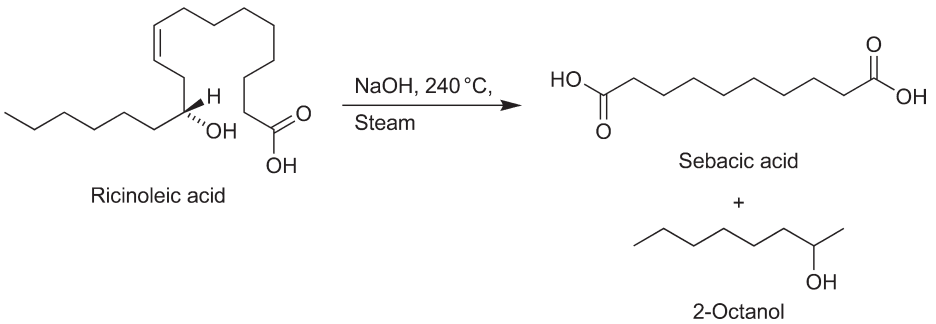

Figure 17 Sebacic acid from ricinoleic acid.

approach, which is "an overall concept of a processing plant where biomass feedstocks are converted and extracted into a spectrum of valuable products, based on the petrochemical refinery" (US Department of Energy, 1997).[40] This concept will not be discussed at this point, due to the different focus of this chapter.

5.03.2.2.2 Sebacic acid

Sebacic acid (C10) is produced from the triglyceride castor oil, which is the extraction product of castor beans, the seed of a plant called *Ricinus communis*. The plant is mainly grown in India. Hydrolysis of castor oil yields ricinoleic acid, which is further oxidized and split into sebacic acid and 2-octanol (Figure 16).[41] Sebacic acid is commercially available and used as a valuable building block in polyamides, polyesters, and polyurethanes (Figure 17).

5.03.2.2.3 Azelaic acid and brassylic acid

Oleic acid and erucic acid as components of rapeseed or sunflower oil can be converted into azelaic acid (C9) and brassylic acid (C13) by oxidative ozonolysis (Figure 18).[41b,41c,41d]

5.03.2.2.4 Long-chain dicarboxylic acids

Through microbial ω-oxidation of fatty acids with *Candida tropicalis*, long-chain dicarboxylic acids can be obtained.[42] Further microorganism engineering opens up the possibility to produce long-chain hydroxyacids.[43] The catalytic carbonylation of fatty acids like oleic acid or erucic acid can also lead to C19-dicarboxylic acid or C23-dicarboxylic acid, respectively.[44]

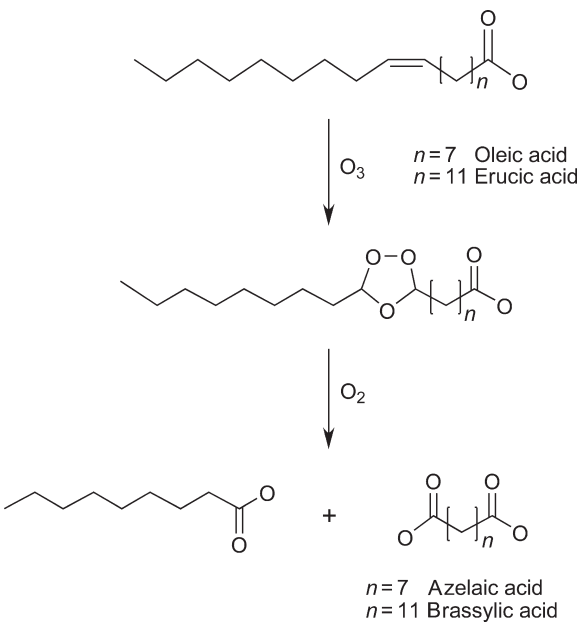

Figure 18 Synthesis of azelaic acid and brassylic acid.

Dimerization of C18-fatty acid with one or more double bonds at 210–250 °C in the presence of a layered silicate catalyst leads to a complex mixture of C36-dicarboxylic acids (dimer acids).[41b] These products are already commercialized.

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By applying metathesis[45] to plant oils and olefins, the synthesis of new bio-based building blocks is also reported.[46]

5.03.2.2.5 *p*-α-Methylstyrene

The styrene monomer is one of the bulk chemicals next to olefins and vinyl chloride for the use in commodity polymers. Its versatile reactivity in the polymerization process made styrene monomer as a valuable building block in homopolymers and even more in copolymers.

A bio-based styrene derivative, which could at least partially substitute styrene in existing compositions, is *p*-α-dimethylstyrene. This monomer is available from limonene through oxidation with nitrobenzene[47] or selective palladium-catalyzed dehydrogenation.[48] Limonene can be obtained from the peels of citrus fruits, such as oranges (Figure 19).

5.03.2.2.6 Terephthalic acid

One bio-based route for terephthalic acid starts from 3-carene, which is obtained from pine trees. Further dehydrogenation leads to *p*-cymene and *m*-cymene, which is then converted into bio-based terephthalic acid or isophthalic acid by an oxidation step.[49] The second route starts from limonene, which can be obtained from citrus fruits. Dehydrogenation leads to *p*-cymene, which is then also oxidized into bio-based terephthalic acid. Industrial interest is demonstrated by patents (Figure 20).[50]

Another route reported in the literature is the thermal cracking of lignin using a zeolite catalyst (H-ZSM-5; H^+ exchange zeolite sieve of molecular porosity catalyst).[51] At 550 °C cracking temperature, about 10% of the total liquid fraction contains xylenes. Through an oxidation step of *p*-xylene, it is possible to obtain terephthalic acid.[17]

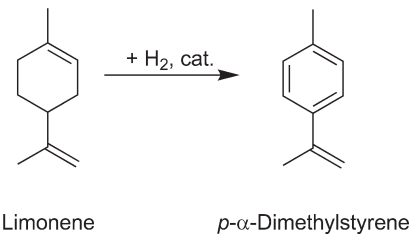

Figure 19 Synthesis of bio-based *p*-α-dimethylstyrene from limonene.

5.03.2.3 Aromatic Monomers via Biochemical Pathways

The source for the biosynthesis of various aromatic monomers is the aromatic amino acid pathway.[52] Its metabolites serve as building blocks for further downstream processing into functional aromatics, either by genetically engineered microbial catalysts or by traditional chemical transformations. The important intermediates are 3-dehydroquinate (DHQ) and 3-dehydro-shikimic acid (DHS). Both DHQ and DHS can be obtained in high yield from glucose, currently converted from starch, or ultimately, from other sugars such as xylose or arabinose, available from cellulose hydrolysate (Figure 21).

Hydroquinone, a high-volume chemical, is produced in industrial scale from the Friedel–Crafts reaction product of benzene and propylene followed by Hock oxidation. Besides the application of hydroquinone as an intermediate in antioxidants and stabilizers, it is used in polymer synthesis as a comonomer for polyesters (polyarylates and liquid crystalline polymers) and for polyetherketones.

Alternative, benzene-free bio-based routes to hydroquinone like the oxidative decarboxylation of quimic acid[53] or the chemical reduction of hydroxybenzoic acid are reported. Routes to catechol and pyrogallol follow a similar scheme: shifting the metabolism of the amino acid pathway to protocatechuic acid leads to the production of catechol and pyrogallol.[54]

Chorismic acid is the key intermediate in the biological pathway to hydroxy- or amino-substituted benzoic acid. Recent academic and industrial efforts aim to a bio-based route to *p*-hydroxybenzoic acid by overexpression of ubiC-encoded chorismate lyase.[55] Alternatively, shikimic acid can be chemically transformed into hydroxy benzoic acid (HBA).[56]

p-Aminobenzoic acid is an intermediate in the biochemical pathway to folic acid. However, little is known about the route from chorismic acid to *p*-aminobenzoic acid.[57] In principle, *p*-aminobenzoic acid could be a valuable building block for polymers of the aramid type.

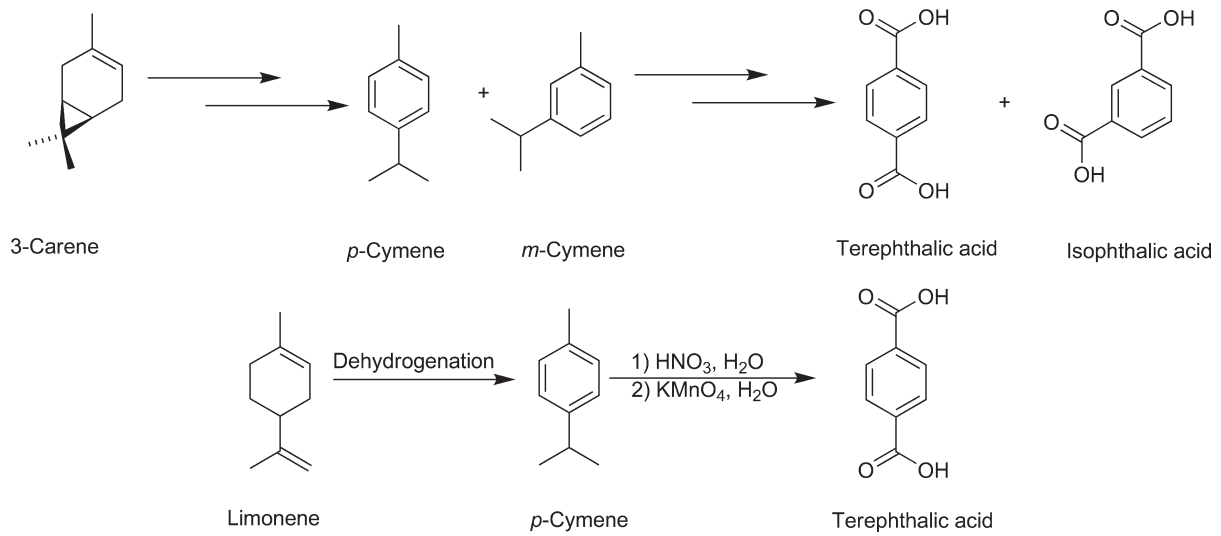

Figure 20 Bio-based terephthalic acid from 3-carene or limonene.

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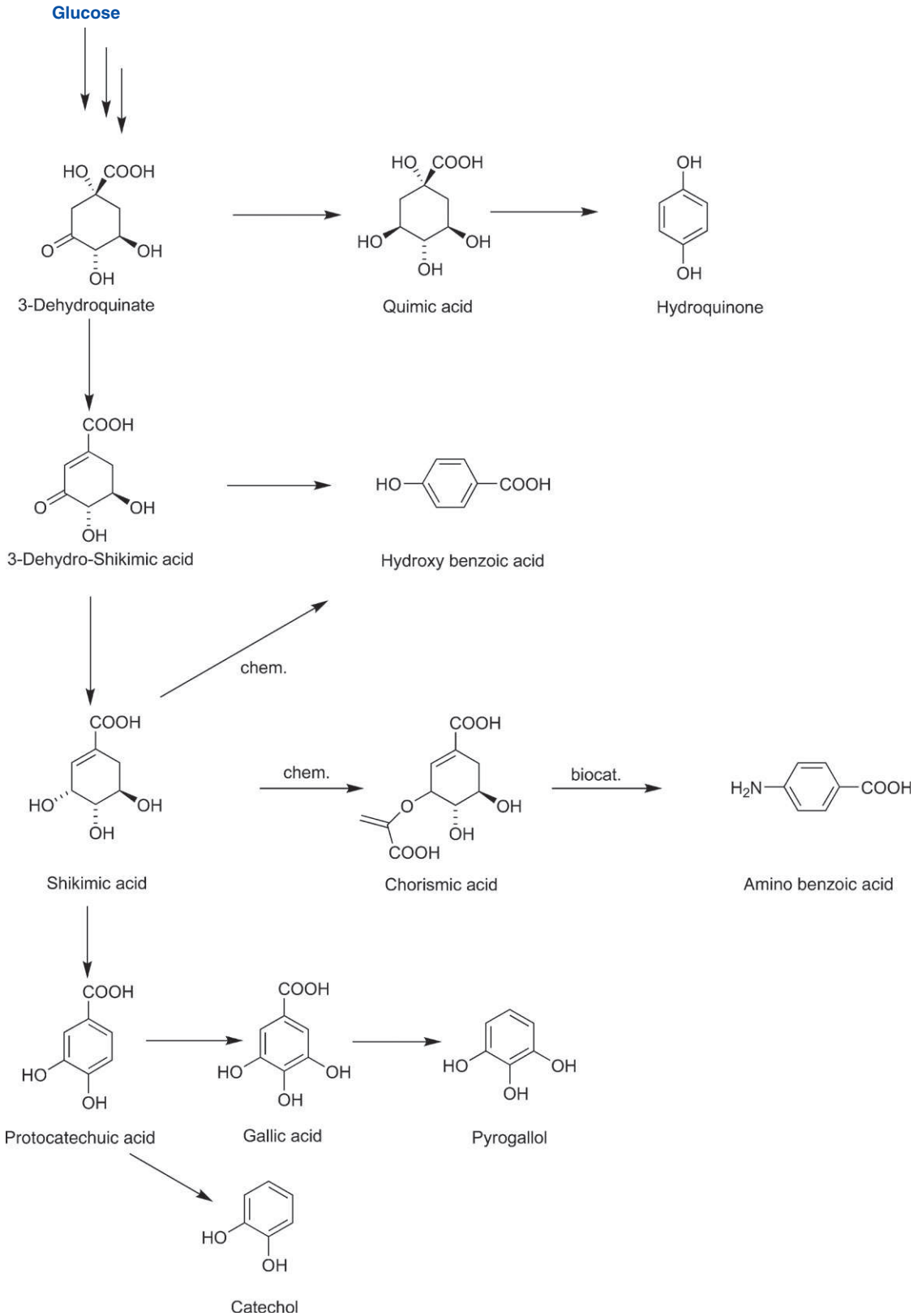

Figure 21 Biosynthesis of various aromatic monomers; the polyphenols, hydroquinone, catechol, pyrogallol, as well as hydroxy- and aminobenzoic acid.

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5.03.3 Approaches in Commodity Polymers

For a clear and precise overview, general schemes will be used for the next three sections. Within Tables 1–6 polymer type, feedstock, bio-based intermediate, monomers, and thermal properties are shown. It starts with a summary of the possibilities for bio-based building blocks in commodity polymers (Table 1).

5.03.3.1 Polyolefins from Renewable Resources

5.03.3.1.1 Polyethylene/polypropylene/polyvinylchloride

The products that are currently produced out of bio-based ethylene are a large variety of high-density polyethylene (HDPE) and linear low-density polyethylene (LLDPE). Bio-based polyethylene has exactly the same chemical, physical, and mechanical properties as fossil-based polyethylene (Figure 22).[11,39b–f]

The monomer for polyvinylchloride, vinylchloride, can be also produced from bio-based ethylene through addition of chlorine to 1,2-dichlorethane and through thermal cleavage.[17] It is then conventionally polymerized in existing equipment with well-established procedures. Commercial production of bio-based polyvinylchloride was announced by Solvay in 2007 (Figure 23).

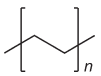
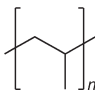
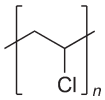
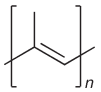
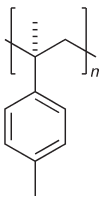
5.03.3.1.2 Polyisoprene

It has been recently reported that certain cells can convert carbon that is available in a cell culture medium into bio-based isoprene. The cells contain a heterologous nucleic acid, which is linked to a promoter and encodes an isoprene synthase polypeptide. The isoprene can be recovered from the culture medium and then polymerized into bio-based synthetic rubbers. Synthetic 1,4-polyisoprene is used in manufacturing tires and many other applications (Figure 24).[16]

5.03.3.1.3 Polystyrene derivatives

From limonene through catalytical partial dehydrogenation, it is possible to obtain *p*-dimethylstyrene.[48] By combining

Table 1 Possibilities in commodity polymers

Polymer type		*Feedstock*	*Bio-based intermediate*	*Monomer*	*T_g/T_m (°C)*
Polyethylene		Carbohydrates	Ethanol	Ethylene	LDPE, –100/110–125 HDPE, –70/130–145
Polypropylene		Carbohydrates	Ethanol	Propylene	–10/176
Polyvinyl chloride		Carbohydrates	Ethanol	Vinyl chloride	79/–
Polyisoprene		Carbohydrates		Isoprene	–60/–
Polystyrene derivative		Plant oil	Limonene	4-Methyl-α-methylstyrene	178/–

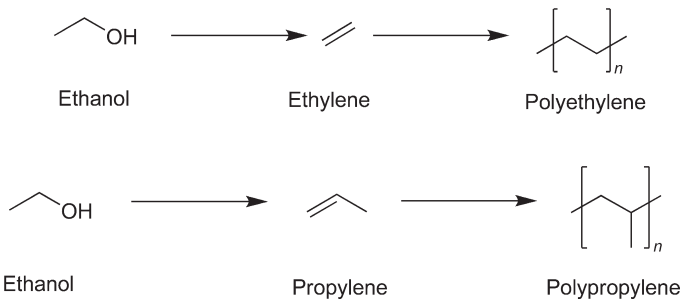


Figure 22 Synthesis of bio-based polyethylene and polypropylene.

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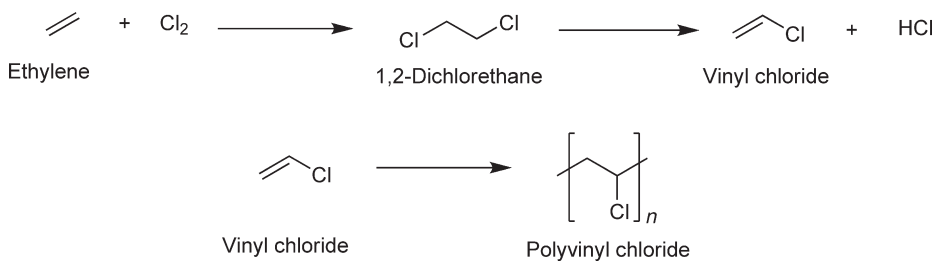


Figure 23 Synthesis of bio-based polyvinylchloride.

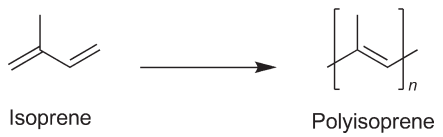


Figure 24 Bio-based 1,4-polyisoprene.

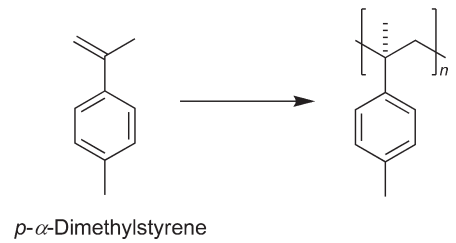


Figure 25 Synthesis of bio-based polystyrene derivatives from *p*-α-dimethylstyrene.

bio-based acrylonitrile produced from bio-based propylene, it is possible to synthesize a product that is analogous to styrene-acrylonitrile copolymer. Another possibility is combining bio-based butadiene or isoprene, which will lead to a bio-based version of acrylonitrile-butadiene-styrene (ABS) copolymer (Figure 25).[58]

5.03.3.2 Biodegradable Polymers from Renewable Resources

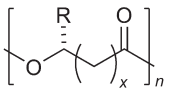
5.03.3.2.1 Polylactic acid

Polylactic acid is a rigid thermoplastic polyester from renewable resources. It was commercialized by Cargill in 1994 (Table 2). The production of polylactic acid can be carried out via direct condensation of lactic acid or via ring-opening polymerization of lactides (Figure 26).[59]

Direct condensation of lactic acid is an equilibrium reaction. Small traces of water in the reaction limit the achievement of high-molecular-weight polymers over this reaction route. Large-scale production of polylactic acid is done via a tin-catalyzed, ring-opening polymerization of lactide in the melt. NatureWorks, a subsidiary of Cargill, has developed a low-cost process for the continuous production of high-molecular-weight polylactic acid.[59–61] The product is commercially available under the tradename Ingeo®.

5.03.3.2.2 Polyhydroxyalkanoates

Polyhydroxyalkanoates (PHAs) are aliphatic polyesters produced from renewable feedstocks. PHAs are synthesized directly via fermentation of a carbon substrate inside a microorganism. Depending on the microorganisms and the cultivation conditions, homo- or copolyesters with different hydroxylalkanoic acids can be obtained.[62]



Polyhydroxyalkanoate

$x = 1, 2, ...$
$R = H, Me, Et, ...$

The most prominent commercially available PHAs are poly-3-hydroxybutyrate (PHB), poly-3-hydroxybutyrate-*co*-4-hydroxybutyrate (P(3-HB-*co*-4-HB)), poly-3-hydroxybutyrate-*co*-valerate (PHBV), and polyhydroxybutyrate-*co*-hexanoate (PHBH).[63]

In principal, bacterial fermentation of PHA is done in a fermentation vessel. It is filled with a growth medium containing mineral salts and inoculated with bacteria containing seed ferment. A carbon source is added during the fermentation until it is completely consumed and until the cell growth and PHA accumulation is finished. A PHA fermentation usually takes between 38 and 48 h.[5d] In Figure 27, a biochemical pathway of PHB is shown.[64]

A lot of the PHB-producing microorganisms produce PHB through a three-enzyme pathway containing β-ketothiolase, acetoacetyl reductase, and PHA synthase. Starting from acetyl-CoA converted into acetoacetyl-CoA, which is then converted into (*R*)-3-hydroxybutyryl-CoA. The most important step is the transformation of (*R*)-3-hydroxybutyryl-CoA into the polymer, which is enzymatically done by the PHA synthase.[64] Crucial for the production of PHAs is the isolation and purification of the polymer from the microorganisms. The microorganisms have to be lysed and chemically extracted with organic solvents. These solvent extraction methods are based on the solubility and insolubility of PHAs in defined solvent systems.[65] Recently, a new way of isolation and purification was reported.[66] The process is based on high-pressure homogenization and subsequent continuous centrifugation for cell disruption and biomass separation. This is followed by water-based chemical treatments to remove residual cell constituents as well as alkali ions that otherwise have a negative impact on the thermal stability of the purified PHB.

5.03.3.2.3 Aliphatic aromatic copolyesters – polybutylene adipate-terephthalate

Polybutylene adipate-terephthalate (PBAT) is a compostable/biodegradable random aliphatic–aromatic copolyester that is

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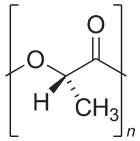
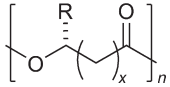
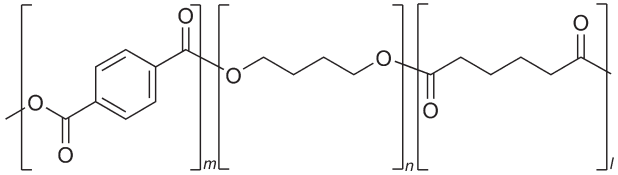
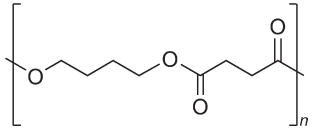
Table 2 Biodegradable polymers from renewable resources

Polymer type		*Feedstock*	*Bio-based intermediate*	*Monomer*	*T_g/T_m (°C)*
Polylactic acid		Carbohydrates	Lactic acid	Lactide	60/170
Polyhydroxyalkanoate		Carbohydrates			4/180
Polybutylene adipate-terephthalate		Carbohydrates Carbohydrates Plant oil	Succinic acid *cis, cis*-Muconic acid Limonene	1,4-Butanediol Adipic acid Terephthalic acid	–32/115
Polybutylene succinate		Carbohydrates Carbohydrates	 Succinic acid	Succinic acid 1,4-Butanediol	–32/115

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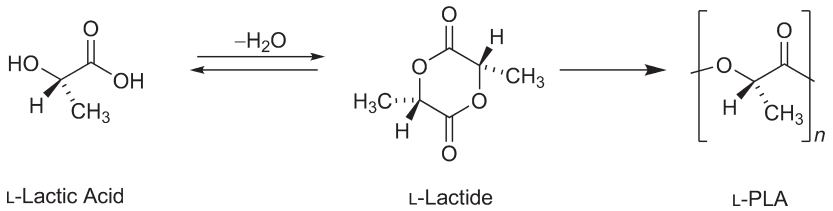


Figure 26 Synthesis of L-PLA.

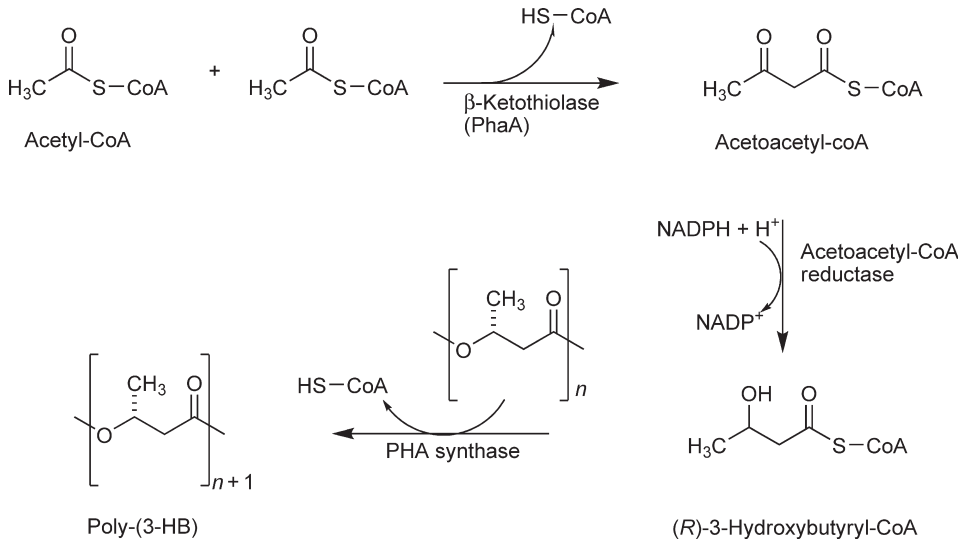


Figure 27 Biochemical pathway of poly-3-hydroxybutyrate fermentation.

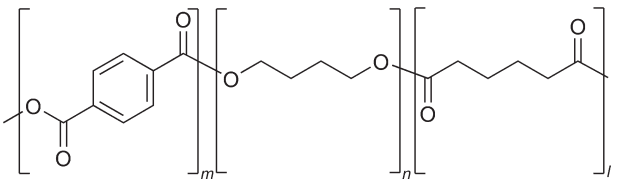


Figure 28 Chemical structure of polybutylene adipate-terephthalate.

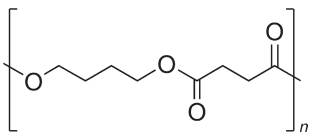
synthesized by melt condensation from adipic acid, terephthalic acid, 1,4-butanediol, and modular units. The product has been commercialized under the trade name Ecoflex®. The polymer has a melting point of ~110 °C and the mechanical properties are similar to those of low-density polyethylene (LDPE). The material can be processed into films on a conventional blown film line for LDPE (Figure 28).

By combining Ecoflex® with renewable resources like starch, Polylactic acid (PLA), PHA, or cellulose through processing techniques like compounding or coating, negative properties and functionality of renewable materials like moisture uptake, low barrier, and poor processability can be improved, so that the utilization of renewable resources can be increased. For example, starch is not water-resistant; however, by compounding starch and Ecoflex®, the hydrophobicity of starch is improved and thermoplastically processed. PLA is a relatively brittle material and Ecoflex® is a flexible polymer. By blending PLA with Ecoflex®, properties of PLA can be adjusted for different applications. Thus, Ecoflex® can be called 'enabling polymer'.

The major applications of Ecoflex® and its compounds are film products like shopping bags, organic waste bags, paper coating, and foamed materials. Mulch films for agricultural application are also very important applications.[63,67] With the use of bio-based building blocks, it is also possible to synthesize bio-based Ecoflex®.

5.03.3.2.4 Aliphatic polyesters – polybutylene succinate

Polybutylene succinate (PBS) is an aliphatic polyester produced from succinic acid and 1,4-butanediol.



High-molecular-weight PBS was first introduced in the market by Showa Denko under the trade name Bionolle®. PBS has a melting point of ~115 °C and the product can be processed into films and injection molded parts. The film properties are similar to those of HDPE.[68] The monomers succinic acid and 1,4-butanediol can be produced from renewable origin (*see* Section 5.03.2.1.2).[69]

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5.03.4 Approaches in Engineering Polymers

Engineering polymers are predominantly used in applications wherever the combination of heat resistance above 100 °C and good mechanical properties are required. Main fields of use are parts for the automotive industry or for electrical or electronic devices.

The improvement in heat resistance compared to the commodity polymers is achieved by introducing less flexible moieties into the backbone (polyesters, polycarbonates) or by strengthening the interaction between the polymer chains through hydrogen bonds (polyamides). Because the preferred synthesis route is the condensation process, there are several options to introduce renewability with the monomers discussed in Section 5.03.2. The solution can be either the 1:1 replacement of the fossil monomer by its bio-based alternative or the extension of the product range by incorporation of new bio-based monomers that are not commercially feasible with fossil resources. In all cases, production of such bio-based polymers can be run in existing plants (drop-in solution) – a big advantage on the way for a commercial realization.

5.03.4.1 Polyesters

Figure 29 summarizes bio-based options with polyesters (Table 3). The monomers ethylene glycol and 1,3-propanediol are – in addition to the established fossil route – already commercially available from renewable resources.[13,70] This new degree of choice resulted in the development of partially bio-based polyethylene terephthalate (PET) and polytrimethylene terephthalate (PTT).[49a,50,71] 'Bio-PET' is used for water bottles and marketed as an environmentally friendly alternative to the fossil-based PET.

Bio-based 1,3-propanediol can replace its fossil counterpart in PTT, a polyester with unique resilience properties as fiber.[72] Advantages of the bio-based monomer are a higher purity and a lower environmental impact at costs comparable with the fossil product.[73]

Bio-based butanediol as a component for polybutylene terephthalate (PBT) might be accessible through hydrogenation of succinic acid (*see* Section 5.03.2.1.2). Critical for the commercial success will be a cost-effective route compared to the traditional Reppe synthesis.

Even further from industrial realization is the use of bio-based terephthalic acid as a monomer in polycondensates, whereas some potential is seen for 2,5-FDCA as bio-based dicarboxylic acid.[74] Such activity is reported from Avantium.

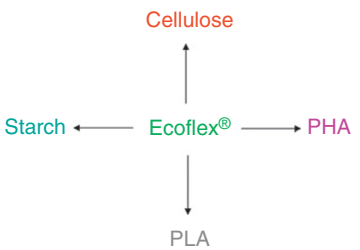

Figure 29 Ecoflex® as an enabler for renewable resources.

5.03.4.2 Polyamides

5.03.4.2.1 Aliphatic polyamides

Figure 30 lists opportunities in bio-based aliphatic polyamides. The figure shows the full spectrum of bio-based polyamides from products already commercialized to those that are under development or still in its academic infancy. In addition, the bio-content can be varied from 100% down to 20%, depending on the available monomers.

The prime example is polyamide 11 (PA11), which is produced in commercial scale from castor oil-derived 11-aminoundecanoic acid and thus is 100% bio-based. Applications of PA11 are extruded parts such as flexible pipelines, tubes, fuel lines, and optical fiber sheathing. Special features for PA11 include excellent chemical and impact resistance and low-moisture absorption together with the feature 'derived from renewable resources'.[75]

Although sebacic acid as a potential building block for polyamides has been available for a long time, only recently has it attracted interest from industry as a bio-based source for polyamides. In particular, its combination with HMDA proved to be an easy and cost-efficient entry into the bio-based polyamide arena. All major PA6.6 players have a PA6.10 in their portfolio. With a 60% renewable content, it resembles PA6 in thermal properties, but has a lower water uptake and a lower density.[76] Similarly, other polyamides of the X.10 type were introduced (PA4.10, PA10.10) from various companies (e.g., DSM, DuPont, Evonik). Whereas decamethylene diamine is accessible through sebacic acid, the synthesis of 1,4-butanediamine *in vivo* through decarboxylation of the amino acid ornithine is still not economically viable for larger-scale production.[31]

There are considerable activities to produce adipic acid through fermentation from carbohydrates[18b,77] to enter the PA6.6 chain. The benefit would be a process without nitrous oxide, the byproduct of the current route to adipic acid.

The amino acid lysine, made through fermentation from glucose, is the starting material for a bio-based polyamide 6 (PA6) (*see* Section 5.03.2.1.4). The hurdle for transferring this process into a commercial scale is the deamination step, which is not economically feasible yet.[27]

5.03.4.2.2 Partially aromatic polyamides

The incorporation of aromatic units like terephthalic acid into aliphatic polyamides raises the glass transition temperature as well as the melting temperature. The resulting partially aromatic semicrystalline polyamides (polyphthalamide, PPA) represent the utmost performance polyamides can deliver. With melting points well above 300 °C and processing temperatures around 340 °C, they reach the inherent limits of these materials. The scientist's task is to design polymers with high crystallinity, but with good processability – without sacrificing the other typical properties of polyamides. The approach is to use homopolyamides with long aliphatic chains or copolyamides with only a small amount of comonomer. Therefore, commercial products are either copolymers of HMDA and terephthalic acid with small amounts of isophthalic acid or ε-caprolactam as disruption units, or homopolymers from long-chain diamines with terephthalic acid. Table 4 shows examples of partially aromatic polyamides and the potential to incorporate renewable monomers.

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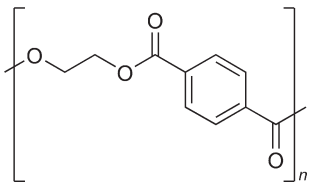
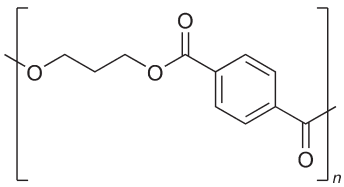
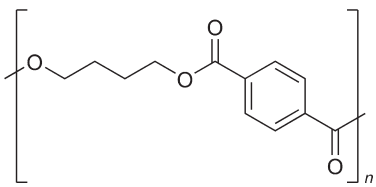
Table 3 Opportunities in bio-based polyesters

Polyester type		*Feedstock*	*Bio-based intermediates*	*Monomer(s)*	*T_g/T_m (°C)*
Polyethylene terephthalate		Plant oil Carbohydrates	Limonene Ethanol	Terephthalic acid Ethylene glycol	80/255
Polytrimethylene terephthalate		Plant oil Carbohydrates	Limonene	Terephthalic acid 1,3-Propanediol	60/227
Polybutylene terephthalate		Plant oil Carbohydrates	Limonene Succinic acid	Terephthalic acid 1,4-Butanediol	60/223

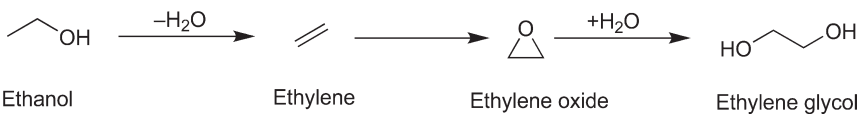


Figure 30 Ethylene glycol conversion from bio-based ethanol.

Basically for the realization of bio-based PPAs, the same limitations apply as for the aliphatic polyamides. Availability of the monomers on a cost-efficient basis is a prerequisite for a successful commercialization. For ε-caprolactam, terephthalic acid, and HMDA, any new synthetic route has to compete with the economics of the established world-scale capacities.

The situation might be different for the long-chain diamines and diacids. From renewable sources, special chain lengths might be available, which give the polymers specific properties that can be of high interest for different applications. Examples are the slightly modified polyamides 9T and 10T that are commercial. At the moment, 1,9-nonandiamine is produced from fossil resources via butadiene;[78] however, it is possible to obtain this diamine from rapeseed oil via azelaic acid. 1,10-Decanediamine is of natural origin from castor oil.

Considering other long-chain fatty acids as source, there are many new diacids and diamines conceivable that might lead to new specialty polyamides with properties not achievable by the fossil product spectrum.[79]

5.03.5 Approaches for High Performance Polymers

High performance polymers are typically characterized by high heat resistance (>150 °C), nonflammability, and retention of mechanical properties at elevated temperatures. The general synthetic concept is to link only aromatic units. This interrupts the linearity, reduces crystallinity, and increases flexibility. As a consequence, the intractable fully aromatic polymers are processable either via solution (e.g., film casting) or melt (e.g., injection molding). Prominent examples are polyetherketones, liquid crystalline polyesters, or polyaramides as shown in Table 5.

Today, the sources for the corresponding monomers for these polymers rely exclusively on a few aromatic primary building blocks from the refining of crude oil, such as benzene, toluene, or xylenes (the so-called BTX fraction). The further cost-efficient downstream processing into monomers of the A-A/B-B or A-B type (diphenols, aromatic amines, and acids) is well established in the industry along with the large-scale production of the corresponding polymers.

Nevertheless, with the monomers described in Chapter 2.03, there are in principle alternatives available that could increase the bio-based content of high performance polymers.

Possible examples could be:

1. Bio-based terephthalic acid in liquid crystalline polyesters, polyetherketones, or in polyaramides.
2. Bio-based *p*-aminobenzoic acid as monomer for poly-(*p*-benzamide), a polymer with properties similar to Kevlar®.[80]
3. Bio-based hydroquinone in polyetherketones and liquid crystalline polyesters.

Closer to realization is the approach of using bio-based *p*-hydroxybenzoic acid as a substitute for the oil-based

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Table 4 Opportunities in bio-based aliphatic polyamides

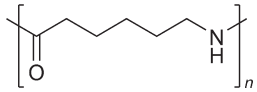
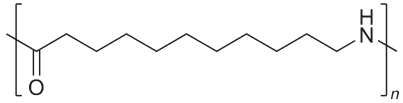
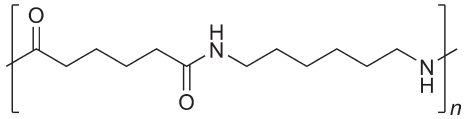
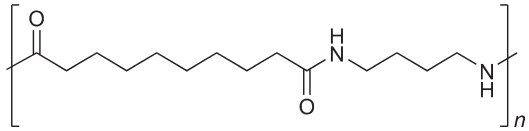
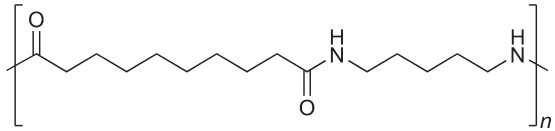
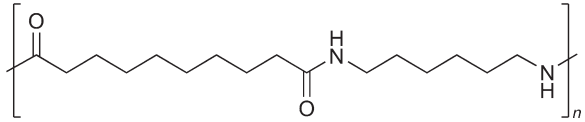
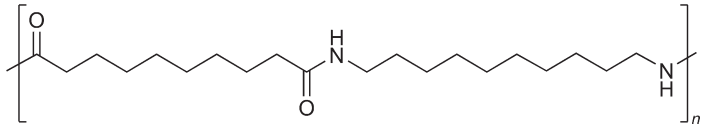
Polyamide type		*Feedstock*	*Bio-based intermediates*	*Monomer(s)*	T_g/T_m (°C)
PA6		Carbohydrates	Lysine	ε-Caprolactam	53/220
PA11		Castor oil	Ricinoleic acid	11-Aminoundecanoic acid	42/190
PA6.6		Carbohydrates Glucose Carbohydrates	*cis, cis*-Muconic acid Glucaric acid Propene	Adipic acid Adipic acid Hexamethylene diamine	50/260
PA4.10		Castor oil Carbohydrates	Ricinoleic acid Ornithine	Sebacic acid 1,4-Butane diamine	58/253
PA5.10		Castor oil Carbohydrates	Ricinoleic acid Lysine	Sebacic acid 1,5-Pentamethylene diamine	51/215
PA6.10		Castor oil Carbohydrates	Ricinoleic acid Propene	Sebacic acid Hexamethylene diamine	50/223
PA10.10		Castor oil Castor oil	Ricinoleic acid	Sebacic acid 1,10-Decanediamine	41/205

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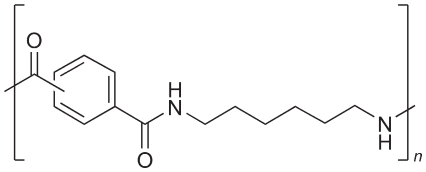
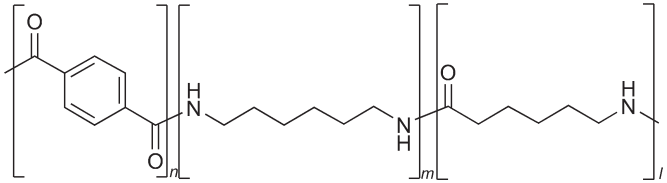
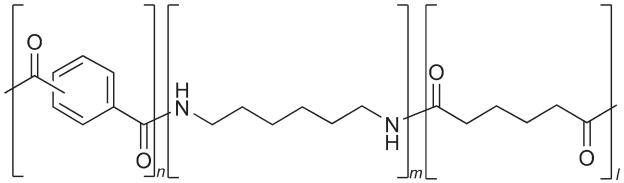
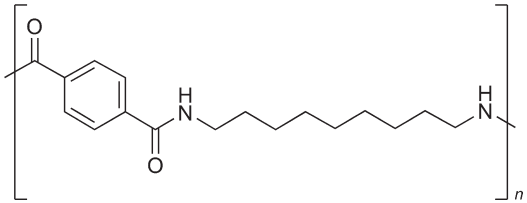
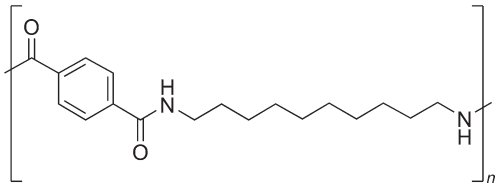
Table 5 Opportunities in bio-based partially aromatic polyamides

Polyamide type		*Feedstock*	*Bio-based intermediates*	*Monomer(s)*	*T_g/T_m (°C)*
PA6T/6I		Carbohydrates Plant oil	Propylene Limonene	Hexamethylene diamine Terephthalic acid Isophthalic acid	130/320
PA6T/6		Carbohydrates Plant oil Carbohydrates	Propylene Limonene Lysine	Hexamethylene diamine Terephthalic acid ε-Caprolactam	100/295
PA6T/66		Carbohydrates Plant oil Carbohydrates	Propylene Limonene *cis, cis*-Muconic acid	Hexamethylene diamine Terephthalic acid Adipic acid	120/310
PA9T		Plant oil Plant oil	Limonene Azelaic acid	Terephthalic acid 1,9-Nonanediamine	124/310
PA10T		Plant oil Castor oil	Limonene Ricinoleic acid	Terephthalic acid 1,10-Decanediamine	115/318

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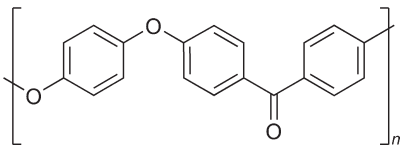
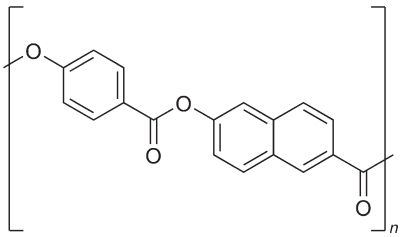
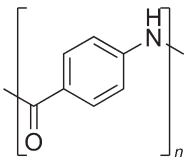
counterpart in poly-*p*-hydroxybenzoate (e.g., Ekonol®)[81] or as comonomer in liquid crystalline polyesters (e.g., Vectra®).[82] This would result, according to the literature,[55a] in lower production costs for those polymers in addition to the potential of having lower impact to the environment.

5.03.6 Conclusions

The challenge of finite fossil resources has been addressed by academic and industrial research with the development of polymers based on renewable resources. The corresponding monomers are accessible either through fermentation of carbohydrate feedstocks by microbes, often genetically modified, or by chemical processing of plant oils. The last 20 years of intensive research has resulted already in a broad variety of bio-based monomers and polymers that have shown the general feasibility of introducing renewability into the current oil-based polymer portfolio.

The opportunities are manifold. Nature can provide monomers that are chemically identical to the oil-based ones (e.g., PE, PP, PET, PA6) or deliver new monomers, which can potentially substitute oil-based counterparts (e.g., PLA, PHA). The polymer pyramid can be also filled with bio-based alternatives (**Table 6** and **Figure 31**).

Table 6 Examples for bio-based options for high performance polymers

Polymer type		*Feedstock*	*Bio-based intermediates*	*Monomer(s)*	*T_g/T_m (°C)*
Polyetherketone		Carbohydrates	Quimic acid	Hydroquinone	143/343
Liquid crystalline polyester		Carbohydrates	Shikimic acid	4-Hydroxybenzoic acid	103/275
Polyaramide		Carbohydrates	Shikimic acid	4-Aminobenzoic acid	–/>450

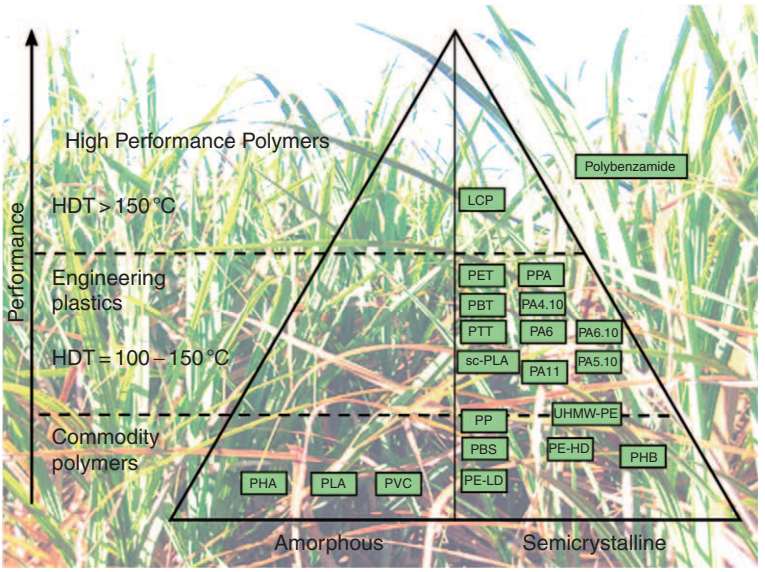


Figure 31 The polymer pyramid – based on renewable resources.

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However, there is a caveat: with respect to sustainability, it does not necessarily mean that every bio-based solution is *per se* more sustainable than the current fossil ones. As a consequence, it has to be carefully considered case-by-case whether it makes sense economically and ecologically to use polymers based on renewable resources.

Nevertheless, nature provides the tools to alternatives, and we are just at the beginning of a new learning curve. There are many new opportunities ahead!

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5.04 Sequence Control in One-Step Polycondensation

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5.04.1 Introduction

Condensation polymers are those polymers that are formed from polyfunctional monomers, which are typically prepared by the reaction between two kinds of bifunctional symmetric monomers. The two monomers, here called XaaX and YbbY, can yield the -aabb- repeating units without problems on sequence control, where aa and bb represent symmetric monomer substrates, and X and Y represent the leaving groups. However, when another symmetric monomer ZccZ is added to the polycondensation system mentioned above in an attempt to prepare a sequential polymer with the repeating unit of -(aabbcc)-, the situation becomes very complicated. If one looks at other sides brought by *Mother Nature*, even much more complicated synthetic procedures have been well established. For instance, the synthesis of proteins from activated amino acids in a living cell takes place on the surface of a ribosome. The resulting polypeptide molecules have a specific amino acid sequence governed by the *m*-RNA that is coded by DNA present in the nucleus of the cell. In our artificial procedures, there are no such active templates that are able to direct the sequence of amino acids. Therefore, the chemical synthesis of polypeptides is typically carried out step by step with the addition of each amino acid residue, resulting in tedious procedures that require a lot of time.

In general, sequential polycondensation polymers can be prepared by multisynthetic steps as shown in **Scheme 1**.

In **Scheme 1**, the first step is the synthesis of a sequential monomer (YbbaabbY) from two symmetric monomers, namely XaaX and YbbY. The following step is copolymerization with another symmetric monomer, ZccZ. The resulting polymer has a completely sequential structure with a repeating unit of -bbaabbcc-. To simplify the above reaction, the polymerization of XabX as a nonsymmetric monomer and YccY as a symmetric one is the most common system to give a sequential polycondensation polymer, -abcc-, and will be discussed in the following section.

The other aspect for sequentially ordered polymers is constitutional isomerism. Constitutional isomerism arises from differences in the nature of or sequence of chemical bonding in chemical compounds (e.g., CH_3OCH_3 and CH_3CH_2OH), or even polymers. They have the same molecular formula but different molecular structure and chemical properties. In the case of constitutional isomeric polymers, they have the same overall chemical composition but different functional groups and/or different sequential orders. Typical examples for this type of polymers are polyvinyl acetate $-(CH_2-CHOC{=}OCH_3)-$, poly (methyl acrylate) $-(CH_2-CHC{=}OOCH_3)-$, and a series of vinyl polymers that are derived from nonsymmetric vinyl monomers ($CH_2{=}CH-R$).[1,2] In the latter case, the constitutional isomeric vinyl polymers are obtained in the order of head-to-tail (H-T), head-to-head (H-H), tail-to-tail (T-T), and random polymers through chain propagation reaction in 1,2-addition, 1,1-addition, 2,2-addtion, and all three reactions taken at the same batch, respectively.

Such isomerism of polymers has great influence on the polymer properties such as solubility, crystallinity, mechanical and thermal properties like glass transition temperature (T_g), melting point (T_m), and so on. Many reports on the syntheses of sequential condensation polymers have been published. For example, sequential aromatic polyamides were prepared by polycondensation of aromatic diacid chlorides with symmetric diamines which contained aromatic amide units preformed in a sequential arrangement.[3] The aromatic diamine monomer containing preformed-amide linkages was prepared from phenylene diamine and two nitro-substituted aromatic acid chlorides, with the subsequent reduction of the dinitro intermediate. Similarly, sequential aromatic polyamide-esters were prepared from preformed diphenol-amide monomers and diacid chlorides.[4,5] The synthesis of sequential aromatic

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$$\text{XaaX} + 2\text{YbbY} \longrightarrow \text{YbbaabbY}(+\,2\text{XY}) \xrightarrow{\text{ZccZ}} \text{-(bbaabbcc)- (+YZ)}$$

Scheme 1

polyamides and copolyamides by polycondensation of diacid chlorides with preformed methyl-substituted symmetric diamines has also been reported.[6] Furthermore, the polycondensations of aromatic dianhydride with aromatic diamines containing preformed bisbenzoheterocyclic groups yielded the sequential benzoazole-imide copolymers.[7]

These synthetic methods need several steps for the synthesis of sequential polymers, and thus would be troublesome. To remedy this problem, a straightforward synthetic method would be required for the preparation of new sequential condensation polymers. This chapter reviews the synthesis of sequential condensation polymers using one-step synthetic methods utilizing different reactivities of functional groups.[8]

5.04.2 Analysis of Constitutional Regularity

There are a few reports on quantitative analysis of constitutional regularity. Three typical examples are as follows:

First, the transesterification between two polyesters was investigated and the average sequence length and the degree of randomness in the copolymers were determined by using ^{1}H NMR spectroscopy,[9] where a parameter B representing the degree of randomness was introduced. Transesterification of poly(ethylene terephthalate) (PET) and poly(ethylene sebacate) (PES) was undertaken to determine the parameter B as follows. The resulting copolyesters (PET/PES) have three kinds of ethylene glycol (EG) residues (-G-), one of which is sandwiched by terephthalate (T) on both sides, T-G-T, one by sebacate (S) on both sides, S-G-S, and the other by terephthalate and sebacate on each side, T-G-S. The molar fractions of terephthalate (P_T) and sebacate (P_S) are estimated from the intensities of three NMR signals.

$$P_T = \frac{P_{(\text{T-G-S})}}{2} + P_{(\text{T-G-T})} \qquad [1]$$

$$P_S = \frac{P_{(\text{T-G-S})}}{2} + P_{(\text{S-G-S})} \qquad [2]$$

where $P_{(\text{T-G-T})}$, $P_{(\text{S-G-S})}$, and $P_{(\text{T-G-S})}$ represent the ratios of the integrated intensities of T-G-T, S-G-S, and T-G-S signals, respectively, to the total intensity of the EG residues. If one could examine the units along the PET/PES copolymer chain from one end to the other, the probability of finding a T unit next to an S unit would be:

$$P_{ST} = \frac{P_{(\text{T-G-S})}}{2P_S} \qquad [3]$$

Similarly, an S unit exists next to a T unit with a probability of

$$P_{TS} = \frac{P_{(\text{T-G-S})}}{2P_T} \qquad [4]$$

The parameter B is defined by:

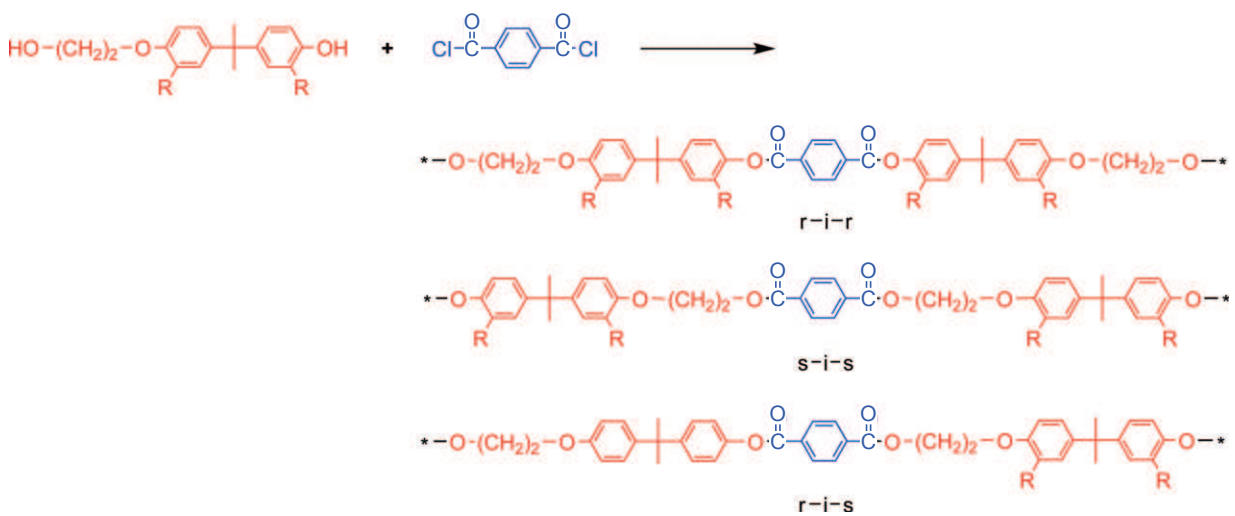
$$B = P_{ST} + P_{TS} \qquad [5]$$

If $B < 1$, these units tend to cluster in blocks, and become $B = 0$ for a homopolymer mixture. If $B > 1$, the sequence length becomes shorter, where $B = 2$ represents an alternating copolymer.

Second, the influence of reaction conditions on the structures of polymers formed from symmetric (terephthaloyl chloride: C-i-C) and nonsymmetric (β-hydroxyethyl ether of 4,4′-diphenylol propane-2,2: A-rs-B) monomers was studied in nonequilibrium polycondensations (Scheme 2).[10] The polycondensation of C-i-C with A-rs-B yields polymeric chains containing both the homotriads (r-i-r and s-i-s) corresponding to H-H and T-T addition and heterotriads (r-i-s) corresponding to H-T addition.

The coefficient of microheterogeneity, K_m, for the polymer was introduced:

$$K_m = \frac{P_{rs}}{(P_{rs} + 2P_{rr})} + \frac{P_{rs}}{(P_{rs} + 2P_{ss})} \qquad [6]$$



Scheme 2

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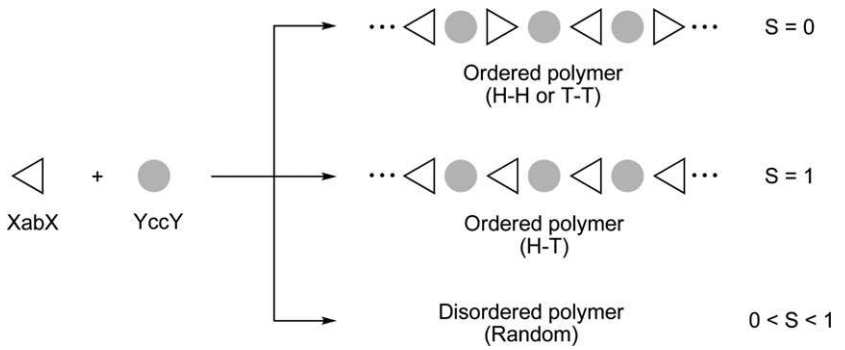


Scheme 3

where P_{rs}, P_{rr}, and P_{ss} are the mole contents of the r-i-s, r-i-r, and s-i-s triads, respectively. $K_m = 0$ for H-H (or T-T) addition ($P_{rs} = 0$), $K_m = 1$ for random addition ($1/2\ P_{rs} = P_{rr} = P_{ss}$), and $K_m = 2$ for H-T addition ($P_{rr} = P_{ss} = 0$).

Third, the influence of constitutional isomerism on the physical properties of polycondensates was also investigated,[11] where the probability s of two adjacent nonsymmetric units in a chain pointing in the same direction was used to quantify structural regularity. When XabX is reacted with YccY, the shortest structure elements in the polymer are -acca-, -accb-, -bcca-, and -bccb-, where the two structures -accb- and -bcca- are indistinguishable. The probability s of an -accb- placement is given by

$$s = \frac{[\text{accb}]}{[\text{acca}] + [\text{accb}] + [\text{bccb}]} \qquad [7]$$

where [accb] includes -accb- as well as -bcca- arrangements.

Three general cases are shown in Scheme 3 as a schematic representation of polymers with different values of s. For a chain where all units are pointing in the same direction, $s = 1$ (H-T); when the orientation of the units is strictly alternating, $s = 0$ (H-H or T-T). If no preference for the different enhancement exists, $s = 1/2$ (random chain).

The relationship between K_m (or B) and s depends on the extent of reaction and on the system under consideration. For complete reaction, $K_m = 2s$.

There are kinetic and thermodynamic factors to control the structural regulation of polymers. However, the former factor is a prerequisite and determines mainly the structural regularity. The basic reactions and the relative reactivities of functional groups of both monomers for this polymerization are as follows:

$$-\text{aX} + \text{Yc}- \xrightarrow{k_{\text{aX}}} -\text{ac}- + \text{XY} \quad -\text{bX} + \text{Yc}- \xrightarrow{k_{\text{bX}}} -\text{bc}- + \text{XY}$$
$$r = \frac{k_{\text{bX}}}{k_{\text{aX}}}, \quad 0 < r < 1 \qquad [8]$$

The reactivity ratio r is defined as the ratio of each reaction rate constant, where the -aX group of XabX is arbitrarily chosen to be more reactive.

There are two one-step methods: a one-stage method and a direct method. The former method is a typical procedure for the synthesis of condensation polymers using active intermediates (e.g., acid chloride, isocyanate, etc.). In contrast, the direct method involves direct polycondensation using condensing agents, and has led to the *in situ* activation of carboxylic acids, followed by condensations under mild conditions.

Detailed theoretical treatments have been amply discussed in several papers and review articles[12,13] so they are not presented in this chapter.

5.04.3 Sequential Polymers from Symmetric and Nonsymmetric Monomers

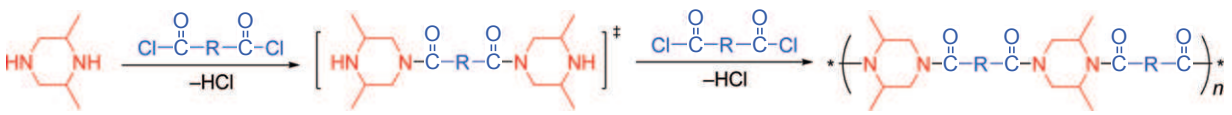
5.04.3.1 Head-to-Head or Tail-to-Tail Polymers

Based on detailed kinetic considerations, it was concluded that a difference in the reactivities of functional groups in a nonsymmetric monomer was not sufficient to produce condensation polymers with $s = 0$.[12] That is, even if the -aX group of the nonsymmetric monomer is more reactive than the -bX group, the immediate mixing of two monomers gives a random polymer. To obtain H-H or T-T polymer with $s = 0$, YccY should be added slowly to XabX, so that there would never be any unreacted functional group, defined as -cY, present in the reaction. After half of the YccY is added, only XbaccabX will be produced. Upon addition of the remaining YccY units, only the -bccb- structure would be formed in the polymer. Accordingly, the resulting polymer would contain -acca- and -bccb- arrangements only, and therefore, $s = 0$.

5.04.3.1.1 One-stage synthesis

There are several reports on sequential polymers from symmetric monomers based on diacid chlorides and nonsymmetric monomers having two functional groups with different reactivities.

The alternating sequential copolymers were prepared from diacid chlorides and *cis*-2,6-dimethylpiperazine as a nonsymmetric monomer (Scheme 4).[14] In this polymerization, the less



Scheme 4

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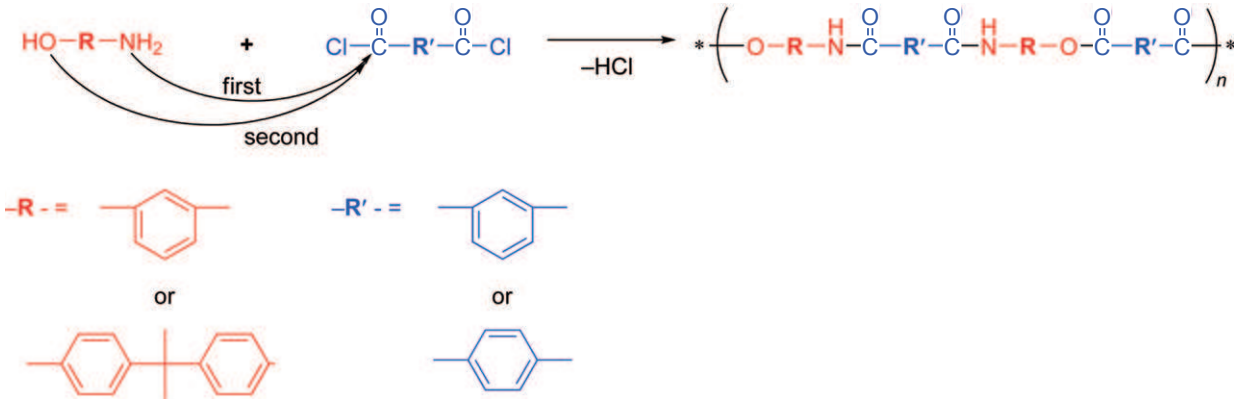


Scheme 5

hindered amine moiety preferentially reacted with the acid chloride to form a symmetric intermediate. However, no characterization of the resulting polymers to support the constitutional regularity was reported in this work.

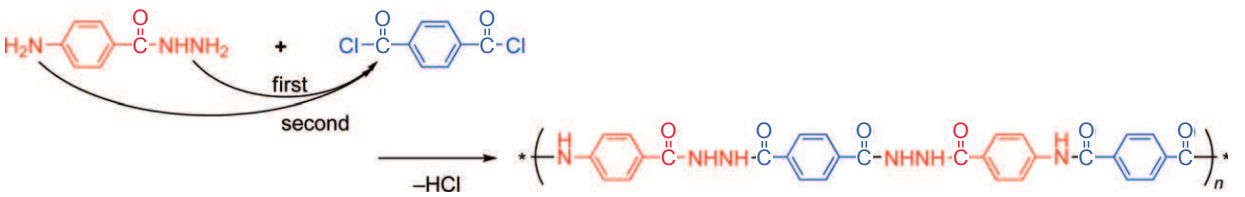
The greater reactivity of an aromatic amino group relative to phenol groups was successfully applied to the synthesis of sequential aromatic poly(amide-ester)s using interfacial and solution polycondensations of *m*- and *p*-aminophenols with diacid chlorides (Scheme 5).[15] The first step of reaction involves the *in situ* preparation of a diphenol-amide that undergoes further condensation. Authentic sequential polyamide-esters were prepared in a two-step procedure, that is, via the preparation of amide-bisphenol monomers from diacid chlorides and *m*- or *p*-aminophenols, and subsequent polycondensation with aromatic dichlorides.

The polycondensation of 4-(4-amino-α,α-dimethylbenzyl) phenol with iso- and terephthaloyl chlorides was studied to determine if the amide-ester polymers obtained were random or sequential.[16,17] It was then concluded that the polymers prepared by the one-stage procedure were random.

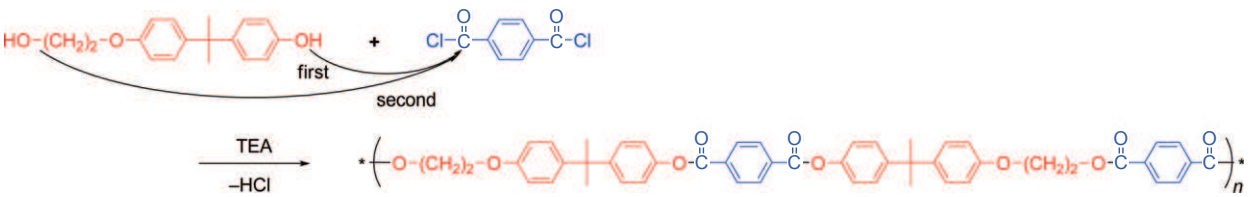
Using the higher reactivity of a hydrazide group toward an acid chloride group compared to an aromatic amine group, the polycondensation of terephthaloyl chloride with *p*-aminobenzhydrazide was investigated under a variety of experimental conditions to determine the degree of sequence in the polyamide-hydrazide. The conclusion was that polyamide-hydrazides were at least 'partially sequential' (Scheme 6).[18]

Similarly, the reactivity of phenols to acid chlorides in the presence of triethylamine (TEA) is higher than that of alcohols. Thus, polycondensations of β-hydroxyethyl ethers of bisphenols and terephthaloyl chloride in the presence of TEA were performed to obtain sequential polymers, and polymers with $K_m = 0.5$ were produced by a gradual addition of terephthaloyl chloride to β-hydroxyethyl ethers of bisphenols (Scheme 7).[10]

To study the difference of the reactivity of aromatic diamines having substituents at *ortho* positions to acid chlorides and to see if the regularity of H-H or T-T orientations could be tuned, the rigid-rod aromatic polyamides were prepared in a one-stage method with terephthaloyl chloride and one diamine – either 2,6-dichloro-*p*-phenylenediamine or nitro-*p*-phenylenediamine or methoxy-*p*-phenylenediamine – with varying regularities ranging from H-H to T-T orientations (Scheme 8).[19] First, the reaction rates of benzoyl chloride with substituted *p*-phenylenediamines were determined in *N*-methylpyrrolidinone/tetrahydrofuran (NMP/THF = 10/1) (Table 1). The *r* values were about 9×10^{-2}. Based on these findings, polyamides with regularities ranging from $s = 0.005$ to 0.65 determined by ^{1}H NMR were obtained by changing the mode and feed rates for the monomer addition.



Scheme 6



Scheme 7

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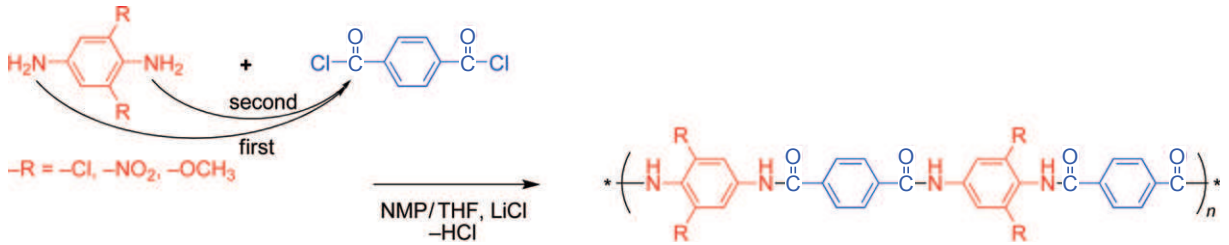
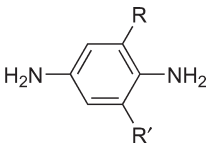


Scheme 8

Table 1 Kinetic data for the reaction systems investigated



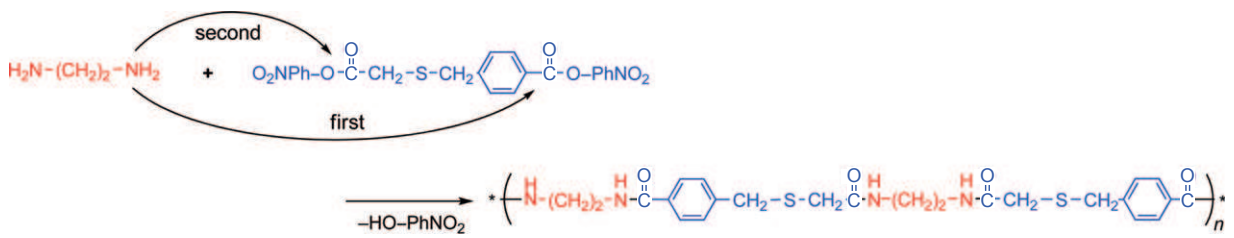
Substituent			
–R	*–R′*	*r* ($\times 10^2$)	k_{ax} ($l\,mol^{-1}\,s^{-1}$)
–Cl	–Cl	9.2	2.9
$–NO_2$	–H	8.7	1.3×10^{-3}
$–OCH_3$	–H	9.0	4.0×10^{3}

Changing from acid chlorides to *p*-nitrophenoxy groups as a leaving group, a synthesis of sequential polyamides by the polycondensation of (*p*-nitrophenyl) [4-(*p*-nitrophenyloxycarbonylmethylenethiomethylene)]benzoate with ethylenediamine was investigated (Scheme 9) and the reaction kinetics and control of the polymer chain regularity were described in detail.[20,21] The aminolysis of aliphatic and aromatic *p*-nitrophenyl esters to aliphatic amines was carried out in dimethyl sulfoxide/dimethyl formamide (DMSO/DMF = 2/1) at 0 °C, and the *r* value was determined to be 1.65×10^{-2}. A polymerization was performed at room temperature by slow addition of ethylenediamine to (*p*-nitropheny) [4-(*p*-nitrophenyloxycarbonyl-methylenethiomethylene)]benzoate, yielding a polyamide with $s = 0.079$. The probability *s* of these polymers was determined using quantitative degradation and subsequent analysis of the fragments by ^{1}H NMR spectroscopy.

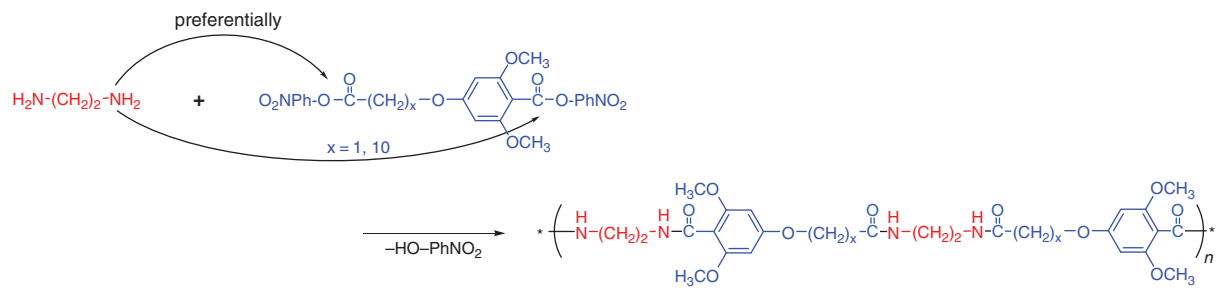
Sterically hindered (*p*-nitrophenyl)[4-(*p*-nitrophenyloxycarbonylalkyleneoxy)] 2,6-dimethoxybenzoates were used as nonsymmetric monomers to improve the regularity, and *r* values of 1.1×10^{-5} and 2.8×10^{-4} were obtained for compounds with $x = 1$ and 10, respectively (Scheme 10).[21] The values of *s* were 0 for the compound with $x = 1$ and ethylenediamine, and 0.03 for the compound with $x = 10$ and ethylenediamine.

A series of polyurethanes with H-H (or T-T) sequence was synthesized by polyaddition of *p*-isocyanatobenzyl isocyanate (IBI, XabX) and EG (YccY).[22] As an aromatic isocyanate has higher reactivity to nucleophiles than an aliphatic isocynate (Scheme 11), IBI can be a good candidate for an asymmetric reactive monomer.

For the synthesis of H-H (T-T) ordered polyurethane, the polymerization was conducted by slow addition of the first half amount of EG to IBI solution in the presence of TEA at 0 °C, followed by rapid addition of the rest of EG in the presence of



Scheme 9



Scheme 10

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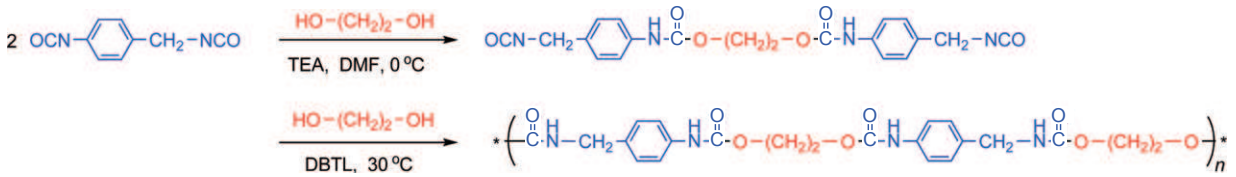
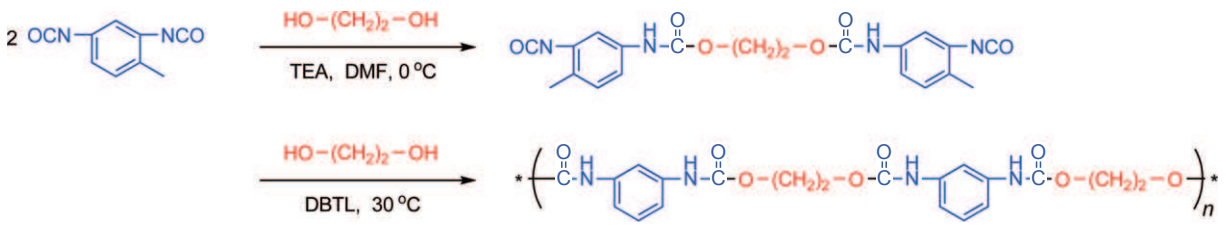
Scheme 11



Scheme 12



Scheme 13

dibutyltin dilaurate (DBTL) at 30 °C (Scheme 12). The difference in the microstructure of the ordered (H-H or T-T) and unordered (random) polyurethane was confirmed by ^{13}C NMR spectroscopy, proving that the ordered polymer had the expected structural regularity.

A similar approach was demonstrated with a different type of H-H (or T-T) ordered polyurethane derived from tolylene-2,4-diisocyanate (TDI) instead of IBI (Scheme 13).[23] TDI is a nonsymmetric monomer and thus it brings an unequal reactivity due to steric hindrance by the methyl group on the benzene ring.

5.04.3.1.2 Direct method

Direct polycondensation using condensing agents has been developed to allow for the *in situ* activation of carboxylic acids, followed by condensation under mild conditions. Various organophosphorus reagents have been found to be useful for the activation of carboxylic acids.[24–31]

One of the excellent condensing agents is diphenyl(2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate (**1**).[32] This condensing agent **1** reacts with a carboxylic acid to form a reactive intermediate, a mixed carboxylic-phosphoric anhydride, whose reactivity to nucleophiles is lower than that of the corresponding acid chloride. The reactivity of a species generally varies inversely with its selectivity (details on reactivity of (**1**) are described in Section 5.04.4.2). Thus, selective amidation using **1** was expected to be higher than that using acid chloride. The kinetic parameters of interest are related to the rate constants for the reactions of functional groups of the nonsymmetric monomer XabX, $r = k_{ax} = k_{bx}$. The overall second-order rate constants for the reaction of benzoic acid with substituted anilines in NMP in the presence of **1** were investigated,[31,32] and these results are summarized in Table 2. The rate constants varied by around 100 when substituted anilines were changed from aniline to 2,6-dimethylaniline. The difference in reactivity of aniline and 2,6-dimethylaniline to the active intermediate is sufficient enough to produce H-H or T-T polyamides.

The slow addition of a symmetric monomer, isophthalic acid, to a nonsymmetric monomer, 2,6-dimethyl-*p*-phenylenediamine, in the presence of **1** produced a sequential polyamide (Scheme 14).

The authentic H-H (or T-T) polyamide was prepared by the direct polycondensation of isophthalic acid with *N*,*N*′-di(4-amino-3,5-dimethylphenyl)isophthalamide, which was obtained from isophthalic acid and 2,6-dimethyl-*p*-phenylenediamine (Scheme 15). The authentic H-T polyamide sample was prepared as shown in Scheme 16. The condensation of methyl hydrogen isophthalate with 2,6-dimethyl-*p*-phenylenediamine in the presence of **1** yielded 4′-amino-3-methoxycarbonyl-3′,5′-dimethylbenzanilide, which was treated with an alkaline solution to give 4′-amino-3-carboxy-3′,5′-dimethylbenzanilide. The direct polycondensation of 4′-amino-3-carboxy-3′,5′-dimethylbenzanilide produced the authentic polyamide. The random polyamide was prepared by the polycondensation of isophthaloyl chloride with 2,6-dimethyl-*p*-phenylenediamine by adding both monomers at once (Scheme 17). Spectroscopic analyses including IR, ^{1}H, and ^{13}C NMR spectroscopy clearly indicated that the direct polycondensation reaction produced the desired H-H or T-T ($s = 0$) polyamide.

Another method to prepare H-H (or T-T) polyamides using amines with different p*K*a values was reported.[33] The overall second-order rate constants *k* for the reaction of benzoic acid with substituted anilines in NMP in the presence of **1** were determined. A linear relationship with a slope of 1 was found

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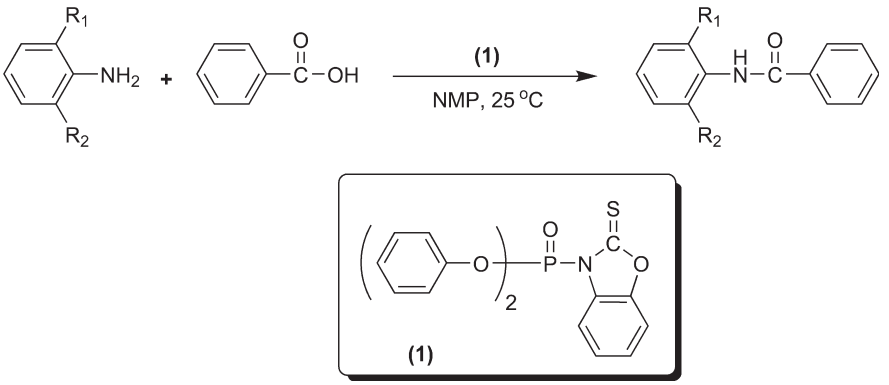
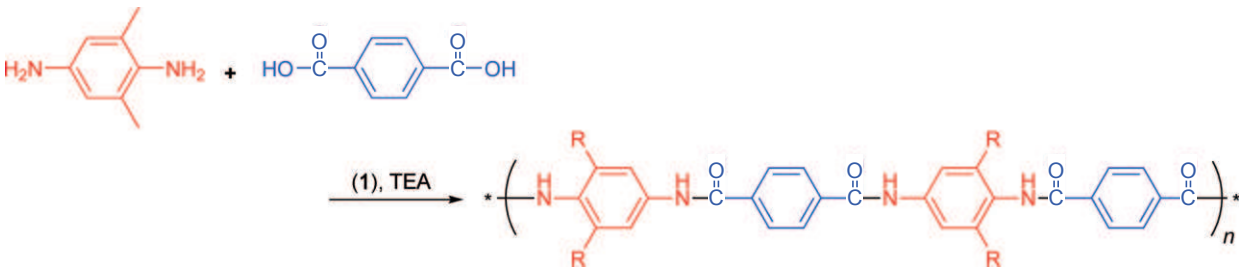
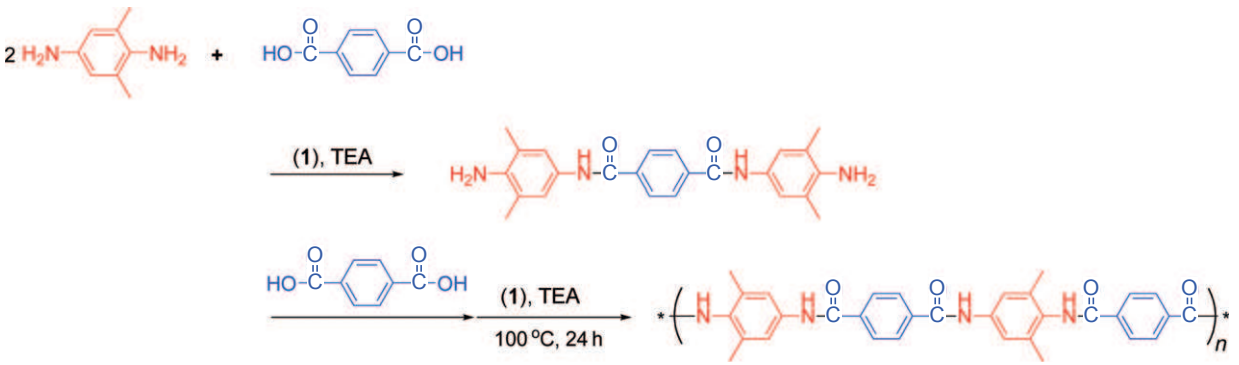
Table 2 Overall second-order rate constants for the reaction of benzoic acid with substituted anilines in NMP at 25 °C in the presence of **1**



Substituent		
$-R^1$	$-R^2$	k_x (l mol^{-1} min^{-1})
–H	–H	1.12
$-CH_3$	–H	3.07×10^{-1}
$-CH_3$	$-CH_3$	1.19×10^{-2}



Scheme 14



Scheme 15

between log k and the pKa values for aniline derivatives (Figure 1).[34] As the difference in pKa values between an aliphatic amine and an aromatic amine is about 6, aliphatic and aromatic amines are expected to have 10^6-fold different rate constants for aminolysis of the active species. Thus, 2-(4-aminophenyl)ethylamine was selected as the XabX monomer.

The slow addition of isophthalic acid to 2-(4-aminophenyl)ethylamine in the presence of **1** produced a sequential ($s = 0$) polyamide. The microstructure of the polyamide was determined by comparing ^{13}C NMR chemical shifts of the amide carbonyl groups to those for the authentic polyamide (Scheme 18).

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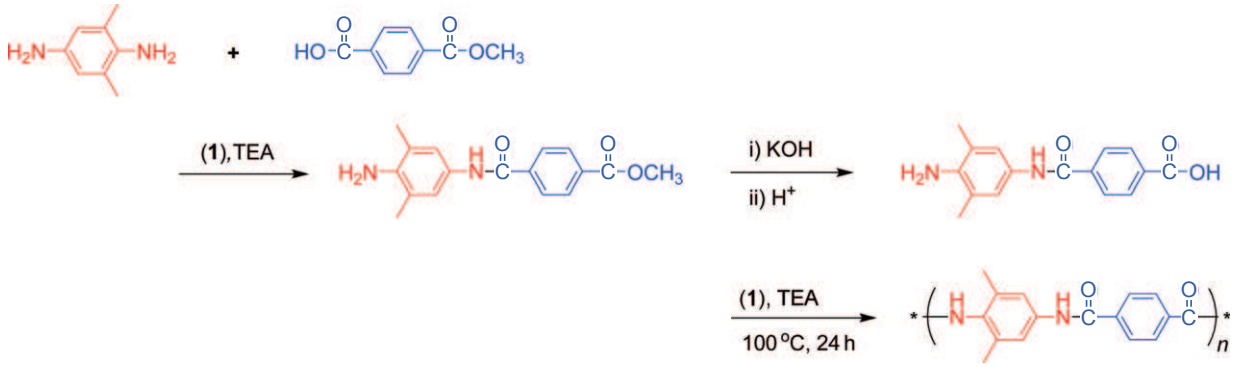
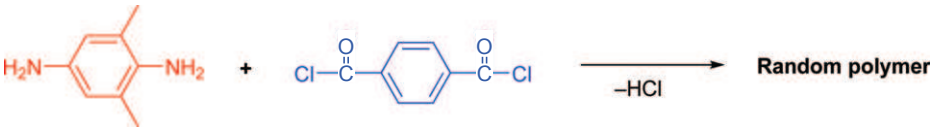


Scheme 16



Scheme 17

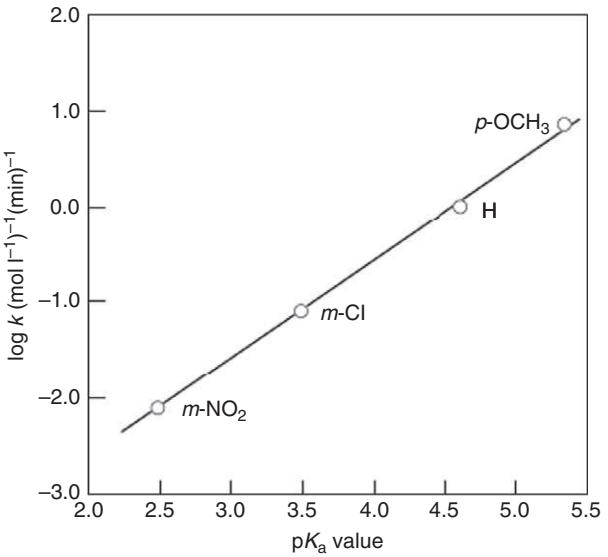


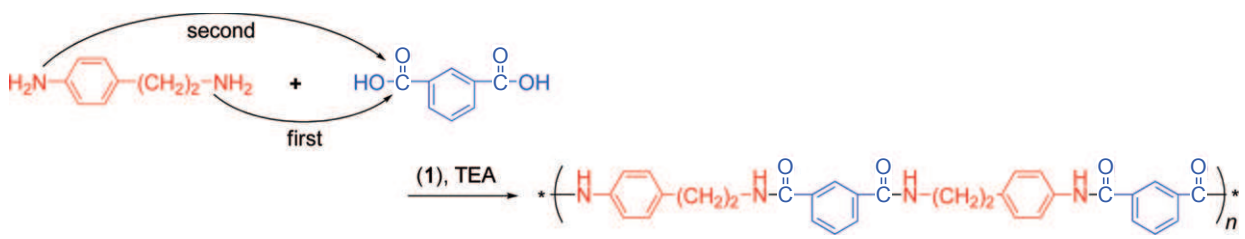
Figure 1 Hammett plot of log *k* vs. p*Ka* for condensation of benzoic acid with aniline derivatives using **1.** Reprinted with permission from Ueda, M. *Prog. Polym. Sci.* **1999**, *24*, 699.[8] Copyright 1999, Elsevier.

5.04.3.2 Head-to-Tail Polymers

For the synthesis of the H-T polymer ($s = 1$), two new parameters, g_a and g_b, are introduced, where parameter g_a is the ratio of the reaction rate constants of the second reacting functional group on the YccY monomer to that of the first reacting functional group if the first one has reacted with an -aX group. Thus,

$$g_a = \frac{k_{cY,second}}{k_{cY,first(aX)}} \quad g_a > 0$$
$$g_b = \frac{k_{cY,second}}{k_{cY,first(bX)}} \quad g_b > 0 \qquad [9]$$

Deactivation of induction means that g_a (or g_b) < 1, while in the case of activation of induction g_a (or g_b) is greater than unity. These inductions arise from electronic or steric effects. The effect of a change of g_a on the polymer sequence for both types of additions at a constant value of $r = 0.01$ is shown in Figure 2. For $g_a = g_b = 0.067$, the regularity s changes from 0.049 to 0.864 with an increasing rate of addition of the YccY monomer to the XabX monomer. The maximum value of s is obtained by mixing both monomers at once. The monomer feed rate on the abscissa is dimensionless. On the x-axis, moving to the right approaches the



Scheme 18

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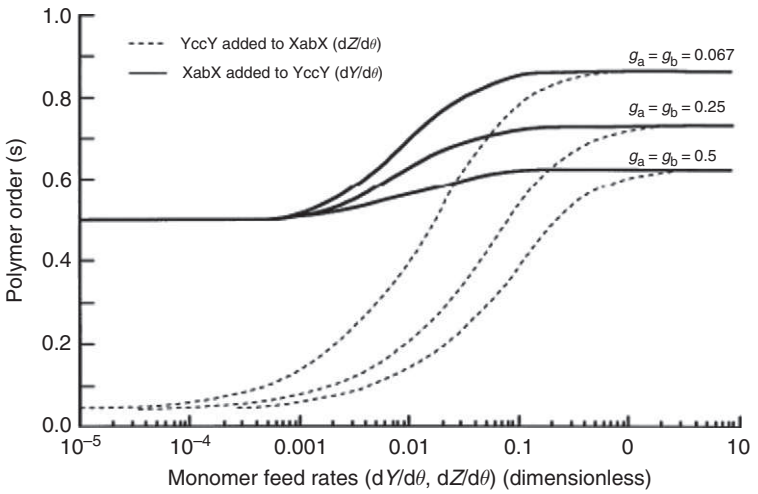


Figure 2 Plot of *s* as a function of monomer feed rates d*Y*/dθ (θ is time) (when XabX is fed continuously), and d*Z*/dθ (when YccY is fed continuously) for $r = 0.01$. The functional groups on the symmetric monomer YccY are dependent on each other, but show equal degrees of induction g ($g = g_a = g_b$). Reprinted with permission from Ueda, M. *Prog. Polym. Sci.* **1999**, *24*, 699.[8] Copyright 1999, Elsevier.

limit of fast addition of one monomer to the other and moving to the left approaches the limit of slow addition.[13]

A H-T polymer is produced when the following requirements are met: (1) r is sufficiently small, (2) the second reacting group on the YccY monomer is strongly deactivated by the reaction of the first (i.e., $g_a = g_b < 1$), and (3) the two monomers are mixed at once. Therefore, it is important for the molecular design of YccY and XabX monomers to meet the requirements (1) and (2).

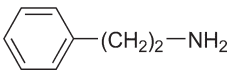
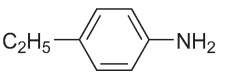
5.04.3.2.1 One-stage synthesis

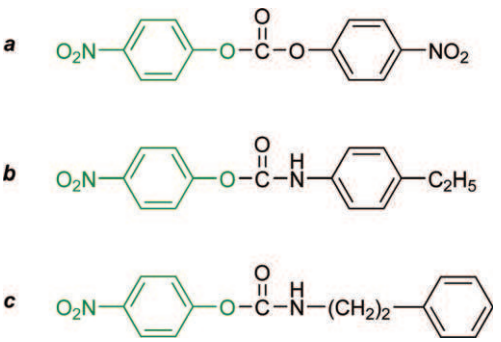
The sequential polyureas were prepared by the polycondensation of aromatic carbonates with nonsymmetric diamines.[35] The reaction rate constants relevant to the aminolysis of bis(4-nitrophenyl) carbonate with aliphatic and aromatic amines were summarized in Table 3. As the p*K*a value for an aliphatic amine is higher than that for an aromatic amine, the rate constant for the former is higher than that for the latter by several orders of magnitude. The value of r (aromatic amine /aliphatic amine) is 1.0×10^{-6}. It was further shown that the induction was very large or absent, depending on the first reactant. The relative rate constants for bis(4-nitrophenyl) carbonate are $g_a = 3.6 \times 10^{-3}$ and $g_b = 6.1 \times 10^{-2}$.

Based on these findings, polycondensations of bis (4-nitrophenyl) carbonate with 2-(4-aminophenyl)ethylamine were carried out by using three different procedures: (1) the diamine is slowly added to the carbonate, (2) both are mixed rapidly (Scheme 19), and (3) the carbonate is slowly added to the diamine. The results are shown in Table 4. The obtained polymers had *s* values of 0.47, 0.89, and 0.05 as estimated by ^{1}H and ^{13}C NMR.

Poly(3-alkylthiophene) is one of the most widely explored polymers in the optoelectronic devices, especially in transistor and photovoltaic applications because of its excellent charge-transporting mobility and highly regioregular structure. The synthesis of H-T poly(3-alkylthiophene)s was reported by Chen *et al.*[36] Rieke zinc undergoes oxidative addition with

Table 3 Aminolysis rate constants of bis(*p*-nitrophenyl) carbonate with aliphatic and aromatic amines at 25 °C in DMSO

Amine	*Ester or amide*	*Rate constant* ($l\,mol^{-1}\,s^{-1}$)
	***a***	1.0×10^3
	b	9.5×10^2
	c	3.6
	***a***	1.0×10^{-2}
	b	6.1×10^{-4}
	c	1.0×10^{-5}



2,5-dibromo-3-alkylthiophene or 2-bromo-5-iodo-3-alkylthiophene regioselectively to afford 2-bromo-5-(bromozincio)-3-alkylthiophene or 2-bromo-5-(iodozincio)-3-alkylthiophene. These intermediates polymerize catalytically to a series of regiospecific poly(3-alkylthiophene)s using Ni(DPPE)Cl_2 (DPPE; 1,2-bis(diphenylphosphino)ethane) (Scheme 20).

The ^{13}C NMR spectrum of the regioregular H-T poly (3-alkylthiophene) clearly exhibited four peaks for the thiophene carbons corresponding to the HT–HT structure. In contrast, for the regiorandom polymer, many peaks were

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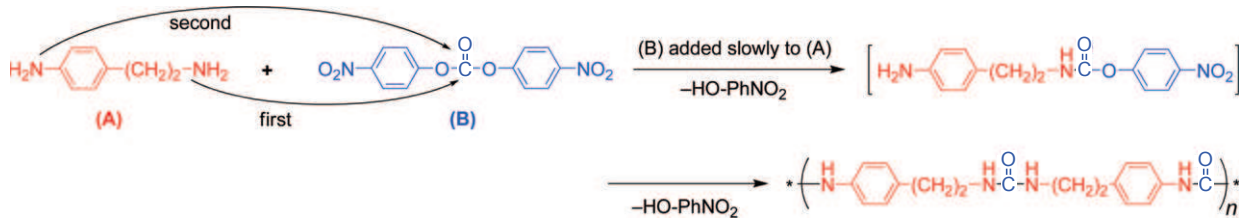


Scheme 19

Table 4 Constitutionally regular and irregular polyureas from 2-(4-aminophenyl)ethylamine (A) and bis (*p*-nitrophenyl)carbonate (B)

Method	*s*	M_n
(A) added slowly to (B)	0.47	4300
(A) and (B) mixed rapidly	0.89	1700
(B) added slowly to (A)	0.05	3700

observed due to an equal distribution of the four triad structures (HT–HT, TT–HT, HT–HH, and TT–HH).

The facile addition of nucleophiles to double bonds activated by electron withdrawing groups is well known, and the Michael-type polyaddition of diamines and carbanions has been extensively studied (Scheme 21).[37,38] In particular, dithiols are powerful nucleophiles, and this Michael-type addition is generally much faster than the nucleophilic substitution reaction of carboxylic acid derivatives, such as acid anhydrides and active esters with nucleophiles. The selective polyaddition of aminobenzenethiol to maleic anhydride due to their different reactivities was reported by Asahara.[39]

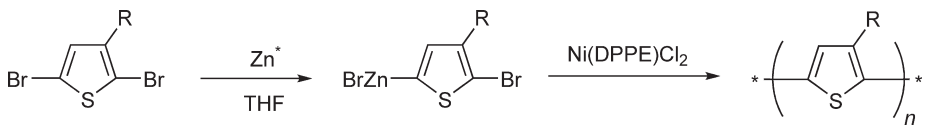
Regarding an H-T ordered polyurethane, the polyaddition reaction was undergone from the same monomers, IBI and EG, as described above for the H-H (or T-T) ordered polyurethane (Scheme 22). H-T regularity was controlled by two factors: (1) different reactivities between aromatic and aliphatic isocyanates and (2) discriminative reactivity between free EG and one-side substituted EG to aliphatic isocyanate due to the steric repulsion of catalyst peripheries.[40] It is noted that an effective catalyst such as 1,1,3,3-tetraphenyl-1,3-dichlorodistannoxane was adopted to enhance steric repulsion around the active site for the formation of H-T regioregular urethane linkage.

Moreover, by changing the molecular design of the catalyst, substituting a –NCS group for the –Cl group, the H-T content was increased up to 93%.[41] The Sn–NCS bond in distannoxane has a high polarity that promotes the formation of alkoxy-distannnoxane of EG. The difference in the microstructure of the H-T ordered polyurethane to other types of ordered polyurethane (e.g., H-H or T-T) as mentioned earlier and unordered (random) polyurethane was confirmed by ^{13}C NMR. A remarkable influence of the polymer's constitutional regularity on the thermal properties and crystallinity was revealed.

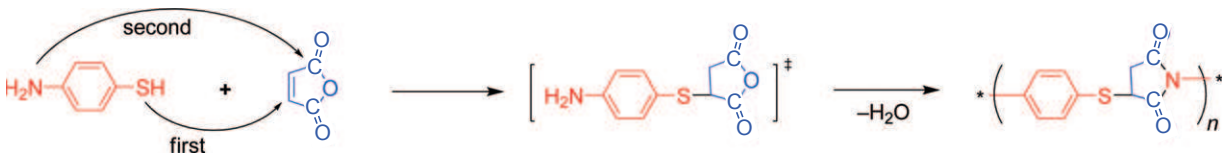
5.04.3.2.2 Direct method

As described above, the rate constant for the aminolysis of the active intermediate is altered about 10^6 fold when an aliphatic amine is replaced with an aromatic amine. 2-(4-Aminophenyl) ethylamine (or a pair of two symmetric monomers such as 4,4′-oxydianiline and *m*-xylylenediamine) was chosen as the XabX monomer for the synthesis of H-T polymers. Succinic anhydride was selected as the YccY monomer, which was expected to have a deactivating induction and give an intermediate. Ordered polyamides were prepared by mixing the two monomers all at once in the presence of **1** in NMP at room temperature (Scheme 23).[42]

Similarly, the H-T polyamide from succinic anhydride and a pair of two symmetric monomers, 4,4′-oxydianiline and *m*-xylylenediamine, in the presence of **1** was prepared. The structure of these polyamides was verified by comparing their spectral data with those of the authentic polyamides.



Scheme 20



Scheme 21

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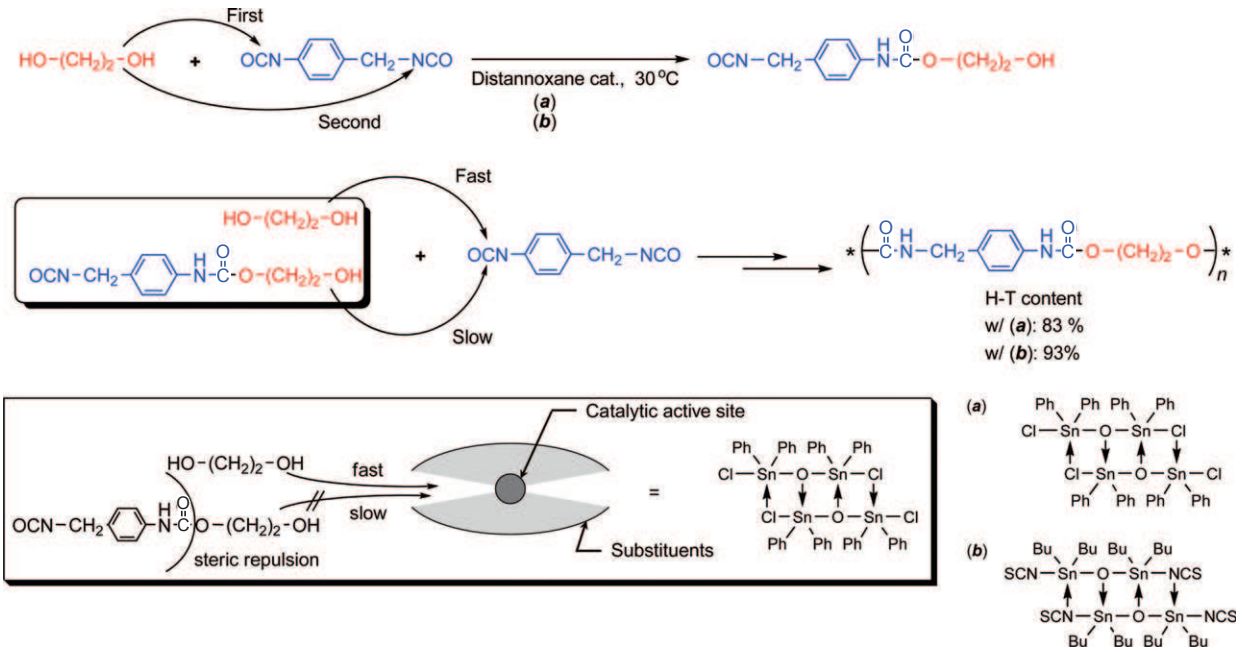
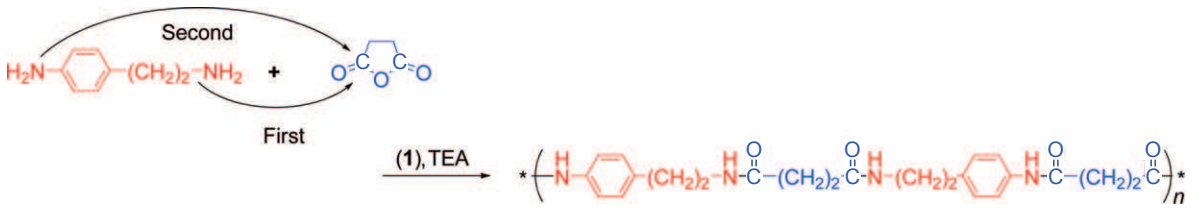


Scheme 22



Scheme 23

5.04.4 Sequential Polymers from Two Nonsymmetric Monomers

The sequential polymers (-bacd-) were prepared from two nonsymmetric monomers, XabX and YcdY, by direct polycondensation as described in the following section. The theoretical aspects of systems with two nonsymmetric monomers were studied.[43] The relevant elementary reactions and the relative reactivities of functional groups of both monomers for this polymerization can be written as follows:

$$\begin{aligned} &\text{–aX} + \text{Yc–} \xrightarrow{k_{ac}} \text{–ac–} + \text{XY}, \quad r_1 = k_{ad}/k_{ac}, \quad 0 < r_1 < 1 \\ &\text{–aX} + \text{Yd–} \xrightarrow{k_{ad}} \text{–ad–} + \text{XY}, \quad r_2 = k_{bc}/k_{ac}, \quad 0 < r_1 < 1 \\ &\text{–bX} + \text{Yc–} \xrightarrow{k_{bc}} \text{–bc–} + \text{XY}, \quad r_3 = k_{bd}/k_{ac}, \quad 0 < r_3 < 1 \\ &\text{–bX} + \text{Yd–} \xrightarrow{k_{bd}} \text{–bd–} + \text{XY} \end{aligned} \qquad [10]$$

Diad orientational arrangements produced by the above reaction are -ac-, -ad-, -bc-, and -bd-. This reaction system is schematically shown in Scheme 24.

The sequential parameter s can be defined as the probability of two consecutive nonsymmetric units pointing in the same direction and is given by

$$s = \frac{([\text{bc}] + [\text{ad}])}{([\text{ac}] + [\text{ad}] + [\text{bc}] + [\text{bd}])} \qquad [11]$$

where [bc], [ad], … denote the concentration of -bc-, -ad-, …, respectively. However, this single parameter is not sufficient to describe the possible structures obtained from the above reactions. Therefore, two more parameters, s_1 and s_2, are introduced. Here, s_1 and s_2 denote the probabilities of the two nearest -ab- and -cd- units pointing in the same direction, respectively.

$$\begin{aligned} s_1 &= \frac{([\text{acdb}] + [\text{adcb}])}{([\text{acda}] + [\text{acdb}] + [\text{adcb}] + [\text{bcdb}])} \\ s_2 &= \frac{([\text{cabd}] + [\text{cbad}])}{([\text{cabc}] + [\text{cabd}] + [\text{cbad}] + [\text{dabd}])} \end{aligned} \qquad [12]$$

All theoretically possible combinations of the values of 0, 0.5, or 1 assigned to s, s_1, and s_2, respectively, are summarized in Table 5.

Figure 3 shows the typical changes of polymer order parameters s, s_1, s_2 as a function of the monomer feed rate for the XabX + YcdY system with $r_1 = 10^{-2}$, $r_2 = 10^{-2}$, $r_3 = 10^{-4}$ and X_n (degree of polymerization) = 100. The simple mixing of two monomers at once produces the most sequential polymer, and

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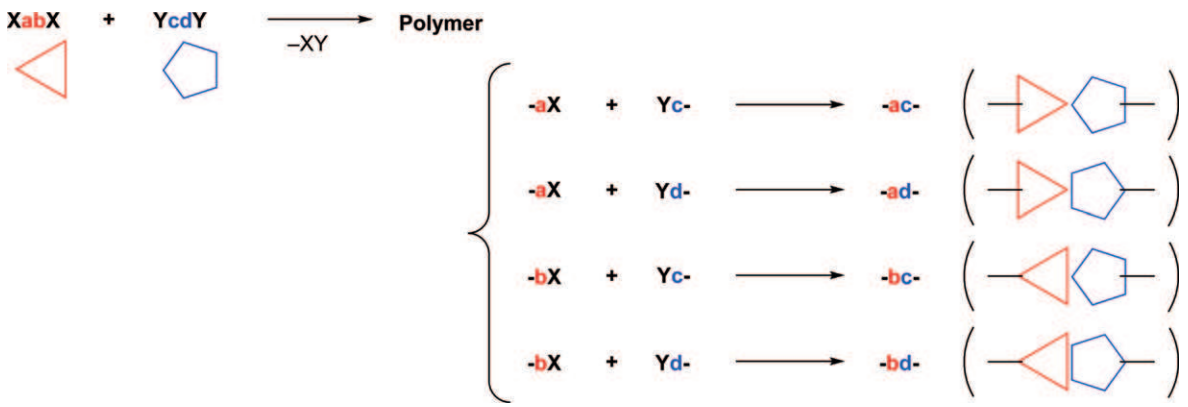

Scheme 24

Table 5 Special and limiting cases for the XabX + YcdY system

Structure		s_1	s_2	s
Ordered polymer	-(abcd)-	1	1	1
	-(abdc)-	1	1	0
	-(abcdabdc)-	1	0	0.5
	-(abcdbacd)-	0	1	0.5
	-(abcdbadc)-	0	0	0.5
Semi-ordered polymer[a]	-(abyy)-	1	0.5	0.5
	-(xxcd)-	1	1	0.5
	-(abyybayy)-	0	0.5	0.5
	-(xxcdxxdc)-	0.5	0	0.5

[a]xx is either ab or ba; yy is either cd or dc.

a synthesis of a truly random polymer is difficult in the one-step polymerization. A polymer with -bacd- sequence is obtained when the relative reactivity ratios r_1 and r_2 are both smaller than unity (less than 0.01). In this case, the first intermediate is XbacdY, which will later polymerize stoichiometrically to a fully sequential polymer (-bacd-).

5.04.4.1 One-Stage Synthesis

As a typical example for one-stage synthesis from two nonsymmetric monomers, sequential poly(urethane-urea) was prepared by polyaddition reaction of two nonsymmetric monomers, such as IBI as XabX and 4-aminophenylethyl alcohol as YcdY in the presence of DBTL.[44] Competitive model reactions were demonstrated as shown in Scheme 25, leading to the following three conclusions: (1) high nucleophilicity of an aliphatic amine such as benzylamine should not be responsible for the selectivity when it reacts with either aromatic or aliphatic isocyanate; (2) an aromatic isocyanate (e.g., phenyl isocyanate) has higher reactivity than an aliphatic isocyanate (e.g., benzyl isocyanate) because of the resonance effect between aromatic ring and isocyanate moiety, which causes the electron density of the carbon in isocyanate group to decrease;[45] and (3) comparison of an aromatic amine and an aliphatic alcohol in the reaction with phenyl isocyanate shows a selective reaction with the aromatic amine occurred to yield diphenyl urea.

On the basis of these model reactions, the ordered poly (urethane-urea) was obtained from IBI and 4-aminophenethyl alcohol as nonsymmetric monomers as shown in Scheme 26. In addition to the synthesis of the ordered polymer, authentic ordered and random poly(urethane-urea)s were prepared to verify the structure of the ordered polymer. The expected ordered structure (-abcd-) was confirmed through the comparison of the three polymers in ^{1}H and ^{13}C NMR spectroscopies. The constitutional regularity influenced the solubility, crystallinity, and thermal and mechanical properties of the polymers.

5.04.4.2 Direct Method

The selection of nonsymmetric dicarboxylic acids and diamines is a key point in the synthesis of the sequential polyamides from two nonsymmetric monomers by direct polycondensation using **1**. In aromatic acid derivatives, the positive charge on the carbonyl carbon can be delocalized into the aromatic ring, while such delocalization is not possible in aliphatic carboxylic acid derivatives. Therefore, aromatic acid derivatives have different reactivities to nucleophiles than aliphatic acid derivatives. Several dicarboxylic acids were selected as the nonsymmetric monomer. The reactivity of an aliphatic carboxylic acid, an aromatic carboxylic acid, and a substituted aromatic carboxylic acid with amines in the presence of **1** was studied (Scheme 27).

The overall second-order rate constants for the reaction of carboxylic acids such as lauric acid, benzoic acid, and *o*-toluic acid with aniline in NMP in the presence of **1** were determined. The active intermediates were the carboxylic-phosphoric mixed anhydride [R-CO-O-PO(O-Ar)$_2$], which reacted rapidly with available nucleophiles such as amines and alcohols to yield the corresponding condensation products.[46,47] However, the reactivity difference between the active intermediates and aniline was 10–50 fold, these differences were not sufficient to afford a sequential polymer. Therefore, other active intermediates were required to accomplish the ordered polymers.

When there are no nucleophiles in the reaction of carboxylic acids with the condensing agent **1**, the intermediate (e.g., carboxylic-phosphoric mixed anhydrides) reacts with the leaving group of **1** to yield an active amide (Scheme 28).

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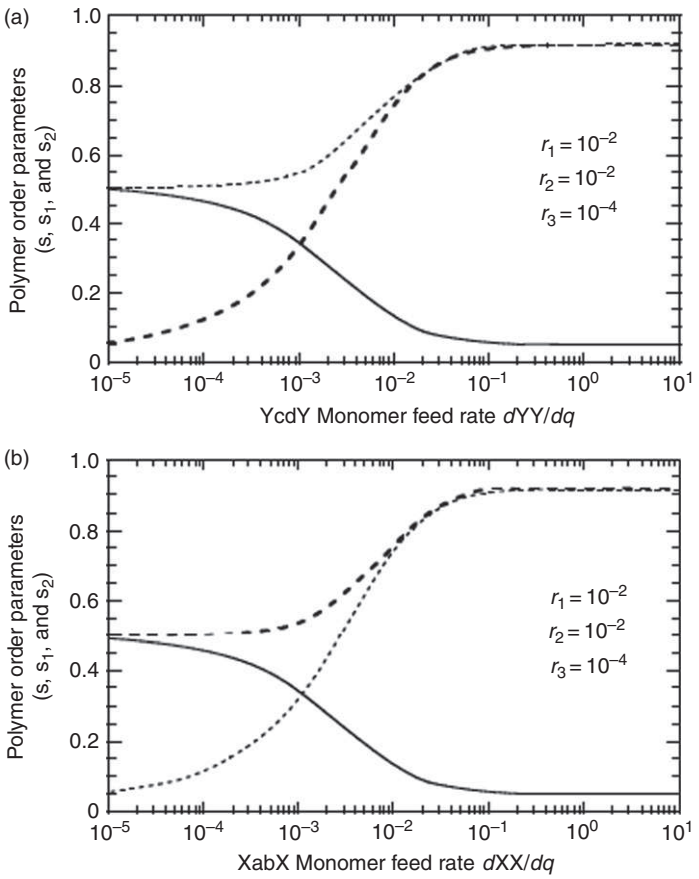
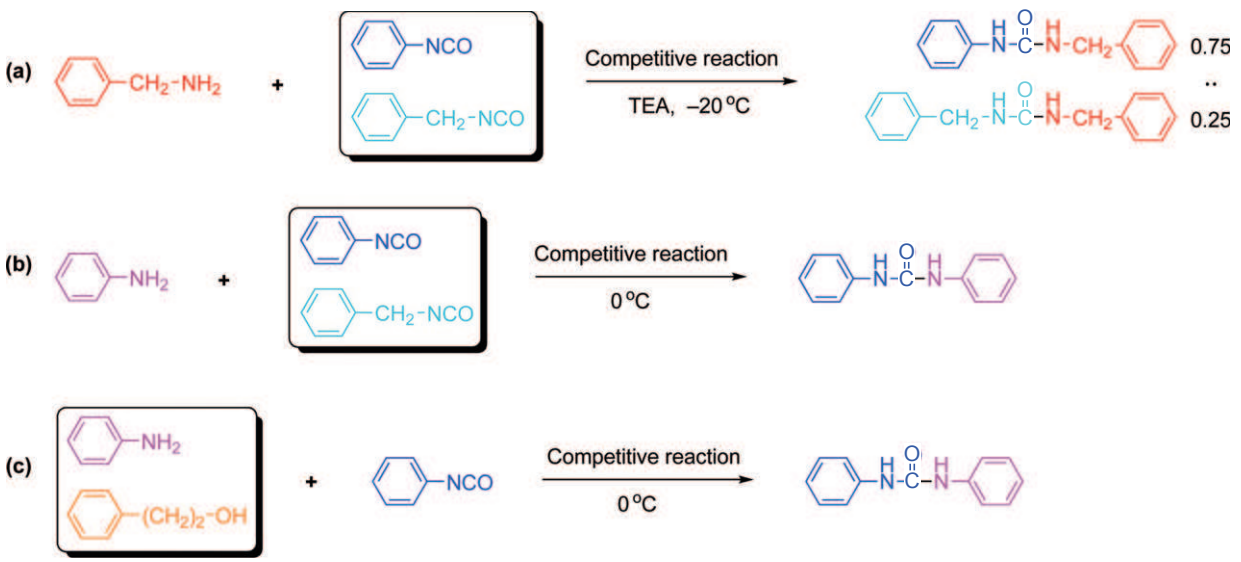


Figure 3 Polymer order parameters s (——), s_1 (– –), and s_2 (- - - -) as a function of the monomer feed rate for [XabX + YcdY] system with $r_1 = 10^{-2}$, $r_2 = 10^{-2}$, $r_3 = 10^{-4}$ and $X_n = 100$. (a) YcdY added to XabX (d YY/dθ) and (b) XabX added to YcdY (dXX/dθ). Reprinted with permission from Ueda, M. *Prog. Polym. Sci.* **1999**, *24*, 699.[8] Copyright 1999, Elsevier.



Scheme 25

The reactivity of the active amide to nucleophiles is lower than that of mixed anhydrides. Thus, a selective amidation was expected. The reaction of active amides with aniline as shown in Scheme 29 was investigated, and the overall second-order rate constants are summarized in Table 6.

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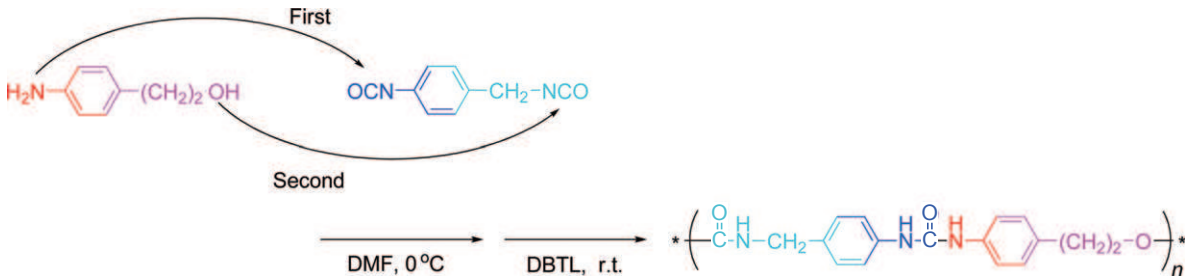
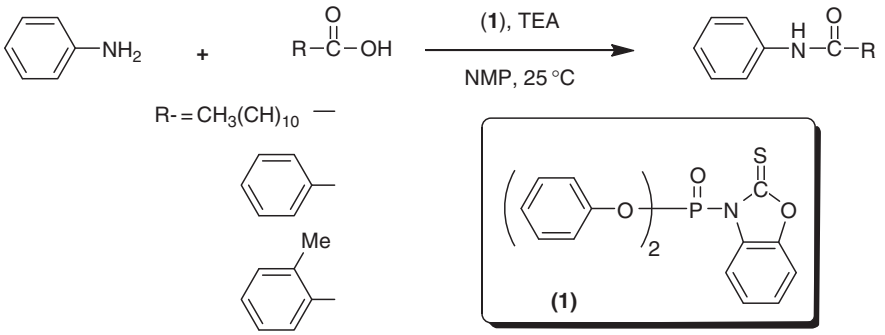
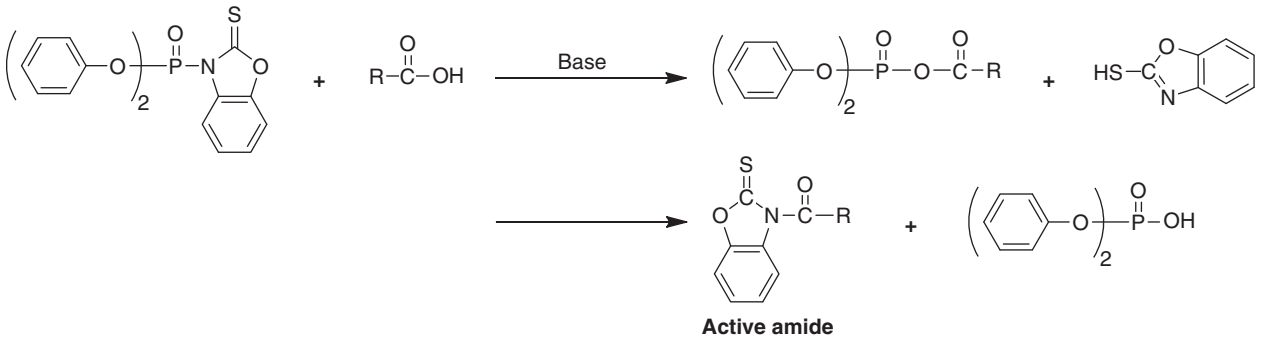


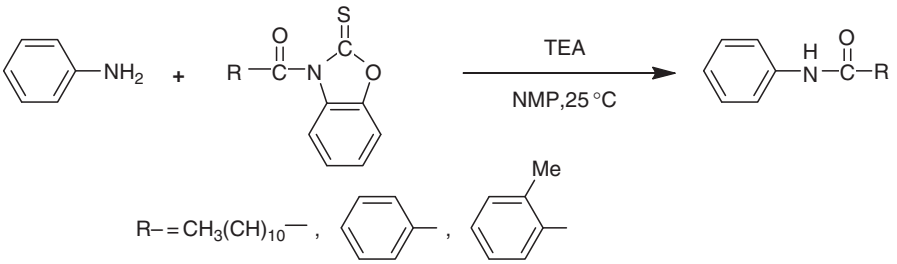
Scheme 26



Scheme 27



Scheme 28



Scheme 29

The difference in rate constants between 3-lauroylbenzoxazoline-2-thione and 3-toluoylbenzoxazoline-2-thione was almost 2×10^2 fold. Furthermore, the competitive reaction between 3-lauroylbenzoxazoline-2-thione and 3-toluoylbenzoxazoline-2-thione with benzhydrazide yielded *N′*-benzoyl laurylolhydrazide in quantitative yield, which indicated that selective amidation occurred (Scheme 30(**a**)).

As described above, there is a linear relationship with a slope of 1 between log *k* (second-order constant) and p*K*a for aniline derivatives where the reaction of benzoic acid with various anilines happens in the presence of **1** in NMP (see Figure 1). A competitive reaction between 3-lauroylbenzoxazoline-2-thione with benzhydrazide (p*K*a = 7) and aniline (p*K*a = 4) yielded a selective acylation product, *N′*-benzoyl

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Table 6 Overall second-order rate constants for the reaction of various active amides with aniline in NMP at 25 °C in the presence of **1**

Substituent R–	*Rate constant ($l\,mol^{-1}\,min^{-1}$)*
$CH_3(CH_2)_{10}$–	5.7
Phenyl-	6.3×10^{-1}
o-Tolyl-	2.6×10^{-2}

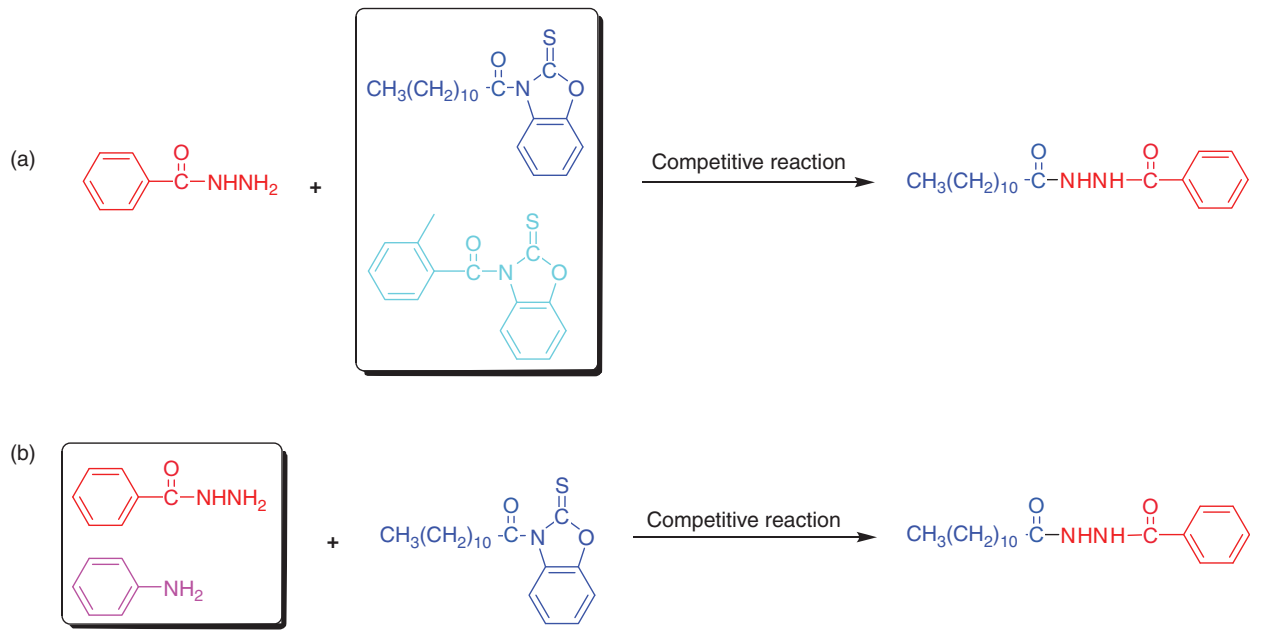
laurylohydrazide. (Scheme 30(b)). On the basis of these model reactions, a pair of dicarboxylic acids, such as 2,5-dimethylterephthalic acid (XaaX) and 4,4′-(oxydi-*p*-phenylene)dibutanoic acid (XbbX), as nonsymmetric monomers (XaaX + XbbX ≈ XabX), and 4-aminobenzhydrazide as another nonsymmetric monomer (YcdY) were selected. The actual procedure for direct polycondensation was described as follows: mixing the condensing agent **1** with two dicarboxylic acids, 2,5-dimethylterephthalic acid and 4,4′-(oxydi-*p*-phenylene) dibutanoic acid, in NMP-HMPA (hexamethylphosphoramide) (3:1) for 2 h at room temperature, followed by the addition of 4-aminobenzhydrazide. The polycondensation proceeded slowly to produce the resulting polymer. This procedure involves two main reactions: (1) activation of a carboxylic acid component as generation of an active amide from **1** and the carboxylic acid and (2) condensation of this intermediate with the amine (Scheme 31).

On the other hand, the authentic polymer was prepared as follows (Scheme 32): 4,4′-(Oxydi-*p*-phenylene)dibutanoic acid reacted with 4-aminobenzhydrazide in the presence of **1** to form 4,4′-(oxydi-*p*-phenylene)di[*N*′-(4-aminobenzoyl)butanohydrazide], which polymerized with 2,5-dimethylterephthaloyl chloride to give poly(acylhydrazide-amide).

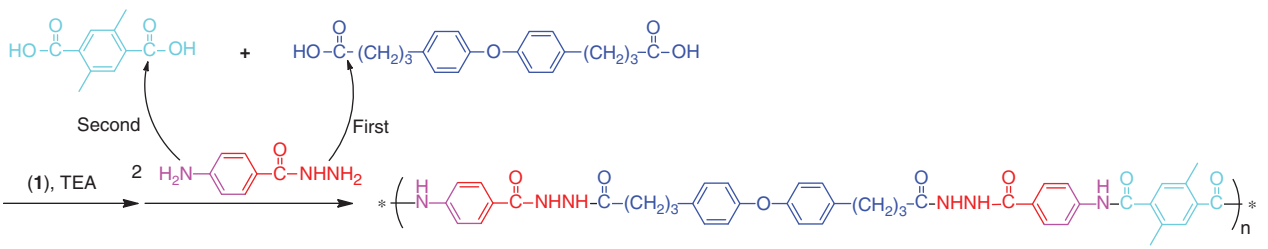
The microstructure of the polymers was determined by ^{13}C NMR spectroscopy. The spectrum of the authentic sequential polyamide was identical to that of the polyamide prepared by the direct method and completely different from that of the random polymer.[48]

Employing a similar strategy, another type of sequential polymer from a pair of symmetric monomers, 4,4′-(oxydi-*p*-phenylene)dibutanoic acid (XaaX) and 2-methoxyisophthalic acid (XbbX), with a nonsymmetric monomer (YcdY), 4-aminobenzhydrazide, was reported, where a methoxy group in place of a methyl group was used as the *o*-substituent group of the aromatic carboxylic acid (Scheme 33).[49]

In order to find another type of nonsymmetric dicarboxylic acids, a competitive reaction of anisic acid and 2,4,6-trichlorophenyl



Scheme 30



Scheme 31

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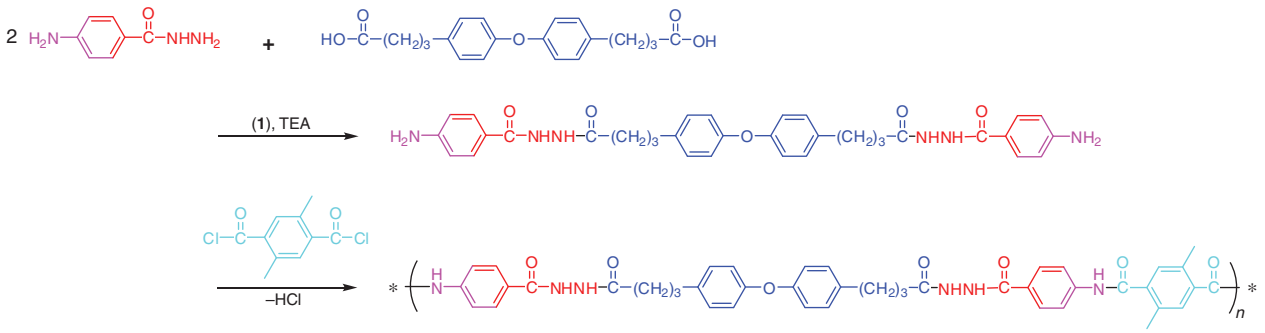
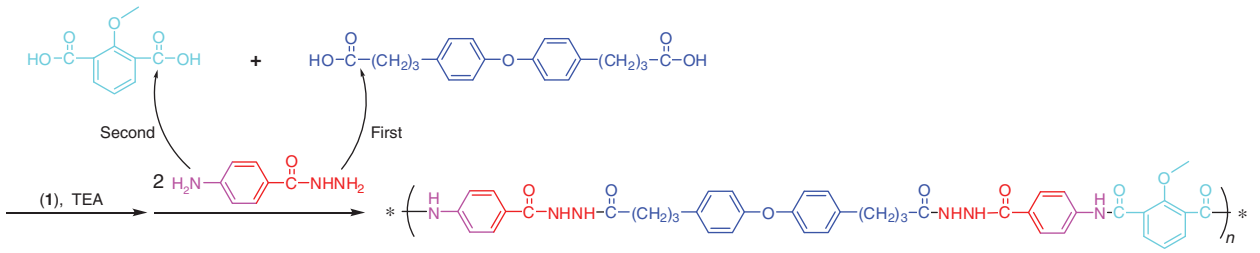
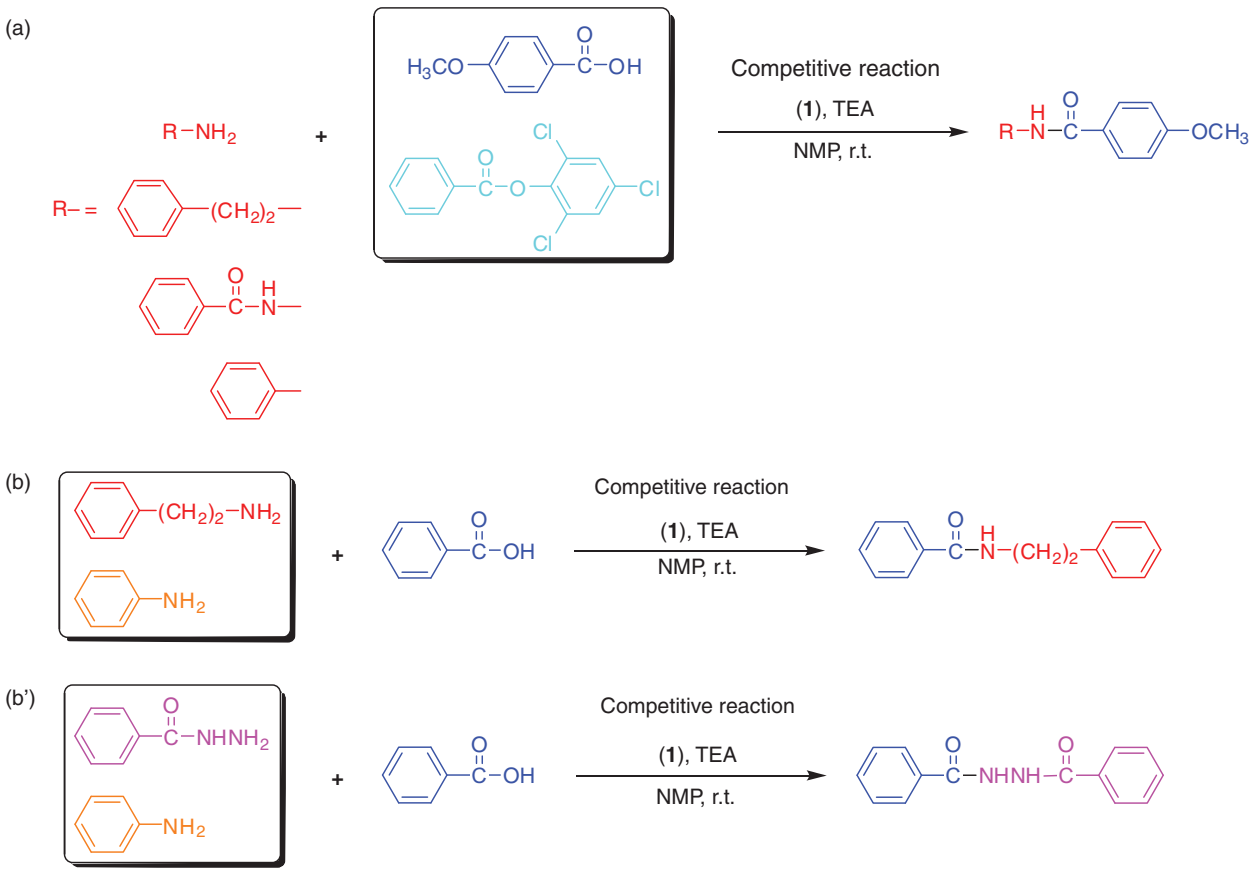


Scheme 32



Scheme 33



Scheme 34

benzoate with amines such as phenethylamine, benzhydrazide, and aniline was conducted in a condition of direct condensation in the presence of **1** and TEA.[50] It was found that selective amidation was observed in all cases, and thus *N*-phenethyl-4-methoxybenzamide, *N'*-benzoyl-4-methoxybenzhydrazide, and 4-methoxybenzanilide were obtained in quantitative yields (Scheme 34(**a**)).

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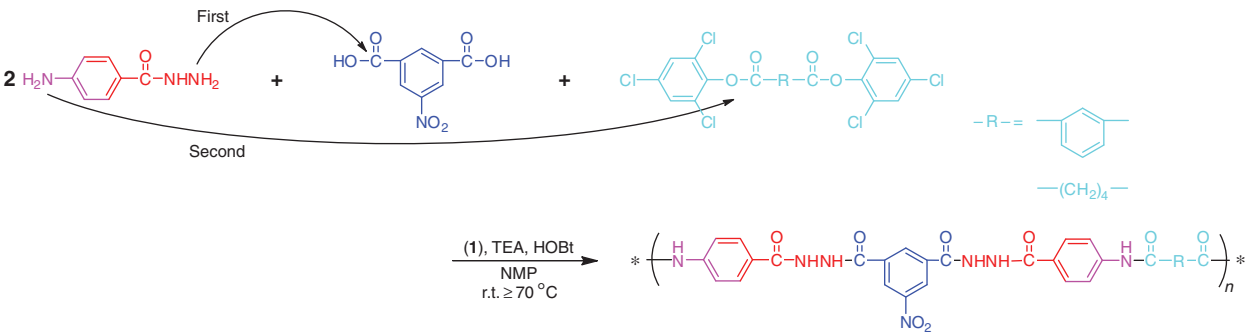
For the selection of nonsymmetric amines, competitive reactions between phenethylamine (p*Ka* = 10) or benzhydrazide (p*Ka* = ~7) and aniline (p*Ka* = 4) with benzoic acid were studied and found that the desired products, *N*-phenethylbenzamide and *N*′-benzoylbenzhydrazide, were formed in quantitative yields (Schemes 34**(b)** and 34**(b)**).

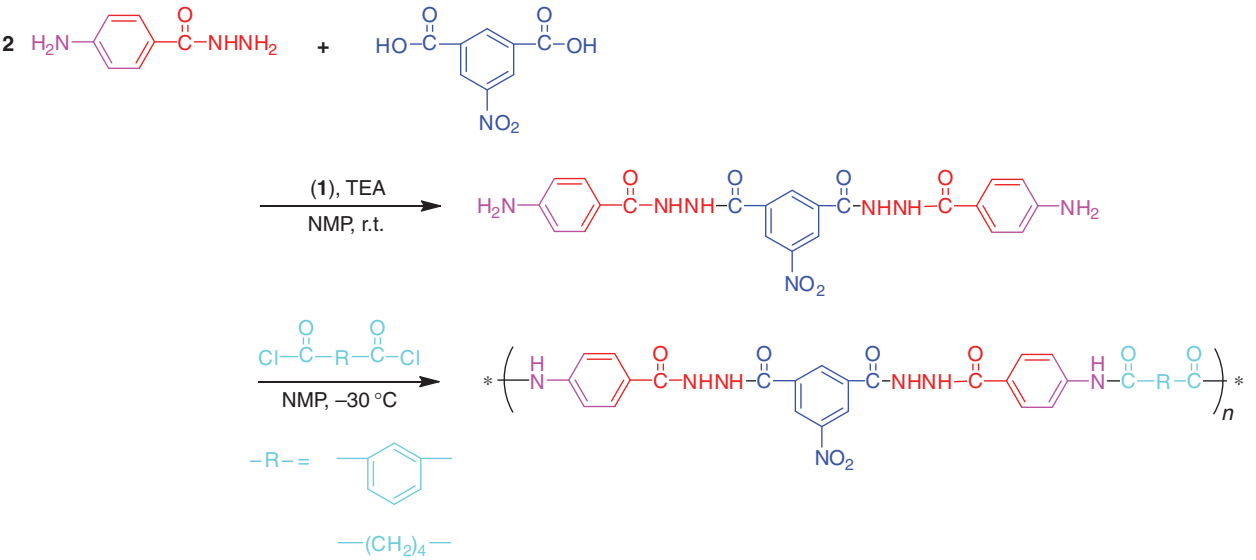
Based on these model reactions, the direct polycondensation of a pair of two dicarboxylic acid derivatives, bis(2,4,6-trichlorophenyl)isophthalate or bis(2,4,6-trichlorophenyl)adipate (XaaX) and 5-nitroisophthalic acid (XbbX) to play the role of nonsymmetric monomer (XabX), and 4-aminobenzhydrazide as a nonsymmetric monomer (YcdY) was performed by using **1**, and the sequential polyamides (-aadcbbcd-) were obtained in quantitative yields (Scheme 35).

For the comparison with the polymer obtained in direct method, authentic sequential and random polyamides were prepared as shown in Schemes 36 and 37. The authentic sequential polyamides were obtained by the low-temperature solution polycondensation of isophthaloyl chloride or adipoyl chloride with *N*,*N*′-bis(4-aminobenzoyl)-5-nitroisophthalhydrazide, which had been prepared from 5-nitroisophthalic acid and 4-aminobenzhydrazide.

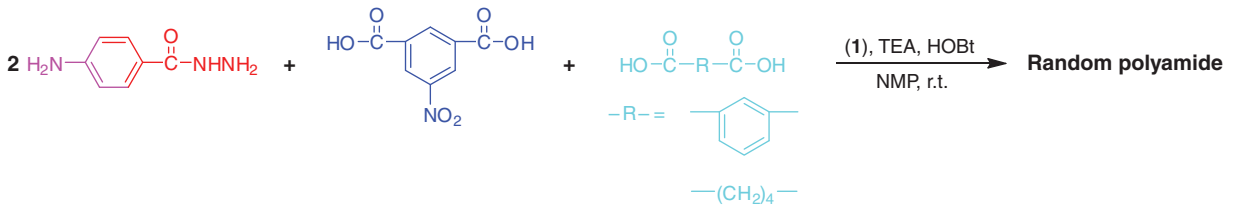
A random polyamide was synthesized by simultaneously mixing 5-nitroisophthalic acid, isophthalic acid, and



Scheme 35



Scheme 36



Scheme 37

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4-aminobenzhydrazide in the presence of **1** (Scheme 37). A similar procedure was utilized for the preparation of another random polyamide by replacing isophthalic acid with adipic acid. The microstructure of each polymer was determined by ^{13}C NMR spectroscopy, and the formation of the desired sequential polyamide was confirmed.

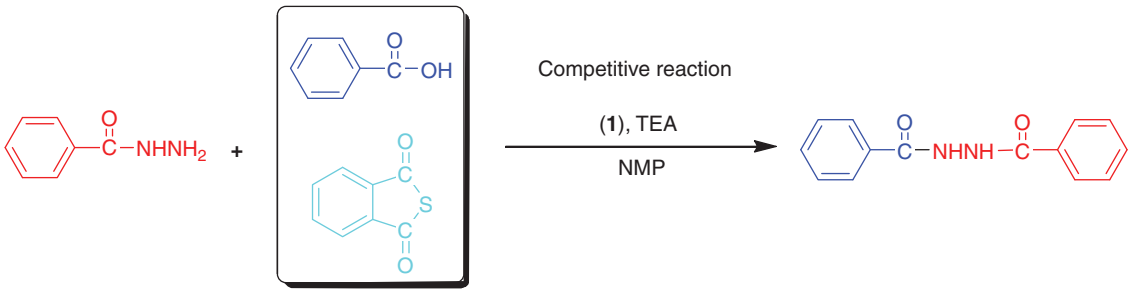
A sequential poly(acylhydrazide-imide) was prepared by direct polycondensation of two nonsymmetric monomers, trimellitic thioanhydride (XabX) and 4-aminobenzhydrazide (YcdY), where phthalic thioanhydride was used as a substitute for the active ester.[51] Phthalic thioanhydride reacts with amines to give *N*-substituted phthalimides without the formation of amic acid, which may induce unfavorable side reactions.[52] The competitive reaction between phthalic thioanhydride and benzoic acid with benzhydrazide in the presence of **1** produced a single product, *N'*-benzoylbenzhydrazide (Scheme 38).

A direct polycondensation was carried out by mixing both monomers in the presence of **1** and TEA in dipolar aprotic solvents at room temperature, yielding the sequential poly (acylhydrazide-imide) (Scheme 39).

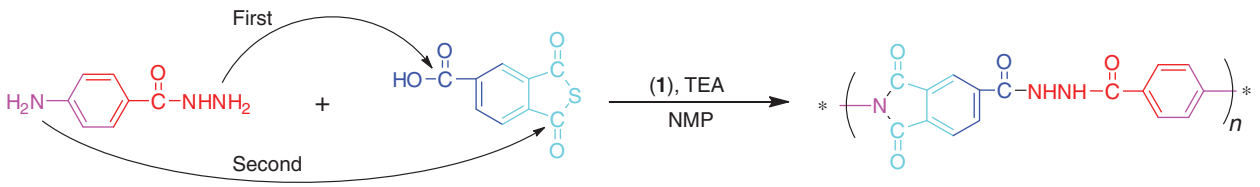
Polyaddition reaction was combined with polycondensation to prepare a sequential polymer. A sequential poly (amide-ester-thioether) was obtained using **1** by direct poly (addition-condensation) of 4-(acryloyloxy)benzoic acid (XabX) and 4-aminobenzenethiol (YcdY).[53]

The competitive reaction between benzenethiol and aniline with phenyl acrylate yielded phenyl 3-phenylthiopropanoate, which indicated that the selective addition reaction of benzenethiol occurred (Scheme 40).

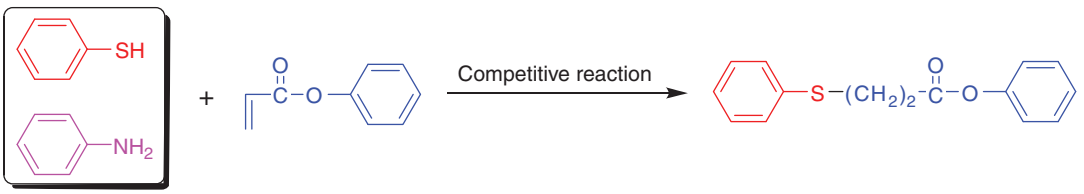
The sequential poly(amide-thioether) was obtained by mixing both monomers, 4-(acryloyloxy)benzoic acid and 4-aminobenzenethiol, in the presence of **1** and TEA in NMP at room temperature (Scheme 41). The microstructure of the polymers obtained was investigated by ^{13}C NMR spectroscopy, proving that the polymers had the expected sequential structure.



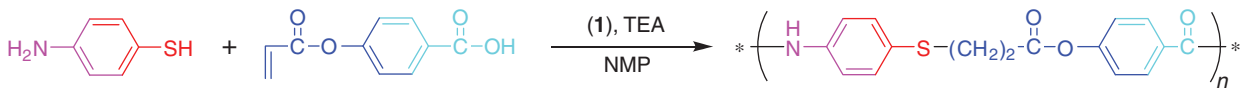
Scheme 38



Scheme 39



Scheme 40



Scheme 41

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5.04.5 Sequential Polymer from Three Nonsymmetric Monomers

The synthesis of a sequential (-abcdef-) polymer from three nonsymmetric monomers, XabX, YcdY, and ZefZ by direct polycondensation was also reported. The selectivity of electrophilicity and nucleophilicity are extremely important considerations in choosing nonsymmetric monomers. To accomplish the synthesis of a sequential (-abcdef-) polymer from three nonsymmetric monomers, three types of nucleophiles and electrophiles must be selected.[54]

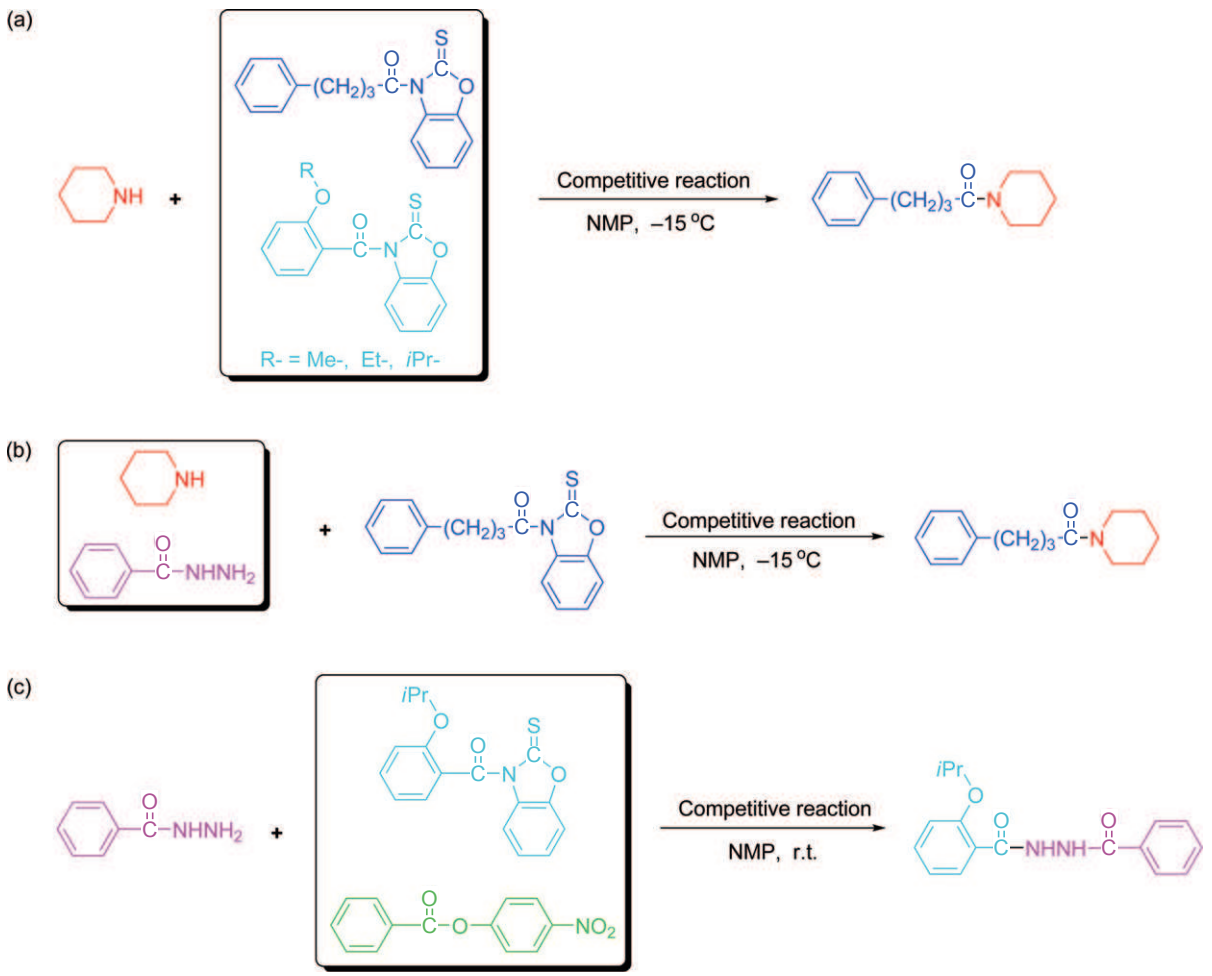
5.04.5.1 Direct Method

As for carboxylic acid components, an aliphatic carboxylic acid, an *o*-substituted aromatic carboxylic acid, and an active ester were employed. An aliphatic amine, an acylhydrazide, and an aromatic amine were selected as the amine components. The results of various model reactions indicated that (1) selective amidation was observed in the reaction of *N*-(4-phenylbutanoyl)benzoxazoline-2-thione with piperidine (Scheme 42(**a**)), (2) a competitive reaction of *N*-(4-phenylbutanoyl) benzoxazoline-2-thione with piperidine and benzhydrazide produced *N*-piperidyl-4-phenylbutyric amide (Scheme 42(**b**)), and (3) the aminolysis of *N*-(*o*-isopropoxybenzoyl)benzoxazoline-2-thione and 4-nitrophenyl benzoate to benzhydrazide yielded *N*′-benzoyl(2-isopropoxy) benzhydrazide (Scheme 42(**c**)).

Based on these results, 5-(3-carboxypropyl)-2-isopropoxybenzoic acid (XabX) and bis(4-nitrophenyl) isophthalate (XccX), as the carboxylic acid components, and piperazine (YddY) and 4-aminobenzhydrazide (YefY) as the amine components were used for the direct synthesis of a sequential (-abcdef-) polymer. A direct polycondensation of these monomers in the presence of **1** produced the desired polymer (Scheme 43). The microstructure of the polymer was determined by comparing the ^{13}C NMR spectrum of the product with that of the authentic sequential polymer.

Polyaddition reaction is also a useful synthetic method for producing sequential polymers as described in the previous section (see Schemes 38 and 39). The poly(addition-condensation) method was successfully applied in the preparation of a sequential polymer from three nonsymmetric monomers, using an acylhydrazide, an aromatic amine, and a thiol as nucleophiles, and a carboxylic acid, an active ester, and a vinyl ester as electrophiles.[55]

A competitive reaction between benzoic acid and 4-nitrophenyl acetate with amines such as benzhydrazide and



Scheme 42

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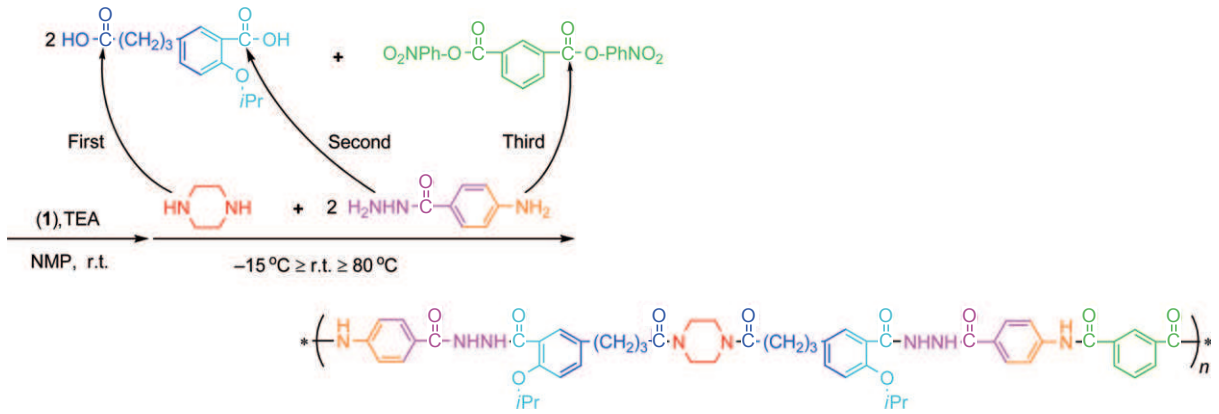
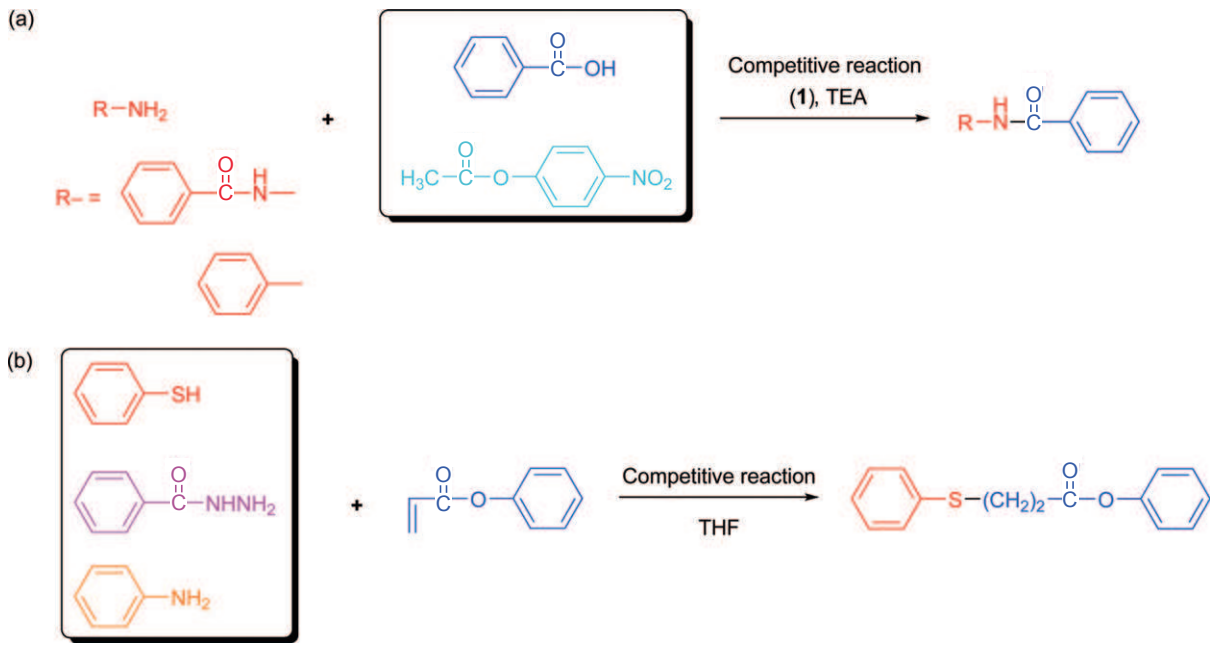


Scheme 43

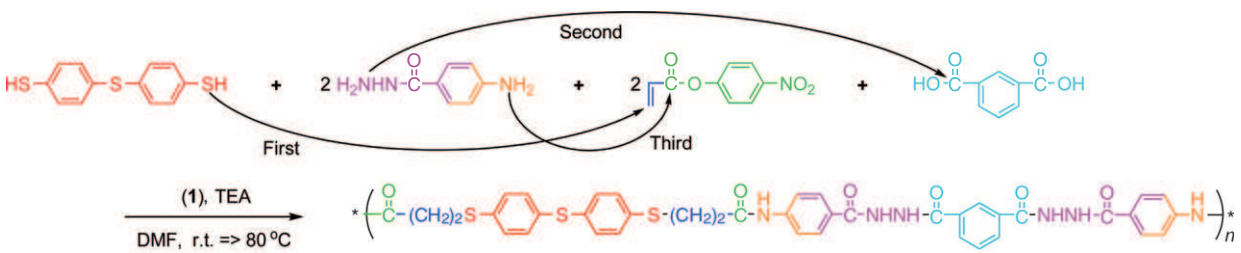
aniline formed dibenzoylhydrazine and benzanilide, respectively (Scheme 44(a)). A competitive addition reaction of phenyl acrylate with benzenethiol, benzhydrazide, and aniline yielded phenyl 3-phenylthiopropanoate (Scheme 44(b)).

The sequential (-abcdef-) polymer was prepared directly from two nonsymmetric monomers, 4-nitrophenyl acrylate (XabX) and 4-aminobenzhydrazide (ZefZ), and a pair of symmetric monomers, that is, a pair of 4,4′-thiobisbenzenethiol (YccY) and isophthalic acid (YddY), which is regarded as a nonsymmetric monomer YcdY (Scheme 45).

The authentic sequential polymers were synthesized as follows: bis(4-nitrophenyl) 3,3′-[thiobis(4,1-phenylenethio)]bis



Scheme 44



Scheme 45

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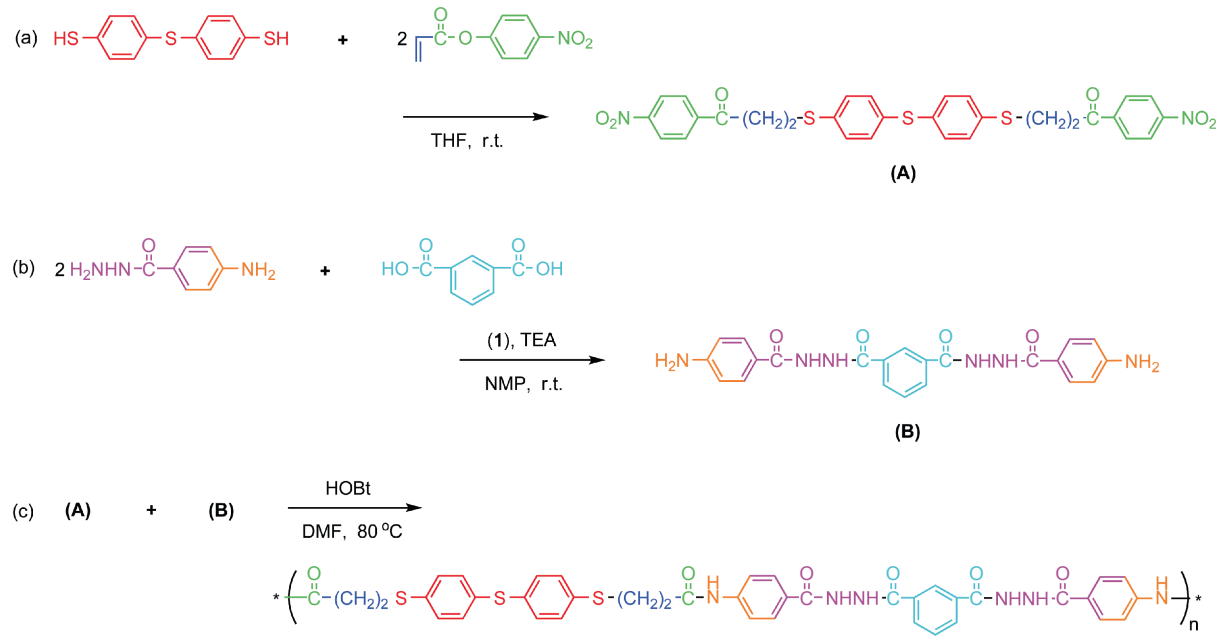

Scheme 46

(propanoate) was prepared by the addition reaction of 4-nitrophenyl acrylate with 4,4′-thiobisbenzenethiol (Scheme 46(a)), and *N*′,*N*′-bis(4-aminobenzoyl)isophthalhydrazide was prepared by condensation of isophthalic acid with 4-aminophenylhydrazide in the presence of **1** (Scheme 46(b)), respectively. Then, the authentic sequential polymer was prepared by the polycondensation of *N*′,*N*′-bis(4-aminobenzoyl)isophthalhydrazide and bis(4-nitrophenyl) 3,3′-[thiobis(4,1-phenylenethio)]bis (propanoate) (Scheme 46(c)). The ^{13}C NMR spectra of the authentic ordered polymer and the polymer prepared by poly (addition- condensation) were identical.

5.04.6 Conclusions

The precise syntheses of sequential condensation polymers from nonsymmetric monomers using either the one-stage method or the direct method have been reviewed. The control of the sequence regularity of the polymers is strongly dependent on kinetic factors. Therefore, only a limited number of polymers can be prepared by these synthetic techniques. If thermodynamic factors such as a template polymerization are taken into consideration for the sequence regularity, more complex sequence control such as a synthesis of sequential polymers derived from four nonsymmetric monomers would be accomplished. Furthermore, the reactivity of carboxylic derivatives to nucleophiles should be controlled more precisely because selective amidation of carboxylic acids would not be perfect using condensing agents. Therefore, a combination of three suitable carboxylic acid components and condensing agents must be developed.

One of the goals of precision polycondensation is accurate sequence control. However, the synthetic methodology is still in its infancy probably because of poor selectivity between functional groups. Thus, more research and development are still required for the synthetic methodology as well as to establish an efficient and general preparative method for the sequential polymers. The discovery of an efficient method for the synthesis of sequential polymers is important for the investigation of fundamental physical properties of such polymers and thus would make this research area very attractive for further study.

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Biographical Sketches

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5.05 Nonstoichiometric Polycondensation

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5.05.1 Introduction

It is necessary to allow the reaction to proceed to a high degree of conversion in order to prepare high molecular weight polymer in condensation polymerization, which means the content of molecular end-group should be decreased. This will generally be possible only when an equal amount of functional groups is maintained throughout the reaction. Not only must the reaction be initiated with stoichiometrically balanced ratio of two functional groups, but the system must also be free of impurities that contain the same functional groups. It had been well known that the stoichiometric balance of functional groups influences the molecular weight of polymers prepared by polycondensation.[1]

Here, let us consider polycondensation of a monomer having two functional groups A with a monomer having two functional groups B. The number of functional groups A and B is represented by N_A and N_B, respectively, and it is assumed that the functional groups B are in excess of the functional groups A ($N_A < N_B$). Polymerization proceeds under nonstoichiometric condition. The initial number of these monomers is given by

$$(N_A + N_B)/2 = [N_A(1 + 1/r)]/2 \quad (r = N_A/N_B < 1)$$

When polymerization proceeds in a step-growth manner and the extent of the reaction reaches p, the numbers of unreacted functional groups A and B are given by $N_A(1 - p)$ and $N_B - N_A p$, respectively. Thereby, the total number of the remaining functional groups is given by

$$N_A(1-p) + (N_B - N_A p) = N_A[2(1-p) + (1-r)/r]$$

The number-average degree of polymerization (DPn) is described in terms of p and r by

$$\mathrm{DPn} = \frac{N_A(1 + 1/r)/2}{N_A[2(1-p) + (1-r)/r]/2} = \frac{1+r}{2r(1-p) + (1-r)} \qquad [1]$$

For $r < 1$, an excess of the functional groups B will be present and the reaction is, therefore, complete when all the functional groups A have reacted. Hence, the maximum DPn (DPn_{max}) possible corresponds to complete conversion of the functional groups A ($p = 1$) and it is given by

$$\mathrm{DPn}_{max} = \frac{1+r}{1-r} \qquad [2]$$

This relation between DPn_{max} and r clearly indicates the necessity of using very pure monomers and ensuring exact stoichiometric balance between two reactive functional groups. An absence of side reactions that destroy stoichiometry must be guaranteed to produce high-molecular-weight polymers in good yield.

However, this discussion is based on the assumption that the reactivity of the functional groups of the molecular chain end is not changed throughout the polymerization and the reaction proceeds stochastically. It is also assumed that polymerization proceeds linearly and cyclic polymer does not form. Furthermore, this is also based on the assumption that polymerization proceeds in a homogeneous system. If the reactivity of a functional group increases when the other functional group has reacted, then the condensation polymerization yields high molecular weight polymers even under the condition of stoichiometric imbalance between two functional groups. Alternatively, if polymerization proceeds in a heterogeneous system, that is, immiscible two liquid phases or solid–liquid phase, stoichiometric imbalance is not of great importance to prepare high molecular weight polymers because the migration of monomers or oligomers from one phase to another phase greatly influences polymerization.

A few studies on the preparation of polymers under nonstoichiometric condition have been reported since the 1970s. For instance, the polymerization of dichlorobenzene and sodium sulfide yielded poly(*p*-phenylene sulfide), but this polymerization did not obey the classical polycondensation theory.[2–4] Yields and molecular weights of polymers were adequate at incomplete monomer conversion. Stoichiometric balance of monomers was not necessary to obtain high-molecular-weight polymers. Another example was the synthesis of polybenzoxazole under nonstoichiometric condition.[5] Polymerization of 4,6-diaminoresorcinol dihydrochloride (DAR) with terephthaloyl chloride (TPC) in the presence of P_2O_5 and polyphosphoric acid had been studied by varying the molar ratio of DAR and TPC in feed. When the monomers were present in equimolar amounts, polymerization gave the highest molecular weight polymer (the inherent viscosity of the polymer was 26.0 dl g^{-1} when measured in methanesulfonic

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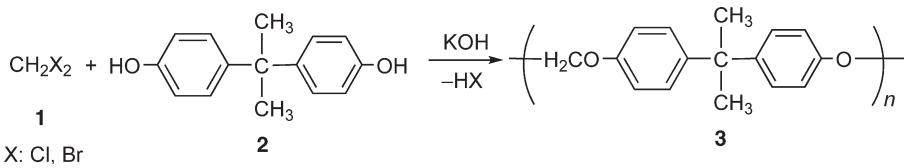
acid at 25 °C). However, when polymerizations were carried out at the molar ratio of DAR and TPC of 1:1.025 and 1:1.05, then also high-molecular-weight polymers were formed, the inherent viscosities of which were 23.0 and 24.0 dl g^{-1}, respectively. In contrast to these, polymerization at the molar ratio of DAR and TPC of 1.05:1 gave only low-molecular-weight polymer, the inherent viscosity of which was 4.8 dl g^{-1}. A substantial molar excess of TPC over DAR did not lower the molecular weight, and high-molecular-weight polymer could be prepared under nonstoichiometric condition. Recently, numerous means of polymer synthesis under nonstoichiometric condition have been found and their mechanisms have also been clarified. The nonstoichiometric polycondensation is quite useful to prepare high-molecular-weight polymers when it is difficult to maintain the stoichiometric condition between two monomers due to side reactions and physical loss from the polymerization system by sublimation or evaporation of the monomers.[6,7]

In this chapter, nonstoichiometric polycondensation is described by categorizing polycondensation into that caused by the change in reactivity and that caused by the change in the structure of polymers. In other words, nonstoichiometric polycondensations are categorized based on the chemical effect and the physical effect (see Chapter 5.02).

5.05.2 Nonstoichiometric Polycondensation Caused by the Change in Reactivity

5.05.2.1 Polycondensation of α,α-Dihalomonomers

A well-known example of stoichiometrically imbalanced polycondensation is the formation of polyformal as shown in Scheme 1.[8,9] Polycondensation of dihalomethane (**1**) such as dibromomethane and dichloromethane with potassium and sodium salt of bisphenol such as bisphenol A (**2**) and hydroquinone gave a high-molecular-weight polyformal (**3**) even when dihalomethane was in excess. When **2** was reacted with dichloromethane (**1**) and excess potassium hydroxide pellets in the presence of monomethyltricaprylyl ammonium chloride (MTCAC) as a phase transfer catalyst (PTC) in dichloromethane as solvent, precipitates of the dipotassium salt were obtained, which gradually disappeared over a long period leaving a viscous solution containing a precipitate of potassium chloride and excess potassium hydroxide. This polymerization initially proceeded in suspension. **1** was used not only as a monomer but also as a solvent, and therefore the stoichiometric balance between **1** and **2** was broken. For example, **2** (0.5 mol) and **1** (11.9 mol) were polymerized,[10] and in the other polymerization reaction **2** (1.99 mol) was polymerized with **1** (9.7 mol) in the mixed solvent of **1** and 1-Methy-2-pyrrolidinone (NMP).[8] The results of polymerization are presented in Table 1.[8] **3** was obtained with a yield of 49% by polymerization at 25 °C for 18 h and precipitation into methanol (run no. 1 in Table 1) even under nonstoichiometric condition. Intrinsic viscosity (η) of the polymer, which is usually used as a measure of molecular weight, was 0.31 dl g^{-1}. At 35 °C, higher molecular weight polymers were formed with higher yield (run no. 2 in Table 1). When polymerization was carried out in a mixed solvent of **1** and chlorobenzene, the polymers were obtained with a yield of 93% (run no. 3 in Table 1). At higher temperature, the molecular weight did not increase due to thermal decomposition. When polymerization was performed in the mixed solvent of **1** and NMP, which was a polar aprotic solvent, in the absence of PTC, polymerization proceeded at a faster rate (run no. 4 in Table 1). The formation of formals is an irreversible reaction. In the polyformal reaction, the intermediate (**5**) having halomethyl ether group is first formed, and this intermediate is much more reactive than the dihalomethane as shown in Scheme 2. The bisphenol salt (**4**) preferentially reacts with the more reactive halomethyl ether groups rather than dihalomethane. The intermediate **5** then reacts with **4** to give intermediate (**6**) or with another **5** to give **7**. Thus, the polymer



Scheme 1 Synthesis of **3**.

Table 1 Results of polymerization of dichloromethane with **2**[a]

	Polymerization conditions						
Run no.	*Base*	*Solvent*[c]	*PTC*	*Temp (°C)*	*Time (h)*	*Yield (%)*	*[η]*[b] *(dl g⁻¹)*
1	KOH	CH_2Cl_2	MTCAC	25	18	49	0.31
2	KOH	CH_2Cl_2	MTCAC	35	21	70	0.60
3	NaOH	CH_2Cl_2/chlorobenzene	MTCAC	75	4	93	0.57
4	NaOH	CH_2Cl_2/NMP	None	70	1	78	0.58

[a]Polymerizations were carried out in the presence of MTCAC.
[b]Measured in chloroform at 25 °C.
[c]An excess amount of CH_2Cl_2 to bisphenol A was used not only as a monomer but also as a solvent.
MTCAC, monomethyltricaprylyl ammonium chloride; PTC, phase transfer catalyst.
Cited from Hay, A. S.; Williams, F. J.; Relles, H. M.; Boulette, B. M. *J. Macromol. Sci. Chem.* **1984**, *A21*, 1065.

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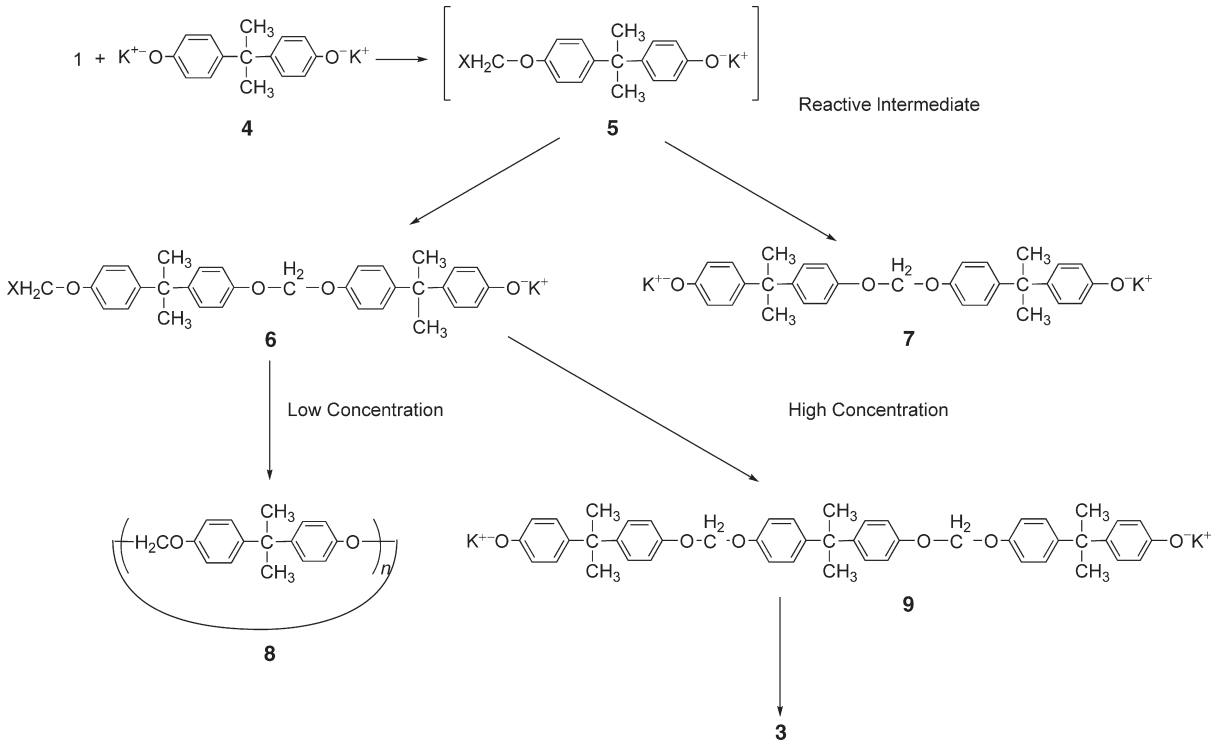
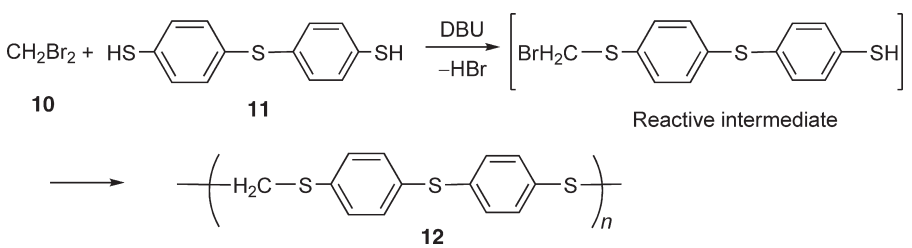


Scheme 2 Formation of **3** from **1** and **2**. Miyatake, K.; Hlil, A. R.; Hay, A. S. *Macromolecules* **2001**, *34*, 4288.[11]

end-groups are always the phenol salt, not the halomethyl group, even in the presence of excess dihalomethane, and then polymerization proceeds in a condensative chain manner without termination with dihalomethane. Under normal stirring conditions where the salt goes very slowly into solution, the concentration of the salt is low, so that **6** could react with itself to give a cyclomer **8**.[11] Higher analogs of **6** could also give cyclomers when the concentration of the salt in solution is low, thus contributing to a broad molecular weight distribution. Under high-intensity mixing conditions, the concentration of the salt is high, so that **6** and its higher analogs would preferentially react with the salt. The soluble intermediate (**9**) and **7** could react with dihalomethane to give reactive halomethyl intermediates. The continuous reaction cycle suppresses the formation of cyclomers, producing high molecular weight polymer. When polymerization was carried out at room temperature by the addition of the bisphenol A potassium salt into the solution of dibromomethane in NMP over several hours, **3** was formed with Mn of 4.96×10^4 and a bimodal and broad distribution (Mw/Mn = 3.1). In addition, this **3** contained 23% cyclomers. On the other hand, when the salt was vigorously stirred, followed by the addition of dibromomethane, high molecular weight polymer with a narrow distribution (Mn = 2.5×10^5, Mw/Mn = 1.3) was obtained after vigorous stirring for only 5 min without the formation of cyclomers.

Polycondensation of dibromomethane (**10**) with 4,4′-thiobisbenzenethiol (**11**), shown in Scheme 3, also gives high-molecular-weight poly(phenylene thioether) (**12**) under nonstoichiometric condition.[12] Although the polymerization of **1** with **2** to yield **3** proceeded in suspension, this polymerization proceeded in homogeneous solution. The polymerizations of **10** with **11** were carried out by varying the molar ratio of the monomers in feed, that is, by varying S (=$[\mathbf{10}]_{\text{init.}}/[\mathbf{11}]_{\text{init.}}$), in the presence of 1,8-diazabicyclo [5,4,0]-undec-7-ene (DBU) in NMP at 75 °C. Figure 1 shows the plots of the inherent viscosity (η_{inh}) of **12** prepared for 2 and 4 h as a function of S values. Although the molecular weight of the polymers depended on S values in the



Scheme 3 Synthesis of **12** from **10** and **11**.

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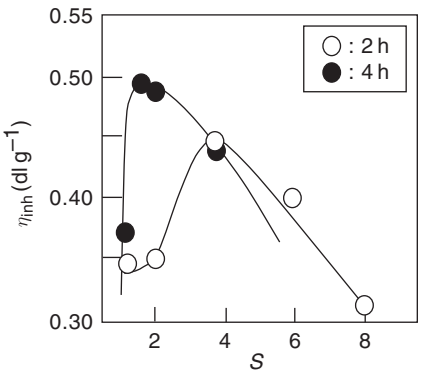


Figure 1 Plots of η_{inh} of polymer **12** prepared for 2 and 4 h as a function of Iimori, H.; Shibasaki, Y.; Ando, S.; Ueda, M. *Macromol. Symp.* **2003**, *199*, 23.[12]

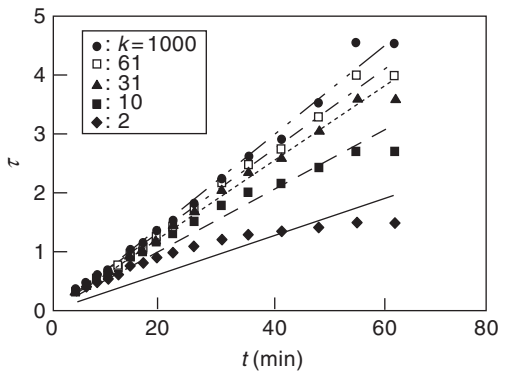
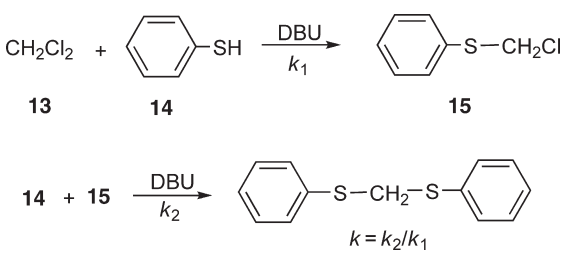


Figure 2 Relationship between real time (t) and normalized time (τ) for various κ values. Reproduced from Iimori, H.; Shibasaki, Y.; Ando, S.; Ueda, M. *Macromol. Symp.* **2003**, *199*, 23.[12]

polymerization, the polymer was formed at $S > 1$ under nonstoichiometric condition. The highest η_{inh} values of 0.44 and 0.50 dl g^{-1} were obtained by the polymerization at S of 4 for 2 h and at S of 1.5 for 4 h, respectively, and the large nonstoichiometric imbalance makes the time when the highest polymer is formed shorter. Increasing the polymerization time to greater than 2 h at S of 4 and 4 h at S of 1.5 did not increase molecular weight, suggesting that polymerizations were already terminated. High-molecular-weight **12** is obtained even in the presence of an excess amount of **10**. The model reaction of thiophenol (**14**) and **10** was examined to estimate the kinetics of this polymerization. However, the reaction was too fast to analyze even at −25 °C, and therefore the model reaction of **14** with dichloromethane (**13**) instead of **10** was performed at 25 °C (**Scheme 4**). The reaction time was normalized as τ ($=k_1[\mathbf{13}]_{init.}t$) and the values of τ were calculated by assuming a certain ratio of two reaction rates κ ($=k_2/k_1$). Based on the definition of τ, it should be linearly proportional to real time t. The value of κ is estimated by the linearity between t and τ. The calculated τ values were plotted as a function of t with varying κ values as shown in **Figure 2** and the correlation coefficients (R^2) of linear relationship between t and τ were calculated. When the value of κ was 61, the maximum R^2 value of ~0.993 9 was obtained, and therefore it was concluded that the second nucleophilic substitution reaction of **14** with intermediate (**15**) occurred 61 times faster than the first one. This kinetic consideration revealed that **15** formed by the substitution of one chlorine with the mercapto group reacted much faster than dichloromethane, and this high reactivity of the intermediate leads to high molecular weight polymers even under nonstoichiometric condition.



Scheme 4 Model reaction of **13** with **14**.

Synthesis of polyorthocarbonate (**16**) is a very well-known and clear example of nonstoichiometric polycondensation.[13] 2,2-Dichloro-1,3-benzodioxole (**17**) reacts with **2** to form a reactive intermediate **18** as shown in **Scheme 5**. Polycondensation of **17** with excess **2** resulted in low-molecular-weight polymer, as summarized in **Table 2**. On the other hand, polycondensation of excess **17** with **2** gave high-molecular-weight **16**. Although the maximum Mn of the polymer by polycondensation of 1.7 equivalents of **17** with **2** was calculated as 693 according to eqn [2], the molecular weight reached 1.2×10^5 after 3-h refluxing in dichlorobenzene. A model reaction was examined as shown in **Scheme 6** to estimate the kinetics of this polymerization (rate constants k_1 and k_2). Phenol (**19**) was used instead of **2** to estimate the ratio of the corresponding rate constants k_1' and k_2' because two phenolic OH groups in **2** possessed similar reactivity and the ratio of two reaction rates κ ($=k_1/k_2$) was expected to be comparable to k_1'/k_2'. The model reaction was conducted in dichloromethane at −40 °C, which was lower than the polymerization temperature, to decrease reaction rate for precise estimation. Although **17** and diphenyl orthocarbonate (**21**) were detected in the reaction mixture, asymmetrical orthocarbonate (**20**) was not detected during the reaction. This model reaction obeyed the second-order kinetics, and the values of k_1' and k_2' were estimated as 2.84×10^{-2} and 7.66×10^{-1} l mol^{-1} min^{-1}, respectively. The ratio k_2'/k_1' was estimated as 27, indicating that the reaction intermediate **20** was much more reactive than monomer **17**. To evaluate the effect of the excess amount of **17** from the viewpoint of the formation of **21**, the time-dependent conversion and the yield of each compound in the reaction system were calculated under the condition of κ of 27. **Table 3** shows the yield of **21** and the consumption of **17** at the time when **19** was entirely consumed. The calculations were carried out for the series of the stoichiometric imbalance parameter S ($2[\mathbf{17}]_{init.}/[\mathbf{19}]_{init.}) = 2$. The times are shown in normalized value $\tau = k_1[\mathbf{17}]_{init.}t$. If the reaction was carried out under stoichiometric condition ($S = 1$), it took an infinite period for the complete consumption of **19**. If the reaction was performed at S of 1.5 (50% excess of **17**), **19** was consumed completely at $\tau = 6.85$. The yield of **21** reached 99.06%, and the consumption of **17** was only 100.94% (based on $[\mathbf{19}]_{init.}$). The excess amount of **17**

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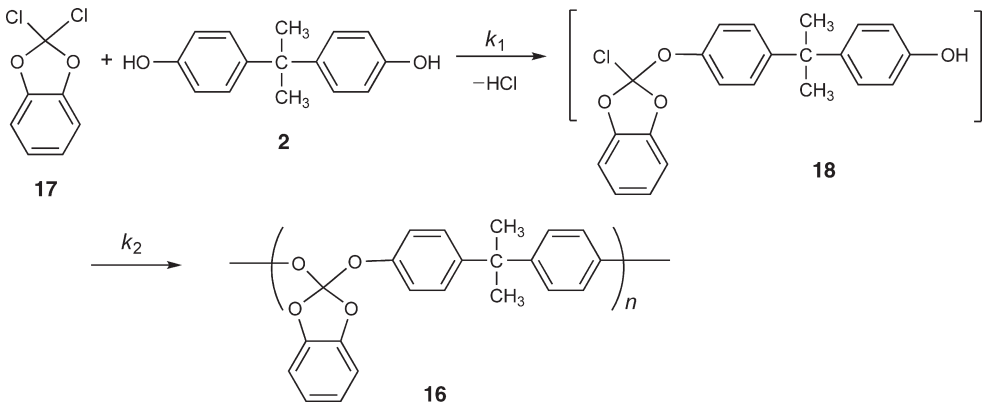
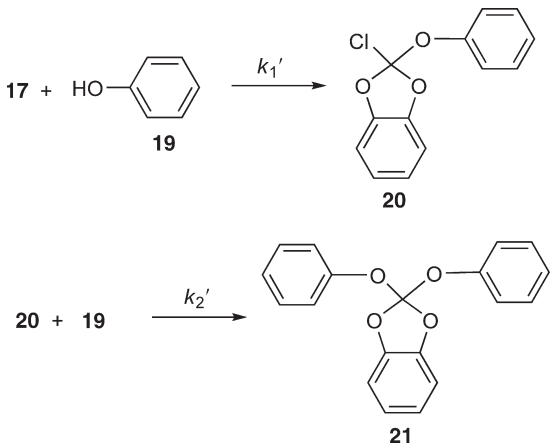


Scheme 5 Synthesis of **18**.

Table 2 Effect of feed ratio on the polycondensation of **17** and **2**[a]

Feed ratio (mmol)					
17	***2***	*Yield of **18**[a] (%)*	*Mn ($\times 10^4$)*[b]	*Calc. Mn*	*Mw/Mn*[c]
3	4	54	0.46	1212	1.18
5	5	99	4.8	∞	2.25
4	3	101	4.2	1212	2.56
5	3	100	12.0	693	2.52
6	3	102	3.0	520	2.86
30	3	63	0.86	212	2.31

[a]Polymerizations were carried out in chlorobenzene at reflux for 3 h.
[b]Insoluble in isopropyl ether.
[c]Estimated by Gel permeation chromatography (GPC).
Cited from Kihara, N.; Komatsu, S.; Takata, T.; Endo, T. *Macromolecules* **1999**, *32*, 4776.[13]



Scheme 6 Model reaction of **17** with **19**.

does not inhibit the formation of **21**. At S from 2 to 4, analogous results were obtained. It is noteworthy that the yield of **21** decreases substantially with an excess amount of **17** if k_2'/k_1' is equal to or less than 1. Normalized time (τ)-dependent yield of **21** was calculated under the condition of $k_2'/k_1' = 27$ as shown in Figure 3. Although the final yield of **13** reaches the highest value at S of 1, it needs a considerably longer time. Although the maximum yield of **13** decreases as the value of S increases, the yield of **13** reaches a high value more rapidly. Number-averaged molecular weight (Mn) of **16** prepared by the polymerization of **17** and **2** was calculated based on the assumption that κ was 27 and as a function of S ($[\mathbf{17}]_{\text{init.}}/[\mathbf{2}]_{\text{init.}}$) and τ by using a modified Case's method. When S was equal to 1, that is, the condition of stoichiometry, Mn increased linearly until infinite τ as expected from the classical theory as shown in Figure 4. In contrast to this, Mn increased nonlinearly at $S > 1$ and it became constant after phenolic OH groups were entirely consumed. Even though the reaction occurred more rapidly as the value of S increased, the maximum Mn became lower. This estimation suggests that nonstoichiometric condition is desirable to prepare polymers of sufficiently high molecular weight within a practical time frame. This kinetic consideration revealed that the intermediate **18** reacted with phenol 27 times faster than **17**, resulting in the formation of oligomers with phenol end-groups. In other words, the second nucleophilic substitution reaction of monochloride formed by the first substitution occurred much faster than the first substitution reaction. Maximum molecular weight is clearly obtained at S of 1 at infinite time, but this is impracticable. Since the first reaction accelerates the rate of the second reaction, polycondensation practically increases the molecular weight under nonstoichiometric condition.

5.05.2.2 Palladium-Catalyzed Polycondensation

The above nonstoichiometric polycondensations are attributed to the formation of reactive intermediate. Catalysts play an important role in nonstoichiometric polycondensation. The palladium-catalyzed allylic substitution reaction between electrophilic bisallylic esters and nucleophilic malonic esters is a versatile carbon–carbon bond-forming reaction, which is well known as the Tsuji–Trost reaction, and this polycondensation proceeds under nonstoichiometric condition.[14,15] This is the first example of nonstoichiometric polycondensation via a carbon–carbon bond-forming reaction. Polycondensation between 1,4-diacetoxybut-2-ene (**22**) and nucleophilic diethyl malonate (**23**) shown in Scheme 7 yielded high-molecular-weight polymer **24** even with an excess of **22** in the presence of a Pd(0) catalyst as

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Table 3 Theoretical yield of **21**, conversion of **17**, and the corresponding molecular weight of **16**[a]

S	*Consumption time (τ) of* ***19***	*Yield of* ***21*** *(%)*	*Consumption of* ***17*** *(%)*	*Mn of* ***16***[b]
1	49 999.56	99.99	99.99	3 399 874
1.5	6.85	99.06	100.94	36 836
2	4.57	98.11	101.89	18 478
3	3.43	96.23	103.77	9 299
4	3.05	04.34	105.66	6 242

[a]Calculated at $\kappa = 27$.
[b]Mn of **16** after complete consumption of phenolic OH groups.
Cited from Kihara, N.; Komatsu, S.; Takata, T.; Endo, T. *Macromolecules* **1999**, *32*, 4776.[13]

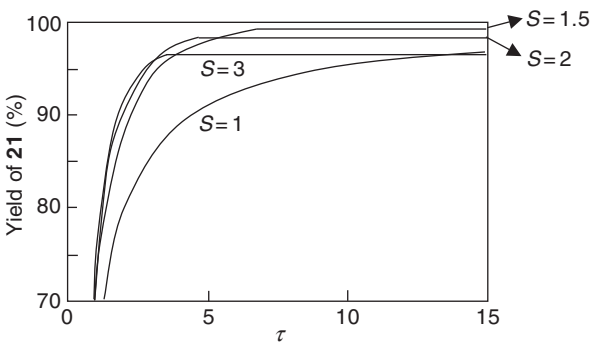


Figure 3 Normalized time (τ)-dependent yield of **21** calculated at various *S* values. Reproduced from Kihara, N.; Komatsu, S.; Takata, T.; Endo, T. *Macromolecules* **1999**, *32*, 4776.[13]

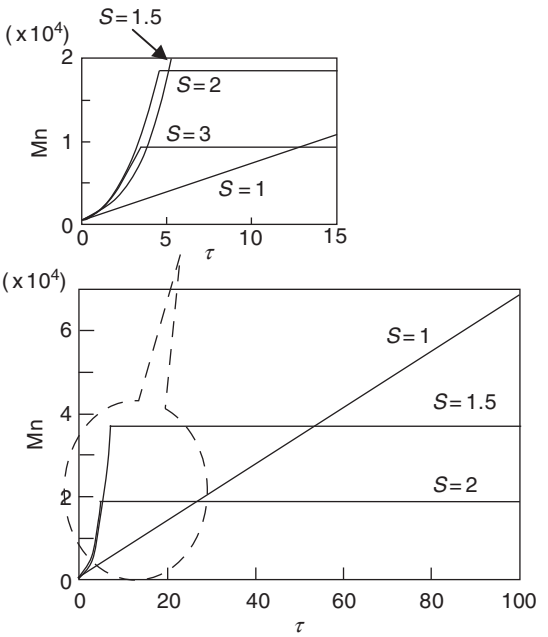
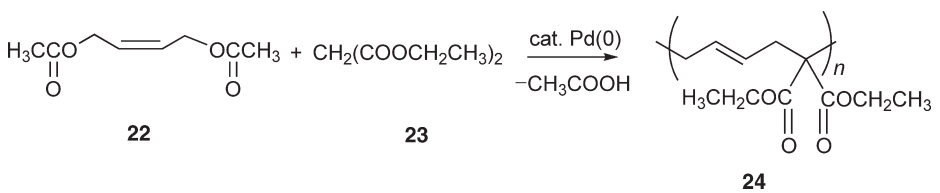


Figure 4 Plots of calculated Mn of **16** as a function of normalized time τ at various *S* values. Reproduced from Kihara, N.; Komatsu, S.; Takata, T.; Endo, T. *Macromolecules* **1999**, *32*, 4776.[13]

summarized in Table 4. According to the classical theory of polycondensation, DPns of polymer **24** obtained in the presence of 10 mol.% excess of **22** or **23**, corresponding to the molar ratio of **22** and **23** of 1.0:1.1 and 1.1:1.0, are expected to be 21. However, the DPn of the obtained **24** was quite different from the calculated values. The DPns were 24 and 66 at the molar ratio of **22** and **23** of 1.0:1.1 and 1.1:1.0, respectively. When 1.3 equivalents of **22** were used, the calculated DPn was 7.7, whereas the DPn of the obtained polymer **24** was quite high at 50. Although a further excess of **22** gradually decreased the DPns, **24** with a high DPn of 37 was unexpectedly obtained even in the presence of 100% excess of **22**. Ninety percent of excess **22** was recovered in this case. An excess of **22** did not significantly affect the molecular weight.

This nonstoichiometric polycondensation was rationalized by including olefin-Pd(0) complex (**26**), which caused the cascade bidirectional allylation as shown in Scheme 8. Thus, **26** is selectively formed after the first allylation, and then the π-allylpalladium(II) complex (**27**) is formed at the other allylic terminal. The reactive site moves stepwise from one side to the other side in **26**. Therefore, the polymers are always end-capped by malonic ester groups even in the presence of an excess of bisallylic ester and polycondensation proceeds in a condensative chain manner without termination by bisallylic ester. The polymerization behavior is dependent on the ligand of the Pd(0) catalyst. Bis(diphenylphosphino)butane (dppb) is indispensable, and the use of Triphenylphosphine (PPh_3) results in low-molecular-weight



Scheme 7 Palladium-catalyzed polycondensation of **22** with **23**.

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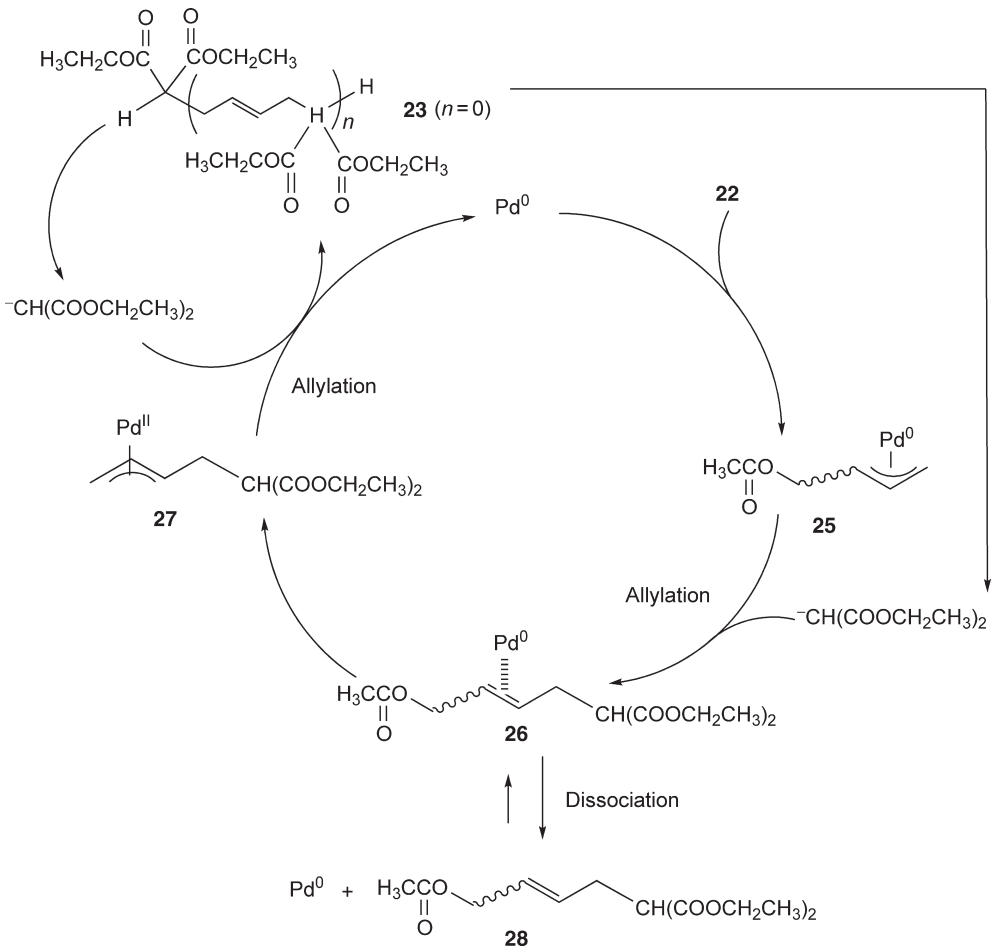
Table 4 Polycondensation of **22** with **23** under nonstoichiometric condition[a]

Ligand	Molar ratio [**22**]/[**23**]	DPn of **24**	
		Calculated	Obtained[b]
Dppb	1.0/1.1	21	24
Dppb	1.1/1.0	21	66
Dppb	1.3/1.0	7.7	50
Dppb	1.5/1.0	5.0	46
Dppb	2.0/1.0	3.0	37
PPh_3	1.5/1.0	5.0	5.0[c]

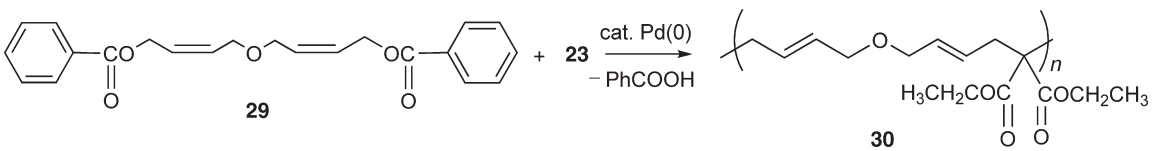
[a]Condition: Tris(dibenzylideneacetone)dipalladium(0) [$(Pd_2(dba)_3)$] (0.01 equiv.), dppb (0.02 equiv.), *N,O*-bis(trimethylsilyl)acetamide, CH_2Cl_2 (1 ml), 40 °C, 11 h.
[b]Estimated by Size exclusion chromatography (SEC) ($CHCl_3$, polystyrene standard).
[c]Estimated by proton nuclear magnetic resonance (^{1}H NMR) spectroscopy.
Dppb, bis(diphenylphosphino)butane.
Reproduced from Nomura, N.; Tsurugi, K.; Okada, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 1932.[16]

polymer due to the formation of **28** by dissociation process. Polycondensation of 4,4′-oxybis(but-2-ene-4,1-diyl)dibenzoate (**29**) with **23**, shown in Scheme 9, under stoichiometric condition also yielded the polymer **30** with DPn of 110 ($Mn = 1.6 \times 10^4$, $Mw/Mn = 1.53$).[16] When polymerization was carried out at the molar ratio of **29** and **23** of 1.5:1.0 or 1.0:1.5, a DPn value of 5.0 was expected according to eqn [2] in both cases. However, with an excess of 50 mol.% **29**, a polymer having DPn of 99 ($Mn = 1.4 \times 10^4$, $Mw/Mn = 1.62$) was obtained. In contrast to this, an excess of 50 mol.% **23** reduced DPn to 6 ($Mn = 0.8 \times 10^3$, $Mw/Mn = 1.76$). This type of nonstoichiometric polymerization of other electrophilic bisallylic esters with nucleophiles was also reported as presented in Table 5 and various high-molecular-weight polymers were successfully obtained with an excess of electrophiles.[17]

Palladium-catalyzed polycondensation of methyl propargyl carbonate (**31**) with bisphenols proceeded to afford polyethers having exomethylene groups (**32**) as shown in Scheme 10.[18,19]



Scheme 8 Cascade bidirectional allylation mechanism of palladium-catalyzed polycondensation. Reproduced from Nomura, N.; Tsurugi, K.; Okada, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 1932.[16]



Scheme 9 Palladium-catalyzed polycondensation of **29** with **23**.

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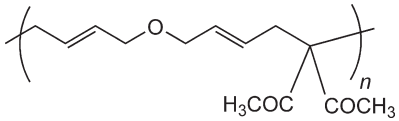
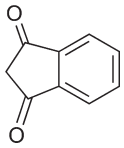
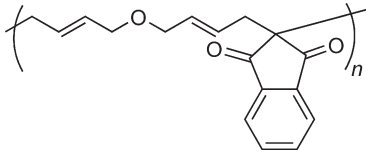
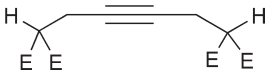
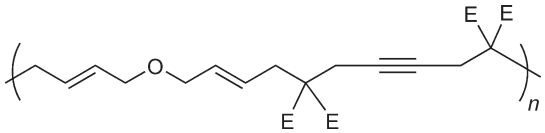
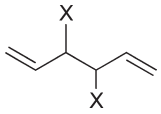
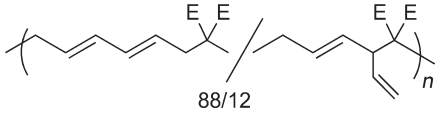
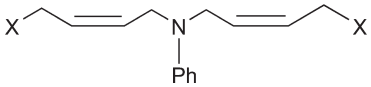
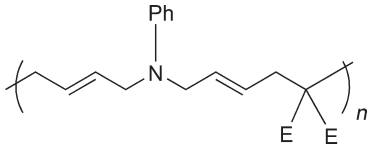
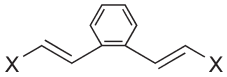
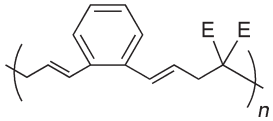
Table 5 Nonstoichiometric polymerization of electrophilic bisallylic esters with nucleophiles[a]

Electrophile (X=OCOPh)	*Nucleophile (E=COOCH$_2$CH$_3$)*	*Molar ratio of E/N in feed*	*Polymer (E=COOCH$_2$CH$_3$)*	*Yield (%)*	*DPn*[b] *Calc.*	*DPn*[b] *Obs.*	*Mn*[b] ($\times 10^3$)	*Mw/Mn*[b]
29	**23**	1.0/1.0	**30**	97	∞	110	16	1.53
		1.5/1.0		98	5	99	14	1.62
		1.0/1.5		[c]	5	6[d]	0.8	1.76
	$CH_2(COCH_3)_2$	1.5/1.0		82[e]	5	120	13	1.39
		1.5/1.0		99	5	100	14	1.52
		1.5/1.0		99	5	65	16	1.47
	**23**	1.0/1.0	 88/12	95	∞	270	32	1.54
		1.5/1.0		94	5	340	41	1.57
		2.0/1.0		96	3	340	41	1.57
		1.0/1.5		[c]	5	6[d]	0.8	1.59
	**23**	1.5/1.0		97	5	73	13	1.47
	**23**	1.5/1.0		92	5	64	10	1.75

[a]Polymerizations were catalyzed by 1 mol.% of $Pd_2(dba)_3$ (5 μmol) and 2.0 mol.% of 1,4-bis(diphenylphosphino)butane (10 μmol) in the presence of 3.0 mmol of *N,O*-bis(trimethylsilyl)acetamide in CH_2Cl_2-DMF (9:1, 1.0 ml).
[b]Determined by SEC.
[c]Not isolated. A crude reaction mixture was analyzed by SEC.
[d]Some amount of an insoluble material was obtained.
[e]Measured by proton nuclear magnetic resonance (^{1}H NMR) spectroscopy.
Cited from Nomura, N.; Tsurugi, K.; RajanBabu, T. V.; Kondo, T. *J. Am. Chem. Soc.* **2004**, *126*, 5354.[17]

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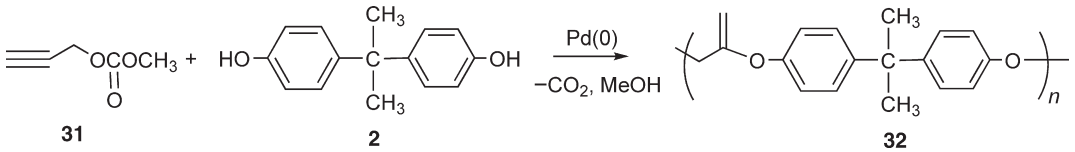

Scheme 10 Synthesis of **32** by palladium-catalyzed polycondensation.

Table 6 Influence of feed ratio of **31** and various bisphenols on molecular weight[a]

Bisphenol	*Molar feed ratio of bisphenol to **31***	*Yield of polyether (%)*[b]	*Mn*[c] ($\times 10^3$)	*Mw/Mn*[c]
2	1.0	78[d]	2.2	1.97
	0.7	74[d]	4.8	2.76
	0.5	0[d]		
	1.0	59	2.1	2.53
	0.5	95	3.1	1.70
	1.0	33	1.2	1.65
	0.5	50	2.5	1.79

[a]Condition: **31**, 1.0 mmol; Tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$), 50 μmol (5.0 mol.%); THF, 3.0 ml; 60 °C; 24 h.
[b]Insoluble in methanol.
[c]Estimated by GPC (based on Polystyrene (PSt)).
[d]17 h.
Cited from Takemura, T.; Sugie, K.; Nishino, H., *et al. J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 2250.[19]

Nonstoichiometric polymerization was examined since this polymerization system was similar to Pd(0)-catalyzed polycondensation of allylic compounds and malonic esters as mentioned before. Pd(0)-catalyzed polycondensation of **31** with bisphenols was carried out at 60 °C in Tetrahydrofuran (THF). The results are presented in Table 6. The molar ratio of **31** and bisphenol affected the polymerization behavior, and polyethers of higher molecular weights were obtained by polymerization in the presence of an excess of **31**. For example, the polymerization of **31** with **2** under stoichiometric condition gave the polyether (**32**) with Mn of 2.2×10^3. **32** with Mn of 4.8×10^3 was also obtained by the polymerization of **31** with 0.7 equivalents of **2**. The polymerization of **31** with 4,4′-dihydroxy diphenylether afforded a polyether with Mn of 2.1×10^3 under stoichiometric condition, while a polyether with Mn of 3.1×10^3 was obtained by the polymerization of **31** with 0.5 equivalents of bisphenol. The polymerization of **31** with 4,4′-dihydroxy benzophenone also afforded a polyether with Mn of 1.2×10^3 under stoichiometric condition, while a polyether with Mn of 2.5×10^3 was obtained by polymerization of **31** with 0.5 equivalents of bisphenol. An excess of **31** did not lower the molecular weight and practically yielded high-molecular-weight polymers. A possible mechanism was proposed from the consideration of the model reaction of **31** with *p*-cresol as shown in Scheme 11. Propargylpalladium intermediate (**33**), generated by oxidative addition of **31** to Pd(0), is attacked by the first *p*-cresol at the central carbon to produce intermediate (**34**), followed by protonation to afford allylpalladium intermediate (**35**). A second *p*-cresol attacks **35** to give ether having exomethylene group (**36**).

Polycondensations involving cascade directional reaction are insensitive to stoichiometric imbalance of two monomers.

5.05.2.3 Phase Transfer Catalyzed Polycondensation

It had been well known that the phase transfer catalyzed polycondensation was not necessary to obtain high-molecular-weight polymers starting from a stoichiometrically balanced ratio of two functional groups as usually requested in polycondensation.[20] Reactions are conducted in two-phase systems consisting of mutually insoluble aqueous and organic layers. Ionic reagents are located mainly in the aqueous phase while the substrate is in the organic phase. Alternatively, ionic reagents can be used in the solid phase as a suspension in the organic phase. In both cases, the transport of the anionic species from the aqueous or the solid phase into the organic phase, under a highly active form, is ensured by small amounts of lipophilic PTCs such as quaternary onium salts and crown ethers. The reaction generally occurs in the organic phase. Most of the nucleophilic substitutions in the liquid–liquid systems were represented by the following mechanism as shown in Scheme 12.[20,21] Anion Y^- is transferred into the organic phase as (Q^+, Y^-) with the aid of quaternary onium salt Q^+X^-. Then anion Y^- reacts with R-X by the nucleophilic substitution to give R-Y. The by-product (Q^+, X^-) is rapidly converted into Q^+Y^- by anion exchange with the nucleophile M^+Y^-. This cycle continues by the phase transfer of quaternary onium salt, affording high-molecular-weight polymers.

The kinetics and mechanism of the phase transfer catalyzed polycondensation of **2** and *trans*-1,4-dichloro-2-butene (**37**) have been reported in detail (Scheme 13).[22,23] Polymerization was carried out to yield polyether **38** in immiscible two phases of aqueous NaOH and toluene at 65 °C using tetrabutylammonium hydrogen sulfate (TBAH) as the catalyst by varying the molar ratio of **2** and **37** as presented in Table 7. Polyether **38** was obtained even under nonstoichiometric

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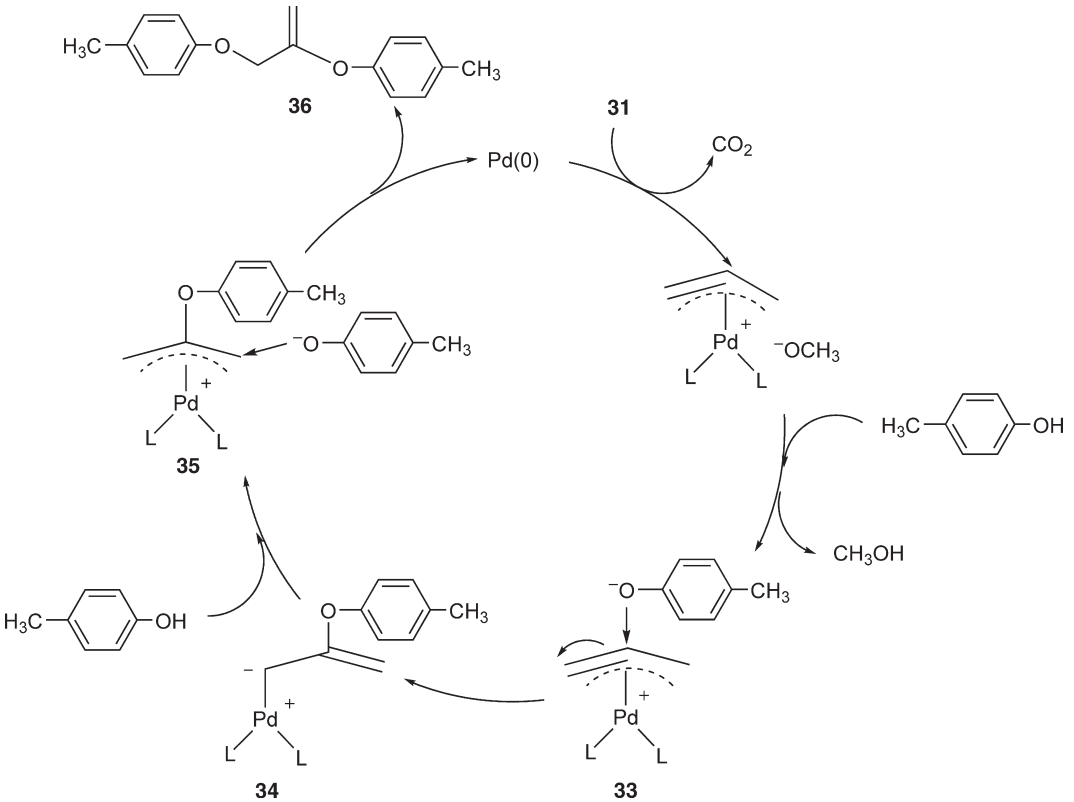
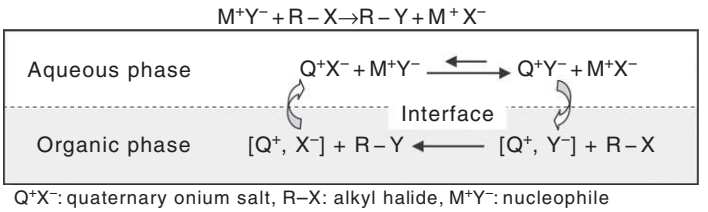
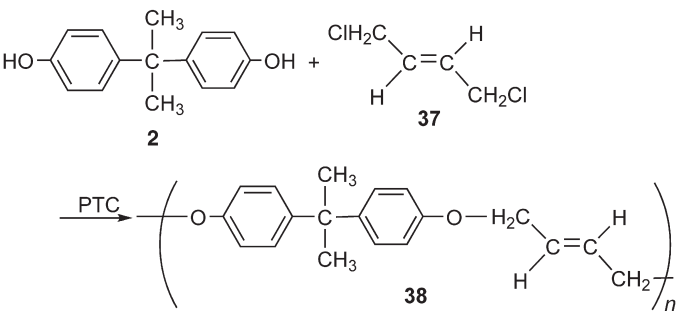


Scheme 11 Possible mechanism of palladium-catalyzed polycondensation of **31**. Reproduced from Koizumi, T.; Sugie, K.; Kiyonaga, O., *et al. Macromolecules* **2004**, *37*, 9670.[18]



Scheme 12 Nucleophilic substitution reaction in immiscible two phases. Reproduced from Boileau, S. In *New Methods for Polymer Synthesis*; Mijs, W.J., Ed.; Plenum: New york, NY, 1992, p 179.[20]



Scheme 13 Synthesis of **38** by phase transfer catalyzed polycondensation in immiscible two phases.

initial monomer ratios, and high-molecular-weight polyether was formed even at a molar ratio of **2** and **37** of 2 with a yield of 74%. The mechanism of this reaction is explained in Scheme 14. Polycondensation occurs via alkylation of a phenolate end-group by **37** in the organic phase. In the first step, sodium bisphenolate located in the aqueous phase undergoes cation exchange with the onium salt to give a mixed salt **39**, and then **39** reacts with **37** through the reactive and lipophilic end-group leading to **40**. After another cation exchange with the catalyst, **40** gives a more lipophilic species (**41**), which is

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Table 7 Influence of the molar ratio of **2** and **37** on the molecular weight of **38** under phase transfer catalyzed conditions[a]

Run no.	Molar ratio [**2**]/[**37**]	Yield of **38** (%)	Mn[b]	Mw/Mn[b]
1[c]	1	0		
2	1	100	3100	1.8
3	2	74	5300	2.5
4[d]	4	58	2600	1.3

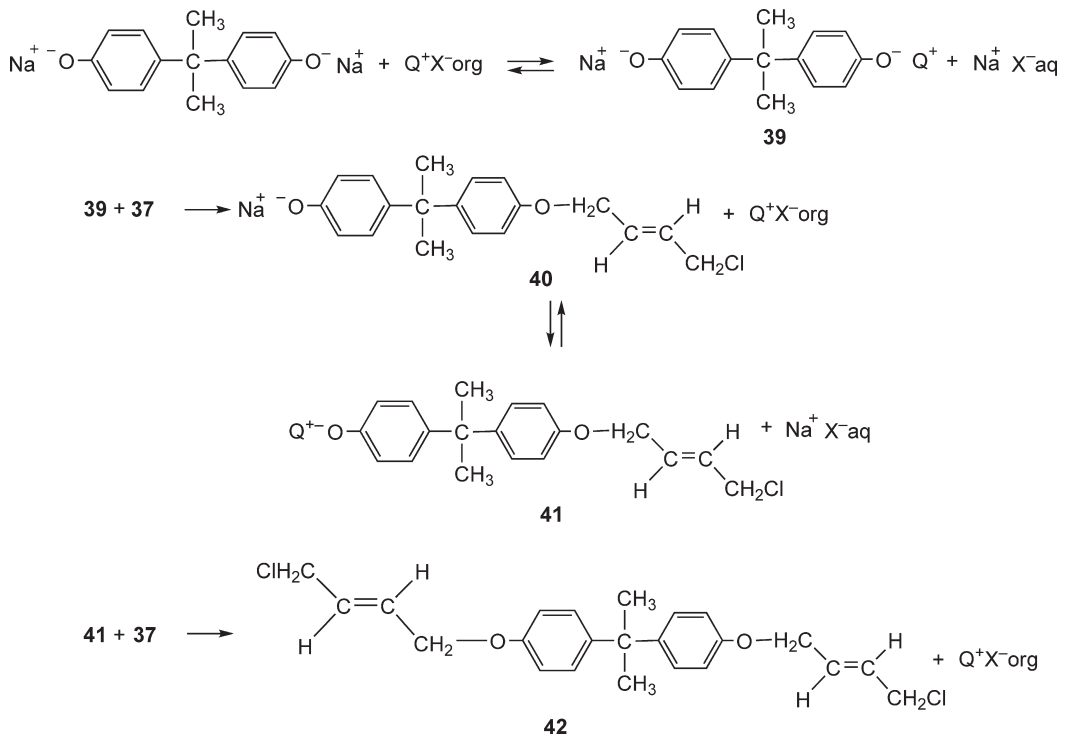
[a]Condition: Toluene/NaOH 3 N (10 ml/10 ml); **37**, 3.07 mmol; tetrabutylammonium hydrogen sulfate (TBAH), 0.614 mmol; 65 °C; 5 h; 500 rpm.
[b]Measured by GPC.
[c]Without TBAH.
[d]Presence of phenolic end-groups in the polymer.
Reproduced from Boileau, S. In *New Methods for Polymer Synthesis*; Mijs, W. J., Ed.; Plenum: New York, NY, 1992; p 179.[20]

presumably located in the organic phase. Then, **41** reacts with another **37** to yield **42**. It has been clarified that the concentration of bisphenolate anion is equal to zero in the organic phase in the absence of catalyst. Therefore, the reaction does not occur between **2** and **37** in the absence of TBAH (run no. 1 in Table 7). The cation of the catalyst Q^+ transports the phenolate from the aqueous phase to the organic phase and transports Cl^- back to the aqueous phase continuously. This process governs the kinetics and it is important to note that the concentration of phenolate end-groups is much lower than that of the chlorine end-groups in the toluene phase resulting in the formation of polyether with chlorine end-groups. Polycondensation does not take place directly between **2** and **37** under stoichiometric molar ratios according to this polymerization mechanism. **2** is continuously supplied in small amounts in a reactive form from the aqueous phase to the organic phase containing **42** with the aid of the catalyst, and therefore, the high-molecular-weight polymer is formed even in the presence of an excess of **2** (run nos. 3 and 4 in Table 7). On the basis of this mechanism, many attempts have been made to increase molecular weight. A higher concentration of more reactive phenolate in the organic phase increases the molecular weight of the polymer. Increasing the stirring rate of the polymerization system accelerates the dissolution of the phenolate into the organic phase by increasing the interface area between two phases, resulting in high molecular weight.

5.05.3 Nonstoichiometric Polycondensation Caused by the Change in the Higher Structure of Polymers

5.05.3.1 Nucleation–Elongation Polycondensation

As shown in Scheme 15, the imine metathesis polymerization of **43** with **44** containing *m*-phenylene ethynylene sequence generated high molecular weight polymer **45** in acetonitrile derived by the folding of the *m*-phenylene ethynylene chains, whereas the metathesis polymerization under nonfolding conditions in chloroform gave only low-molecular-weight oligomers.[24–26] The correlation of the molecular weight of the resulting polymers with the solvent composition of a series of acetonitrile/chloroform binary mixtures, which was related to the stability of the folded conformation (helical structure) of *m*-phenylene ethynylene molecules, indicated that folding shifted the metathesis equilibrium toward high-molecular-weight polymers. Furthermore, the insensitivity of the equilibrated molecular weight to the concentration indicated that intramolecular association rather than



Scheme 14 Mechanism of polyether formation by phase transfer catalyzed polycondensation. Boileau, S. In *New Methods for Polymer Synthesis*; Mijs, W. J., Ed.; Plenum: New York, NY, 1992; p 179.[20]

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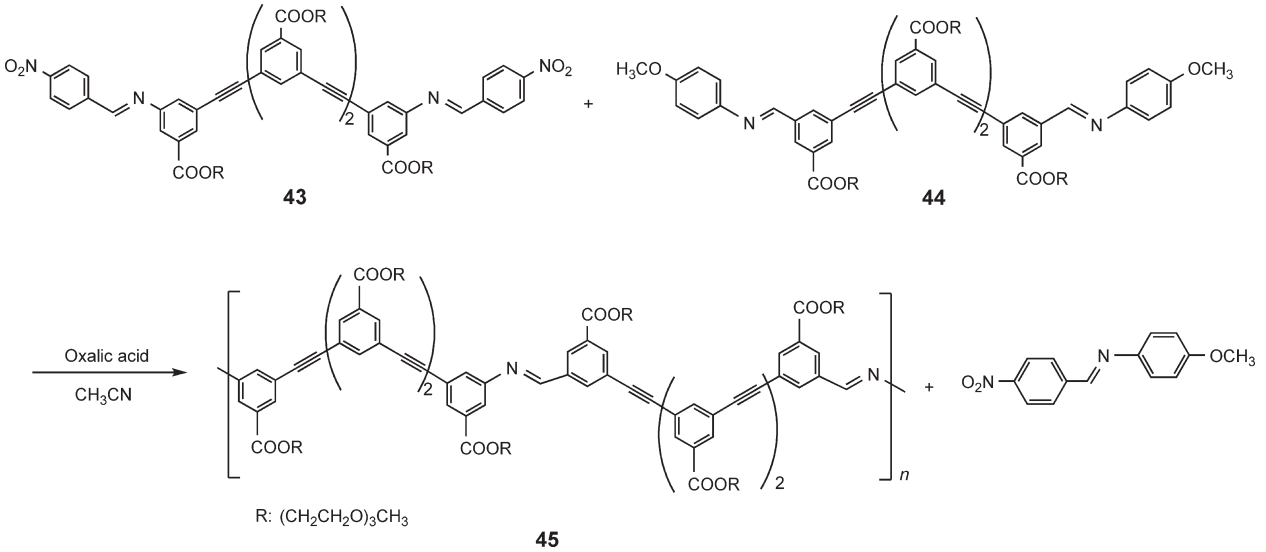


Scheme 15 Imine metathesis polymerization of **43** and **44**. Reproduced from Zhao, D.; Moore, J. S. *J. Am. Chem. Soc.* **2002**, *124*, 9996.[24]

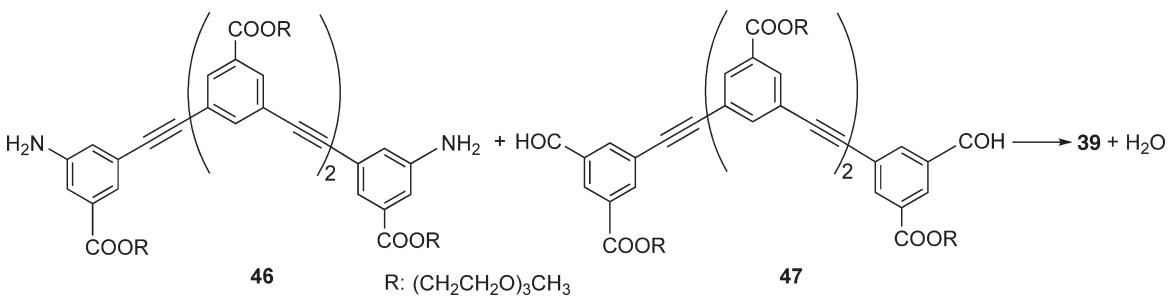
intermolecular aggregation was the dominant driving force for the high molecular weight polymer formation. It was reasonably considered by the formation of the helical conformation that this polymerization followed the nucleation–elongation mechanism. The nucleation–elongation mechanism is fairly tolerant of stoichiometric imbalance between two functional groups. The nucleated polymerization achieved high molecular weight under imbalanced stoichiometry by excluding the excess monomer. This polymerization was performed under nonstoichiometric condition as shown in Table 8.[26] The polymers were obtained under nonstoichiometric conditions and the Mn of the polymers was insusceptible to the stoichiometric balance. The polymers were present at equilibrium along with a substantial amount of monomer but relatively little dimer or trimer. Excess monomer remained unreacted at equilibrium because it did not take part in the formation of the folded polymer. In contrast to this, the polymerization of the corresponding diamine (46) and dialdehyde (47) at the same monomer stoichiometry in the melt produced only low-molecular-weight oligomers predictable from eqn [2] (Scheme 16). Because the helical folding of *m*-phenylene ethynylene chains did not occur under these melt conditions, polymerization under nonstoichiometric condition in solution was proposed to follow the folding-driven nucleation–elongation mechanism as illustrated in Scheme 17. An equilibrium model was examined to clarify the features

Table 8 Polymerization conditions and molecular weight of polymer **45** as a function of stoichiometry[a]

Initial monomer concentration				
*[**43**] (mM)*	*[**44**] (mM)*	*Molar ratio of [**43**]/[**44**]*	*Mn of **45** ($\times 10^3$)*	*Mw of **45** ($\times 10^3$)*
5.0	5.0	1.00	31	419
5.0	5.5	1.10	27	283
5.0	6.0	1.20	21	157
5.0	6.3	1.25	19	94
5.0	6.7	1.33	17	63
5.0	7.5	1.50	12	34

[a]Polymerizations were carried out in the presence of oxalic acid (0.5 mM) for 14 days at room temperature in acetonitrile.
Cited from Zhao, D.; Moore, J. S. *J. Am. Chem. Soc.* **2003**, *125*, 16294.[26]

of nucleation–elongation mechanism under imbalanced stoichiometry. All the different units in the polymerization system were categorized into three energetically distinct groups: monomer, end-group, and internal repeating unit. Each type of moiety included two energetically equivalent species bearing different functional groups. Equation [3] shows the transformations among these species, wherein A and B represent A-A and B-B



Scheme 16 Imine metathesis polymerization of **46** and **47**. Reproduced from Zhao, D.; Moore, J. S. *J. Am. Chem. Soc.* **2003**, *125*, 16294.[26]

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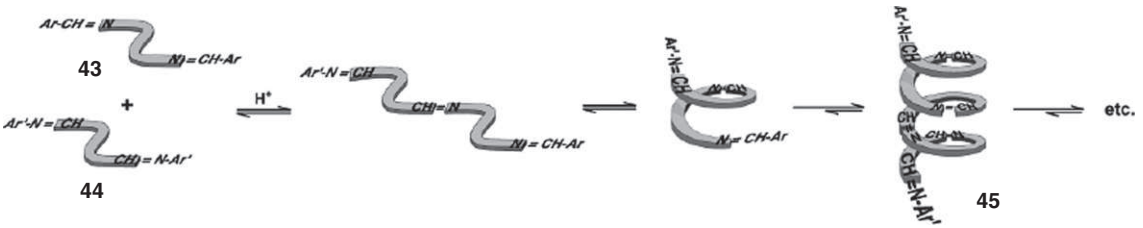

Scheme 17 Folding-driven nucleation–elongation mechanism. Reproduced from Zhao, D.; Moore, J. S. *J. Am. Chem. Soc.* **2002**, *124*, 9996.[24]

type monomers, respectively, EgA and EgB stand for the corresponding units at the end of an oligomer or a polymer, while PA and PB are internal repeating units of a polymer chain containing more than two monomer segments. Each reaction was reversible with a corresponding equilibrium constant (K_1 and K_2).

$$\left.\begin{array}{l} A + B \overset{K_1}{\rightleftharpoons} EgA + EgB \\ A + EgB \overset{K_2}{\rightleftharpoons} EgA + PB \\ B + EgA \overset{K_2}{\rightleftharpoons} EgB + PA \end{array}\right\} \quad [3]$$

When K_1 was nearly equal to K_2, the equilibrium model corresponded to an isodesmic polymerization. If K_1 was much smaller than K_2, the model described a polymerization that had a single nucleation step with all subsequent monomer addition steps having an identical free energy change. DPn′, which is DPn not including the unreacted monomers, and the monomer concentration at the equilibrium of a nucleated system were calculated as presented in Figure 5. A significantly higher DPn′ was found for polymers under the same K_2 from a nucleation–elongation polymerization than from an isodesmic polymerization. Consistently, the monomer concentration at the equilibrium of nucleation–elongation polymerization system was also significantly higher than that found in an isodesmic polymerization. It is clear from Figure 5, that there are important differences in monomer concentration and DPn′ between isodesmic and nucleation–elongation polymerization under nonstoichiometric condition. The thermodynamic formation of the polymers having specific conformation (helical structure in this case) specifically leads the polymerization, resulting in high-molecular-weight polymers under nonstoichiometric condition.

5.05.3.2 Polycondensation Using Reaction-Induced Crystallization

Reaction-induced crystallization of oligomers during polycondensation solves the drawback of nonstoichiometric conditions. This polymerization procedure was first reported to control the morphology of aromatic polymers and many polymer whiskers were successfully prepared.[27] The polymer crystals such as the whiskers were formed as follows: oligomers were first formed in the solution. When the degree of polymerization of the oligomers exceeded the critical value, which depended on the polymerization condition, oligomers were phase-separated by crystallization via the supersaturated state and then the oligomer crystals were formed. The crystals grew by the continuous supply of oligomers from the solution phase. Further polymerization occurred in the crystals leading to high-molecular-weight polymers. Finally, the polymer crystals having clear morphology were obtained. This polymerization is not limited by the intractability of polymers because the morphology is built by the crystallization of oligomers with polymerizing, and therefore many crystals of the intractable rigid polymers have been developed as high-performance materials so far. Based on this formation mechanism of the polymer crystals, it is expected that the molecular weight increases in the crystals by the elimination of end-capped residues from the crystals via solid-state polymerization even if polymerization is carried out with coexisting monofunctional reagents that can act as end-capped reagents.

Preparation of poly(*p*-oxybenzoyl) (**48**) from *p*-acetoxybenzoic acid (**49**) was examined in the presence of 4-alkyloxybenzoic acids (**50**) or 4-alkyloxyphenyl acetates (**51**) as shown in Scheme 18.[28,29] Solvents were of great importance to induce crystallization during polymerization, and a solvent

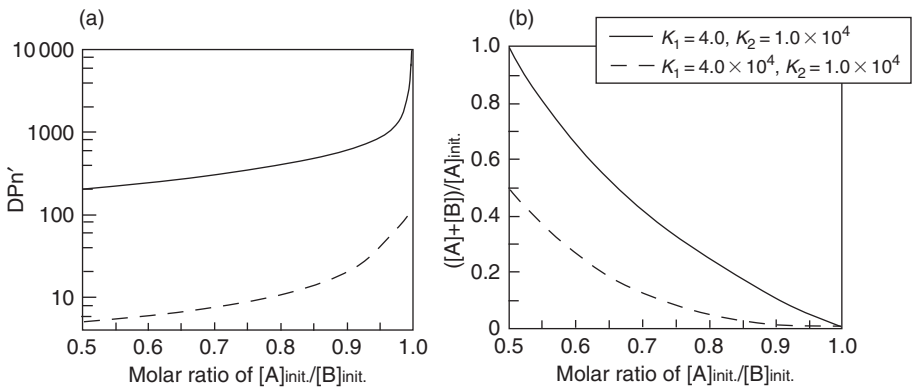

Figure 5 Representative plots of (a) DPn′ of the polymer (excluding the monomer), and (b) the relative monomer concentration at equilibrium, as a function of the initial monomer molar ratio in a nucleation–elongation polymerization. Corresponding results for an isodesmic reaction are also shown for comparison. Reproduced from Zhao, D.; Moore, J. S. *J. Am. Chem. Soc.* **2003**, *125*, 16294.[26]

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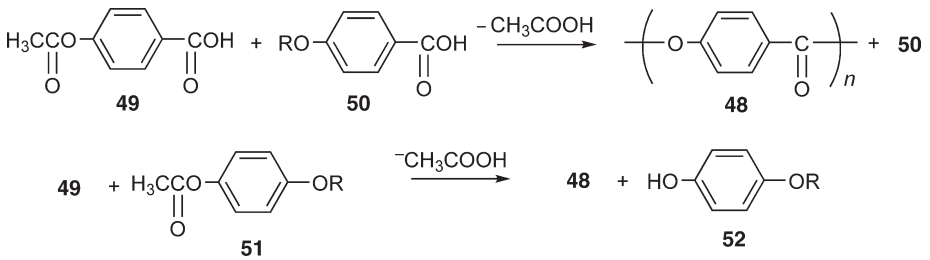

Scheme 18 Preparation of **48** from **49** with monofunctional compound **50** or **51**.

that was a good solvent to monomers and a poor solvent to polymers was adopted. In the polymerization of **49** and **50**, liquid paraffin was the desirable solvent, and therefore polymerizations were performed in liquid paraffin at 320 °C in the presence of three different kinds of **50** such as *p*-hexyloxybenzoic acid (HOBA), *p*-decyloxybenzoic acid (DOBA), and *p*-octadecyloxybenzoic acid (OOBA). **49** and **50** did not dissolve in liquid paraffin at 25 °C, but dissolved on heating. Crystallization of oligomers was induced during polymerization, and needle-like or pillar-like crystals were formed. Table 9 presents the results of polymerization. The range of concentration of **50** in feed to yield the crystals was wider in the system of HOBA than in the system of DOBA and OOBA. DPns estimated by end-group analysis were much higher than the calculated values. DPn of **48** was 34 even at HOBA of 60 mol.%, which means 50 mol.% excess of **50** to **49**. DPns obtained in the system of DOBA and OOBA were higher than that in the system of HOBA, and they were 232 and 283 at the concentration of **50** in feed of 30 mol.%, respectively. In contrast to these, the DPn of the products prepared by melt polymerization at the concentration of **50** in feed of 20 mol.% was 6, and the melt polycondensation of **49** in the presence of **50** obeyed the classical theory. In the systems of HOBA and DOBA, residues of **50** were scarcely contained in polymer crystals, and they were almost concentrated in the liquid phase. This fact suggested that the oligomers not end-capped by **50** were selectively phase-separated to form crystals on the basis of difference in the solubility derived from end-groups, and DPn increased by solid-state polymerization. The oligomers end-capped by **50** were also phase-separated to form crystals, and then residues of **50** contained in the crystals were excluded by solid-state polymerization from the crystal to the liquid phase. The content of residues of **50** in the polymer crystals prepared in the system of OOBA was less than that in the system of HOBA. This implied that the oligomers end-capped by OOBA were harder to contain in the crystals than HOBA due to the bulkiness of the end-groups. The wider range of the concentration of **50** in feed to yield the polymer crystals was attributable to the lower solubility of end-capped oligomers by HOBA than others.

Nonstoichiometric polycondensation of **49** was also examined in the presence of three kinds of aromatic monoacetates **51** such as *p*-hexyloxyphenyl acetate (HOPA), *p*-decyloxyphenyl acetate (DOPA), and *p*-octadecyloxyphenyl acetate (OOPA). Polymerizations were carried out in liquid paraffin at 320 °C by varying the concentration of **51** in feed. Table 10 presents the results of polymerization. **48** was obtained in the form of mostly needle-like crystals as shown in Figure 6. The obtained DPns were much higher than those

Table 9 Polymerization of **49** in the presence of **50**[a]

			*DPn of **48***		
50	*Concentration of **50** in feed (mol.%)*[b]	*Yield of **48** (%)*	*Calculated*	*Obtained*	*Morphology of **48***
HOBA	10	36	10.0	60	Pillar
	20	51	5.0	40	Pillar
	30	53	3.3	57	Pillar
	40	39	2.5	45	Slab
	50	42	2.0	42	Plate
	60	38	1.7	34	Plate
DOBA	10	48	10.0	277	Needle
	20	50	5.9	161	Pillar
	30	53	3.3	232	Pillar
OOBA	10	27	10.0	489	Needle
	20	38	5.0	344	Needle
	30	39	3.3	283	Pillar
	20		5.0	6[c]	

[a]Polymerizations were carried out at 320 °C for 6 h.
[b]Defined as {[**50**]/([**49**]+[**50**])} × 100.
[c]Melt polymerization.
DOBA, *p*-decyloxybenzoic acid; HOBA, *p*-hexyloxybenzoic acid; OOBA, *p*-octadecyloxybenzoic acid.
Cited from Kimura, K.; Kohama, S.; Yamashita, Y. *Macromolecules* **2002**, *35*, 7545.[28]

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Table 10 Polymerization of **49** in the presence of **51**[a]

51	*Concentration of **51** in feed (mol.%)*[b]	*Yield of **48** (%)*	*DPn of **48*** Calculated	*DPn of **48*** Obtained	*Morphology of **48***
HOPA	10	42	18.3	413	Needle
	30	44	5.5	381	Needle
	60	50	2.3	410	Needle
	80	38	1.5	381	Needle
	30		5.5	4[c]	
DOPA	10	41	14.4	435	Needle
	30	41	4.57	430	Needle
	60	50	2.0	493	Needle
	80	17	1.4	453	Needle
OOPA	10	37	12.8	440	Needle
	30	38	4.1	410	Needle
	60	25	1.9	435	Needle
	80	7	1.3	467	Needle, pillar

[a]Polymerizations were carried out at 320 °C for 6 h.
[b]Defined as {[**51**]/([**49**]+[**51**])} × 100.
[c]Melt polymerization.
DOPA, *p*-decyloxyphenyl acetate; HOPA, *p*-hexyloxyphenyl acetate; OOPA, *p*-octadecyloxyphenyl acetate.
Cited from Kohama, S.; Kimura, K.; Yamashita, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 1757.[29]

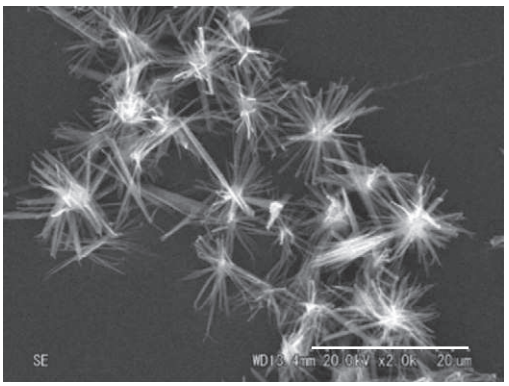

Figure 6 Needle-like crystals of **48** prepared by the polymerization of **49** in the presence of 80 mol.% excess of **51** (*p*-decyloxyphenyl acetate). Scale = 20 μm. Reproduced from Kohama, S.; Kimura, K.; Yamashita, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 1757.[29]

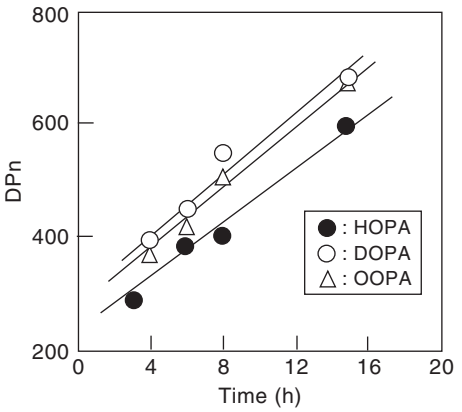

Figure 7 Kinetics of solid-state polymerization in the crystals of **48** prepared in the presence of three kinds of monoacetates **51** (*p*-hexyloxyphenyl acetate (HOPA), *p*-decyloxyphenyl acetate (DOPA), and *p*-octadecyloxyphenyl acetate (OOPA)). Kohama, S.; Kimura, K.; Yamashita, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 1757.[29]

estimated by the feed ratio. The DPn in the system of HOPA was 381, even at HOPA concentration in feed of 80 mol.%. The DPns in the systems of DOPA and OOPA were slightly higher than that in the system of HOPA, and they were 453 and 467, respectively, even at DOPA and OOPA concentrations in feed of 80 mol.%. In contrast to these results, the DPn of the products prepared by bulk polymerization at HOPA concentration in feed of 30 mol.% was 4, and the bulk polycondensation of **49** was terminated by monoacetate according to the classical theory. Figure 7 shows the kinetic considerations of polymerization in the solid state. The solid-state polymerization obeyed second-order kinetics, and the rate constants were estimated and the values of k_2 ranged from 14.5 to 20.8 kg mol^{-1} min^{-1}. They were not significantly influenced by the structure of the monoacetate. Polymerization proceeded effectively in the solid state with the elimination of acetic acid and by-product *p*-alkyloxyphenol (**52**). Polycondensation proceeded even under nonstoichiometric condition through the following mechanisms: when the DPn of oligomers exceeded a critical value, which was approximately 8, oligomers were crystallized to form crystals. End-free oligomers were preferentially crystallized due to the lower solubility compared to oligomers end-capped by monofunctional reagents. End-capped oligomers were also crystallized, and polycondensation proceeded with the elimination of end-capping groups by transesterification just when the oligomers crystallized. Although a part of the end-capped oligomers was contained in the crystals, end-capping groups were excluded by solid-state polycondensation. Even though the monofunctional reagents participated in the polymerization, they could not terminate the polymerization, resulting in the formation of high molecular weight polymers in the form of crystals. If the oligomers precipitated to

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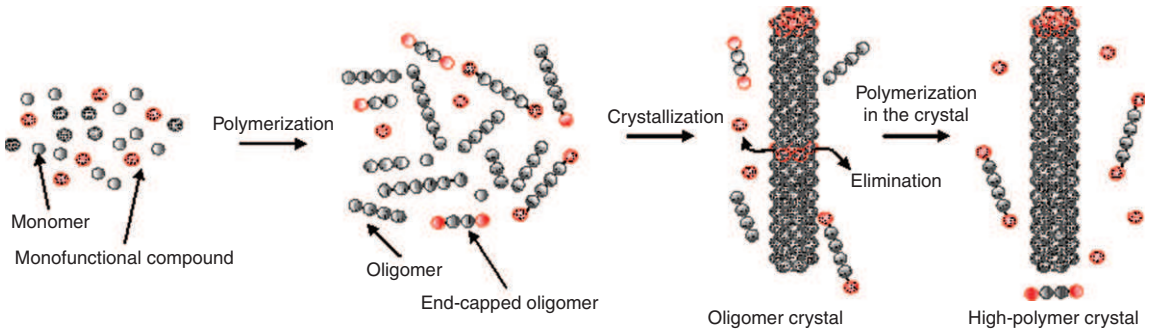
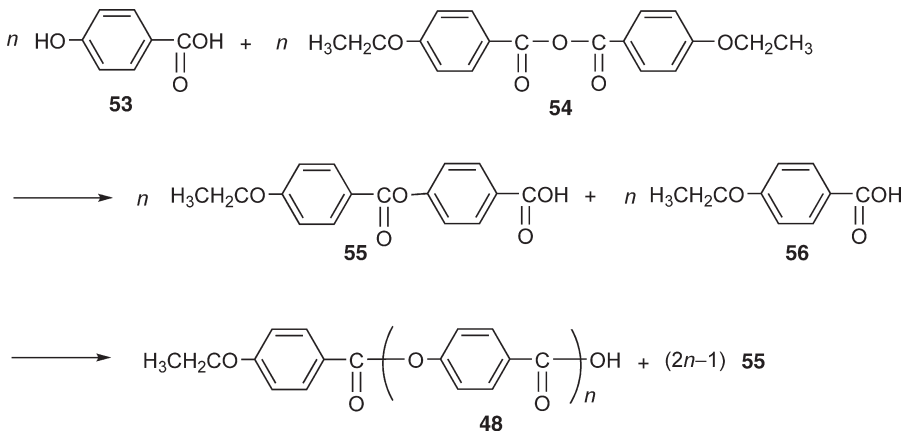


Scheme 19 Schematic illustration of nonstoichiometric polycondensation via crystallization.

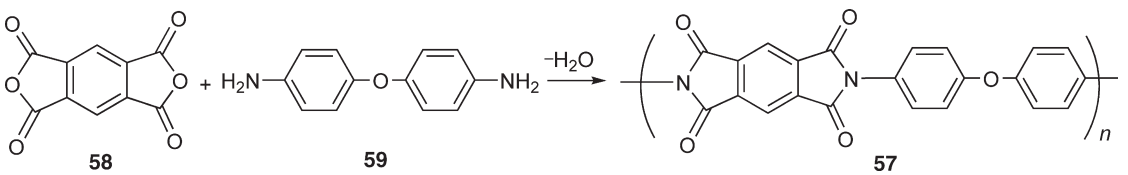
form the crystals, molecular weight increased due to polymerization on/in the crystals. Crystallization of the oligomers is responsible for driving polymer growth by excluding the monofunctional monomer as shown in Scheme 19.

Based on the mechanism of this nonstoichiometric polycondensation accompanied by reaction-induced crystallization of oligomers, direct synthesis of **48** was proposed by polycondensation of *p*-hydroxybenzoic acid (**53**) with equivalents of *p*-ethoxybenzoic anhydride (**54**) as a condensation reagent as shown in Scheme 20.[30] Polymerizations were carried out at 320 °C in aromatic solvents and liquid paraffin. **48** having a DPn of 76 was obtained as fibrillar and pillar-like crystals. **53** was first converted to reactive acyloxyaromatic acid intermediate (**55**) by the reaction of phenolic OH of **53** and anhydride group in **55**. The oligomers precipitated to form crystals via crystallization, and then the DPn increased by an acid–ester exchange reaction between oligomers on and in the crystals. Even though the stoichiometry between two functional groups was imbalanced by by-production of *p*-ethoxybenzoic acid (**56**), polymerization was not terminated and it proceeded under nonstoichiometric condition. Other aromatic polyesters such as poly(4′-oxy-4-biphenylcarbonyl) and poly(2-oxy-6-naphthoyl) were also prepared by the direct polycondensation of 4′-hydroxy-4-biphenylcarboxylic acid and 2-hydroxy-6-naphthoic acid in the presence of **54** or 2-naphthoic anhydride as condensation reagents.[31]

Nonstoichiometric synthesis of polyimide (**57**) called Kapton had also been studied using reaction-induced crystallization of oligomers during solution polymerization.[32] Pyromellitic dianhydride (**58**) and 4,4′-oxydianiline (**59**), shown in Scheme 21, polymerized in aromatic solvents at 330 °C at a low concentration on varying the molar ratio of **58** and **59** in feed, that is, on varying χ (=[58]/[59]). Pale orange precipitates of **57** were obtained even under nonstoichiometric conditions. The precipitated crystals exhibited clear habits, shown in Figure 8, and they possessed quite high crystallinity. To compare the influence of χ on the molecular weight, **57** was synthesized by the conventional homogeneous solution polymerization at various χ values and by thermal imidization. The molecular weights of **57** prepared by both procedures were plotted as a function of χ (Figure 8). A slight shift of χ from 1.0 drastically lowered the molecular weight in the solution polymerization, whereas polymerizations with



Scheme 20 Direct polycondensation of **53** with **54** as a condensation reagent.



Scheme 21 Preparation of **57** under nonstoichiometric condition using reaction-induced crystallization during polymerization.

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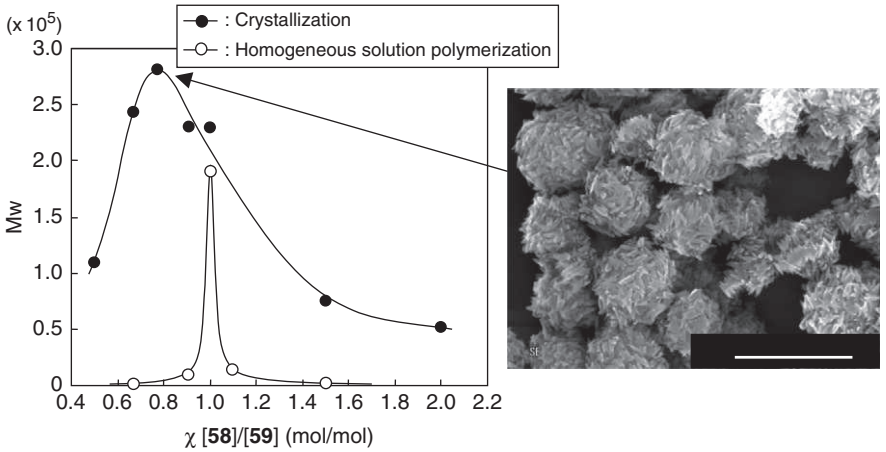
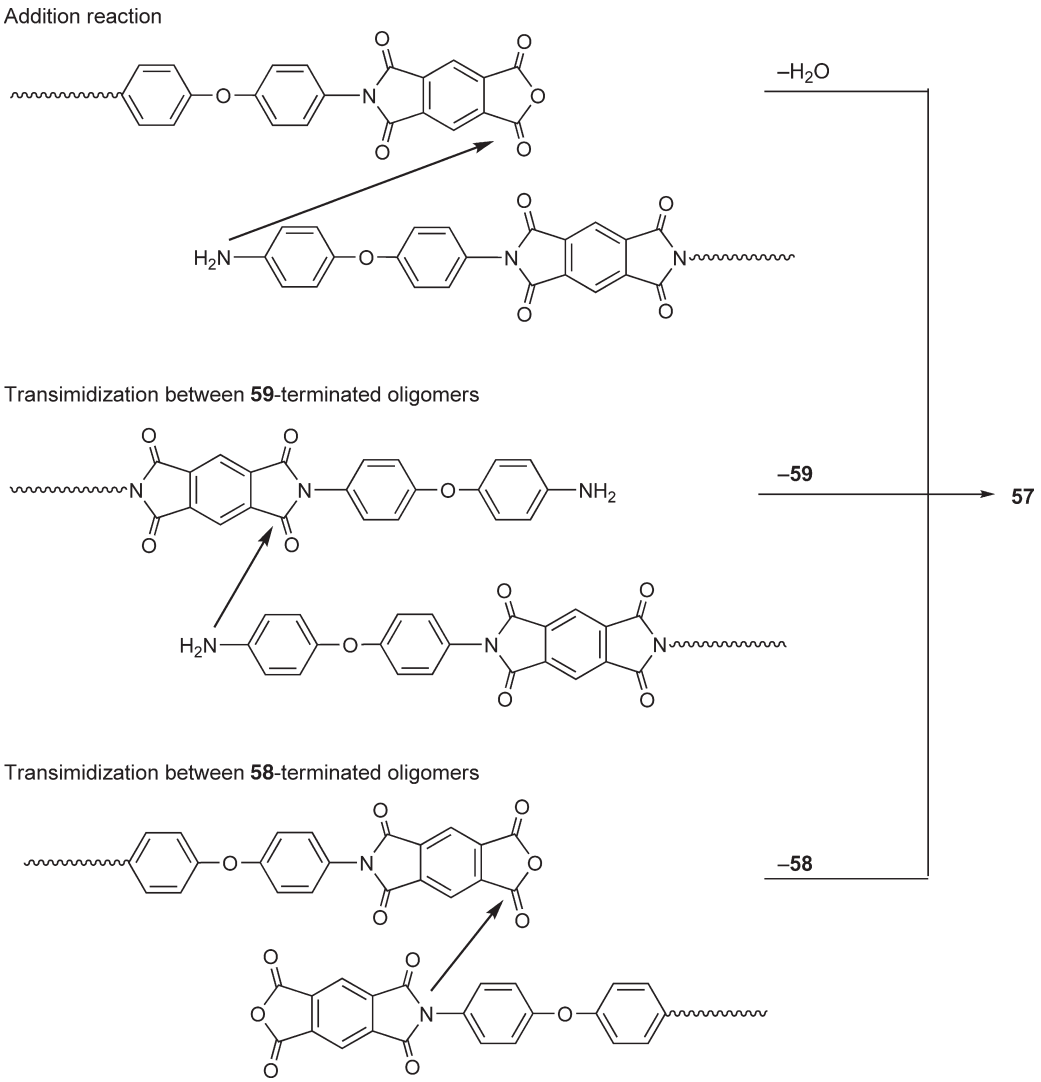


Figure 8 Influence of stoichiometry on Mw of **57** prepared from **58** and **59** by heterogeneous polymerization via crystallization for 6 h and by the homogeneous solution polymerization and by thermal imidization. Scale = 2 μm. Reproduced from Wakabayashi, K.; Kohama, S.; Yamazaki, S.; Kimura, K. *Macromolecules* **2008**, *41*, 1168.[32]



Scheme 22 Solid-state polymerization mechanism of **57**. Reproduced from Wakabayashi, K.; Kohama, S.; Yamazaki, S.; Kimura, K. *Macromolecules* **2008**, *41*, 1168.[32]

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crystallization of oligomers afforded the high-molecular-weight **57** under a wide range of χ. The χ value of 0.77, which was 30 mol.% excess of **59**, afforded aggregates of needle-like crystals having the highest Mw of 2.81×10^5. Mw changed gradually with χ. Even at χ of 0.5 and 2.0, Mws of **57** were 1.09×10^5 and 5.20×10^4, respectively. This polymerization system is unsusceptible to χ. The polymerization proceeded with the formation of crystals due to the continuous supply of oligomers from the solution. The oligomers were end-capped by the excess monomers and the end-groups were nonstoichiometric. The solid-state polymerization in the precipitated crystals occurred not only by the addition reaction between amino end-groups and anhydride end-groups of the oligomers but also by the transimidization reaction as depicted in Scheme 22. Because of this solid-state polymerization, the molecular weight increased even under nonstoichiometric condition.

5.05.4 Conclusion

According to the classical theory of polycondensation, the highest molecular weight polymers are obtained under strictly controlled stoichiometric conditions, that is to say, an exact 1:1 molar ratio of two functional groups is necessary. However, it has been found that an excess of one functional group affords polymers of sufficiently high molecular weight comparable to those prepared under stoichiometrically balanced condition. Sometimes, nonstoichiometric polycondensation affords polymers of sufficiently high molecular weight. The stream of the research on this unusual polycondensation is directed toward not only the chemical effect but also the physical effect:

1. *Chemical effect*. If one functional group of bifunctional monomer **A** becomes more reactive by the reaction of another functional group in the same monomer **A** with a functional group of bifunctional monomer **B**, this intermediate is liable to react faster with a functional group in monomer **B** than the unreacted monomer **A**, leading to the formation of **B-A-B** even under an excess amount of monomer **A** in the reaction mixture. The polymerization proceeds until all monomer **B** is consumed and the polymer is terminated by monomer **A**. Although the stoichiometric balance of two functional groups ideally gives the highest molecular weight at $p = 1$, the polymerization needs infinite time and this is impractical. It is of great advantage that the stoichiometric imbalance between two functional groups often accelerates the reaction and high-molecular-weight polymers are obtained within a practical time frame.
2. *Physical effect*. Formation of higher structure of polymers such as a specific conformation and crystal structure during polymerization can lead the polymerization, and high-molecular-weight polymers are formed even under nonstoichiometric condition. Even under the condition of stoichiometric imbalance, the polymers are synthesized by building up small pieces regularly to form thermodynamically stable conformations. This mechanism is identical to nucleation and growth mechanism, and the physical driving force selects the desirable pieces from monomers and various oligomers. Reaction-induced crystallization during polymerization is also of importance to form the superstructure of polymers. In this polymerization, polymer-forming phase is changed from the solution to crystals by crystallization of oligomers. This unique polymerization can adjust the stoichiometric imbalance by exclusion of excess monomer residues at the end of oligomers from the crystal to the solution, like the exclusion of impurities in crystallization, resulting in an increase in molecular weight.

The future research will bring into focus the nonstoichiometric polycondensation based on both chemical and physical effects possessing a large potential for preparation of polymers, including their architecture, and it will become closer to the true system for the creation of a wide variety of polymers in nature.

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Biographical Sketch

Kunio Kimura received his master's degree in 1983 from Osaka University, Japan. After graduation, he worked for TOYOBO Co. Ltd. from 1983 to 1995 and developed thermally stable polyesters, heterocyclic polymers, and biodegradable plastics. He received his PhD degree from Osaka University in 1995. Then he moved to Okayama University, Japan, and was promoted to professor in 2003. His research interests cover morphology control of polymers using reaction-induced phase separation during polymerization, precision polycondensation, and synthesis of fluorine-containing aromatic polymers.

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5.06 Chain-Growth Condensation Polymerization

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5.06.1 Introduction

Polycondensation is an important method of polymerization that yields not only engineering plastics such as polyamides, polyesters, and polyimides but also π-conjugated polymers. Conjugated polymers have recently received considerable attention as an attractive class of materials owing to their use as organic electronic materials in devices such as field-effect transistors (FETs), organic light-emitting diodes (OLEDs), and photovoltaic cells. However, the molecular weight of these polymers is generally difficult to control and their polydispersity index theoretically approaches 2 at high conversion, which is unlike the behavior of living polymerization. An uncontrolled molecular weight and broad molecular weight distribution do not stem inherently from the reaction type of condensation polymerization, that is, condensation steps with elimination of a small molecule species, but from a polymerization mechanism for step-growth polymerization. Accordingly, if the mechanism of polycondensation could be converted from step growth to chain growth, condensation polymers with controlled molecular weight and low polydispersity could be synthesized. Nature already uses a chain-growth condensation polymerization process to synthesize perfectly monodisperse biopolymers such as polypeptides,[1,2] DNA,[3] and RNA.[4,5] For example, in the biosynthesis of polypeptides, the amino group of an aminoacyl-tRNA monomer, selectively reacts with the terminal ester moiety of polypeptidyl-tRNA in a ribosome to elongate the peptide chain. Even in artificial condensation polymerization of AB monomers, chain-growth mechanism can be involved if the reactivity of the polymer end group becomes higher than that of the monomer. Conventional polycondensation, which proceeds in step-growth polymerization manner, assumes that all functional groups of monomer and polymer are of equal reactivity as described in Flory's statistical treatment. In condensation polymerization of monomers with two functional groups at close position, the reactivity of one functional group of the monomer could be changed after reaction of the other functional group with the polymer end group. In this chapter, several approaches to chain-growth condensation polymerization are described.

5.06.2 *p*-Substituted Aromatic Polymers

5.06.2.1 Polyamides

One way to achieve selective reaction of a monomer with the polymer end group would be the enhancement of reactivity of the polymer end group by the change of the substituent effect induced by bond formation to the monomer. Monomers having both nucleophilic and electrophilic sites at the *p*-position would be susceptible to the change of substituent effect through the resonance effect (**Scheme 1**).

There were some observations of such selective, though not predominant, reactions of monomers with polymer end groups in the polycondensation of 4-halothiophenoxide,[6] 4-chlorophenylsulfonyl phenoxide,[7] 4-fluoro-4′-hydroxy benzophenone,[8,9] 4-halobenzenesulfonate,[10] 2,6-dimethylphenol,[11,12] and 4-bromo-2,6-dimethylphenol.[13–16] About a decade after these reports, Yokozawa *et al.*[17] found that condensation polymerization of phenyl 4-(octylamino)benzoate **1a** in the presence of a base (a combination of *N*-octyl-*N*-triethylsilylaniline, CsF, and 18-crown-6) and phenyl 4-nitrobenzoate **2** as an initiator yielded well-defined aromatic polyamides with very low polydispersities ($M_w/M_n \leq 1.1$) (**Scheme 2**). The number average molecular weight

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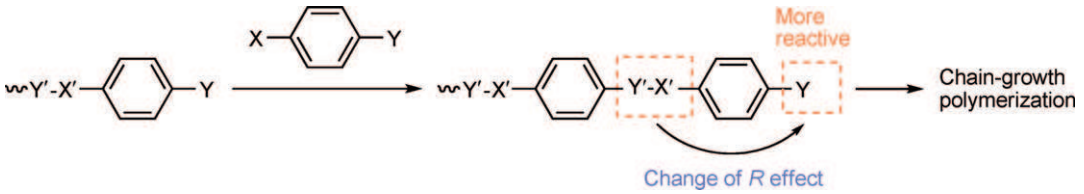
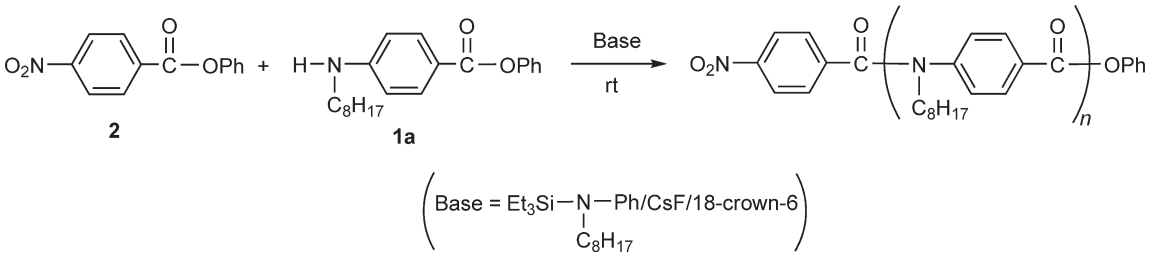


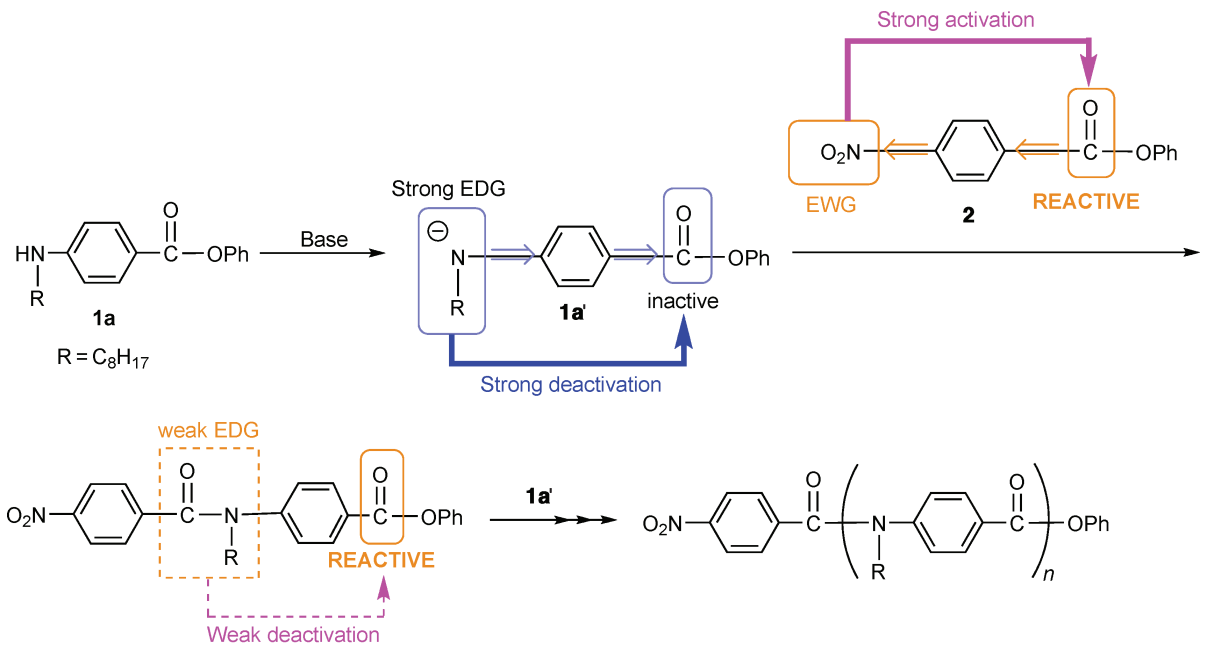
Scheme 1 General scheme of chain-growth condensation polymerization for *p*-substituted aromatic polymers.



Scheme 2 Chain-growth condensation polymerization for aromatic polyamides.

(M_n) of the polymer was controlled by the feed ratio of monomer to initiator, and polymers with molecular weights up to 22 000 g mol^{-1} and low polydispersity index were obtained. Furthermore, the M_n values also increased in proportion to monomer conversion, indicating that this polycondensation proceeded as a chain-growth polymerization.

This result is explained by different substituent effects between the monomer and the polymer (Scheme 3). The base abstracts the proton of the amino group of monomer 1a to generate the amide anion 1a′. This anion deactivates the phenyl ester moiety of 1a′ by its strong electron-donating ability through the resonance effect, thus preventing a monomer from reacting with another one. The monomer anion 1a′ will react with initiator 2, which has an electron-withdrawing group, due to increased reactivity of the phenyl ester moiety of 2. The amide obtained has a weak electron-donating amide linkage, and the phenyl ester moiety of the amide is more reactive than that of 1a′. Thus, the next monomer would selectively react with the phenyl ester moiety of the amide. Growth would continue in a chain polymerization manner by the selective reaction of 1a′ with the polymer terminal phenyl ester moiety. This monomer 1a underwent chain-growth polymerization to yield the polyamide with low polydispersity even under normal conditions for step-growth polycondensation, where the initiator 2 was not



(EDG: Electron-donation group: EWG: Elcetron-withdrawing group)

Scheme 3 Proposed polymerization mechanism of **1a**.

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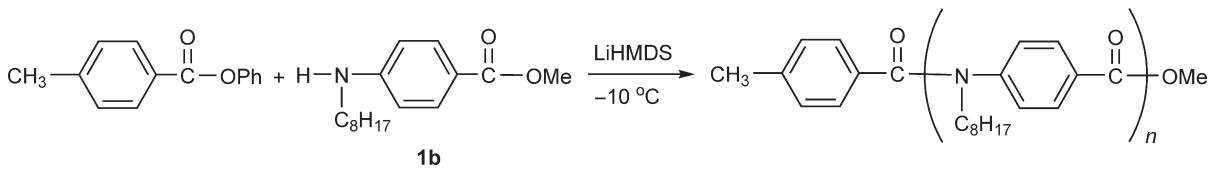
added. The polymerization probably involves the formation of the dimer of **1a**, which initiates chain-growth polymerization faster than step-growth polymerization.[18]

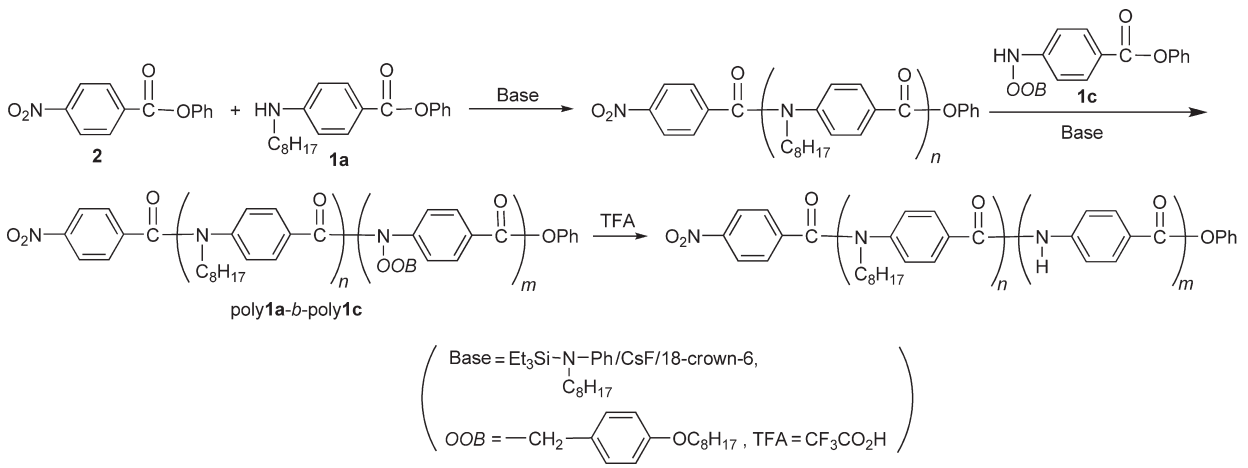
The above synthetic method for well-defined aromatic polyamides, however, requires an unusual base, *N*-octyl-*N*-triethylsilylaniline, along with CsF and 18-crown-6. Additionally, the monomer has a phenyl ester moiety as an electrophilic site, which is not common as compared with a methyl or an ethyl ester. Furthermore, it is necessary to separate the polyamide obtained from by-products such as *N*-octylaniline and phenol by high-performance liquid chromatography (HPLC). For a more convenient synthesis, the polycondensation of the corresponding methyl ester monomer **1b** with a commercially available base has been developed.[19] The methyl ester **1b** is polymerized with lithium hexamethyldisilazide (LiHMDS) in the presence of an initiator in tetrahydrofuran (THF) at −10 °C (**Scheme 4**). The highly pure polyamide with a well-defined molecular weight and low polydispersity was obtained after simple treatment of the reaction mixture with aqueous NaOH solution followed by evaporation. An advantage of this method is the formation of low-boiling-point by-products such as methanol, ammonia, and hexamethyldisiloxane. The condensation polymerization of a similar monomer containing a 3-acyl-2-benzothiazolthione as the electrophilic site instead of the methyl ester moiety of **1b** with Grignard reagent as a base has also been reported.[20]

Block copolymers of aromatic polyamides have been synthesized by chain-growth condensation polymerization of 4-(alkylamino)benzoic acid esters **1**. An example is the block copolymer of *N*-alkyl and *N*-H polyamides shown in **Scheme 5**.[21] First, *N*-octyl monomer **1a** was polymerized, followed by addition of monomer **1c**, with a protecting group on the amino group, and a base to the reaction mixture. The added monomer **1c** polymerized smoothly from the ends of the poly**1a** chains to yield the block copolymer of poly**1a** and poly**1c**. The protecting group was quantitatively removed with trifluoroacetic acid (TFA) to afford the desired block copolymer of *N*-alkyl and *N*-H polyamides with low polydispersity. The reason monomer **1c** was used for this block copolymerization was that a monomer with a primary amino group did not polymerize under the polymerization conditions.[22] The block copolymer self-assembled in THF by virtue of intermolecular hydrogen bonding of the *N*-H polyamide unit. Scanning electron microscope (SEM) images showed micrometer-sized bundles and aggregates of flake-like structures.[21] Block copolymers of *N*-octyl and *N*-fluoroalkyl polyamides with low polydispersity were also synthesized and their self-assembly was studied.[23,24]

Block copolymers of aromatic polyamide and conventional coil polymers were prepared by the reaction of the polymer end group of the polyamide with the living propagating group of the coil polymer. Thus, the phenyl ester moiety of the polyamide reacts with the anionic living end of the coil polymer, whereas the amino group of the polyamide reacts with the cationic living end of the coil polymer. For example, poly(ethylene glycol) (PEG) monomethyl ether was reacted with the polyamide, prepared by the chain-growth condensation polymerization of **1a**, in the presence of NaH to yield a block copolymer of polyamide and PEG (**Scheme 6**). Excess of PEG was used in this polymer reaction, but unreacted PEG was removed by washing with water to isolate the block copolymer.[22] Similar reaction of PEG with a polyamide obtained by the chain-growth condensation polymerization of **1a** with phenyl terephthalate as a bifunctional initiator gave a block copolymer of PEG-aromatic polyamide-PEG.[25]



Scheme 4 Polymerization of methyl ester monomer **1b** with LiHMDS.



Scheme 5 Synthesis of block copolymer of *N*-octyl and *N*-H polyamides.

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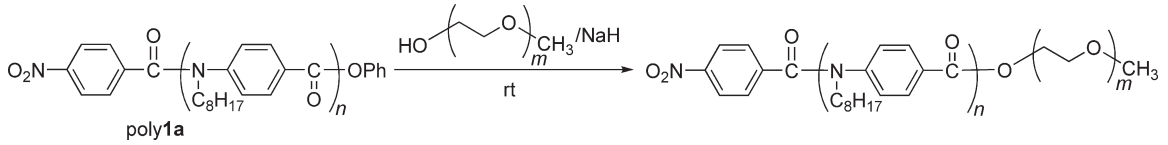
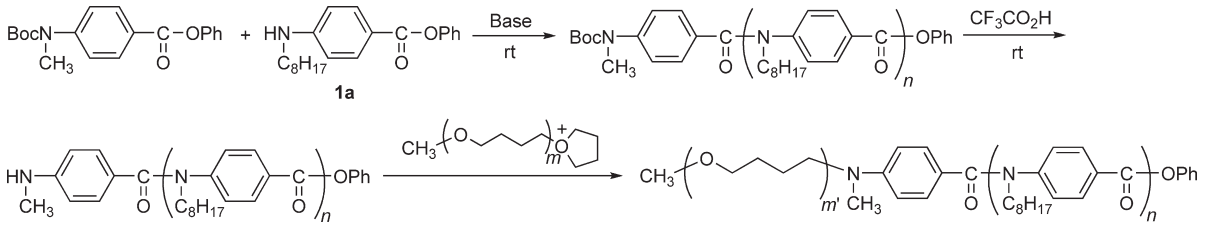


Scheme 6 Block copolymer of aromatic polyamide and PEG.

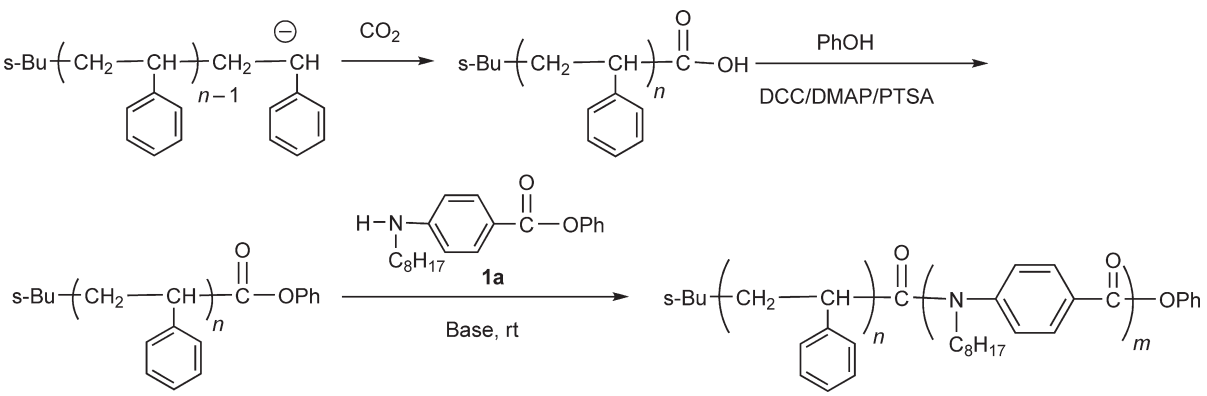


Scheme 7 Block copolymer of aromatic polyamide and poly(THF).

Polyamide with a terminal amino group was prepared by the polymerization of **1a** with an initiator bearing the *tert*-butoxycarbonyl (Boc) protecting group, followed by treatment with TFA to remove the Boc group. The terminal amino group of the polymer reacted with living poly(THF) to yield a block copolymer of polyamide and poly(THF) (**Scheme 7**). When bifunctional living poly(THF) initiated by trifluoromethanesulfonic anhydride was reacted with the above polyamide, polyamide-poly(THF)-polyamide triblock copolymer was produced.[26]

Another approach to block copolymers of the aromatic polyamide and coil polymer was the macroinitiator method involving the chain-growth condensation polymerization of **1a** from a macroinitiator of a coil polymer. A diblock copolymer of polystyrene and the polyamide was synthesized with this approach (**Scheme 8**). First, polystyrene with a terminal carboxyl group was prepared by anionic living polymerization of styrene, followed by quenching with dry ice, and then the carboxyl group was converted to the phenyl ester by using phenol and a condensation agent. From this terminus, chain-growth condensation polymerization of **1a** was carried out to yield the desired block copolymer. When low-molecular-weight macroinitiators were used, the block copolymers with low polydispersity were obtained in good yields. When high-molecular-weight macroinitiators were used, the block copolymer was contaminated with the homopolymer of the polyamide. This is probably because the polymer effect of polystyrene decreased the efficiency of initiation from the macroinitiator to induce self-polycondensation of **1a**.[27] To overcome this problem, a macroinitiator of aromatic polyamide was used for the polymerization of styrene. Thus, the polymer end group of the polyamide was converted to the dithiobenzoate moiety, and reversible addition–fragmentation chain transfer (RAFT) polymerization of styrene was carried out in the presence of this polyamide as a macro-chain transfer agent to yield well-defined diblock copolymer consisting of aromatic polyamide and polystyrene with high molecular weight.[28] A macroinitiator of aromatic polyamide for atom transfer radical polymerization (ATRP), which is more easily synthesized than the chain transfer agent for the RAFT polymerization, was also effective for the synthesis of block copolymer of aromatic polyamide and polystyrene with high molecular weight.[29]

Star-shaped condensation polymers have been prepared by copolycondensation of an A_n monomer with an AB-type monomer or with A_2 and B_2 monomers,[30–33] in which the arm lengths of the polymers obtained are not controlled. Well-defined star-shaped condensation oligomers have been synthesized by the coupling reaction between an A_n monomer and linear monodisperse oligomers, which was prepared by



Scheme 8 Block copolymer of aromatic polyamide and polystyrene.

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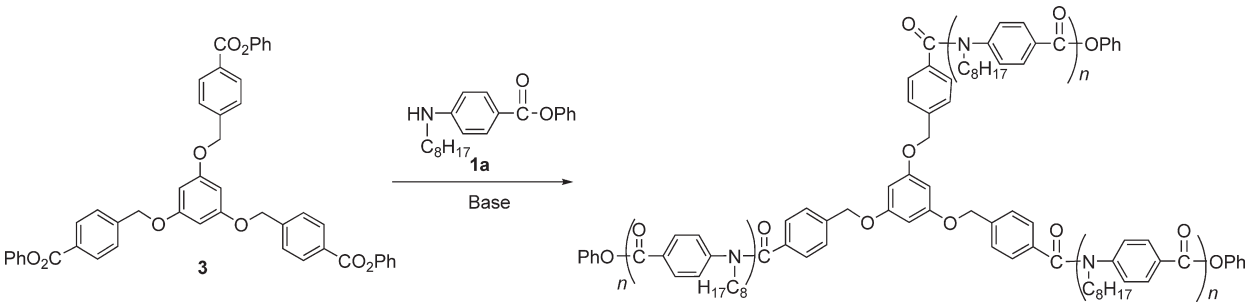


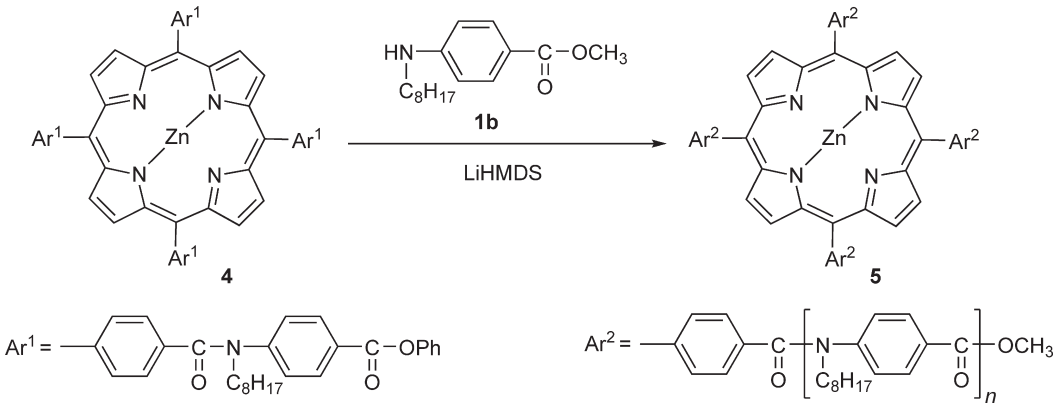
Scheme 9 Synthesis of star polyamides.

sequential condensation procedure.[34–37] Star-shaped aromatic polyamides with low polydispersity by the chain-growth condensation polymerization of **1a** were synthesized from 1,3,5-tris(4-phenyloxycarbonylbenzyloxy)benzene (**3**) having the benzyloxy spacers in the presence of prototype base system (*N*-octyl-*N*-triethylsilylaniline/CsF/18-crown-6) (**Scheme 9**).[38] The benzyloxy linkages of the core of the star polymer were cleaved by hydrogenolysis to yield a polymer with low polydispersity. The M_n of the cleaved polymer was one-third of that of the parent star polymer, indicating that the star polymer possessed three arm chains of uniform length. However, the polymerization at higher feed ratios of $[\mathbf{1a}]_0/[\mathbf{3}]_0$ afforded not only the three-armed polymer but also a linear polymer formed by self-polycondensation of **1a**. In the polymerization of **1a** with a monofunctional initiator, no self-polycondensation of **1a** takes place as long as the feed ratio of $[\mathbf{1a}]_0/[\text{initiator}]_0$ is 100 or less.[17] In the polymerization with trifunctional initiator **3**, however, the self-polycondensation occurred even at the feed ratio of $[\mathbf{1a}]_0/[\text{initiator site of }\mathbf{3}]_0$ of 33, which is much less than 100. Easy occurrence of the self-polycondensation in the polymerization of **1a** with multifunctional initiator **3** is presumably ascribed to the low local concentration of the initiator site in the whole solution except for the area around **3**. Thus, monofunctional initiators homogeneously exist in the solution, whereas multifunctional initiators make both the area of high local concentration of the initiator units and the area of low local concentration of them where self-polycondensation would be liable to occur.

Furthermore, the synthesis of well-defined star-shaped poly (*p*-benzamide) with stronger base, LiHMDS, was investigated by using the porphyrin-cored tetrafunctional initiator **4**. The target star polymer has an absorption at 430 nm due to the porphyrin ring, whereas the linear polymer formed as a by-product does not have this absorption, thus it was easy to differentiate the star polymer from the linear polymer by gel permeation chromatography (GPC) with UV detection and to optimize conditions for the selective synthesis of the star polymer. It then turned out that the polymerization of methyl ester monomer **1b** at 10 °C, which was higher than the optimized temperature (−10 °C) for the synthesis of linear poly**1b** with LiHMDS from a monofunctional initiator, yielded the star polyamide **5** with controlled molecular weight and narrow molecular weight distribution up to the feed ratio of $[\mathbf{1b}]_0/[\mathbf{4}]_0$ of 120 (**Scheme 10**).[39]

5.06.2.2 Polyesters

Synthesis of a well-defined aromatic polyester is more difficult than that of polyamide, because polyester easily undergoes transesterification. The monomer can attack the polymer ester linkage to generate the cleaved chain with the phenoxide moiety and the acyl group at both ends, leading to conventional step-growth polycondensation. Actually, transesterification occurred in the condensation polymerization of monomer **6a**, having an active amide moiety as a good leaving group, even with a weak base such as tertiary amine at room temperature.[40] However, when the polymerization of **6** was carried out at −30 °C with Et_3SiH, CsF, and 18-crown-6 as a base system, transesterification was almost completely suppressed and the molecular weight was controlled up to 7300 with low



Scheme 10 Synthesis of star polyamides from tetrafunctional porphyrin initiator.

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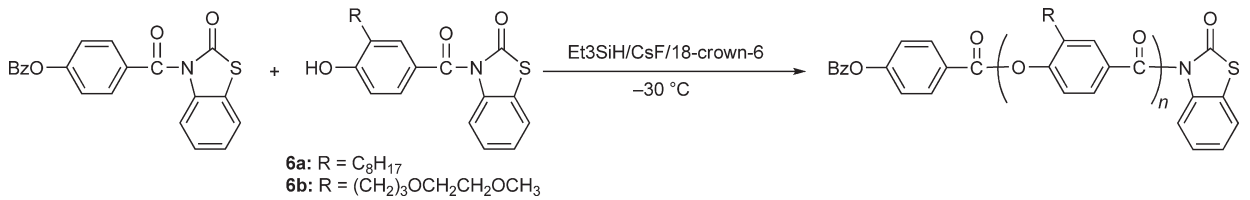
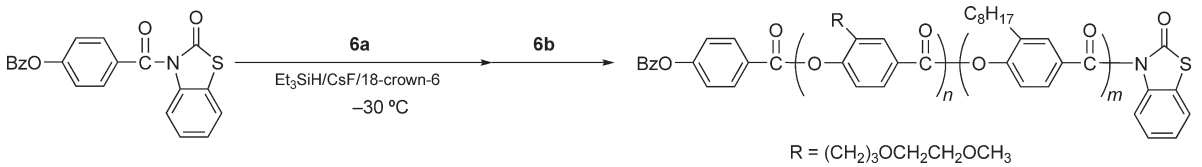


Scheme 11 Chain-growth condensation polymerization for aromatic polyesters.



Scheme 12 Block copolyesters with different side chains.

polydispersity ($M_w/M_n \leq 1.3$) (Scheme 11).[41] Under this condition, a block copolyester bearing different side chains was synthesized in one-pot by monomer addition method (Scheme 12).[41]

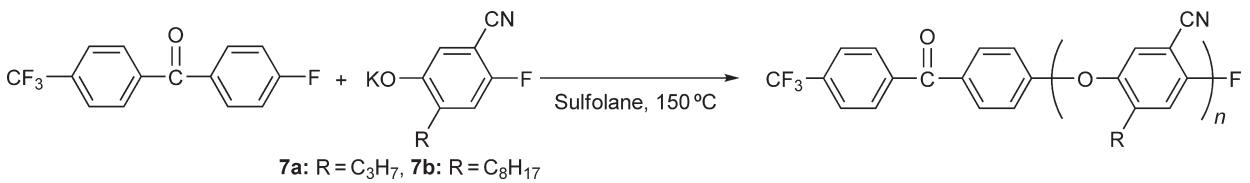
5.06.2.3 Polyethers

From the perspective of the advantages of different substituent effects between monomer and polymer for chain-growth condensation polymerization, the synthesis of well-defined polyethers seems to be difficult because the hydroxyl group in a monomer and the ether linkage of a polymer have similar electron-donating abilities. However, monomer 7a bearing a phenoxide moiety underwent chain-growth condensation polymerization in sulfolane at 150 °C to yield an aromatic polyether with low polydispersity ($M_w/M_n \leq 1.1$). The molecular weight was controlled up to 3500, because polyether with higher molecular weight precipitated during polymerization.[42,43] Monomer 7b substituted with an octyl group instead of the propyl group in 7a also afforded an insoluble polymer in sulfolane when preparation of higher-molecular-weight polymer was attempted (Scheme 13). In other solvents such as *N*, *N*-dimethylimidazolidinone (DMI) and tetraglyme, the polymerization proceeded homogeneously, but both chain-growth and step-growth polymerizations took place to give a polyether with broad molecular weight distribution.[44]

The key to successful chain-growth condensation polymerization of 7 is the use of phenoxide in the monomer instead of phenol. The phenoxide moiety works as a stronger electron-donating group than does the phenol moiety and the ether linkage, and the carbon attached to the fluorine in monomer 7 is strongly deactivated to prevent 7 from reacting with 7. Accordingly, 7 reacts selectively with the initiator and the polymer end group, resulting in chain-growth condensation polymerization (Scheme 14).

It is interesting that the polyether with low polydispersity from chain-growth condensation polymerization was more crystalline than the product with broad molecular weight distribution from conventional step-growth condensation polymerization. The powder X-ray diffraction (XRD) pattern of the former was more intense, and the differential scanning calorimetry (DSC) profile showed an exothermic peak at 172 °C (cold crystallization) on heating from the glassy state.[43] This implies that the crystallinity of condensation polymers may be controlled by polydispersity.

Well-defined diblock copolymers of polystyrene and the aromatic polyether have been synthesized by the combination of ATRP and this chain-growth condensation polymerization from an orthogonal initiator, which has two different initiating sites for two kinds of polymerization, with one of the initiating sites being inert with respect to polymerization from the other initiating site.[45] A polystyrene macroinitiator was first synthesized by the ATRP of styrene in the presence of the orthogonal initiator with the benzylic bromide moiety, then the terminal bromine of the polystyrene was dehalogenated with Bu_3SnH. The chain-growth condensation polymerization of 7a was then carried out with the polystyrene macroinitiator in sulfolane at 150 °C to afford well-defined polystyrene-*b*-aromatic polyether (Scheme 15). This diblock copolymer self-assembled in THF to form spherical aggregates. However, block copolymer of the aromatic polyether and polyacrylonitrile was synthesized in a reverse order of polymerization, because polyacrylonitrile macroinitiator underwent degradation with 7a under the conditions for the polymerization of 7a.[46]



Scheme 13 Chain-growth condensation polymerization for aromatic polyethers.

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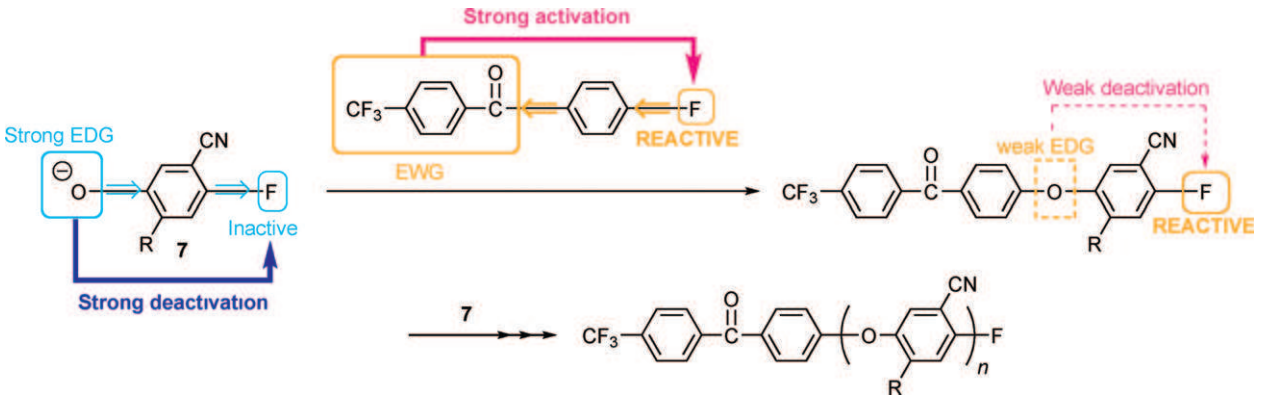
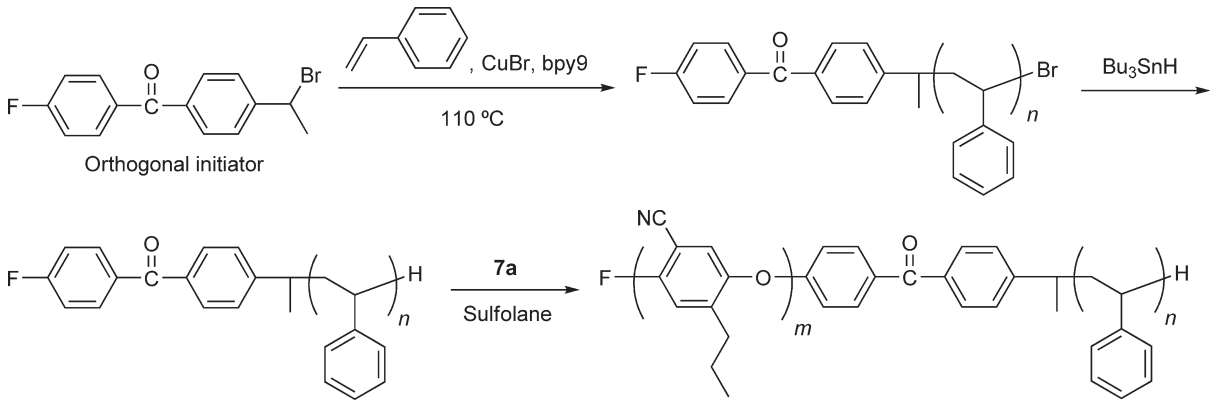
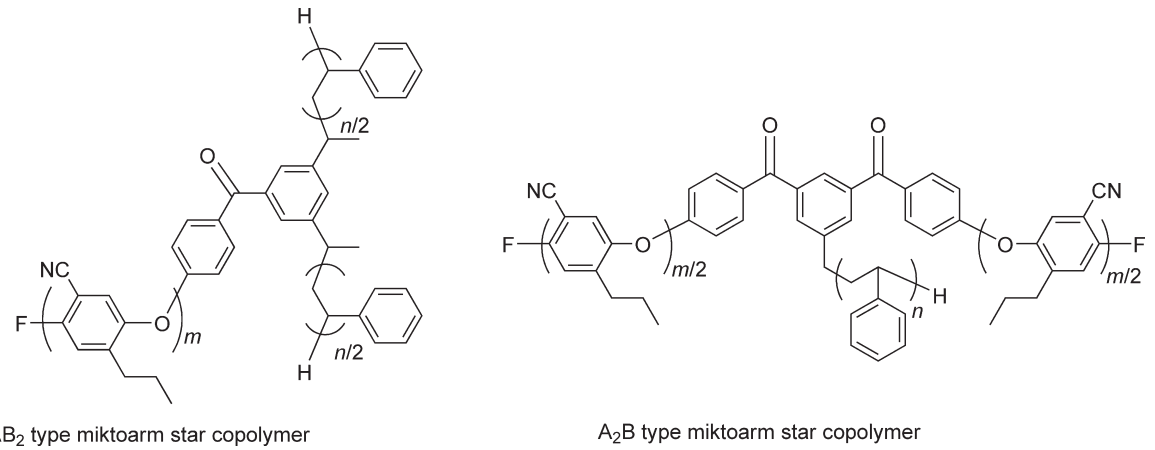


Scheme 14 Proposed polymerization mechanism of **7**.



Scheme 15 Block copolymer of aromatic polyether and polystyrene.



Scheme 16 Miktoarm star copolymers of aromatic polyether and polystyrene.

This orthogonal approach was applied to the synthesis of AB_2- and A_2B-type miktoarm star copolymers consisting of aromatic polyether arms as the A segment and polystyrene arms as the B segment, and their self-assembly was studied in comparison with that of the AB-type diblock copolymer (Scheme 16).[47] As in the case of the AB-type diblock copolymer, the AB_2- and A_2B-type miktoarm star copolymers self-assembled to form spherical aggregates of 150–600 nm diameter when a THF solution of the copolymers was allowed to dry on a glass plate. Similar spherical aggregates were obtained from a THF–methanol solution of the A_2B-type miktoarm star copolymer, whereas the AB_2-type afforded fiber-like structures under the same conditions (Figure 1). The solvent- and polymer structure-dependent changes of morphology would be induced by the lower solubility of the polystyrene and poly7a segments in THF–methanol compared with THF solution. Because the AB_2-type miktoarm star

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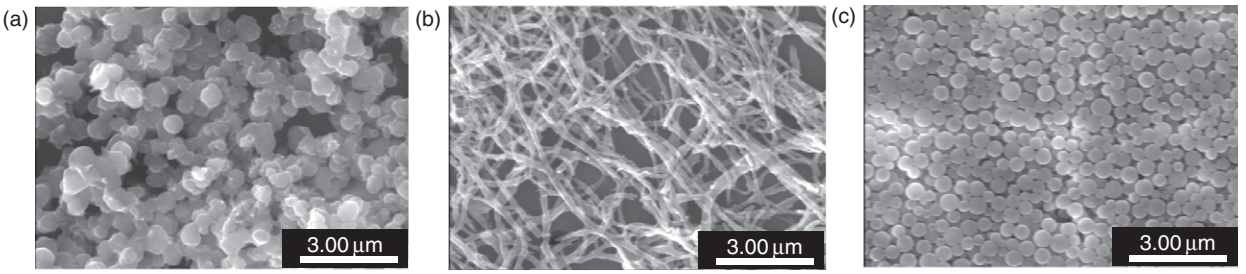


Figure 1 SEM images of self-assembled (a) AB-type diblock copolymer (M_n = 6700, M_w/M_n = 1.16, **7a**$_{14.3}$-*b*-St$_{28.8}$), (b) AB$_2$-type miktoarm star polymer (M_n = 8360, M_w/M_n = 1.14, **7a**$_{14.7}$-*b*-(St$_{17.5}$)$_2$), and (c) A$_2$B-type miktoarm star polymer (M_n = 7900, M_w/M_n = 1.08, (**7a**$_{7.7}$)$_2$-*b*-St$_{37.0}$) in a THF–MeOH solution (2:1, v/v). Reprinted with permission from Ajioka, N.; Suzuki, Y.; Yokoyama, A.; Yokozawa, T. Macromolecules **2007**, 40, 5294–5300.[45] Copyright 2008 American Chemical.

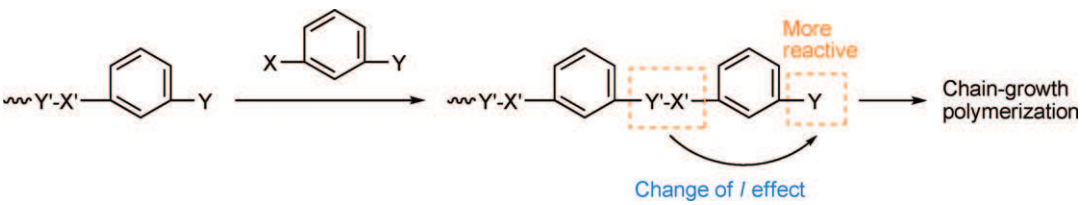
copolymer contains two polystyrene arms, the fiber-like structure of the polymer would result from the combination of enhanced aggregability of the branched polystyrene unit and high crystallinity of the poly**7a** segment in THF–methanol solution. On the other hand, the enhancement of the aggregability of the A$_2$B-type miktoarm star copolymer is thought to be insufficient to induce a change of self-assembled structure, probably due to intrinsically high solubility of this polymer in organic solvents.

5.06.3 *m*-Substituted Aromatic Polymers

In the chain-growth condensation polymerization of *p*-substituted monomers, the anionic nucleophilic site deactivates the electrophilic site on the *p*-position through the resonance effect (+*R* effect), resulting in suppression of self-condensation of the monomer, but selective reaction with an initiator and the propagating end, leading to chain-growth polymerization. If this polymerization method can be applied to the condensation polymerization of *m*-substituted monomers, well-defined aromatic polymers with higher solubility can be obtained compared to that of *p*-substituted aromatic polymers. However, one might think that it would be difficult, because the anionic nucleophilic site of the monomer never deactivates the electrophilic site on the *m*-position through the +*R* effect, and there is a little of possibility of the deactivation through the inductive effect (+*I* effect). The acidity of benzoic acid derivatives, however, shows that the –*I* effect of the *m*-nitro group, a strong electron-withdrawing substituent, is as strong as the –*R* effect of the *p*-nitro group: the pK_a of *m*-nitrobenzoic acid is 3.45, and that of *p*-nitrobenzoic acid is 3.44.[48] Therefore, the strong electron-donating nucleophilic site is expected to show an inductive effect (+*I* effect) on the reactivity of the electrophilic site at the *m*-position as strong as the *R* effect, resulting in suppression of self-condensation of the monomer in a similar manner to the chain-growth condensation polymerization of *p*-substituted monomers (Scheme 17).

5.06.3.1 Polyamides

Ethyl 3-(alkylamino)benzoate **8** was polymerized in the presence of LiHMDS as a base and phenyl 4-methylbenzoate as an initiator in THF at 0 °C to yield *N*-alkylated poly(*m*-benzamide)s with well-defined molecular weights and low polydispersities ($M_w/M_n \leq 1.1$) (Scheme 18). When the *N*-alkyl group was an octyl group, the M_n value of the polymer was controlled up to 12 000 by the feed ratio of the monomer to initiator, and the polydispersity was quite low.[49] In this polymerization, the amide anion of **8** would deactivate the acyl group at the *m*-position through the strong +*I* effect, resulting in suppression of the self-polycondensation of **8**. The anion of **8** then selectively reacts with initiator and the polymer chain end, the acyl group of which is more reactive than that of the monomer with the amide anion, and growth would continue in a chain polymerization manner. To support this mechanism, density functional theory (DFT) calculations were performed. The activation energies for the propagation and self-condensation were 21.6 and 27.0 kcal mol^{-1}, respectively. On the basis of the geometries, energies, and vibrational frequencies obtained, the theoretical rate constants were then evaluated at 298.15 K and 1 atm. The reaction rate constant (1.1×10^{-3} s^{-1}) for the propagation is 8.6×10^3-fold greater than that for the self-condensation (1.3×10^{-7} s^{-1}), and hence is consistent with the experimental finding that propagation was observed exclusively over self-condensation; that is, chain-growth condensation polymerization of *m*-substituted aminobenzoic ester monomers proceeded. A variety of well-defined poly(*m*-benzamide)s were synthesized from the corresponding monomers. All these polymers have higher solubility than the *p*-substituted counterparts.[50] Interestingly, poly



Scheme 17 General scheme of chain-growth condensation polymerization for *m*-substituted aromatic polymers.

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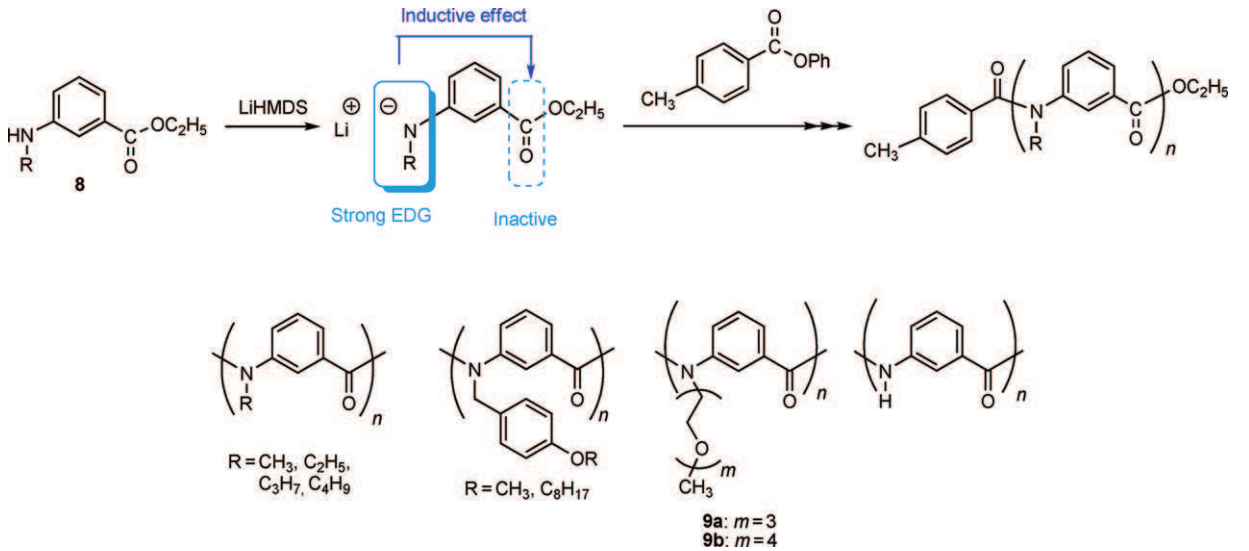
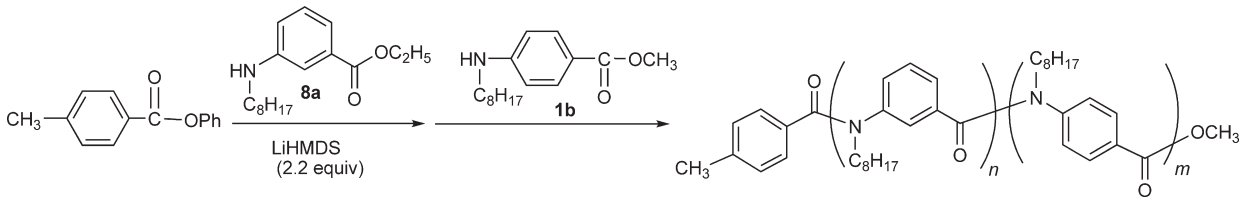


Scheme 18 A variety of *N*-alkylated poly(*m*-benzamide)s.



Scheme 19 Block copolymer of poly(*m*-benzamide) and poly(*p*-benzamide).

(*m*-benzamide)s **9** having oligo(ethylene glycol) are soluble in water, and an aqueous solution of **9** showed a lower critical solution temperature (LCST).[51] For **9a** (degree of polymerization (DP) = 29.8, $M_w/M_n = 1.19$), a phase separation occurred at around 55 °C, where the solubility of the polymers sharply altered. In contrast, the phase separation of **9b** (DP = 32.7, $M_w/M_n = 1.15$) gradually occurred between 58 and 72 °C, that is, at a higher temperature than that of **9a**.

Under the conditions for the polymerization of ethyl 3-(alkylamino)benzoate **8** with LiHMDS as the base, a well-defined diblock copolymer of *m*- and *p*-substituted poly(benzamide) was synthesized.[49] Ethyl 3-(octylamino)benzoate **8a** was polymerized with 2.2 equiv of LiHMDS at 0 °C to give a prepolymer. A fresh feed of methyl 4-(octylamino)benzoate **1b** was added to the prepolymer in the reaction mixture at the same temperature to obtain the block copolymer (**Scheme 19**). It should be noted that excess LiHMDS in the polymerization of **8a** as the first step did not react at all with the terminal ester moiety of poly**8a**, which was able to initiate the polymerization of **1b** as the second step.

Furthermore, *N*-alkyl poly(*m*-benzamide)-*b*-*N*-H poly (*m*-benzamide), *N*-alkyl poly(*m*-benzamide)-*b*-*N*-H poly (*p*-benzamide), and *N*-alkyl poly(*p*-benzamide)-*b*-*N*-H poly(*m*-benzamide) were synthesized by the above sequential chain-growth condensation polymerization of *N*-alkyl and *N*-octyloxybenzyl monomers, followed by removal of the octyloxybenzyl group with TFA. These block copolymers showed gelating properties at low concentration in various solvents.[52,53] The SEM analysis of the dried CH_2Cl_2 gel revealed that the block copolymers self-assembled to form a three-dimensional network structure, in which the solvent might be confined to afford a gel (**Figure 2**). The gelating properties are dependent on the substitution position (*m*- or *p*-) and the composition ratio of the *N*-H poly(benzamide) segment in these block copolymers. Among them, the block copolymer containing *N*-H poly(*p*-benzamide) showed extensive gelating properties in solvents ranging from aromatic to aprotic polar solvents.

There are several reports on the synthesis of block copolymers composed exclusively of rigid or semirigid condensation oligomers or polymers, and these block copolymers appear to have unique and intriguing characteristics due to strong intermolecular interaction. In general, however, such block copolymers have been composed of polymers with a broad molecular weight distribution or oligomers synthesized in a stepwise manner. However, diblock copolymers composed of poly(*m*-benzamide) and aromatic polyether were synthesized by means of successive chain-growth condensation polymerizations.[54] When an orthogonal initiator for the synthesis of the polyamide and aromatic polyether segments was used, side reactions occurred at the 4-fluorobenzophenone unit of the initiator or the macroinitiator. On the other hand, polymerization of polyamide monomer **8a** with a monofunctional initiator afforded well-defined polyamide, which was subsequently converted to a macroinitiator **10** bearing the terminal 4-fluorobenzophenone unit. Polymerization of polyether monomer **7a** in the presence of **10** proceeded in a chain-growth condensation manner from the

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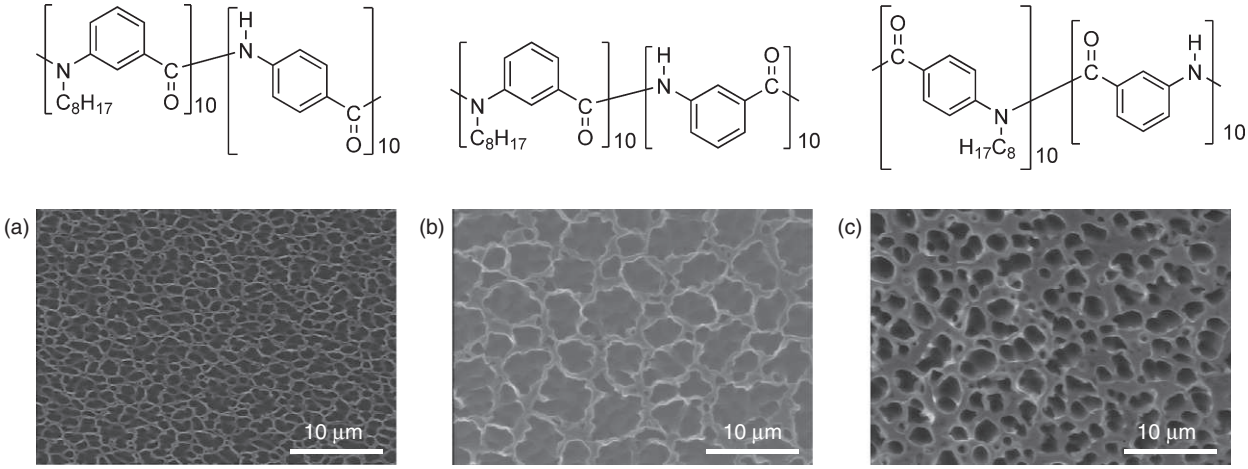
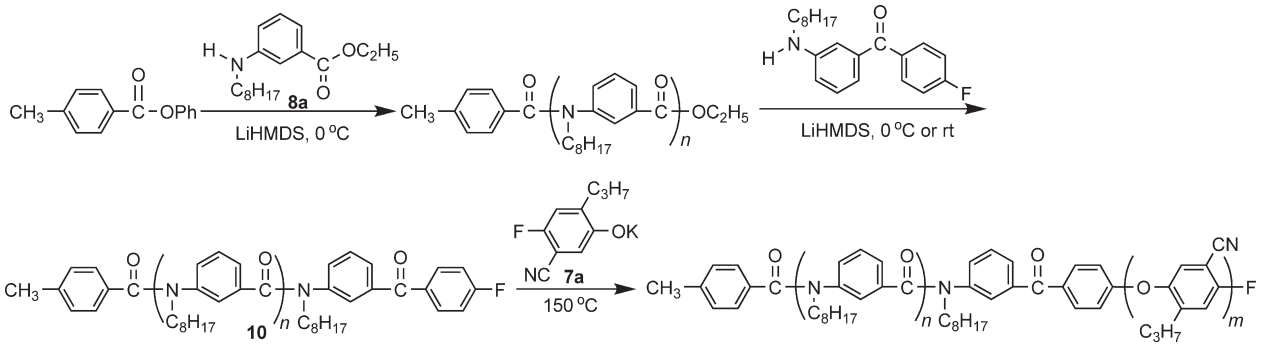


Figure 2 SEM images of (a) dried CH_2Cl_2 gel at 5 wt.% of diblock copolymer and (b, c) structures after drying 5 wt.% solution of diblock copolymer in CH_2Cl_2. Reprinted with permission from Ajioka, N.; Suzuki, Y.; Yokoyama, A.; Yokozawa, T. *Macromolecules* **2007**, *40*, 5294–5300.[45] Copyright 2008 American Chemical Society.



Scheme 20 Block copolymer of aromatic polyamide and polyether.

initiation site of 10 to yield the diblock copolymers of aromatic polyamide and polyether with controlled molecular weight and low polydispersity (Scheme 20).

5.06.3.2 Hyperbranched Polymers

Most of hyperbranched polymers are synthesized by polycondensation or polyaddition, which proceeds through a step-growth polymerization mechanism, so that they generally possess uncontrolled molecular weight and broad molecular weight distribution. The synthesis of hyperbranched polymers with low polydispersity has been tried by slow monomer addition to a core molecule[55,56] or by the use of a highly reactive core molecule.[57] In both methods, however, the polydispersity increased when attempts were made to synthesize polymer with higher molecular weight, because self-polycondensation of the monomer was not fully suppressed. For the synthesis of hyperbranched polymers with defined molecular weight and low polydispersity, irrespective of the amount of the core molecule, the AB_m monomer needs to be polymerized in a chain-growth polymerization manner. On the basis of the above successful chain-growth condensation polymerization of *m*-substituted monomer, the amide anion of 5-(methylamino) isophthalic acid ethyl ester (11) as an AB_2 monomer would also deactivate both the ester moieties through the inductive effect to suppress self-polymerization of the anion of 11, leading to chain-growth polymerization of AB_2 monomer (Scheme 21). Thus, the monomer 11 was polymerized with LiHMDS as a base in the presence of a core initiator and LiCl at −30 °C to yield hyperbranched aromatic polyamide (HBPA) with low polydispersity ($M_w/M_n \leq 1.14$) and a degree of branching of about 0.5.[58] The matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra showed that all HBPAs with different molecular weights contained the initiator unit. The M_n value of HBPA increased linearly in proportion to the ratio of $[11]_0/[\text{initiator}]_0$ up to 40 000, while the M_w/M_n ratio remained at 1.14 or less. Therefore, the polymerization of 11 proceeds through a chain-growth polymerization mechanism from the initiator without side reactions.

Taking advantage of the character of chain-growth polymerization of AB_2 monomer, a well-defined diblock copolymer of linear and hyperbranched polymer was synthesized. Thus, methyl 3-(4-octyloxybenzylamino)benzoate (8b) was polymerized in the presence of an initiator, LiHMDS, and LiCl to give a prepolymer. A fresh feed of 11 was added to the prepolymer in the reaction mixture. The added 11 feed was smoothly polymerized, resulting in successful production of the linear-hyperbranched block copolymer (Scheme 22).

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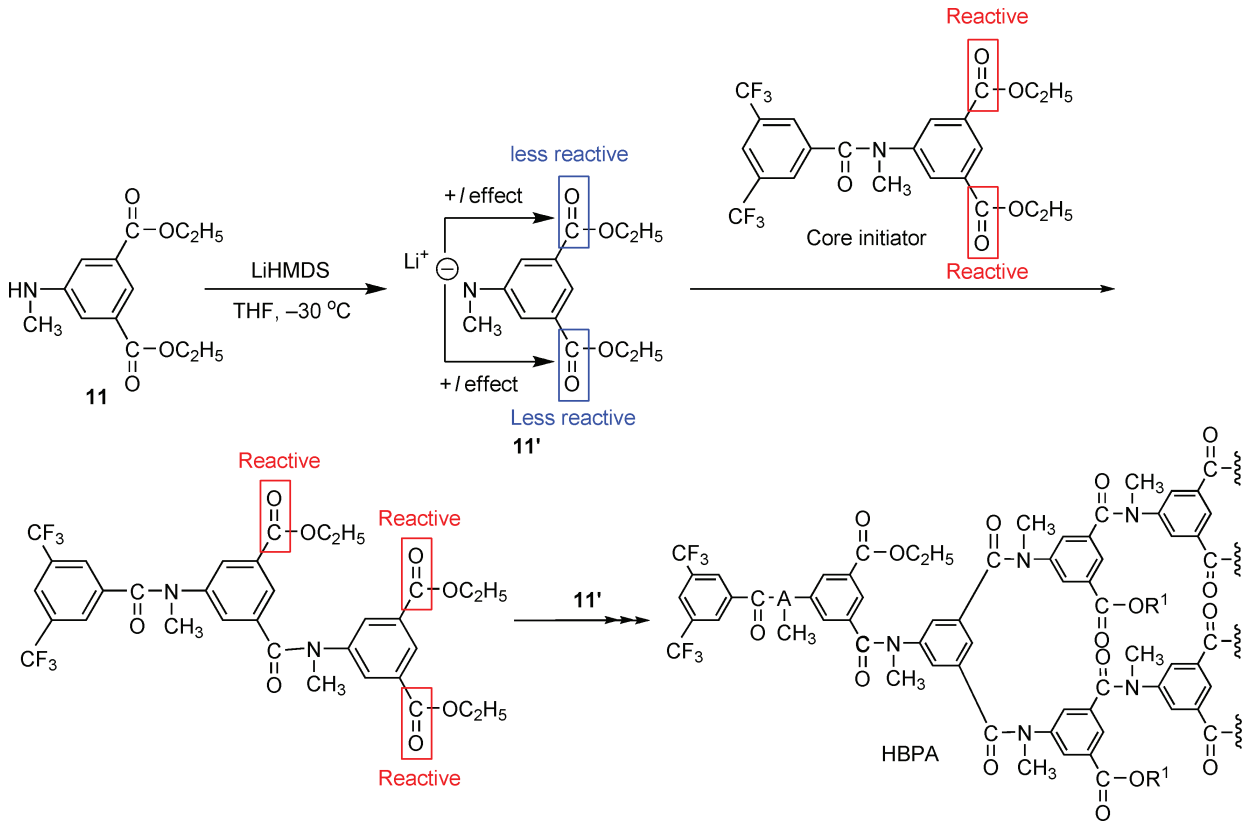
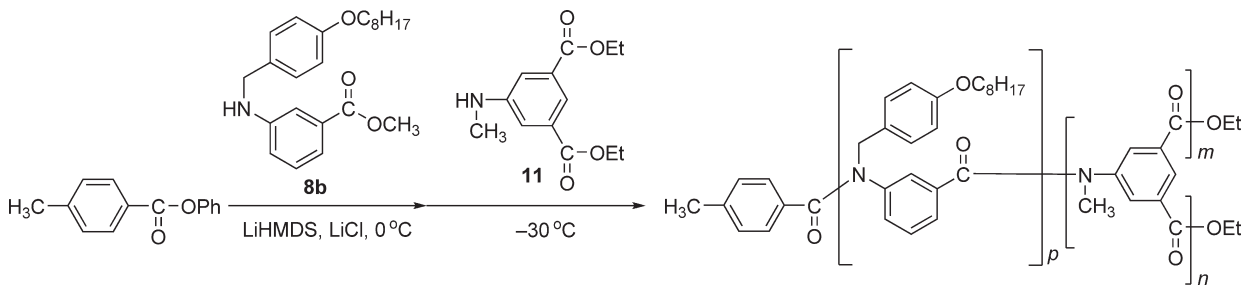


Scheme 21 Chain-growth condensation polymerization for hyperbranched polymers.



Scheme 22 Block copolymer of linear and hyperbranched aromatic polyamides.

5.06.4 Nonaromatic Polymers

5.06.4.1 Polysulfides and Polyesters

In the early 1980s, Percec[59] pointed out that biphasic phase-transfer-catalyzed condensation polymerization showed the behavior of chain-growth condensation polymerization. High-molecular-weight polymers were usually obtained at low conversions. In several cases, even at 100% conversion the polydispersity of the obtained polymers was low ($M_w/M_n < 1.3$). At any conversion, the organic phase contained only polymers with electrophilic chain ends, even when the nucleophilic monomer was used in excess. They speculated that when the nucleophilic anion monomer becomes a polymer chain end, the extraction constant of its onium salt should be molecular weight dependent based on the fact that the hydrophobicity of the nucleophilic anion increases with the increase of the polymer molecular weight. In several cases, the electrophilicity of the polymer end group should be enhanced by *n*-participation (anchimeric assistance) (Scheme 23).[60]

Shaffer and Kramer[61] studied the phase-transfer-catalyzed polymerization of sodium sulfide and a variety of α,ω-dibromoalkanes in detail and found that very high-molecular-weight polysulfide with low polydispersity ($M_n = 683\,000$, $M_w/M_n = 1.24$) was obtained when 1,8-dibromooctane 12 was used as a monomer, together with a catalytic amount of tetrahydrothiophene (THT). In the proposed polymerization mechanism, THT served as an inverse phase-transfer catalyst (PTC). THT reacted with 12 to afford a sulfonium salt, which reacted with sodium sulfide in the water phase. The resulting sulfide was extracted into the organic phase as a quaternary ammonium salt of 8-bromooctyl sulfide by virtue of the PTC QX. Finally, the transferred ammonium

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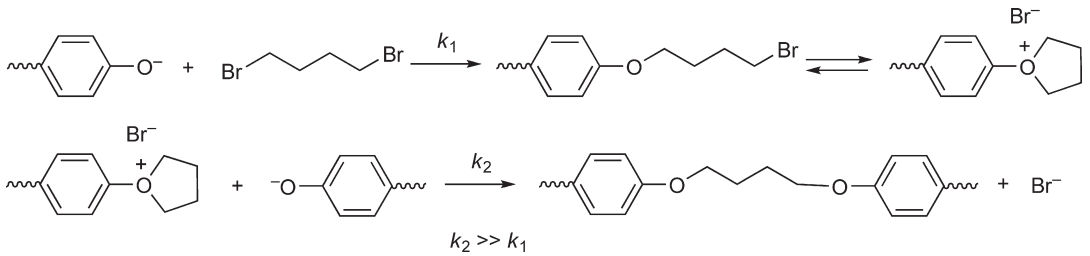
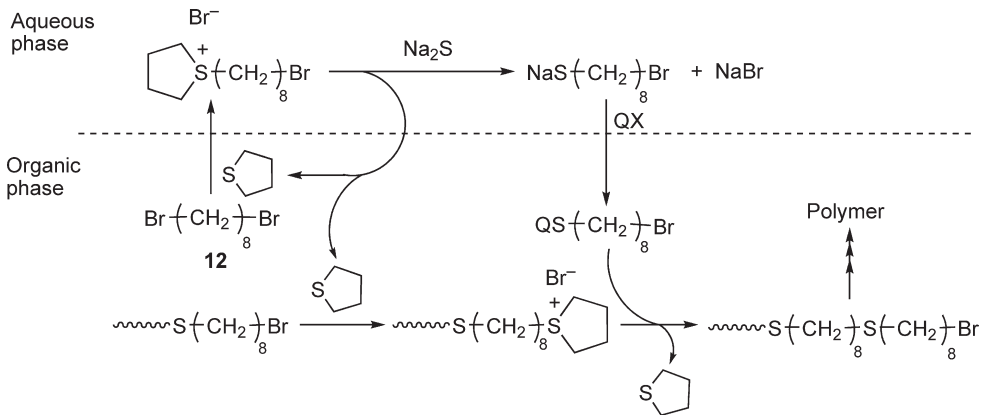


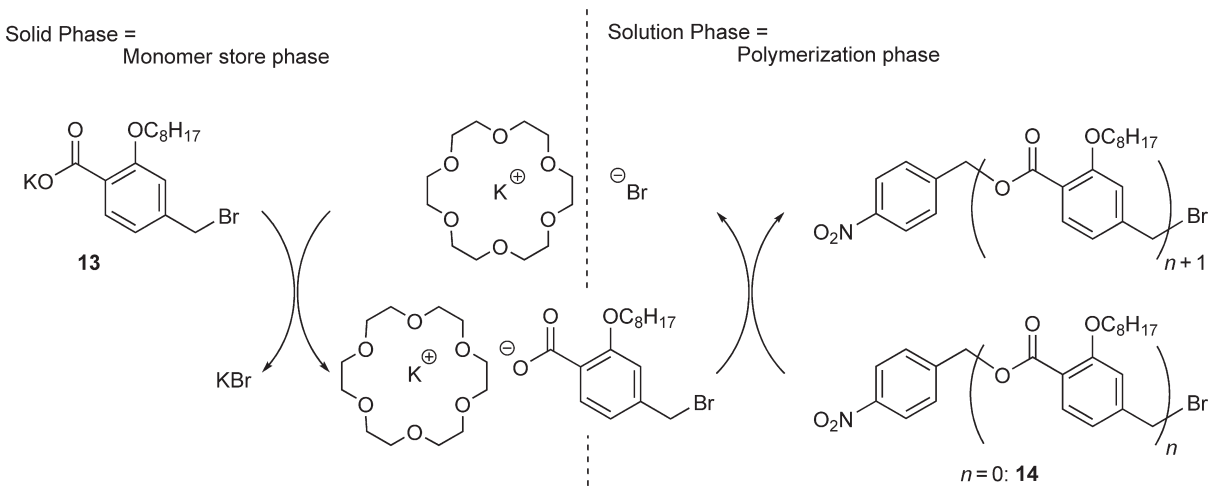
Scheme 23 Anchimeric assistance in biphasic phase-transfer-catalyzed polymerization.



Scheme 24 Phase-transfer-catalyzed polymerization for polysulfides.

salt reacted with the reactive sulfonium polymer chain end in the organic phase. This chain-end sulfonium was electrophilically more reactive to polymerization than the monomer. This may explain the high molecular weight and low polydispersity (Scheme 24). However, controlling molecular weight by addition of a chain initiator was not attempted in this study.

In another approach to chain-growth condensation polymerization with PTC, Yokozawa and Suzuki[62] conducted the polymerization of solid monomer potassium 4-bromomethyl-2-octyloxybenzoate (13) in the presence of 18-crown-6 as a PTC and 4-nitrobenzyl bromide (14) as an initiator in acetone. The polymerization proceeded by chain-growth polymerization mechanism to yield polyesters with M_w/M_n ratio less than 1.3 until the feed ratio of $[13]_0/[14]_0$ reached 15. With a feed ratio of 20 or above, the control of polymerization was not perfect: polymers having M_n values close to the calculated ones as well as oligomers without the initiator 14 were obtained. In the proposed mechanism, the solid phase of the monomer would prevent the reaction of monomers with each other, and the monomer dissolving in an organic solvent with the aid of a PTC in a certain amount would react with an initiator and the polymer end group in the solution phase. (Scheme 25). Similar chain-growth polymerization was also attained with tetrabutylammonium iodide as the PTC instead of 18-crown-6.[63]



Scheme 25 Phase-transfer-catalyzed chain-growth condensation polymerization for polyesters.

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5.06.4.2 Polysilanes

Silicon atom in polysilanes is conjugated through the d-orbital of silicon, so that the terminal chlorosilyl group of polysilanes is preferentially reduced with alkali metal, followed by reaction with monomer, dichlorosilane. Matyjaszewski *et al.*[64] synthesized monomodal polysilanes with relatively narrow molecular weight distributions ($M_w/M_n < 1.5$) by the reductive coupling of methylphenyldichlorosilane **15** with alkali metals in toluene at ambient temperature under ultrasound condition. The sonochemical synthesis was accompanied by selective degradation, which decreased the molecular weight to the limiting value of $M_n \approx 50\,000$ and also reduced polydispersities ($M_w/M_n < 1.2$). High-molecular-weight polysilane was formed at low conversion, indicating that the polymerization resembled a chain-growth polymerization.

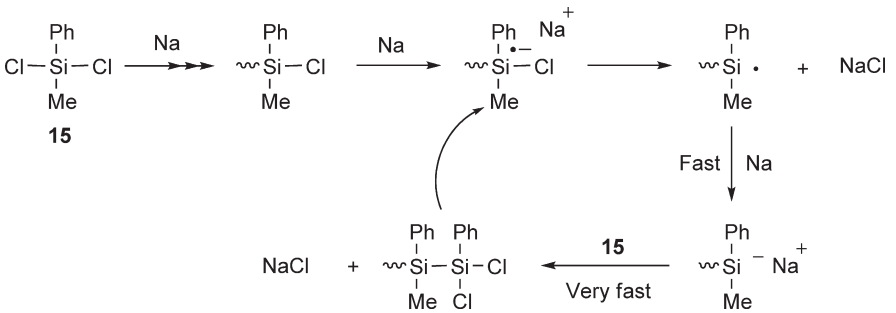
In this polymerization, cyclic oligomers were also formed in high yields by end-biting reactions of silylsodium with chloro-terminated oligosilanes. To reduce the intramolecular cyclization, $Ph(n\text{-}Hex_2Si)_4I$ was used as a chain initiator. The polymer yield increased, but the cyclics were still formed in high yield (≈80%). The ^{1}H-NMR spectrum of the polymer showed that 15–20% of the initiator was incorporated into the polymer. These results were explained by consumption of the initiator by the coupling reaction between the initiators and/or by nonselective generation of the initiator sodium anion.

Initiation may proceed by the coupling of monomeric radicals at the surface of sodium and subsequent reactions to form chloro-terminated oligosilanes of a length sufficient to have a reductive coupling potential similar to that of chloro-terminated polymer chains. Propagation involves the sequential reactions. A chloro-terminated chain rapidly takes up one electron to form a radical anion and eventually a silyl radical. The silyl radical takes a subsequent electron from a metallic sodium particle to form polymeric silylsodium. Silylsodium reacts preferentially with the monomer possessing two electron-withdrawing chloride atoms rather than with the chloro-terminated chain end (**Scheme 26**).

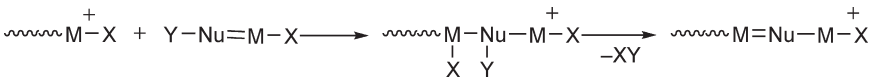
5.06.4.3 Polyphosphazenes

N-Silylated phosphoranimine is polymerized with a cationic catalyst in a chain-growth polymerization manner through transfer of cationic species, stemmed from the initiator. A general scheme of the propagation can be described as **Scheme 27**.

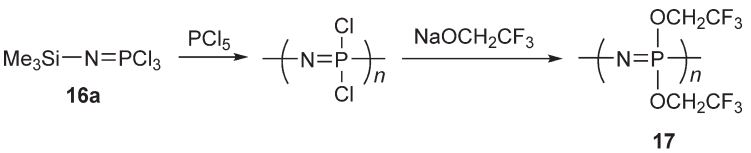
Although *N*-silylated trialkoxyphosphoranimine was reported to polymerize with $SbCl_5$ at 100 °C,[65] Allcock and co-workers found that trichloro(trimethylsilyl)phosphoranimine **16a** polymerized with PCl_5 at ambient temperature with elimination of trimethylsilyl chloride. The resulting poly (dichlorophosphazene) was treated with an excess of $NaOCH_2CF_3$ to give polymer **17** (**Scheme 28**). When the polymerization was carried out in dichloromethane, the molecular weight increased with increasing ratio of **16a** to PCl_5 ($M_w = 7000–14\,000$), and the molecular weight distribution

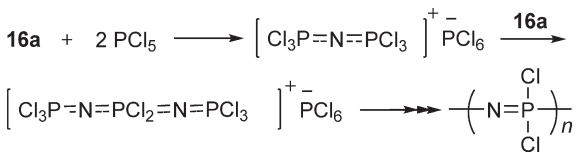


Scheme 26 Chain-growth condensation polymerization for polysilanes.



Scheme 27 General scheme of chain-growth condensation polymerization via transfer of the reactive species from initiator.





Scheme 28 Chain-growth condensation polymerization for polyphosphazenes.

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remained narrow (M_w/M_n = 1.04–1.20).[66] The polymerization proceeded faster in toluene than in dichloromethane to give polymers with high molecular weights in the range of 10^5 and low polydispersities (< 1.3).[67] Phenyl-substituted monomer **16b** ($PhCl_2P{=}NSiMe_3$) also underwent controlled polymerization until the feed ratio of **16b** to PCl_5 was 100. Other related initiators such as $SbCl_5$, $TaCl_5$, or $PhPCl_4$ also appear to initiate the ambient temperature polymerization of **16a** and **16b**. The polymerization is initiated by the reaction of **16a** and 2 equiv of PCl_5 with elimination of Me_3SiCl to generate a salt, with which **16a** successively reacts with elimination of Me_3SiCl, resulting in the elongated cation.

Monomer **16a** was synthesized by the reaction of PCl_5 with either $LiN(SiMe_3)_2$ or $N(SiMe_3)_3$. These methods give relatively low product yields, because PCl_5 is an initiator for the polymerization of **16a**. To circumvent this concurrent polymerization, a new method for synthesizing **16a** and the subsequent polymerization in one pot has been reported.[68] PCl_3 was reacted with $LiN(SiMe_3)_2$ to afford $Cl_2P{-}N(SiMe_3)_2$, which was oxidized with SO_2Cl_2 to yield **16a**. To the mixture, mainly containing **16a**, Me_3SiCl and LiCl, PCl_5 was added to produce the polyphosphazene. Under optimized conditions, the polymer **17** showed a relatively narrow molecular weight distribution (M_w/M_n = 1.24) even in this one-pot reaction from PCl_3 (**Scheme 29**).

Cationic successive polymerization of phosphoranimines with different side chain yields block copolymers. For example, the polymerization of **16a** with PCl_5 was carried out at ambient temperature, followed by addition of a second phosphoranimine to yield a block copolymer with M_w/M_n ratio of 1.1–1.4 (**Scheme 30**).[69]

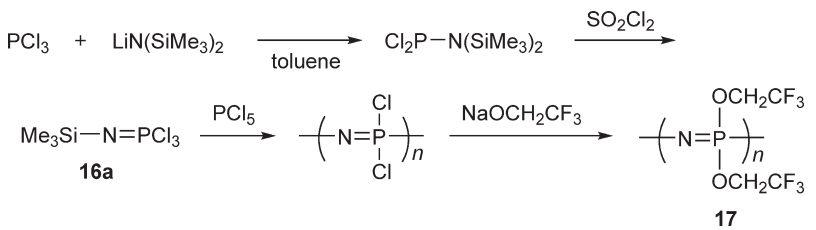
Some block copolymers of polyphosphazene and conventional polymers such as polystyrene,[70,71] PEG,[72–75] and poly (dimethylsiloxane),[76–78] graft copolymers of polynorbornene,[79] polystyrene,[70] or poly(methyl methacrylate) (PMMA)[80] with polyphosphazene, and triarm star polyphosphazene were synthesized.[81]

5.06.4.3.1 Polymerization of ylides

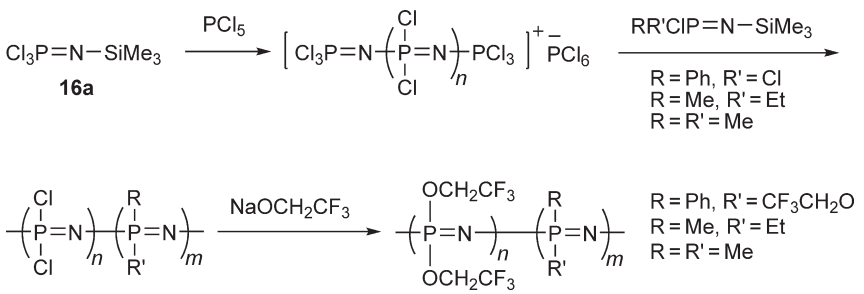
Ylide is polymerized with a trialkylborane initiator accompanying elimination of a neutral compound from the ylide. As shown in a general scheme (**Scheme 31**), the propagation involves insertion of the ylide monomer to the terminal $M{-}BR_2$ bond, so that the propagating end group and the initiator have the same structure, and the polymerization proceeds in a chain-growth polymerization manner.

Shea *et al.* reported the polymerization of dimethylsulfoxonium methylide **18** initiated by trialkylborane. Propagation involves insertion of **18** at the terminal C–B bond with elimination of dimethyl sulfoxide (DMSO). The polymerization was carried out in toluene at 70–80 °C, followed by oxidative work up to yield hydroxyl-terminated polymethylene (**Scheme 32**). The M_n values were very close to the calculated values from the feed ratio of **18** to trialkylborane, and the M_w/M_n ratio ranged from 1.04 to 1.17. These results are consistent with a living polymerization. The insertion mechanism involves an initial attack of the ylide on the alkylborane. The borate complex undergoes 1,2-migration of the alkyl group to produce the homologated alkylborane and a molecule of DMSO.[82,83]

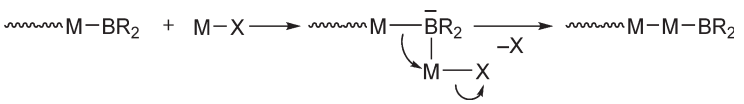
This polyhomologation with alkylboranes is amenable to the synthesis of telechelic polymethylene, because alkylboranes can be prepared by hydroboration of a variety of α-olefins. For



Scheme 29 One-pot synthesis and polymerization of **16a**.



Scheme 30 Block polyphosphazenes.



Scheme 31 General scheme of chain-growth condensation polymerization of ylide with trialkylborane.

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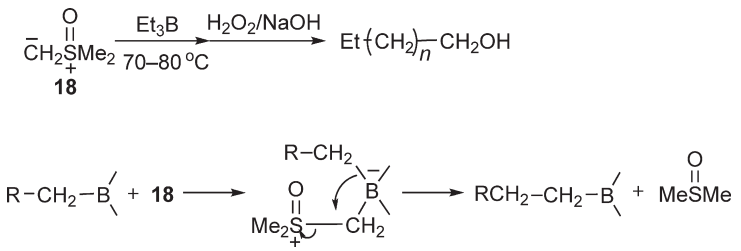
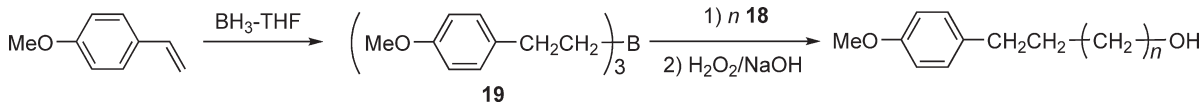
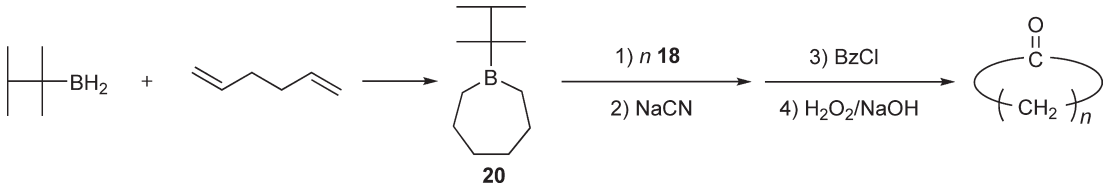


Scheme 32 Polymethylene from the polymerization of **18.**



Scheme 33 Telechelic polymethylene.

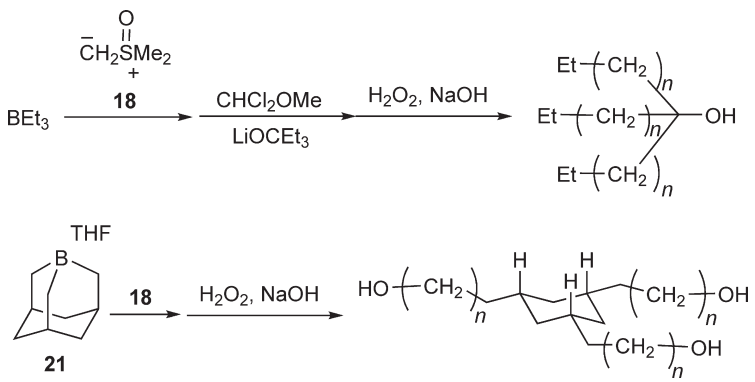


Scheme 34 Synthesis of cyclic ketone from polymethylation.

example, polymethylene with 4-methoxyphenyl and hydroxy groups at both ends was synthesized from initiator **19** prepared by hydroboration of 4-vinylanisole with BH_3•THF (**Scheme 33**).[82] Other functional groups, including biotin, carbohydrates, primary and secondary amines, and dansyl and pyrene fluorescent groups, were also introduced as end groups from the corresponding α-olefins.[84] When *B*-thexylboracycloheptane **20**, prepared by the hydroboration of 1,5-hexadiene with thexylborane, was used as an initiator, methylene was inserted only into the C–B bond of boracyclane, not the thexyl–B bond, resulting in ring expansion. The expanded boracycle was treated with sodium cyanide, followed by benzoyl chloride, and then it underwent peroxide oxidation to yield cyclic ketone (**Scheme 34**).[85]

Shea *et al.* also synthesized star polymethylenes (**Scheme 35**). Polymethylene from **18** was reacted with α,α-dichloromethyl methyl ether, followed by treatment with $LiOCEt_3$, and oxidation with H_2O_2 and NaOH to give the star polymethylene methanol. The M_n value of the polymer obtained agreed well with the calculated value based on the feed ratio of **18** to triethylborane, and the M_w/M_n ratio ranged from 1.02 to 1.13. GPC revealed the absence of linear polymethylene.[86] When 1-boraadamantane•THF **21** was used as the initiator for polymerization of **18**, star polymethylene triol was formed.[87]

Mioskowski and co-workers reported similar polymerization of arsonium ylide **22** initiated by trialkylborane.[88,89] The reaction of **22** at 0 °C in THF did not lead to polymers with substitutions on every carbon atom like the polymerization of sulfoxonium ylide **18**, but rather to a polymer in which the main chain has been elongated by three carbon atoms at a time (**Scheme 36**). Polymers of varying the DP were obtained by using varying ratios of ylide **22** to trialkylborane, but the DP was larger than expected from these ratios. The M_w/M_n ratio



Scheme 35 Synthesis of star polymethylenes.

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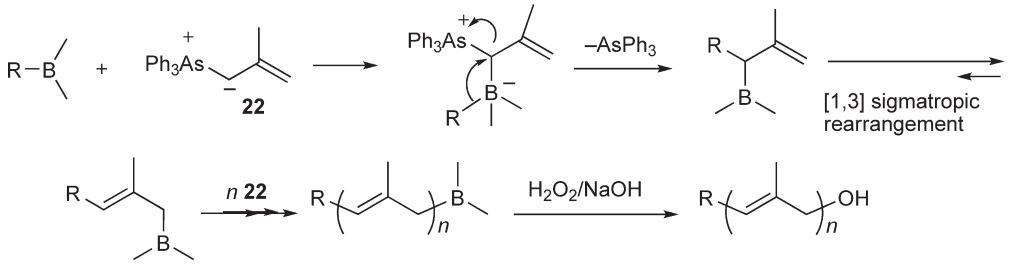


Scheme 36 Chain-growth condensation polymerization of allylic arsonium ylide.

ranged from 1.21 to 1.58. This suggests that the initiation of the polymerization was not completely efficient, but the propagation was controlled. The polymerization mechanism, which is different from that of the polymerization of ylide **18**, involves [1,3] sigmatropic rearrangement after 1,2-migration of the alkyl group of borate. This is the reason for the elongation by three carbons at each step of this insertion polymerization. Block copolymers were also synthesized by successive polymerization of different arsonium ylides.[89]

5.06.5 π-Conjugated Polymers

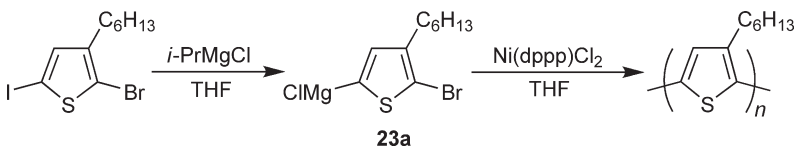
Condensation polymerization with a catalyst can involve another mechanism for chain-growth condensation polymerization, that is catalyst-transfer mechanism, in which the catalyst activates the polymer end group, followed by reaction with the monomer and transfer of the catalyst to the elongated polymer end group, in a similar manner to biological condensation polymerization.

5.06.5.1 Polythiophenes

Poly(alkylthiophene) has received much attention in recent years because of its small band gap, high electrical conductivity,[90,91] and interesting properties such as light-emitting ability[92] and high field-effect mobility.[93,94] The polymerization of Grignard thiophene monomer **23a** with Ni(dppp)Cl_2 (dppp = 1,3-bis(diphenylphosphino)propane) was well known as a regioregulated synthetic method for poly(alkylthiophene)s developed by McCullough *et al.*, but the polymers obtained possessed a broad molecular weight distribution.[95–98] However, Yokoyama *et al.*[99] found that the M_n values of polymers increased in proportion to monomer conversion, with low polydispersities being retained, and were controlled by the amount of the Ni catalyst; the M_n values were proportional to the feed ratio of $[\mathbf{23a}]_0/[\text{Ni catalyst}]_0$ when the polymerization was carried out at room temperature, with care to use the exact amount of isopropyl magnesium chloride for generation of monomer **23a** from the corresponding bromoiodothiophene (**Scheme 37**). Furthermore, the M_w/M_n ratios were around 1.1 up to the M_n value of 28 700 when the polymerization of **23a** was quenched with hydrochloric acid.[100] Sheina *et al.*[101] also reported that a similar zinc monomer and **23a** from the corresponding dibromothiophene showed the same polymerization behavior.[102]

Yokozawa and co-workers studied the polymerization mechanism by using MALDI-TOF mass spectrometry and clarified the following points: (1) the polymer end groups are uniform among molecules, one end group is Br and the other is H (Iovu *et al.*[102] also confirmed it by ^{1}H-NMR spectroscopy); (2) the propagating end group is a polymer–Ni–Br complex; (3) one Ni molecule forms one polymer chain; and (4) the chain initiator is a dimer of **23a** formed *in situ*. On the basis of these results, a catalyst-transfer condensation polymerization mechanism has been proposed (**Scheme 38**).[103] Thus, Ni(dppp)Cl_2 reacts with 2 equiv of **23a**, and the coupling reaction occurs with concomitant generation of a zero-valent Ni complex. The Ni(0) complex does not diffuse to the reaction mixture but is inserted into the intramolecular C–Br bond. Another **23a** reacts with this Ni, followed by the coupling reaction and transfer of the Ni catalyst to the next C–Br bond. Growth would continue in such a way that the Ni catalyst moves to the polymer end group. This catalyst-transfer process has been recently investigated in detail, and Tkachov *et al.*[104] have revealed that a combination of a random transfer of the Ni catalyst along the chain and a sticking effect at the end group is operative in the catalyst-transfer polymerization of **23a**.

Several other reactions involving similar intramolecular transfer of metal catalysts have been reported.[105–113] Zenkina *et al.*[112] demonstrated that the reaction of Ni(PEt_3)$_4$ with a brominated vinyarene resulted in selective η^2–C=C coordination, followed by intramolecular 'ring-walking' of the metal center and aryl-bromide oxidative addition, even in the presence of aryl iodide containing an activating substrate (**Scheme 39**). Nakamura and co-workers studied the Ni-catalyzed cross-coupling reaction by analysis of kinetic isotope effects and theoretical calculations, and indicated that the first irreversible step of the reaction is the π-complexation of the Ni catalyst on the π-face of haloarene. In other words, once a Ni/haloarene



Scheme 37 Poly(3-hexylthiophene) from polymerization of **23a** with a Ni catalyst.

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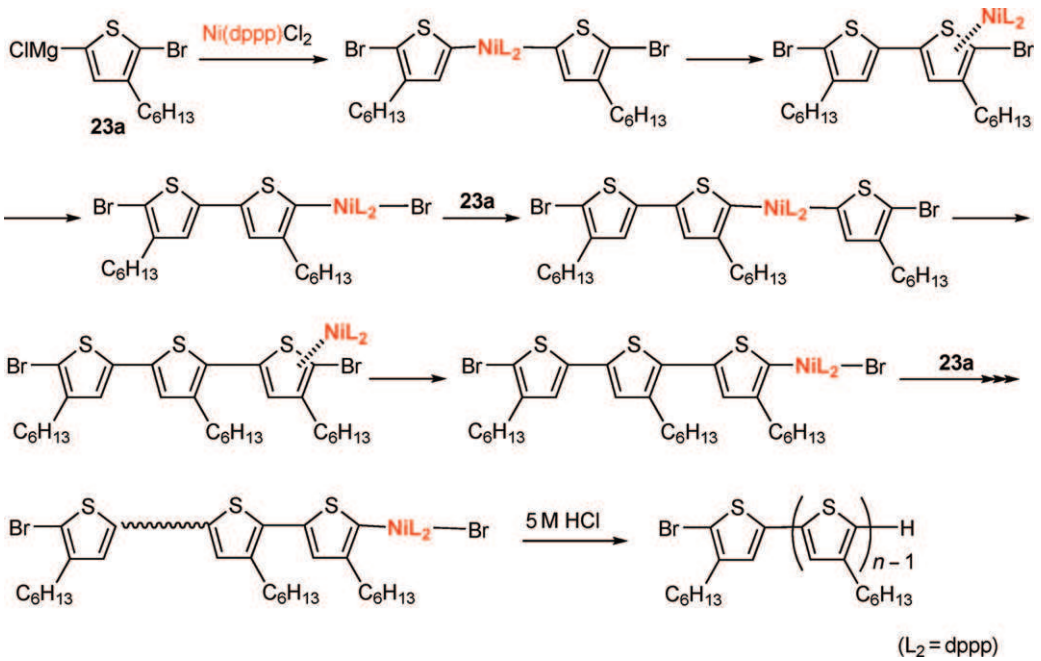
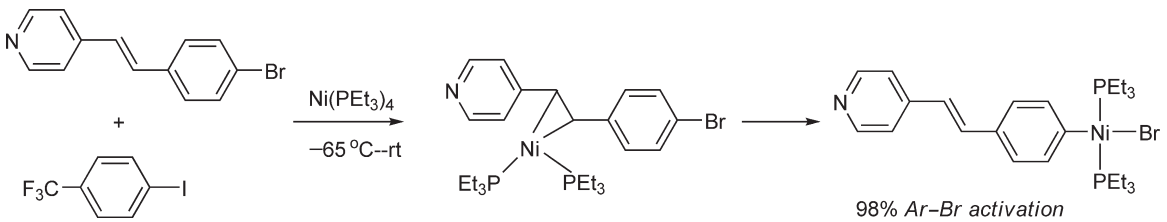


Scheme 38 Catalyst-transfer condensation polymerization for the synthesis of poly(3-henxylthiophene).



Scheme 39 Intramolecular transfer of Ni catalyst.

π-complex forms through ligand change, it does not dissociate and proceeds quickly to the oxidative addition step in an intramolecular manner.[113]

The influence of the phosphine ligand of the Ni catalyst on the catalyst-transfer condensation polymerization of **23a** was investigated.[114,115] The M_n value and the M_w/M_n ratio of polymer were strongly affected by the ligands of the Ni catalyst: $Ni(dppe)Cl_2$ (dppe = 1,2-bis(diphenylphosphino)ethane) and $Ni(PPh_3)_4$ gave a polymer with a slightly lower M_n value and a slightly broad molecular weight distribution, whereas $Ni(PPh_3)_2Cl_2$, $Ni(dppb)Cl_2$ (dppb = 1,4-bis(diphenylphosphino)butane), and $Ni(dppf)Cl_2$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene) gave polymers with low M_n values and broad molecular weight distributions. After all, $Ni(dppp)Cl_2$ resulted in the M_n value close to the theoretical value based on the feed ratio of monomer to the catalyst and the narrowest M_w/M_n ratio. Lanni and McNeil[116] recently conducted kinetic studies and have revealed that the rate-determining step is dependent on the phosphine ligand of the Ni catalyst: the rate-determining steps are transmetalation and reductive elimination in the polymerization with $Ni(dppp)Cl_2$ and $Ni(dppe)Cl_2$,[117] respectively.

Taking advantage of the polythiophene end group containing the Ni complex, McCullough and co-workers introduced functional groups to one or both ends of the polymer by Grignard reagents. Allyl, ethynyl, and vinyl Grignard reagents afford monofunctionalized polythiophenes, whereas aryl and alkyl Grignard reagents yield difunctionalized polythiophenes. By utilizing the proper protecting groups, hydroxyl, formyl, and amino groups can also be incorporated into the polymer chain ends.[118]

In the chain-growth polymerization of **23a** with $Ni(dppp)Cl_2$, the chain initiator is a dimer of **23a** formed *in situ* as mentioned above. Kiriy and coworkers conducted polymerization of **23a** with an externally added initiator, $PhNi(PPh_3)_2Br$, to obtain Ph-terminated poly(3-hexylthiophene), although the polymerization was less controlled than the polymerization of **23a** with $Ni(dppp)Cl_2$.[119,120] This method was applied to growing conductive polymer brushes of poly(3-hexylthiophene) via surface-initiated chain-growth condensation polymerization. Thus, the Ni(II) macroinitiator was prepared by the reaction of $Ni(PPh_3)_4$ with photo-cross-linked poly(4-bromostyrene) films. Exposure of the initiator layers to the monomer solution led to the polymerization from the surface, resulting in poly(3-hexylthiophene) brushes (**Scheme 40**). Recently, Bronstein and Luscombe[121] and Senkovskyy *et al.*[122] have independently reported the synthesis of more effective initiator, ArNi(dppp)X (X = Cl, Br), which

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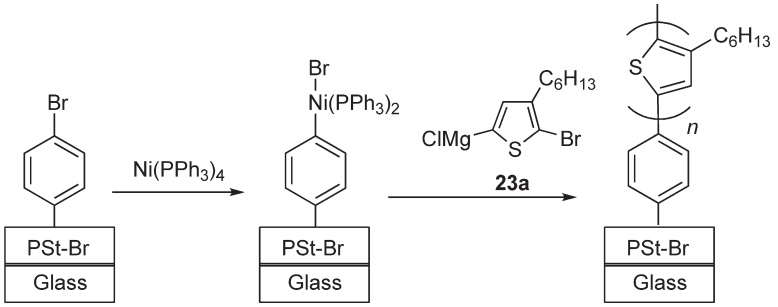
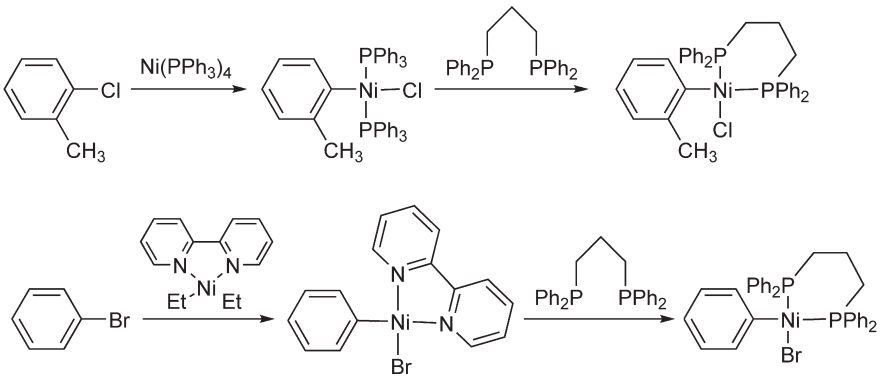


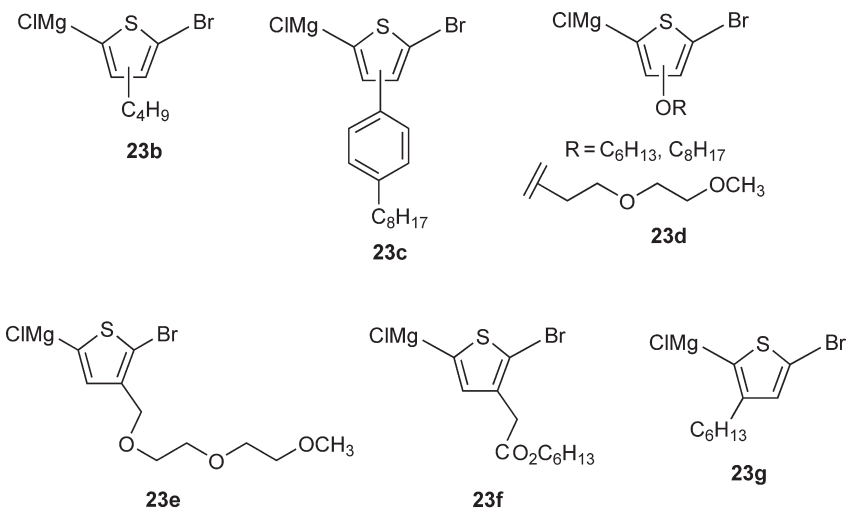
Scheme 40 Poly(3-henxylthiophene) brushes by catalyst-transfer condensation polymerization from surface initiator.



Scheme 41 Synthesis of initiator for catalyst-transfer condensation polymerization leading to poly(alkylthiophene)s.

yields poly(3-hexylthiophene) with narrow molecular weight distribution. Both methods used ligand exchange reaction of the primary ArNi(II)X complex with dppp, although Bronstein and Luscombe and Senkovskyy *et al.* generated the primary Ni(II) complex by using $Ni(PPh_3)_4$ and Et_2Ni(2,2′-bipyridine), respectively (Scheme 41). Protected functional group was introduced to the Ar group of the above initiator according to the Luscombe method.[123]

The chain-growth polymerization of other substituted thiophene monomers instead of 23a with the hexyl group was investigated (Scheme 42). The polymerization of butylthiophene monomer 23b with $Ni(dppp)Cl_2$ afforded polymer with low polydispersity ($M_w/M_n = 1.33–1.43$), although the M_n value is less than 5500 due to the low solubility of poly23b.[124] Aryl-substituted monomer 23c, the polymer of which may have a stabilized π-conjugated main chain system by virtue of the pendant aromatic group, gave a polymer with the M_w/M_n ratio of 2.15, probably due to the low solubility of the conjugated poly23c in the reaction solvent.[125] The polymers from alkoxy-substituted monomers 23d possessed the



Scheme 42 Thiophene monomers for Kumada-Tamao coupling polymerization with a Ni catalyst.

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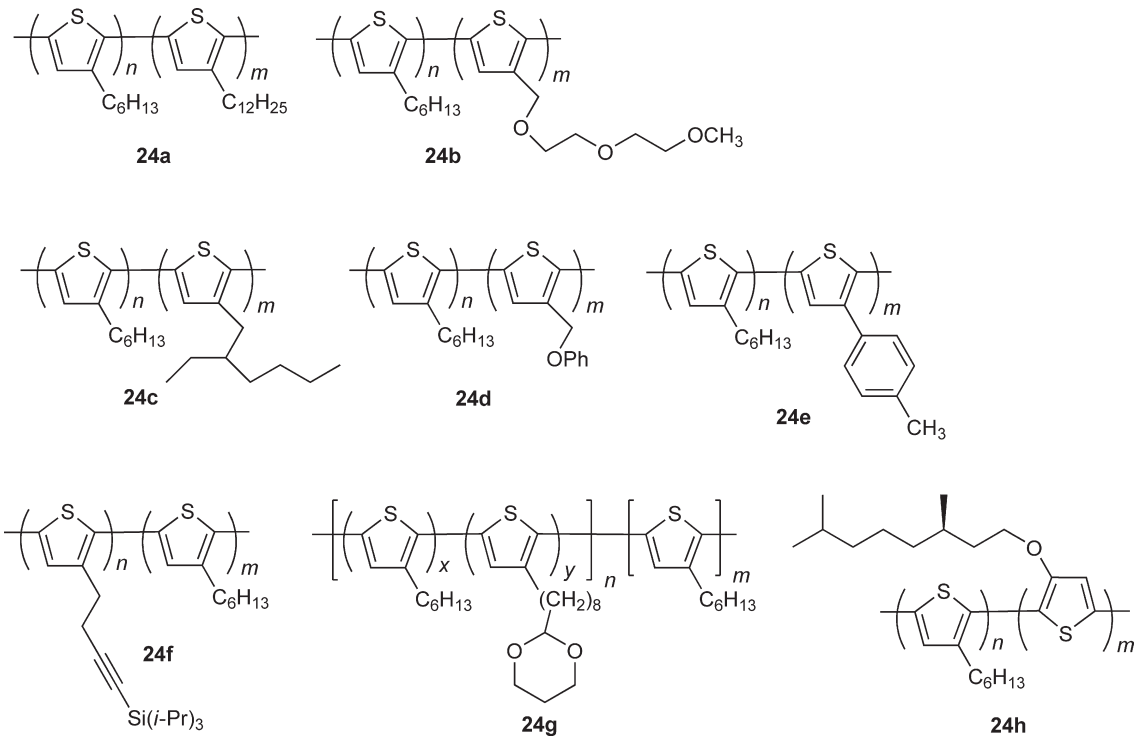


Scheme 43 Block copolythiophenes.

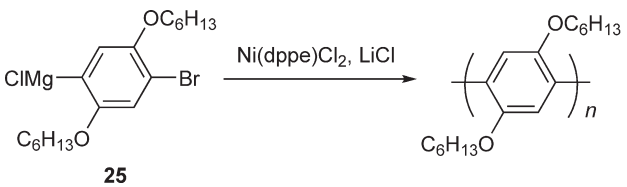
M_w/M_n ratio of 1.5–1.7.[126,127] The polymerization of alkoxymethyl-substituted monomer **23e** with Ni(dppp)Cl_2 gave a polymer with the M_w/M_n ratio of 1.42, whereas the polymerization with Ni(dppe)Cl_2 resulted in decrease of the M_w/M_n ratio up to 1.15.[128] The polymerization of a thiophene monomer **23f** containing an ester moiety also showed chain-growth polymerization behavior to afford polymers with the M_w/M_n ratio of 1.25–1.5.[129] Recently, Boyd *et al.*[130] showed that **23g**, a regioisomer of **23a**, was not polymerized with Ni(dppp)Cl_2 and ArNi(dppp)Cl, either.

Since several substituted thiophene monomers undergo chain-growth polymerization in a living polymerization manner, a lot of block copolythiophenes (**24**) have been synthesized by successive polymerization in one pot. Examples reported earlier are shown in **Scheme 43**. The first reported block copolymer **24a** was synthesized by Iovu *et al.*[102] Yokozawa *et al.*[131] synthesized block copolymer **24b** having both hydrophobic and hydrophilic side chains in each segment. The thin films of **24c**,[132] **24d**,[133] and **24e**[134] showed nanofiber structures after annealing probably because of microphase separation of the crystalline poly(hexylthiophene) segment and the other amorphous segment. The side chain of block copolymer **24f**[135] was converted to the naphthalimide moiety. The diblock copolymer **24g**[136] consists of a block made from a random copolymerization of hexylthiophene monomer and (1,3-dioxa-2-octyl)thiophene monomer and the pure poly (hexylthiophene) block. The 1,3-dioxane moiety was converted to the formyl group, followed by introduction of fullerene C_{60} with the aid of *N*-methylglycine. In the block copolymer **24h**, the chiral segment influences the supramolecular organization of poly(hexylthiophene) segment.[137]

5.06.5.2 Polyphenylenes

It is important to clarify whether catalyst-transfer condensation polymerization is specific to polythiophene, or whether it is generally applicable to the synthesis of well-defined π-conjugated polymers. Yokozawa and co-workers investigated the synthesis of poly(*p*-phenylene) to see whether a monomer **25** containing no heteroatom in the aromatic ring would undergo catalyst-transfer polymerization. However, all polymers obtained in the polymerization with Ni(dppp)Cl_2, Ni(dppe)Cl_2, or Ni(dppf)Cl_2 possessed low molecular weights and high polydispersities. Nevertheless, LiCl was found to be necessary for optimizing the chain-growth condensation polymerization with Ni(dppe)Cl_2, leading to poly(*p*-phenylene) with low polydispersity, and the molecular weight was controlled by the feed ratio of **25** to the Ni catalyst (**Scheme 44**).[138] Lanni and McNeil[117] conducted kinetic study of this polymerization and revealed that the rate-determining step is reductive elimination.

Block copolymers of polythiophene and poly(*p*-phenylene) were tried to be synthesized by the successive catalyst-transfer condensation polymerization of monomers **23a** or **23e** and **25**



Scheme 44 Catalyst-transfer condensation polymerization for the synthesis of polyphenylenes.

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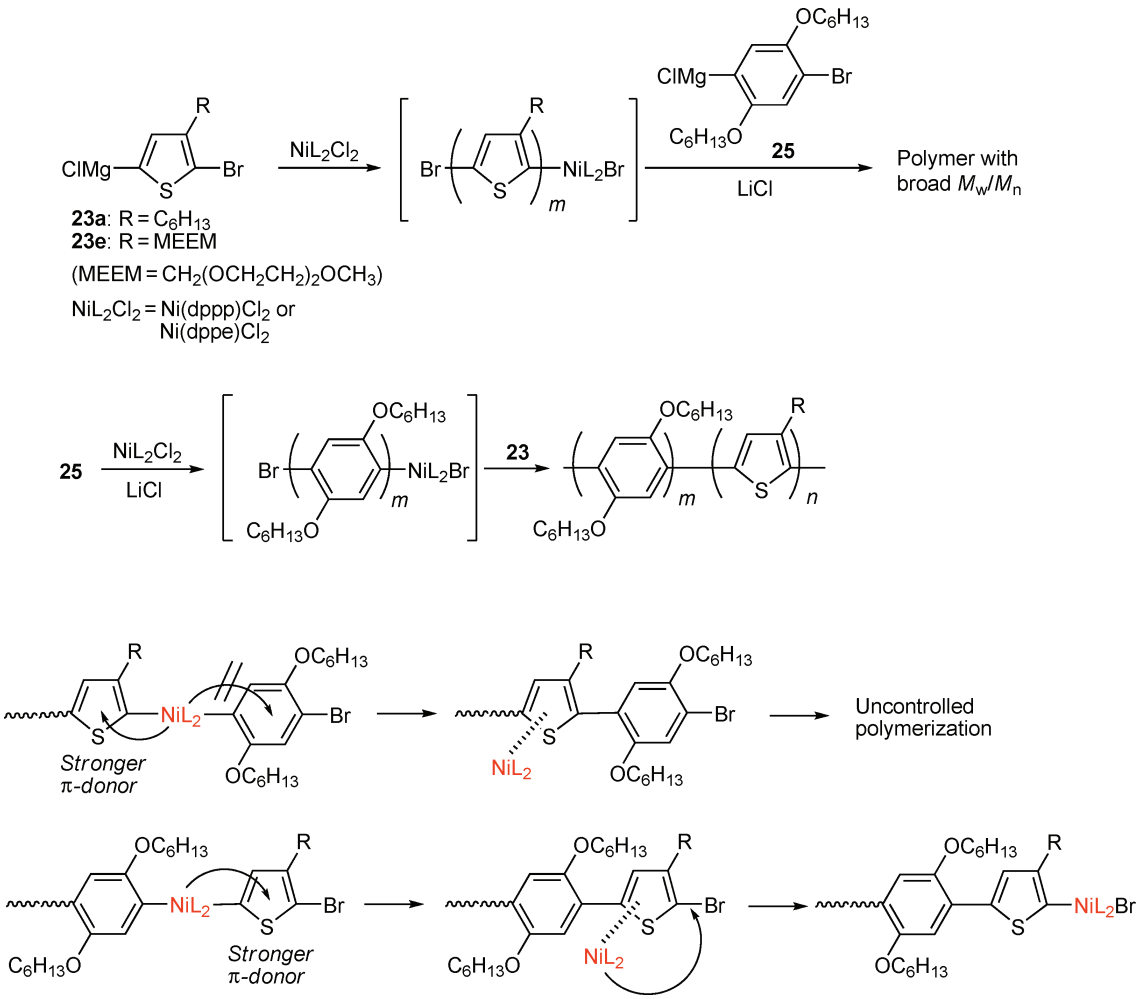
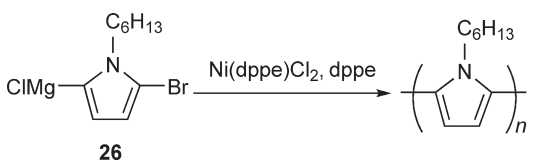


Scheme 45 Synthesis of block copolymer of polythiophene and polyphenylene by catalyst-transfer condensation polymerization.

with a Ni catalyst.[139] This is the first example of the successive catalyst-transfer condensation polymerization for the synthesis of block copolymers consisting of different type of π-conjugated polymers. The polymerization of **23** and then **25** with a Ni catalyst yielded polymers with broad molecular weight distribution, whereas the reverse order of polymerization resulted in well-defined block copolymers of poly (*p*-phenylene) and polythiophene (**Scheme 45**). Successful block copolymerization of **25** and then **23** may be accounted for by the π-donor ability of polythiophene and poly(*p*-phenylene) because the π-electrons of the polymers are considered to assist the transfer of the Ni catalyst in catalyst-transfer polymerization. When **25** is added to the reaction mixture of polythiophene as a prepolymer, the Ni catalyst would be difficult to move to the terminal C–Br bond of the phenylene ring of the elongated **25** unit, because the thiophene ring has stronger π-donor ability than the phenylene ring. On the other hand, when **23** is added to poly(*p*-phenylene) as a prepolymer, the Ni catalyst would smoothly move to the C–Br bond of the thiophene ring with stronger π-donor ability (**Scheme 45**). Photophysical and thermal properties of the block copolymers were also reported.[140]

5.06.5.3 Polypyrroles

Yokozawa and co-workers investigated the condensation polymerization of Grignard-type *N*-hexylpyrrole monomer **26**, which was generated by the reaction of the corresponding dibromopyrrole with *i*-PrMgCl, with a Ni catalyst (**Scheme 46**). When $Ni(dppp)Cl_2$ was used as a catalyst in a similar manner to the case of polymerization of hexylthiophene monomer **23a**, a polymer with the M_w/M_n ratio of 1.26 was obtained, accompanied by low-molecular-weight oligomers. On the other hand, polymerization with $Ni(dppe)Cl_2$ afforded the polymer with a lower polydispersity ($M_w/M_n = 1.19$), though oligomeric by-products were still formed. To suppress the formation of the oligomeric



Scheme 46 Catalyst-transfer condensation polymerization for the synthesis of polypyrroles.

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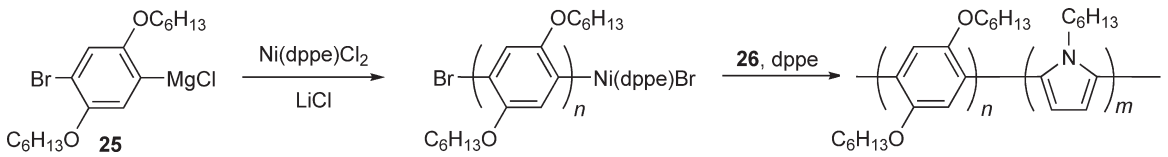
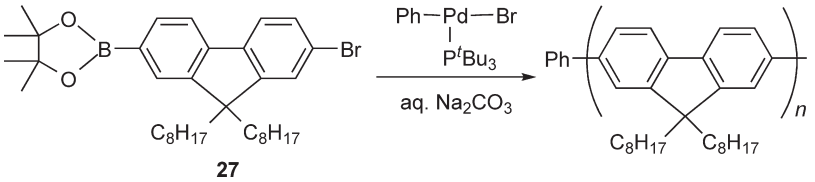


Scheme 47 Block copolymer of polyphenylene and polypyrrole.



Scheme 48 Catalyst-transfer Suzuki-Miyaura coupling polymerization for the synthesis of polyfluorenes.

by-products, they examined the effect of several additives, and found that polymerization of 26 with Ni(dppe)Cl_2 in the presence of additional dppe equimolar to the catalyst at 0 °C gave the polypyrrole with a narrow molecular weight distribution ($M_w/M_n = 1.11$) without formation of by-products. The conversion–M_n and feed ratio–M_n relationships indicated that this polymerization proceeded in a catalyst-transfer polymerization manner.[141] Stefan *et al.*[142] used *i*-PrMgCl•LiCl for generation of Grignard-type *N*-dodecylpyrrole monomer and polymerized with Ni(dppp)Cl_2 to afford a polypyrrole with the M_n value of 11 900 and the M_w/M_n ratio of 1.4.

A block copolymer of poly(*p*-phenylene) and polypyrrole was similarly synthesized. The *p*-phenylene monomer 25 was polymerized first with Ni(dppe)Cl_2 in the presence of LiCl, followed by addition of 26 and dppe to yield the desired block copolymer with a low polydispersity ($M_w/M_n = 1.16$) (Scheme 47). The block copolymerization in reverse order afforded polymer with a somewhat high polydispersity ($M_w/M_n = 1.38$).[141]

5.06.5.4 Polyfluorenes

Yokozawa and co-workers investigated chain-growth Suzuki–Miyaura coupling polymerization for the synthesis of polyfluorene. In this polymerization, stable arylpalladium(II) halide complex was used as an externally added initiator, and the aryl group of the complex served as an initiator unit of the polymer. The polymerization of a fluorene monomer 27 was carried out in the presence of PhPd(^{t}Bu$_3$P)Br as a catalyst to yield polyfluorene with a low polydispersity (Scheme 48). The molecular weight of the obtained polymer increased linearly in proportion to the conversion of monomer with low polydispersity throughout the polymerization, and also increased linearly in proportion to the feed ratio of 27 to the initiator up to 17 700 with low polydispersity, indicating that this Suzuki–Miyaura coupling condensation polymerization proceeded through a chain-growth polymerization mechanism,[143] as shown in the model reactions.[107–109] The MALDI-TOF mass spectrum of the obtained polyfluorene showed that all the polymers bore the phenyl group at one end. This observation strongly supported the view that PhPd(^{t}Bu$_3$P)Br served as an initiator. Beryozkina *et al.*[144] synthesized a surface-bound Pd complex initiator and conducted this chain-growth Suzuki–Miyaura coupling polymerization to yield surface-grafted polyfluorene.

Huang *et al.*[145] reported the polymerization of Grignard-type fluorene monomer 28 with Ni(dppp)Cl_2. The monomer 28 was generated from the corresponding bromoiodofluorene with *i*-PrMgCl/LiCl (1:1). The polymerization proceeded very fast at 0 °C and was almost over in 10 min. High-molecular-weight polyfluorene ($M_n = 18\,800$–$86\,000$) was obtained in the very beginning and the M_n value almost kept identical at different conversion of 28. The M_w/M_n ratio of the resulting polymers was in the range of 1.49–1.77. The behavior of this polymerization resembles that of conventional radical polymerization that proceeds in chain-growth polymerization manner accompanying chain transfer reaction. The ^{1}H-NMR spectrum of polymer indicated that noticeable amount of polymers were the Br/Br-ended polyfluorene, which would be formed by reductive elimination followed by intermolecular transfer of the Ni(0) catalyst that can initiate polymerization of another chain (Scheme 49). Javier *et al.*[146] added the second monomer to the reaction mixture of the polymerization of 28 in the initial stage, where the polymerization still showed pseudo-living polymerization nature before starting the intermolecular transfer of the Ni(0) catalyst, to obtain block copolymers, polyfluorene-*b*-polythiophene and polyfluorene-*b*-polyphenylene.

Yokozawa *et al.*[147] have recently found that well-defined polyphenylene was also obtained by catalyst-transfer Suzuki–Miyaura polymerization by using CsF/18-crown-6 instead of aqueous Na_2CO_3 as a base and synthesized block copolymer of polyfluorene and polyphenylene (Scheme 50).

5.06.6 Future Remarks

The change of polymerization mechanism in condensation polymerization from a step-growth to a chain-growth process has been attained in several ways: (1) activation of the polymer

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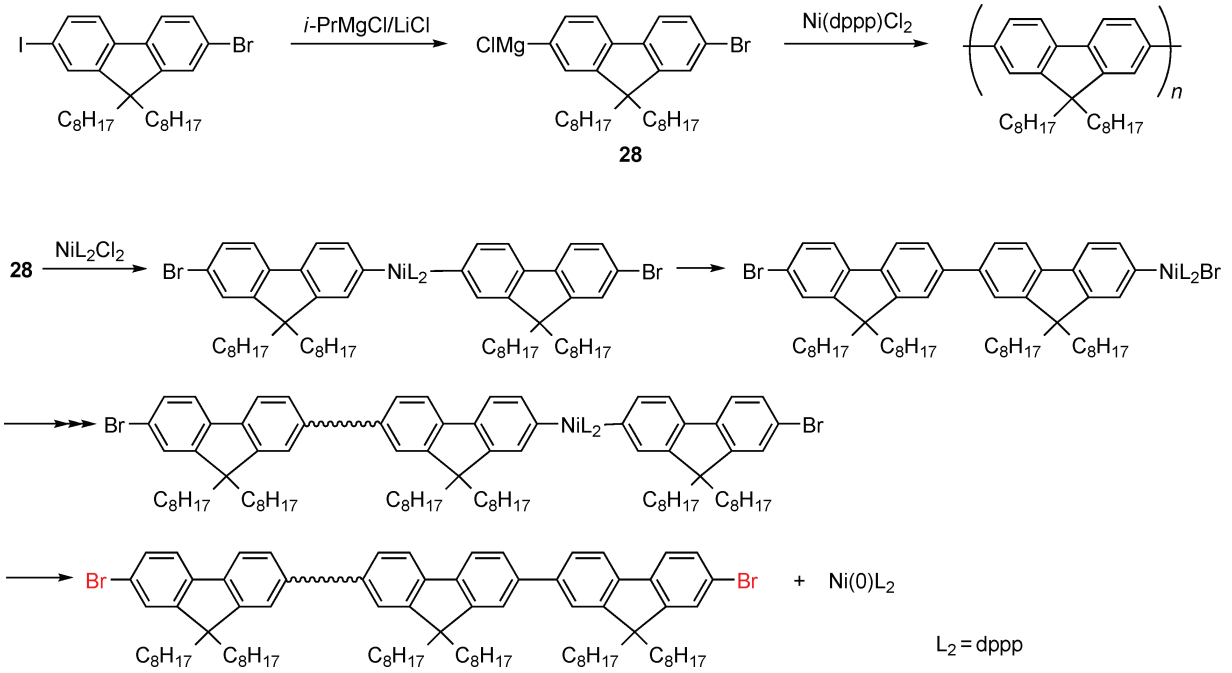
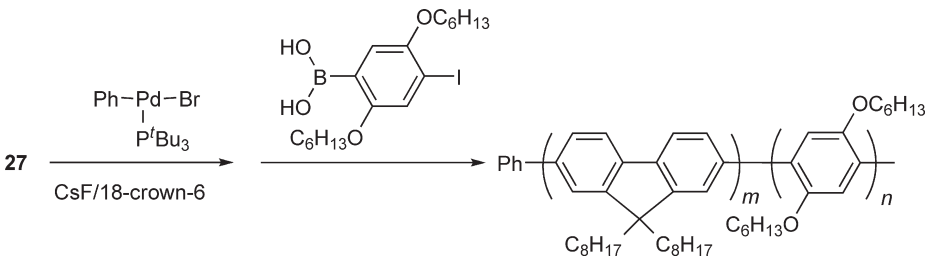


Scheme 49 Kumada-Tamao coupling polymerization for the synthesis of polyfluorenes.



Scheme 50 Block copolymer of polyfluorene and polyphenylne from catalyst-transfer Suzuki-Miyaura coupling polymerization.

end group by differing substituent effects between the monomer and the polymer; (2) phase-transfer polymerization in a biphase system comprising a monomer storage phase and a polymerization phase; (3) transfer of the reactive species, derived from the initiator, to the polymer end group; and (4) activation of the polymer end group by transfer of the catalyst to it. Chain-growth condensation polymerization enables us to produce architectures containing well-defined condensation polymers, such as block copolymers, star polymers, and graft copolymers. Some of these self-assemble to form supramolecular nano- to microorder structures by virtue of the strong intermolecular forces between condensation polymer units. Furthermore, architectures containing π-conjugated polymers have been rapidly developed and applied to organic electrical materials for photovoltaic devices and FET. Future research efforts will be directed toward the development of chain-growth condensation polymerization of AA and BB monomers, which is more general condensation polymerization than that of AB monomers, as well as discovery of specific physical properties of condensation polymers with narrow molecular weight distribution.

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Biographical Sketch

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5.07 Oxidative Coupling Polymerization

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5.07.1 Introduction

Oxidative coupling polymerization, described below as oxidative polymerization, is one type of condensation polymerization, formally defined as the elimination of two hydrogen atoms from a monomer to produce a polymer (Figure 1). In general, one-electron oxidation of the monomer forms a cation radical species or a radical species with removal of a proton, and two molecules of such species couple to give a dimer, followed by repetitive oxidative coupling to produce the polymer. The reaction mechanisms of oxidative polymerizations remain unclear and the coupling selectivity is not easy to regulate, because the active radical species tends to be too reactive to detect and control.

Any oxidizable aromatic compound in which no leaving groups, such as halogen atoms, are necessary for oxidative polymerization, and that has at least two removable hydrogen atoms, can be used as a monomer. Electrochemical oxidation is available, but chemical oxidation with an oxidizing agent is generally preferred. In chemical oxidation, catalysis with dioxygen or hydrogen peroxide is the most favorable because the reaction temperature is moderate and the by-product is only water. Therefore, oxidative polymerization is one of the cleanest and low-loading methods for the synthesis of aromatic polymers. The resulting aromatic polymers are useful in various fields, such as electronics, automobiles, aerospace, and medicine, due to their heat resistance, mechanical strength, electrical conductivities and photoelectric properties, among others.

This chapter describes oxidative polymerizations of phenols, naphthols, diphenyl disulfides, anilines, pyrroles, thiophenes, benzenes, and other monomers from the viewpoints of monomer variation, polymerization method, reaction mechanism, and coupling selectivity. The polymers obtained such as poly(phenylene oxide)s, polyphenols, poly

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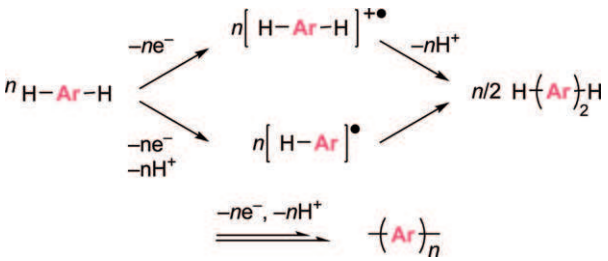

Figure 1 General reaction scheme of oxidative polymerization.

(phenylene sulfide)s, polyanilines, polypyrroles, polythiophenes, and polyphenylenes are also explained on the basis of their physical properties, substituent variation, nanostructure formation, and composite preparation.

5.07.2 Oxidative Polymerization of Phenols and Naphthols

Phenols and naphthols are easily oxidizable, and many studies on their oxidative polymerization have already been reported. However, unless the reactive points of the monomers are confined to two, it is difficult to obtain linear polymers. In the case of phenol, four reactive points arise from radical contribution of an oxygen atom and three carbon atoms at the *para* and *ortho* positions (Figure 2). 2,6-Disubstituted phenols have been selected as monomers for synthesizing useful linear polymers, and enzyme catalysts or enzyme model catalysts have been developed for the oxidative polymerization of 2- and/or 6-unsubstituted phenols. For naphthol monomers, regioselective and stereoselective polymerizations have been investigated.

5.07.2.1 2,6-Dimethylphenol

Some studies on the oxidative coupling of phenols were performed in the early 1950s, but only dimeric or oligomeric products were obtained. The coupling of 2,6-dimethylphenol (2,6-Me_2P) with benzoyl peroxide[1] or alkaline ferricyanide[2] as oxidant mainly gave 3,3′,5,5′-tetramethyldiphenoquinone (DPQ), as shown in Figure 3. In 1956, oxidative polymerization of 2,6-Me_2P to produce poly(2,6-dimethyl-1,4-phenylene oxide) (P-2,6-Me_2P) was discovered.[3] In this method, a solution of 2,6-Me_2P with CuCl (5 mol.%)/pyridine (Py) catalyst in nitrobenzene was stirred under dioxygen (1 atm) at room temperature for less than 1 h. The reaction mixture was then mixed with HCl/methanol, and the product P-2,6-Me_2P was obtained as the methanol-insoluble part in 84% yield with an osmotic molecular weight of 28 000. This was the first example of oxidative polymerization yielding a linear phenolic polymer with a high molecular weight. After this discovery, a variety of catalysts, such as copper, manganese, and cobalt complexes, were studied for their ability to catalyze oxidative polymerization. The activity of amines in copper complex catalysts was found to be in the following order: *N*,*N*′-di-*t*-butylethylenediamine > *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmed) > diethylamine > Py.[4] Such copper/diamine catalysts are now generally used for manufacturing P-2,6-Me_2P industrially.

P-2,6-Me_2P needs a very high temperature for melt processing because its T_g is 208 °C, but oxidative degradation of methyl groups at the 2,6-positions also occurs at this temperature. The discovery that P-2,6-Me_2P was completely miscible with polystyrene (PSt) resulted in a lowering of the T_g of the P-2,6-Me_2P/PSt alloy, which is widely used as an engineering plastic with sales approaching one billion dollars per year (*see* Chapter 5.17).

5.07.2.1.1 Coupling reaction mechanism

P-2,6-Me_2P is a C–O coupling product and DPQ is a C–C coupling product. How the C–O coupling can be controlled has remained unknown since the discovery of this reaction in the late 1950s. The three possible reaction mechanisms proposed for C–O coupling selectivity are as follows (Figure 4): (a) coupling of free phenoxy radicals resulting from one-electron oxidation of 2,6-Me_2P; (b) coupling of phenoxy radicals coordinated to the catalyst complex; and (c) coupling through a phenoxonium cation formed by two-electron oxidation of 2,6-Me_2P.[5]

5.07.2.1.1(i) Coupling of phenoxy radicals coordinated with catalyst

Since oxidative coupling of 2,6-Me_2P with benzoyl peroxide or alkaline ferricyanide affords DPQ as the main product,[1,2] the free phenoxy radical could cause C–C coupling, assuming that C–O coupling would result from the phenoxy radical coordinated to the copper complex catalyst (Figure 4(**b**)). In addition, the selectivity for C–O/C–C coupling was greatly influenced by the ratio of amines to copper in the catalyst, as increasing the ratio of Py and tmed to copper favored C–O coupling, as illustrated in Figure 5.[4] This observation suggested that a dinuclear copper complex would be formed when a small amount of Py was present, affording DPQ, while the addition of excess Py would generate a mononuclear copper

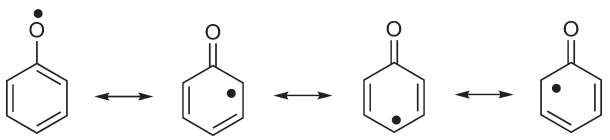

Figure 2 Resonance structures of phenoxy radical.

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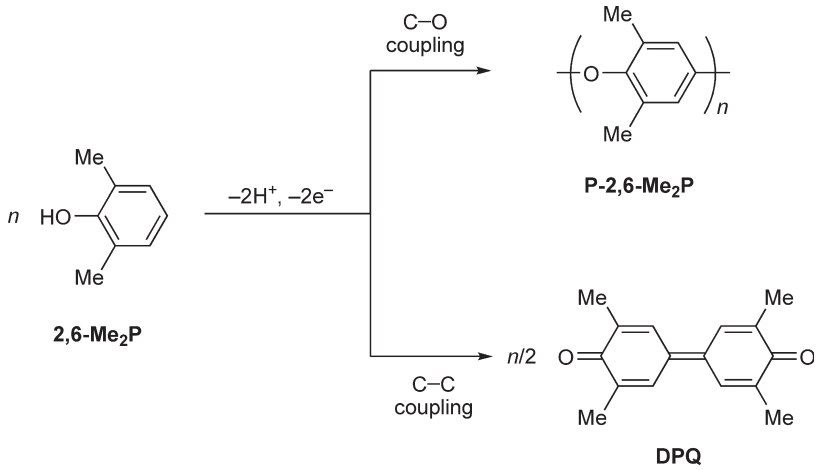

Figure 3 Oxidative coupling of 2,6-dimethylphenol (2,6-Me_2P). P-2,6-Me_2P, poly(2,6-dimethyl-1,4-phenylene oxide); DPQ, 3,3′,5,5′-tetramethyldiphenoquinone.

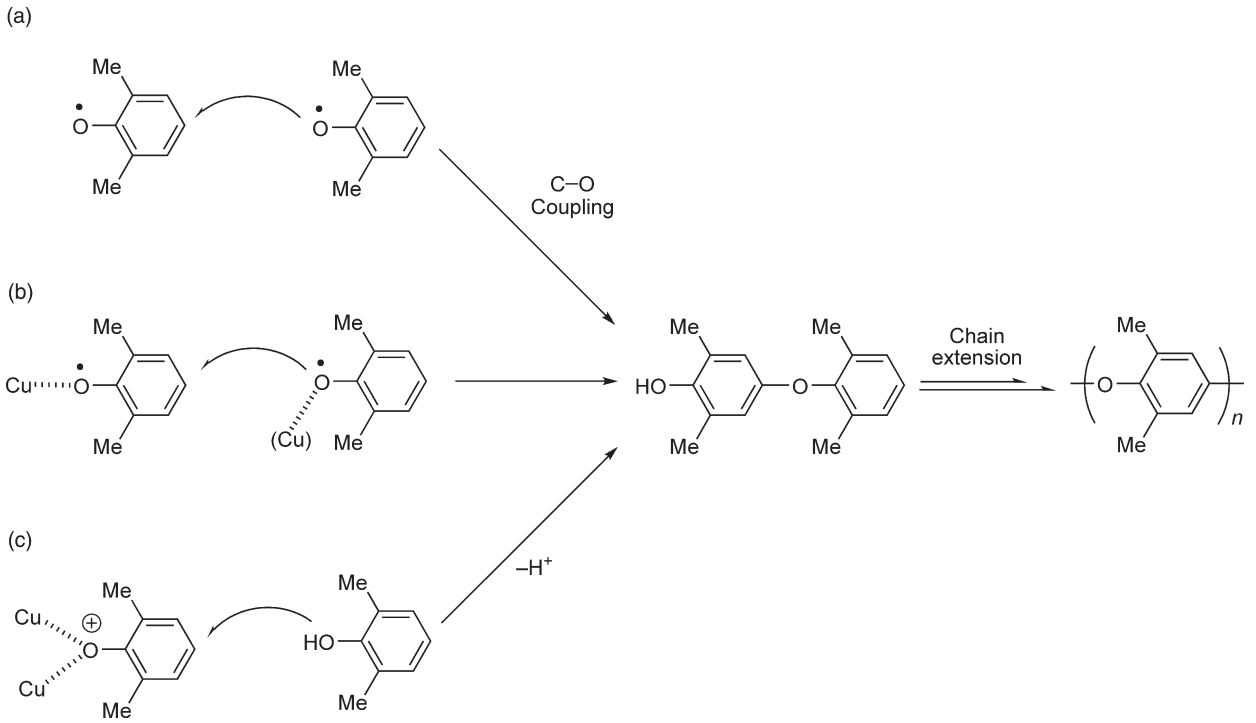

Figure 4 Reaction mechanisms proposed for oxidative polymerization of 2,6-dimethylphenol. Reproduced with permission from Kobayashi, S.; Higashimura, H. *Prog. Polym. Sci.* **2003**, *28*, 1015. © 2003 Elsevier Science Ltd.

complex, leading to P-2,6-Me_2P.[6] However, there is no adequate evidence to support this theory.

The kinetic study indicated that oxidative polymerization proceeded via a Michaelis–Menten-type reaction mechanism, including the phenoxy radical coordinated to the copper complex, as expressed in Figure 6.[7] As the ratio of Py to copper increased, favoring C–Ocoupling, the Michaelis-type constant ($K_m = (k_{-1} + k_2)/k_1$) became smaller, demonstrating that the formation of the phenoxo–copper(II) complex (ES) would be more favorable. This result suggested that C–O coupling might be preferred when at least one of the radicals is coordinated to copper.

The coordinated phenoxy radical can be expressed as the following resonance equation: phenoxo–copper(II) complex ↔ phenoxy radical–copper(I) complex. From the electron spin resonance (ESR) measurement[8] at a Py to Cu ratio of 20, two phenoxo–copper(II) species were observed at the beginning of the reaction, and the following oxidative polymerization gave mainly P-2,6-Me_2P. For Py/Cu = 2, no phenoxo–copper(II) complex was detected, and the major

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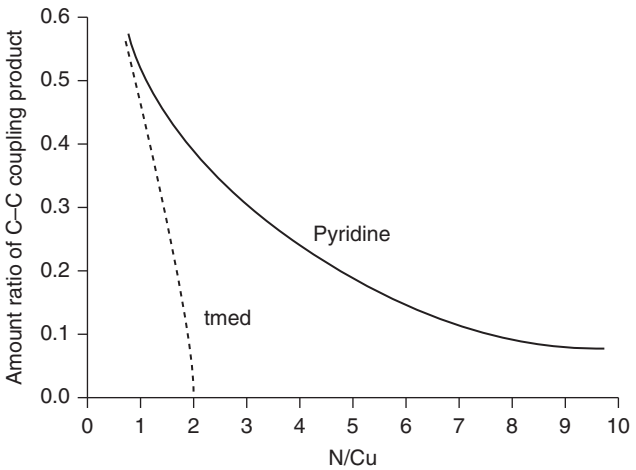

Figure 5 Amount ratio of C–C coupling product vs. nitrogen/copper ratio of catalysts in oxidative polymerization of 2,6-dimethylphenol. tmed, *N,N,N′,N′*-tetramethylethylenediamine. Reproduced with permission from Hay, A. S. *J. Polym. Sci. A: Polym. Chem.* **1998**, *36*, 505. © 1998 Wiley.

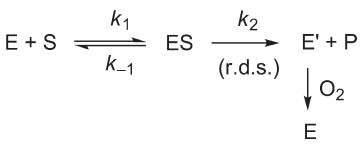

Figure 6 Michaelis–Menten-type analysis of copper-catalyzed oxidative polymerization of 2,6-dimethylphenol. E, copper(II) complex; E′, copper(I) complex; S, phenolate anion; P, coupling products; r.d.s., rate determining step.

product was DPQ. These data suggested that the coupling via the phenoxo–copper(II) complex led to C–O coupling.

5.07.2.1.1(ii) Coupling of phenoxonium cation with neutral phenol

The reaction mechanism of coupling through the phenoxonium cation of 2,6-Me_2P (**Figure 4(c)**) was based on the following data. Although the free phenoxy radical of the polymer was seen in the oxidation of 2,6-Me_2P with Ag_2O by the ESR flow technique,[9] no ESR signals of free phenoxy radicals in the oxidation of 2,6-Me_2P with the [CuCl(OCH_3)Py] complex were detected by a similar technique.[10] It was assumed that the phenoxy radical might be further oxidized by one more Cu(II) complex to the phenoxium cation, the two-electron-oxidized form of the phenol, to give the phenoxonium cation, which would couple with the phenol leading to C–O coupling.

The kinetic and spectroscopic studies of a Cu/*N*-methylimidazole (NMI) catalyst indicated that the reaction order of copper changed from 1.22 at NMI/Cu = 10 to 1.70 at NMI/Cu = 75, while the reaction rate and selectivity for C–O coupling reached a maximum at the NMI/Cu ratio of 30 or more.[11] The Cu/NMI complex did not react with 2,6-Me_2P in the absence of water, but reacted in the presence of water even under nitrogen, and, therefore, some water was required for oxidation. From these data, the key intermediate could be a (μ-hydroxo)(μ-phenoxo)–dicopper(II) complex, in which two-electron transfer from the phenoxo moiety to the two copper atoms would give a phenoxonium cation.

By *ab initio* calculation, the atomic charges for the phenol, phenolate anion, phenoxy radical, and phenoxonium cations (singlet and triplet) of 2,6-Me_2P were determined and are shown in **Figure 7**.[12] Since the oxygen atoms in all species were negative, the species susceptible to C–O coupling was considered to have a positive charge on the *para*-carbon and, therefore, could be the phenoxonium cation (singlet) reacting with either the phenol or the phenolate anion. In this study, the coupling of phenoxy radicals with each other leading to C–O coupling was excluded because the treatment of 2,6-Me_2P with benzoyl peroxide yielded DBQ.[1]

If the oxidative coupling of 2,6-Me_2P proceeds via the phenoxo cation, then in the presence of a more nucleophilic reagent in amounts exceeding that of 2,6-Me_2P, the phenoxo cation would react with the nucleophile, interfering with the production of P-2,6-Me_2P. However, the oxidative polymerization of 2,6-Me_2P catalyzed by the $[Cu(tmed)(OH)Cl]_2$ complex in the presence of *n*-pentylamine (*n*PA) in amounts fivefold that of 2,6-Me_2P produced P-2,6-Me_2P in 75% yield. To compare the nucleophilicity of *n*PA with that of 2,6-Me_2P, their reaction with benzyl chloride was investigated under similar conditions, giving *N*-benzyl-*n*-pentylamine in a quantitative yield and none of the benzyl 2,6-dimethylphenyl ether. These data strongly indicated that electrophilic intermediates, like the phenoxonium cation, are not involved in the oxidative polymerization of 2,6-Me_2P,[5] although a conflicting opinion is reported.[13]

5.07.2.1.1(iii) Coupling of free phenoxy radicals

The above two reaction mechanisms (**Figures 4(b)** and **(c)**) are derived from the assumption that the coupling via free phenoxy radicals of 2,6-Me_2P must lead to C–C coupling based on the data from the oxidation of 2,6-Me_2P with alkaline ferricyanide and benzoyl peroxide.[1,2] With alkaline ferricyanide, DPQ was produced in 45–50% yields, but the other half of the oxidized material was a yellow nonketonic polymer, which could have been P-2,6-Me_2P.[2] In the case of benzoyl peroxide, DPQ and C–C coupling of the diphenol were the sole oxidative coupling products, and the kinetic analysis showed that the reaction mechanism could not be due to phenoxy radical intermediates but due to benzoyl perester intermediates.[14] Moreover, the thermal decomposition of benzoyl 2,6-dimethylphenyl carbonate, which should generate the phenoxy radical, instead produced P-2,6-Me_2P and DPQ in 35–38% and 10% yields, respectively.[15] From these studies, it seemed that some complicated experimental results and misinterpretations were included in the above assumption of C–C coupling selectivity via free radical coupling.

Many studies on the oxidative coupling of 2,6-Me_2P with inorganic oxidants have been performed, and in some cases, the free radical was observed. For example, oxidative coupling with MnO_2, PbO_2, and Ag_2O (indicative of basic conditions) produced P-2,6-Me_2P.[16] Furthermore, the free radicals of 2,6-Me_2P and P-2,6-Me_2P were detected by ESR for reactions using MnO_2 and Ag_2O. Through the addition of triethylamine to the PbO_2 oxidation, the formation of DPQ was suppressed, and the yield of P-2,6-Me_2P was increased.[17] The oxidation with hexachloroiridate(IV) anion in acidic aqueous solution afforded DPQ.[18]

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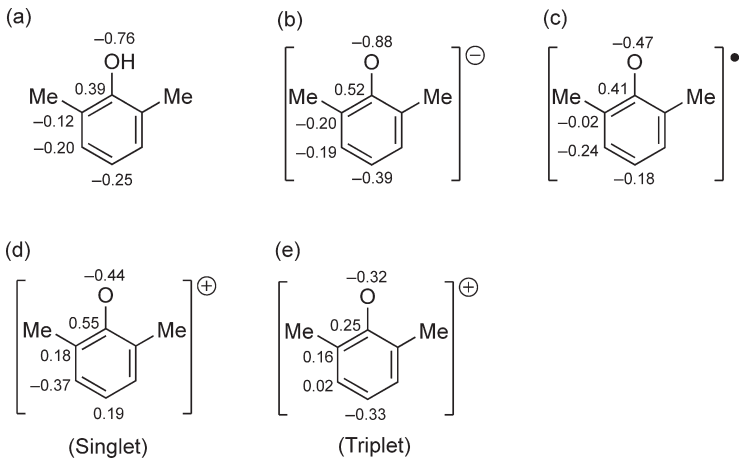
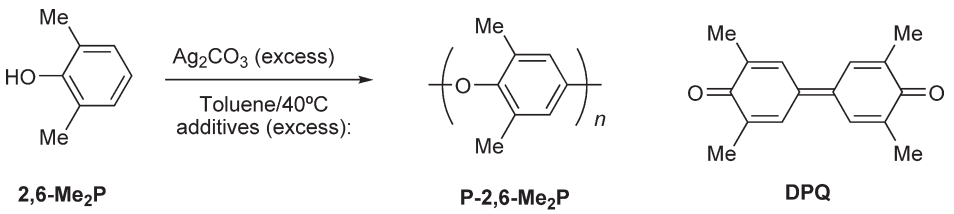


Figure 7 Atomic charges calculated for (a) neutral phenol, (b) phenolate anion, (c) phenoxy radical, (d) phenoxonium cation (singlet), and (e) phonoxonium cation (triplet) of 2,6-dimethylphenol. Reproduced with permission from Baesjou, P. J.; Driessen, W. L.; Challa, G.; Reedijk, J. *J. Am. Chem. Soc.* **1997**, *119*, 12590. © 1997 American Chemical Society.



Additives	P-2,6-Me_2P	DPQ	Total yield (%)
$nC_5H_{11}NH_2$	>99	~0	93
(No addition)	50	50	74
CH_3CO_2H	0	100	79

Figure 8 Oxidative polymerization of 2,6-dimethylphenol (2,6-Me_2P) with Ag_2CO_3 in the absence and presence of $nC_5H_{11}NH_2$ or CH_3CO_2H. P-2,6-Me_2P, poly(2,6-dimethyl-1,4-phenylene oxide); DPQ, 3,3′,5,5′-tetramethyldiphenoquinone. Reproduced with permission from Kobayashi, S.; Higashimura, H. *Prog. Polym. Sci.* **2003**, *28*, 1015. © 2003 Elsevier Science Ltd.

From the above studies, the selectivity for C–O or C–C coupling of 2,6-Me_2P seemed to be affected by a coexisting base or acid. Figure 8 shows the oxidative coupling of 2,6-Me_2P with Ag_2CO_3 in the presence of excess *n*PA or acetic acid (AcOH).[5] The resulting product ratio of P-2,6-Me_2P/DPQ was 50:50 in the absence of additives, while the ratios were >99:0 and 0:100 in the presence of *n*PA and AcOH, respectively. These data showed that, in the oxidative coupling of 2,6-Me_2P, the addition of a base would lead to C–O coupling and the addition of an acid to C–C coupling.

The above observations could be explained by the following proposal:[19] under basic conditions, free phenoxy radicals would be formed leading to C–O coupling (Figure 4(a)); while under acidic conditions, phenoxonium cations could be generated to give C–C coupling. Moreover, the electrochemical oxidation of 2,6-Me_2P above pH 5.2 took place via two monoelectronic steps, the first of which formed the free phenoxy radical, while oxidation below pH 5.2 underwent dielectronic one-step oxidation, which generated the phenoxonium cation (Figure 9).[20] The phenoxonium cation, therefore, seems to be easier to form under acidic conditions than under basic conditions.

The plausible reaction mechanism for the C–O/C–C coupling selectivity in the oxidative polymerization of 2,6-Me_2P is summarized as follows:

1. The coupling of free phenoxy radicals under basic conditions and the coupling via coordinated phenoxy radicals would mainly lead to C–O coupling.
2. The coupling of free phenoxy radicals under acidic conditions or the coupling of phenoxonium cations with phenol would favor C–C coupling.

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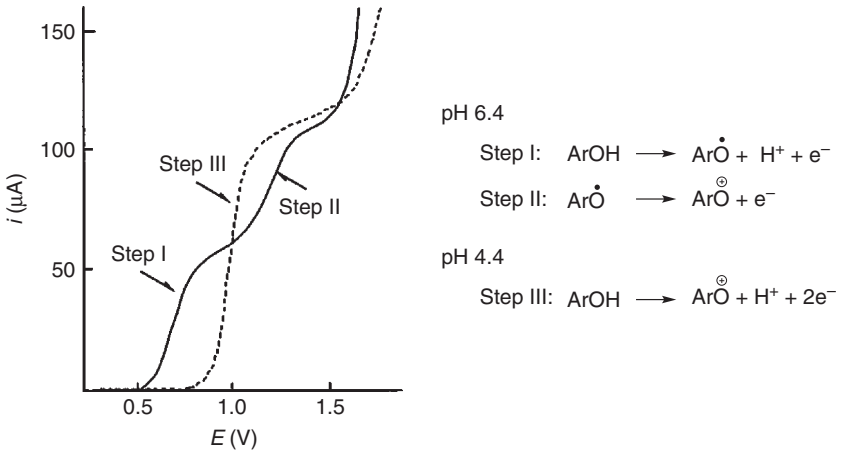

Figure 9 Electrochemical oxidation of 2,6-dimethylphenol. Dotted curve, pH 4.4; solid curve, pH 6.4; *i*, intensity of the electronic current; *E*, electropotential difference. Reproduced with permission from Roubaty, J. L.; Bréant, M.; Lavergne, M.; Revillon, A. *Makromol. Chem.* **1978**, *179*, 1151. © 1978 Wiley-VCH Verlag GmbH & Co. KGaA.

5.07.2.1.2 Chain extension mechanism for 2,6-dimethylphenol

The chain extension mechanism for the oxidative polymerization of 2,6-Me_2P has been almost established (Figure 10). Since an ether bond cuts off π-conjugation, the tail phenoxy group of the dimeric phenoxy radical shows no reactivity,[21] so two molecules of dimeric phenoxy radicals couple with each other to give a quinone-ketal intermediate. The formation of this intermediate is supported by data indicating that oxidative

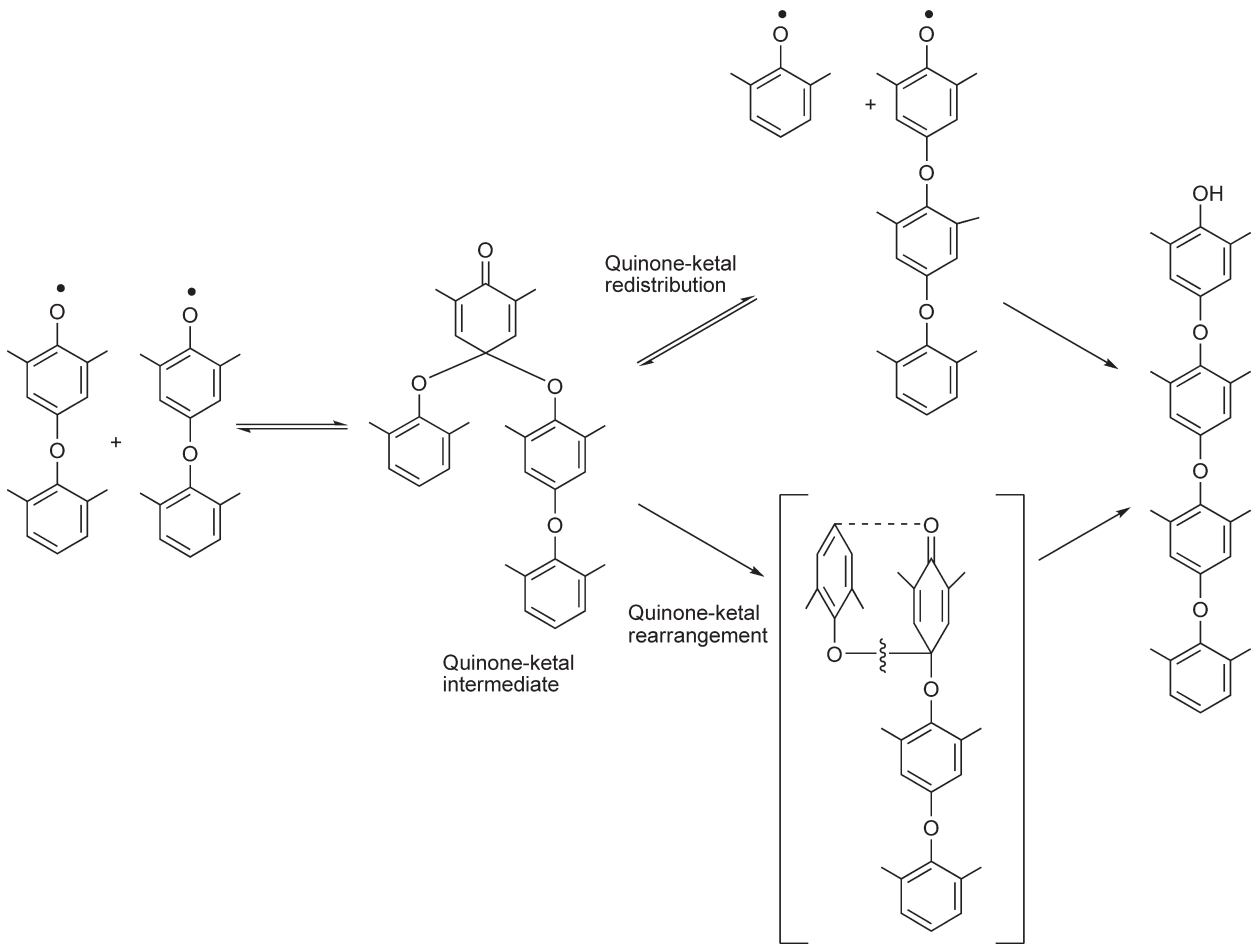

Figure 10 Chain extension mechanism for the oxidative coupling of 2,6-dimethylphenol dimer.

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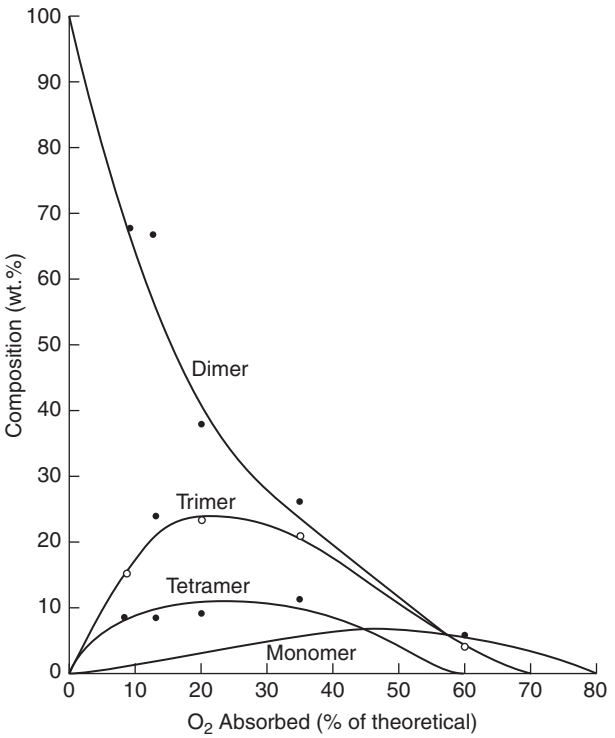

Figure 11 Composition ratio of monomer, dimer, trimer, and tetramer of 2,6-dimethylphenol vs. O_2 absorbed in the oxidative polymerization of the dimer as the starting substrate. Reproduced with permission from Cooper, G. D.; Blanchard, H. S.; Endres, G. F.; Finkbeiner, H. *J. Am. Chem. Soc.* **1965**, *87*, 3996. © 1965 American Chemical Society.

coupling of a 4-phenoxyphenol (PPL) marked with a methyl group (let it be A–B as two distinguishable aromatic rings) yielded none of the dimer through head–tail coupling (A–B–A–B) but did yield the dimer through the quinone-ketal intermediate (B–A–A–B).[22]

Two reaction routes from a quinone-ketal intermediate to a tetramer have been proposed. One is a quinone-ketal redistribution to give a monomer radical and a trimer radical[23] and the other is a quinone-ketal rearrangement via intramolecular rearrangement.[24] It was reported that oxidative polymerization of a 2,6-Me_2P dimer produced oligomers of even numbers, such as 2,6-Me_2P itself and the trimer (**Figure 11**). According to these data, the extension mechanism for the oxidative polymerization of 2,6-Me_2P must include a quinone-ketal redistribution. This redistribution mechanism for 2,6-Me_2P can then be applied to the modification[25] and depolymerization[26] of P-2,6-Me_2P. In addition, for 2-methyl-substituted and 2,6-unsubstituted PPLs, only quinone-ketal rearrangement took place at a low temperature; however, with increasing reaction temperature, quinone-ketal redistribution also occurred.[22]

5.07.2.2 Other 2,6-Disubstituted Phenols

Oxidative coupling of various 2,6-disubstituted phenols possessing alkyl, aryl, alkoxyl, chloro, and nitro groups was examined.[4] When 2- and/or 6-substituted groups are bulky, such as 2-methyl-6-*t*-butyl, 2,6-di-*i*-propyl, and 2,6-di-*t*-butyl, the polymers cannot be obtained, but diphenoquinones are formed. Oxidative coupling of 2,6-diphenylphenol can produce poly(2,6-diphenyl-1,4-phenylene oxide) with a T_g of 235 °C and a T_m of 480 °C. However, no oxidation occurred when both substituents were chloro or nitro groups because of their high oxidation potentials.

Some studies succeeded in applying 2,6-difluorophenol to oxidative polymerization, and then, poly(2,6-difluoro-1,4-phenylene oxide)s with crystallinity by enzyme catalyst[27] and with no crystallinity by copper catalyst[28] were obtained. Oxidative polymerization of 2,6-difluorophenol was achieved without additives only by the use of a copper catalyst in a base-condensed dendrimer capsule (**Figure 12**).[29]

Oxidative polymerization of 3,5-dimethoxy-4-hydroxybenzoic acids with the liberation of carbon dioxide produced poly(2,6-dimethoxy-1,4-phenylene oxide).[30] A photosensitive copolymer containing 2-(tetrahydropyran-2-yl)oxy-6-methylphenol[31] and a polymer of 2-methylthio-6-methylphenol convertible to a heterocyclic ladder polymer[32] were synthesized.

5.07.2.3 2- and/or 6-Unsubstituted Phenols

Since phenoxy radical intermediates have four reactive positions at the oxygen and *para*-carbon, as well as the two *ortho*-carbons, it is difficult to regulate the selectivity of oxidative coupling of phenols having at least one open *o*-position. However, enzyme catalysts, enzyme model catalysts, and other catalysts have been studied for the oxidative polymerization of 2- and/or 6-unsubstituted phenols.

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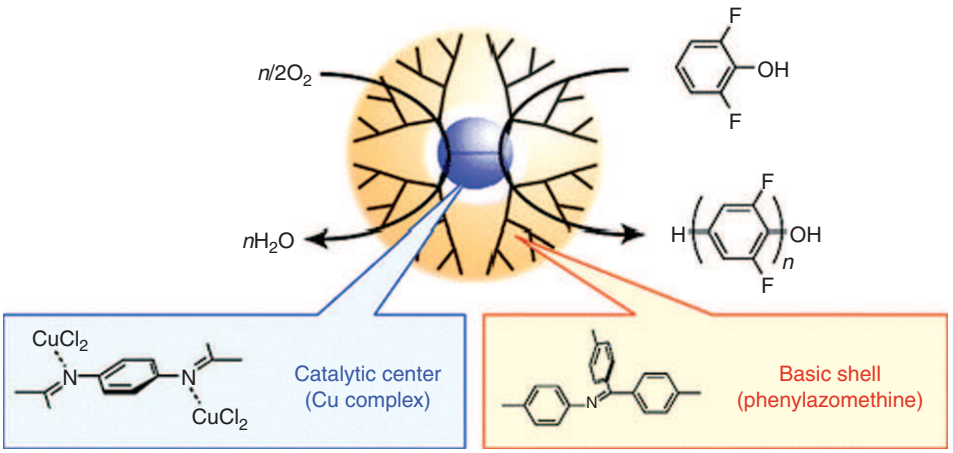

Figure 12 Oxidative polymerization of 2,6-difluorophenol by CuCl complex catalyst in base-condensed dendrimer capsule. Reproduced with permission from Yamamoto, K.; Kawana, Y.; Tsuji, M.; *et al. J. Am. Chem. Soc.* **2007**, *129*, 9256. © 2007 American Chemical Society.

5.07.2.3.1 Peroxidase catalyst

Oxidative coupling of phenols is involved in some biological reactions; for example, the formation of lignin or melanin is catalyzed by the oxidoreductase enzymes such as peroxidase, oxidase, or oxygenase.[33] Peroxidases, such as horseradish peroxidase (HRP), are heme proteins having an iron porphyrin as the active site (**Figure 13(a)**); they catalyze oxidation with hydrogen peroxide. The reaction mechanism for this transformation has already been established (**Figure 14**),[34] as the two active oxygen complexes abstract hydrogen atoms from substrates.[35,36] HRP shows high catalytic activity for generating free radicals from phenols but is unable to control the coupling selectivity as well as other enzymes.[37] The enzyme-catalyzed oxidative polymerizations of phenol, alkylphenols, biphenols, and various functional phenols have been reported[38] (*see* Chapter **5.10**).

In 1983, the removal of phenols from coal-conversion wastewater solutions was achieved with HRP catalyst and hydrogen peroxide, in which the oxidative coupling of phenols afforded water-insoluble low-molecular-weight polymers.[39] Furthermore, HRP-catalyzed oxidative polymerization of several phenols in aqueous–organic solvents was observed to produce polyphenols with M_n of 400–26 000.[40] The use of mixtures of buffer with water-miscible organic solvents is very important for the synthesis of phenolic polymers with higher molecular weights because such polymers are insoluble in water. Structural studies of poly(4-phenylphenol) prepared by HRP catalysis by Fourier transform infrared (FTIR) analysis and ^{13}C nuclear magnetic resonance (^{13}C NMR) analysis with cross polarization/magic angle spinning (CP/MAS) showed that the major linkage in these types of polymers was through C–C coupling across the *o*-positions.[41]

Interestingly, it was found that the oxidative polymerization of phenol catalyzed by HRP in 1,4-dioxane/buffer solvent produced polyphenol, which contained both phenylene and oxyphenylene units (**Figure 15**).[42] Using a mixture of methanol and buffer as a solvent, completely soluble polyphenol with an M_n of 2800 was obtained, which may replace phenol-formaldehyde resins derived from toxic formaldehyde.[43] Furthermore, HRP-catalyzed regioselective oxidative polymerization of phenol using poly(ethylene glycol) (PEG) as a template in water produced poly(hydroxy-*m*-phenylene).[44] The FTIR and differential scanning calorimetry (DSC) analyses indicated the formation of a miscible complex of polyphenol and PEG through hydrogen bonding, leading to high regioselectivity for a phenylene unit content higher than 90%. Carbon nanotubes are also used as templates for HRP-catalyzed polymerization of phenol in water, affording

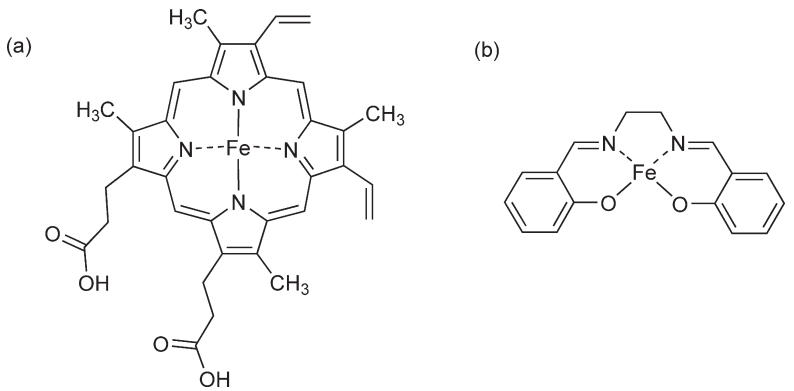

Figure 13 For HRP (a) heme as the active site of HRP, and (b) Fe(salen) complex as the reaction model of HRP.

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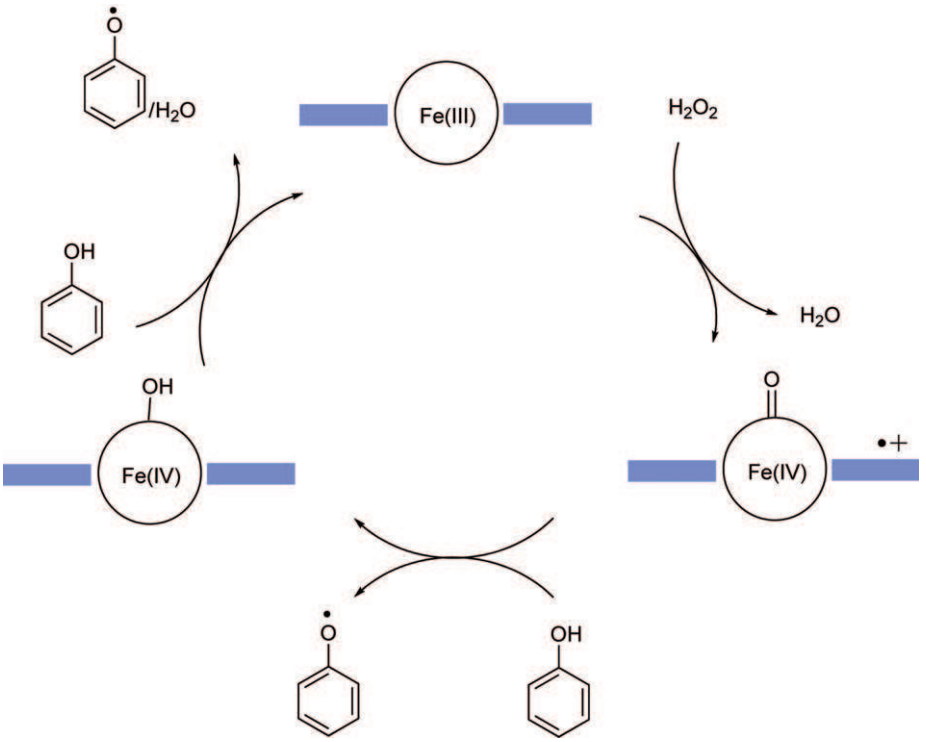

Figure 14 Catalytic reaction mechanism of oxidation of phenol by HPR with hydrogen peroxide. Reproduced with permission from Kobayashi, S. *J. Polym. Sci. A: Polym. Chem.* **1999**, *37*, 3041. © 1999 Wiley.

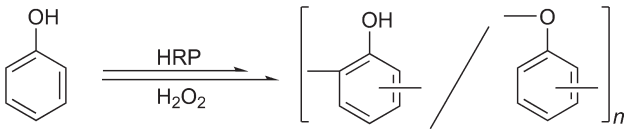

Figure 15 Oxidative polymerization of phenol catalyzed by HRP.

about 90% of the total monomer units in the obtained polymers as the highly thermally stable oxyphenylene.[45]

In the case of phenols possessing functional groups, chemoselectivity between the phenolic moiety and the other reactive groups can be achieved by peroxidase catalysis. In addition, regioselectivity in oxidative coupling is occasionally controlled by the functional substituents present. For example, a phenol derivative with a methacryloyl group was chemoselectively polymerized by HRP catalysis, where only the phenolic moiety was subjected to oxidative coupling without involving the vinyl of the methacryloyl group, as shown in Figure 16(**a**).[46] Chemoselective oxidative polymerization of 3-ethynylphenol with HRP produced a polyphenol having ethynyl groups, whereas the reaction of 3-ethynylphenol with a copper/diamine complex and dioxygen exclusively gave a diacetylene derivative as the oxidation product (Figure 16(**b**)).[47]Additionally, a new redox polymer was obtained via peroxidase-catalyzed oxidative polymerization of glucose-β-D-hydroquinone (arbutin), as shown in Figure 16(**c**).[48] The arbutin polymer consisted of C–C coupling units at the *o*-position, and after acidic deglycosylation, the resulting poly(hydroquinone) showed reversible redox properties. Furthermore, the HRP-catalyzed polymerization of 4-sulfonated phenol yielded a polymer consisting mainly of 1,2-phenylene oxide units, as indicated in Figure 16(**d**).[49] The reason for the regioselectivity of this coupling seemed to be the strong substituent effect of the sulfonate group at the *p*-position.

In organic solvent only, oxidative polymerization of 4-hexyloxyphenol by HRP ion-paired with anionic surfactant aerosol OT (AOT) using *t*-butyl peroxide as an oxidant produced a C–C coupling polymer with mainly quinonoid segments.[50] HRP was introduced into four bilayer poly(styrenesulfonate)/poly(allylamine hydrochloride) capsules, and through enzyme-catalyzed oxidative polymerization, a fluorescent polymer containing 2,2′-diphenoquinone structures was obtained from 4-(2-aminoethyl)phenol hydrochloride (tyramine).[51] Nanoscale patterning and enzymatic oxidative polymerization of caffeic acid on gold surfaces functionalized with *p*-aminothiophenol (*p*-ATP) were demonstrated with dip-pen nanolithography (DPN).[52] The polymer obtained from the surface reaction possessed only C–C coupling structures (Figure 17), showing that the *p*-ATP monolayer acted as a template and the inducer of the regioselective polymerization. In addition, HRP-catalyzed polymerization of 5,6-dihydroxyindolyl-1-thio-β-D-galactopyranoside produced a water-soluble polymer that was a model for the black chromophore of eumelanin.[53]

5.07.2.3.2 Peroxidase model catalyst

Oxidoreductase enzymes, such as HRP, are more expensive than conventional copper/amine catalysts. Hematin (Figure 13(**a**)) is a direct model of the active site of HRP,[54] and an *N*,*N*′-bis(salicylidene)ethylenediamino iron complex (Figure 13(**b**)),

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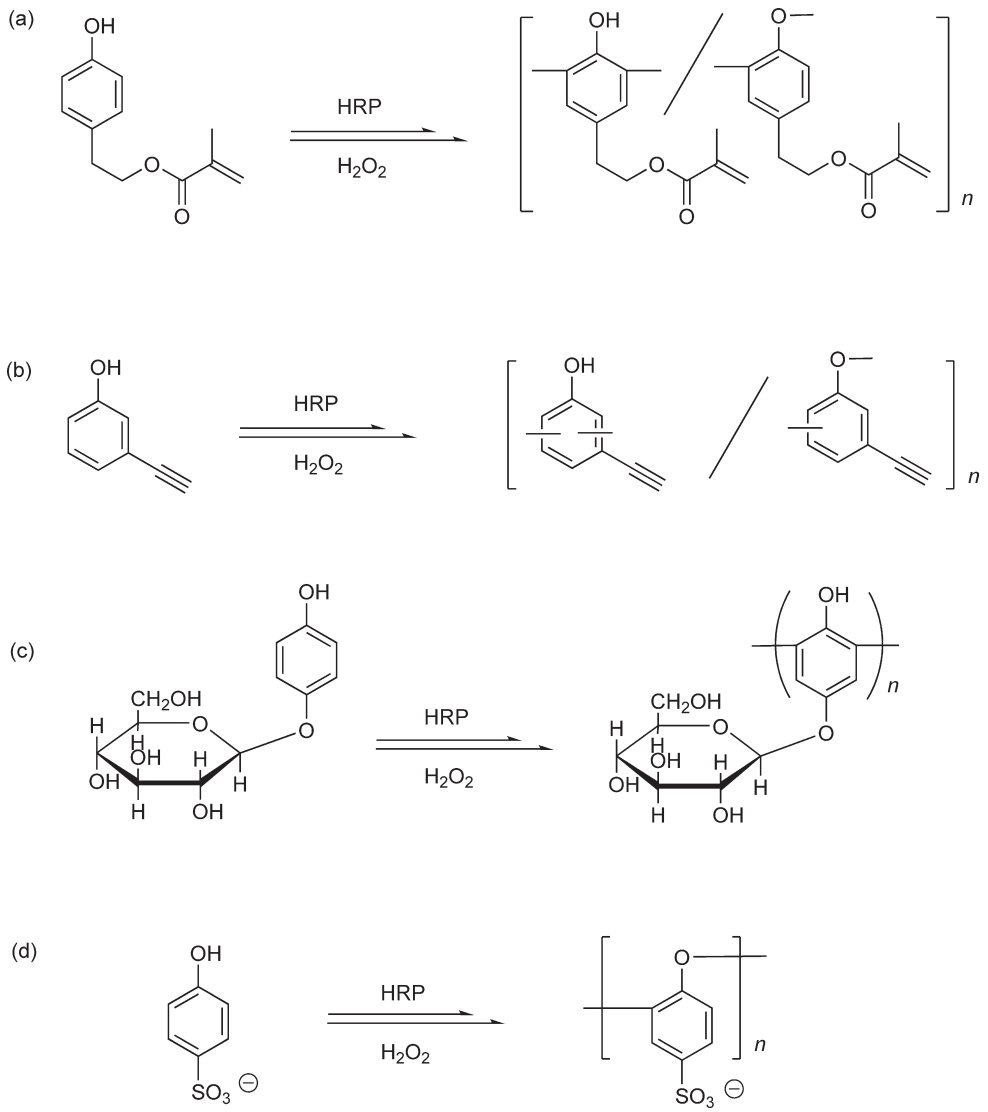

Figure 16 HRP-catalyzed oxidative polymerization of various phenols.

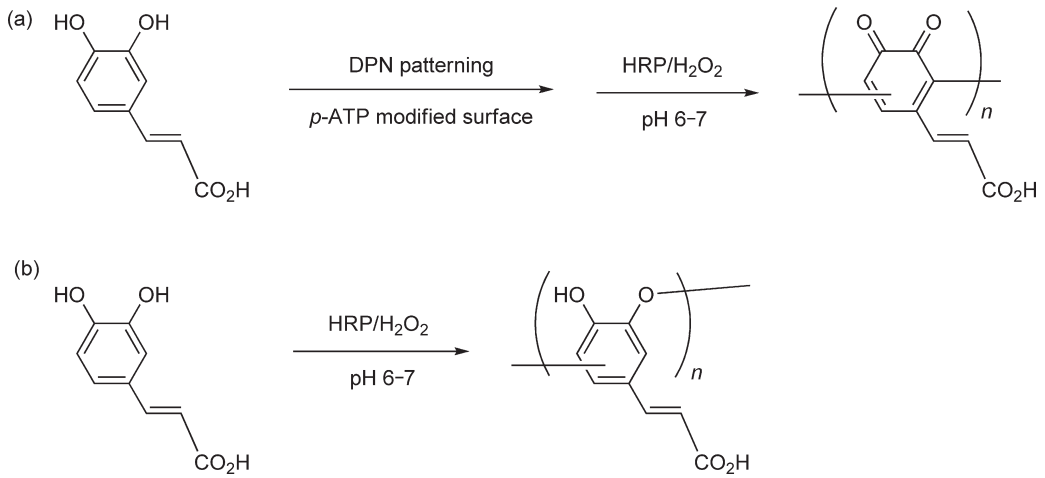

Figure 17 Proposed structures of the polymers obtained by (a) surface polymerization and (b) solution polymerization. Reproduced with permission from Xu, P.; Uyama, H.; Whitten, J. E.; *et al. J. Am. Chem. Soc.* **2005**, *127*, 11745. © 2005 American Chemical Society.

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which can be easily synthesized from cheap materials, is also a catalytically functional model of HRP.[55] Both complexes were capable of oxidative polymerization of phenols with hydrogen peroxide, indicating almost no difference in the catalytic activity of these complexes and HRP.

5.07.2.3.3 Tyrosinase model catalyst

Conventional copper catalysts, typically copper/diamine catalysts, are used industrially to produce P-2,6-Me_2P by oxidative polymerization, but they cannot yield useful polymers from phenols having at least one open *o*-position.[56,57] Peroxidase and peroxidase-model catalysts change coupling selectivity with different solvents or templates and show chemoselectivity toward phenolic moieties. However, these catalysts have limited ability to control the coupling selectivity of 2- and/or 6-unsubstituted phenols, and this was attributed to the following reasons:[58] Copper(I)/diamine complexes, typical conventional catalysts, reacted with dioxygen to give bis(μ-oxo) dicopper(III) complexes.[59] In the reaction of HRP with hydrogen peroxide, Fe(IV)=O intermediates are formed.[35] These active oxygen complexes are subjected to reaction with phenols to afford phenoxy radicals.[36,59] Therefore, catalysts generating 'electrophilic' or 'radical' active oxygen species, which abstract hydrogen atoms from phenols to give 'free' phenoxy radicals, cannot achieve regioselective coupling.

Based on this view (Figure 18), much attention was paid to generate a 'nucleophilic', strictly speaking 'basic', active oxygen species, which came in the form of a μ-η^2:η^2-peroxo–dicopper(II) complex (1), a copper–dioxygen model complex for tyrosinase.[60] The working hypothesis starts with complex 1 abstracting protons (not hydrogen atoms) from phenols to give phenoxo–copper(II) complex (2), equivalent to phenoxy radical–copper(I) complex (3). Intermediate 3 is not a 'free' radical but a 'controlled' radical, which is identical to the coordinated radical described above. Thus, if a catalyst generates (and regenerates) only a nucleophilic active oxygen intermediate, followed by the reaction with phenols to give 'controlled' radicals without formation of 'free' radicals, the regioselectivity of the subsequent coupling will be entirely regulated. This concept is characterized by the exclusive formation of 'controlled' phenoxy radicals, and hence, the new concept was termed 'radical-controlled' oxidative polymerization.[58]

5.07.2.3.3(i) Radical-controlled oxidative polymerization of PPL

Radical-controlled oxidative polymerization of PPL by a tyrosinase model catalyst was developed as illustrated in Figure 19.[58,61] This was the first simple synthesis of crystalline poly(1,4-phenylene oxide) (PPO) by catalytic oxidative polymerization, although another more expensive procedure by Ullmann coupling of sodium 4-bromophenolate was reported.[62] For the tyrosinase model, (hydrotris(3,5-diphenyl-1-pyrazolyl) borate)copper (Cu(Tpzb)) complex and (1,4,7-R_3-1,4,7-triazacyclononane)copper (Cu(L^R): R = isopropyl (iPr), cyclohexyl (cHex), and *n*-butyl (nBu)) complexes were selected.

To quantify coupling selectivity, the ratio of oxidative coupling dimers formed at the initial stage of oxidative polymerization of PPL was examined (entries 1–4 in Table 1). CuCl/*N*,*N*,*N*′,*N*′-tetraethylethylenediamine (teed), which was the sole catalyst reported for oxidative coupling of PPL, was also used (entry 5). As a model system of free phenoxy radical coupling, oxidation by an equimolar amount of 2,2′-azobisisobutyronitrile (AIBN) was also performed (entry 6).

In the case of the CuCl/teed catalyst, four dimers were detected and identified as p-4, o-4, oo-22, and oo-13 (Figure 20). Dimers p-4 and o-4 are formed through C–O coupling, and formation of oo-22 and oo-13 is based on C–C coupling. For the CuCl/teed, considerable amounts of C–C coupling dimers of oo-22 and oo-13 were detected, and p-4 selectivity was low (79%). The dimer ratio was very similar to that for free radical coupling by AIBN oxidation (entry 8), in which the formation of the C–C coupling dimers was characteristic. However, for the Cu(Tpzb), Cu(L^{iPr}), Cu(L^{cHex}), and Cu(L^{nBu}) complexes, none or very little of the C–C coupling dimers was detected, showing high regioselectivity for p-4. The order of p-4 selectivity was Cu(L^{nBu}) (90%) < Cu(L^{iPr}) (93%) < Cu(L^{cHex}) (95%), which was in good agreement with the steric effects of the substituents wrapping the copper centers. These data showed that the regioselectivity of phenoxy radical coupling can be controlled by these catalysts.

After oxidative polymerization, the products were isolated as the methanol-insoluble part. In the systems with no or very little C–C dimer formation (entries 1–4), white polymers with M_w up to 4700 were obtained. The resulting polymers were identified with near certainty as PPO from the IR spectra, and showed T_m values up to 194 °C from DSC analysis. In

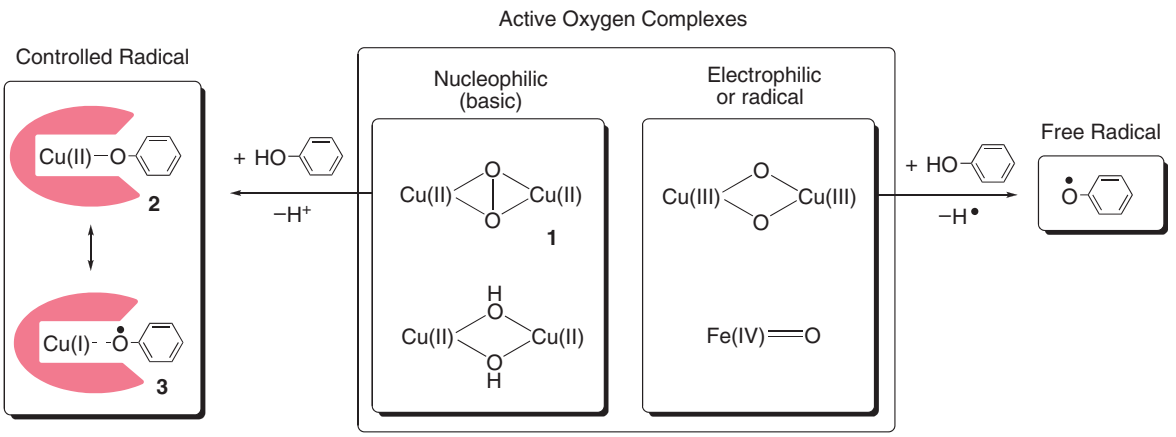

Figure 18 Working hypothesis for controlling phenoxy radical coupling. Reproduced with permission from Higashimura, H.; Kubota, M.; Shiga, A.; *et al.* *Macromolecules* **2000**, *33*, 1986. © 2000 American Chemical Society.

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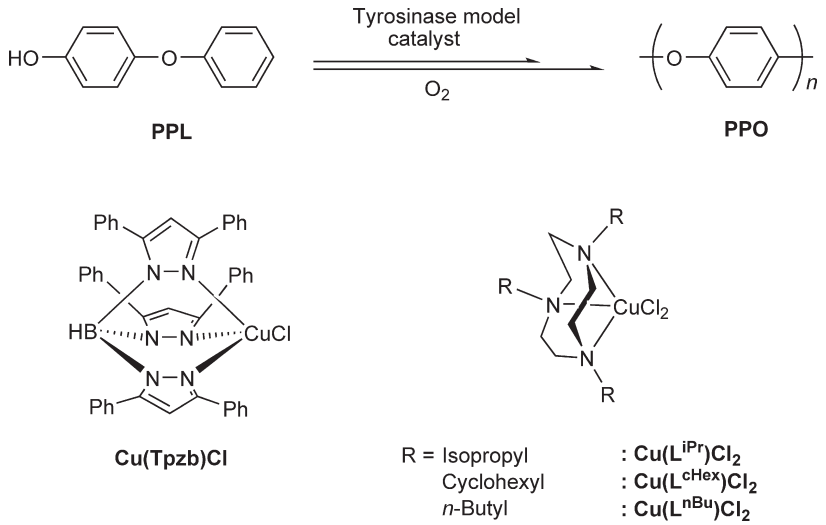

Figure 19 Oxidative polymerization of 4-phenoxyphenol (PPL) by tyrosinase model catalysts. Cu(L^R)Cl_2, (1,4,7-R_3-1,4,7-triazacyclononane) copper dichloride (R=isopropyl (iPr), cyclohexyl (cHex), and *n*-butyl (nBu)); Cu(Tpzb)Cl, (hydrotris(3,5-diphenyl-1-pyrazolyl)borate) copper chloride.

Table 1 Dimer ratio at the initial stage of oxidative polymerization of 4-phenoxyphenol

			Initial dimer ratio (%)			
Entry	*Catalyst*	*Oxidant*	*p-4*	*o-4*	*oo-22*	*oo-13*
1	Cu(Tpzb)Cl[a]	O_2	91	9	0	0
2	Cu(L^{iPr})Cl_2[a]	O_2	93	7	0	0
3	Cu(L^{cHex})Cl_2[a]	O_2	95	5	0	0
4	Cu(L^{nBu})Cl_2[a]	O_2	90	9	0	1
5	CuCl/teed[a]	O_2	79	6	2	13
6	-[b]	AIBN	82	4	2	12

[a]Polymerization of 4-phenoxyphenol (0.60 mmol) with Cu complex (0.030 mmol) and 2,6-diphenylpyridine (0.30 mmol) in toluene (1.2 g) under dioxygen (1 atm) at 40 °C. CuCl (0.030 mmol) and teed (0.015 mmol) was used as the Cu complex in entry 7.
[b]Oxidized by 2,2′-azobisisobutyronitrile (AIBN; 0.60 mmol) under nitrogen at 40 °C.
Cu(L^R)Cl_2, (1,4,7-R_3-1,4,7-triazacyclononane) copper dichloride (R = isopropyl (iPr), cyclohexyl (cHex), and *n*-butyl (nBu)); Cu(Tpzb)Cl, (hydrotris(3,5-diphenyl-1-pyrazolyl)borate) copper chloride.
Reproduced with permission from Higashimura, H.; Kubota, M.; Shiga, A.; *et al.* *Macromolecules* **2000**, *33*, 1986. © 2000 American Chemical Society.[58]

polymerizations giving considerable amounts of C–C dimers (entries 5 and 6), the brownish polymers showed no clear melting points in the DSC traces.

The reaction mechanism for the catalytic cycle of the tyrosinase model complexes is speculated in Figure 21. First, the starting copper(II) chloride complex Cu(Tpzb)Cl or Cu(L^R)Cl_2 (6) reacts with PPL or oligomers to give phenoxo–copper(II) complex (2), equivalent to phenoxy radical–copper(I) complex (3). Regioselective coupling then takes place between two molecules of 3 to produce copper(I) complex (7) and phenylene oxide products having *p*-linkages because the steric hindrance of the catalyst blocks the coupling at *o*-positions in 3.

In the case of Cu(Tpzb)Cl and Cu(L^R)Cl_2, complex 1 is formed from two molecules of 7 with dioxygen. Complex 1 reacts with two molecules of phenol to regenerate two molecules of 2 and hydrogen peroxide. Hence, this catalytic system would constrain only the regioselective coupling process from 3 by completely excluding free radical coupling reactions. The present system can be thus recognized as a radical-controlled oxidative polymerization. On the other hand, for the CuCl/teed complex, two molecules of 7 afford bis(μ-oxo) dicopper(III) complex (4) with dioxygen. Complex 4 abstracts hydrogen atoms from phenols to give bis(μ-hydroxo) dicopper(II) complex (8) and free phenoxy radicals (5). Therefore, this catalytic cycle would involve free radical coupling with the formation of C–C linkages, although 8 reacts with phenols to regenerate two molecules of 2.[63] Two computational studies were performed to further investigate this reaction; one disagreed with the above reaction mechanism,[64] but the other was in good agreement.[65]

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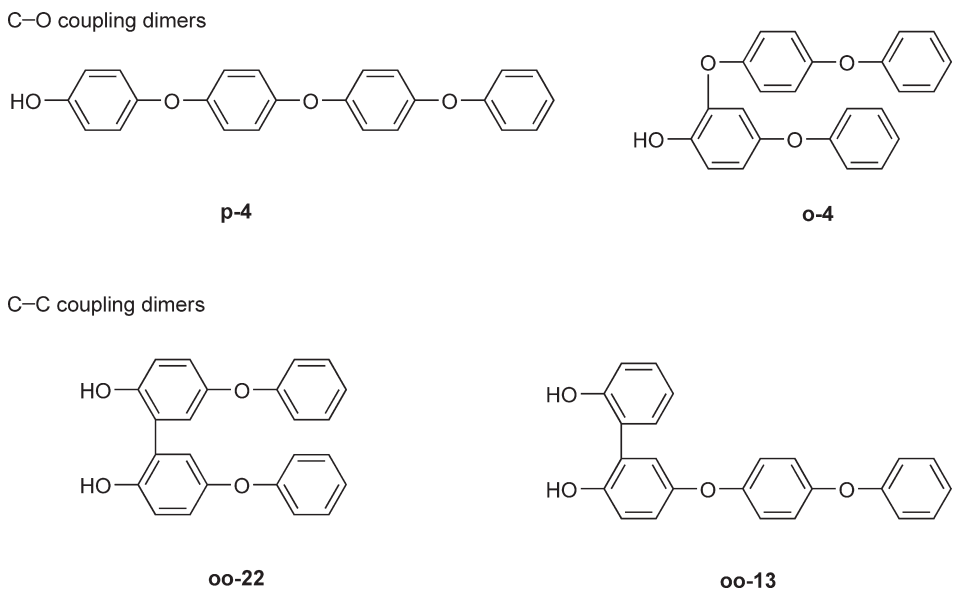

Figure 20 C–O and C–C coupling dimers of 4-phenoxyphenol.

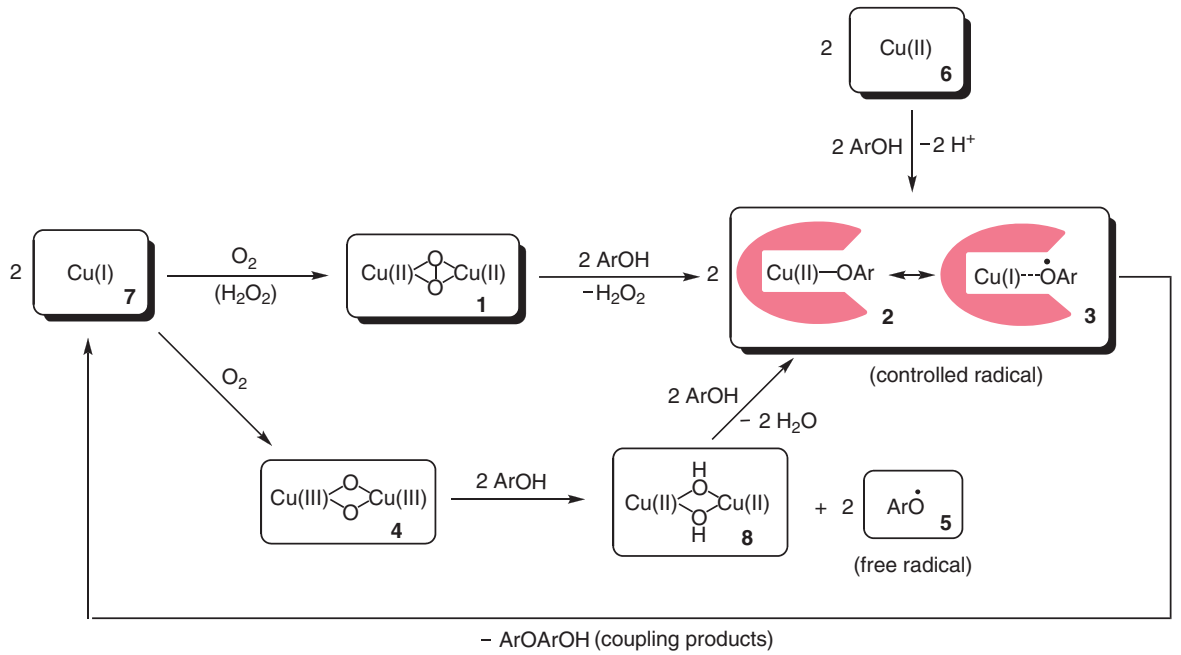

Figure 21 Speculated reaction mechanism for the catalytic cycle in oxidative polymerization of phenols by copper catalysts.

The reaction mechanism of oxidative coupling and chain extension of PPL is speculated in Figure 22.[66] For simplicity, controlled radicals are expressed by free radicals with the elimination of copper moieties. First, two molecules of PPL are oxidized, and the generated radicals couple with each other (radical coupling). Since radical coupling does not occur on the 4-phenoxy group of PPL, only three reaction routes (**a**, **b**, and **c**) can take place, giving rise to a quinone-ketal intermediate, o-4, and oo-22, respectively. From the quinone-ketal, the redistribution path (quinone-ketal redistribution, **d**) is ruled out owing to no detection of phenol or 4-(4-phenoxyphenoxy) phenol, and therefore, the rearrangement path (quinone-ketal rearrangement) is proposed in the oxidative coupling of PPL. Upon cleavage of the ketal C–O bond, synchronous bond formation of route **e** to p-4, that of **f** to oo-13, and that of **h** to oo-22 can occur, although that of **g** regenerates the quinone-ketal.

In the radical-controlled oxidative coupling of PPL, the entire radical coupling takes place with controlled radicals. The steric effect of the catalyst moiety would suppress o-4 formation (route **b**) and inhibit oo-22 formation (route **c**), thereby regioselectively generating the quinone-ketal intermediate (route **a**). Moreover, almost no detection of oo-13, as well as oo-22 in the radical-controlled oxidative coupling

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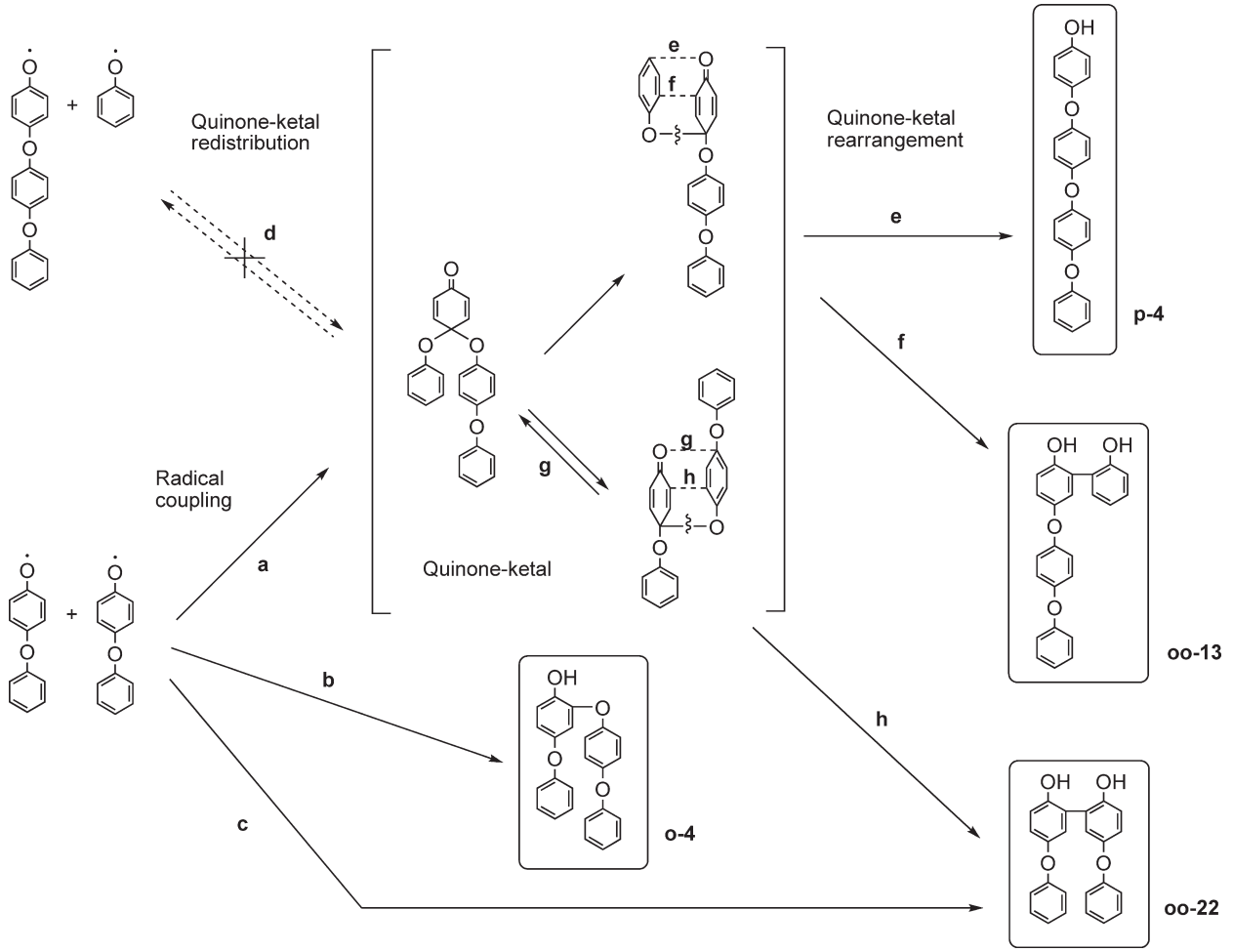

Figure 22 Speculated reaction mechanism for the oxidative coupling and chain extension of 4-phenoxyphenol.

of PPL, indicated that the catalyst must remain in contact with the quinone-ketal intermediate in the rearrangement. To achieve this, the carbonyl group of the quinone-ketal probably coordinates to the copper(I) atom of the catalyst. In the rearrangement, bond formation at the *o*-position to oo-13 and oo-22 via routes **f** and **h**, respectively, could be disfavored, and regioselective production of p-4 via route **e** should predominate. Hence, in radical-controlled oxidative coupling, the tyrosinase model catalyst can control regioselectivity in not only the radical coupling step but also the quinone-ketal rearrangement step.

In a similar way to dimerization, oxidative coupling of controlled radicals from PPL and p-4 will give a trimeric quinone-ketal intermediate, from which the corresponding rearrangements will afford linear C–O trimers (six oxyphenylene units). Further oxidative couplings between controlled radicals generated from PPL, dimer, trimer, and higher oligomers will lead to linear PPO. However, such linear crystalline PPO shows low solubility and precipitates in reaction solvents, so future studies should aim at increasing the molecular weight of the PPO while maintaining high crystallinity.

5.07.2.3.3(ii) Radical-controlled oxidative polymerization of other phenols

In the oxidative polymerization of phenol, the Cu(L^{iPr}) catalyst showed high selectivity for C–O coupling at the *p*-position, but it did not exclude the formation of C–C coupling at the *p*-position.[67] This type of coupling never occurred in the oxidative polymerization of PPL because of the 4-phenoxy group. The resulting polymer consisted mainly of a 1,4-phenylene oxide unit but contained a considerable amount of C–C coupling structures with no crystallinity. The temperature of 10% weight loss for this poly (phenylene oxide) (~500 °C), however, was much higher than that for the polyphenol obtained by peroxidase-catalyzed polymerization (<400 °C). The plot of monomer conversion versus polymer yield for phenol showed a linear relationship, like a chain growth mechanism, while PPL followed a typical stepwise growth mechanism (**Figure 23**). This observed behavior for phenol was due to the much higher reactivities of the dimers and oligomers than that of the monomer, as often seen in oxidative polymerization. Until the monomer is almost consumed, the reaction mixture consists mainly of the monomer and the polymer in a manner similar to a chain reaction mechanism and was therefore named reactive intermediate polycondensation.[68]

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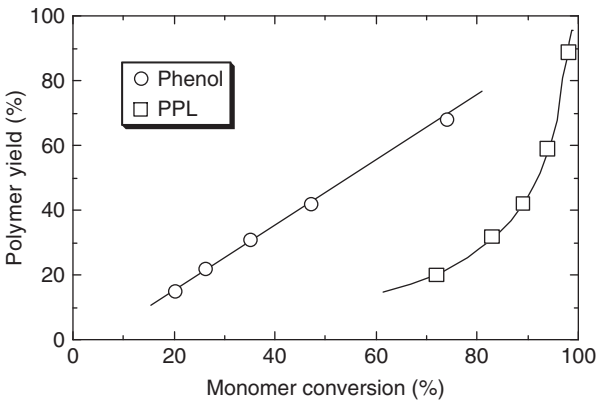

Figure 23 Polymer yield vs. monomer conversion in the oxidative polymerization of phenol and PPL. Reproduced with permission from Higashimura, H.; Fujisawa, K.; Kubota, M.; Kobayashi, S. *J. Polym. Sci. A: Polym. Chem.* **2005**, *43*, 1955. © 2005 Wiley Periodicals.

The substituent effect of methylphenols and dimethylphenols on the reaction rates was examined.[69] For the Cu(tmed) catalyst, the reaction rates were dominated by the O–H homolytic bond dissociation energies of the monomers, and were closely related to the electronic effects of substituents. On the other hand, for the Cu(L^{iPr}) catalyst, the steric effect of the substituents at the *o*-positions was more likely to decrease the reaction rates. Interestingly, Cu(L^{iPr})-catalyzed oxidative polymerization of 2- and 3-methylphenol regioselectively produced soluble poly(phenylene oxide)s with good thermal stability.[70,71]

The polymers obtained by radical-controlled oxidative polymerization of 2,5-dialkylphenols (2,5-R_2P:R = methyl (Me), ethyl (Et), and *n*-propyl (*n*Pr)) are shown in Figure 24.[72] The oxidative polymerization of 2,5-Me_2P catalyzed by Cu(L^{iPr})Cl_2 in toluene under dioxygen produced a white polymer composed exclusively of a 2,5-dimethyl-1,4-phenylene oxide unit and possessed an M_w of 19 300. The melting temperatures in the first and second heating scan (T_{m1} and T_{m2}) were detected at 308 and 303 °C, respectively, demonstrating the synthesis of a P-2,5-Me_2P with heat-reversible crystallinity for the first time. Surprisingly, the isomeric polymer P-2,6-Me_2P showed a melting point at 237 °C (T_{m1}), but once the crystal part had been completely melted, recrystallization never occurred (T_{m2} not detected) via slow cooling or annealing.[73] Since thermoplastic polymers are mainly used as melt-moldings, P-2,6-Me_2P is generally accepted as an amorphous polymer; however, P-2,5-Me_2P can be practically considered as a crystalline one. For 2,5-Et_2P and 2,5-nPr_2P, white polymers with M_w of 23 100 and 32 200, respectively, only 1,4-phenylene oxide units were present. The latter showed heat-reversible crystallinity with a T_{m2} at 276 °C, but the former did not show a detectable T_{m2}. Therefore, the recrystallization of poly(alkylated phenylene oxide)s after melting seems to be governed by both the position and the nature of their alkyl substituents.

5.07.2.3.4 Other catalysts

Oxidative polymerization of 2,5-Me_2P catalyzed by CuCl/2-substituted Py such as 2-phenylpyridine and 2-(4-tolyl) pyridine yielded P-2,5-Me_2P with a crystallization degree of 42%.[74] For the polymerization, a mesoporous catalyst, copper/diamine complex immobilized on a mesoporous silica SBA-15, prevented the formation of branching and cross-linking.[75]

5.07.2.4 Naphthols

Enzyme-catalyzed oxidative polymerization of 2-naphthol[76] and 1,5-dihydroxynaphthalene[77] was reported. In the polymerization of 2,6-dihydroxynaphthalene (Figure 25(a)), Cu (tmed) catalysis with dioxygen[78] and $FeCl_3$ oxidation in the solid state[79] produced poly(2,6-dihydroxy-1,5-naphthalene), in which the regioselectivity is potentially based on the monomer nature.

A 1,1′-binaphthalene structure has a high rotation barrier, so asymmetric induction is possible in 1,1′-coupling polymerization of naphthalene-type derivatives.[80,81] Asymmetric oxidative coupling polymerization of 2,3-dihydroxynaphthalene (Figure 25(b)) was developed using a CuCl/(*S*)-2,2′-methylenebis (4-phenyl-2-oxazoline) catalyst[82] and a VO(stearate)$_2$/sodium D-tartrate catalyst,[83] proceeding in 43% ee and 88% ee, respectively. Furthermore, for a monomer with unequal reactive points (Figure 25(c)), cross-coupling polymerization was also achieved with a head-to-tail selectivity of 96%.[84]

5.07.3 Thiophenols and Their Derivatives

Oxidative coupling of thiophenol does not generally give a polymer but instead diphenyldisulfide (Figure 26(a)) because the formation of S–S bond from the coupling of thiophenoxyl radicals takes place more readily than C–S bond formation.[85] Applying this reaction to oxidative polymerization, poly(1,3-phenylene disulfide) was obtained from 1,3-dimercaptobenzene.[86]

Poly(1,4-phenylene sulfide) (PPS) is one of the so-called super engineering plastics with a high melting point at 282 °C. It is manufactured by polycondensation of 1,4-dichlorobenzene with Na_2S, eliminating NaCl (*see* Chapter 5.17). The synthesis of PPS by oxidative polymerization was achieved by further

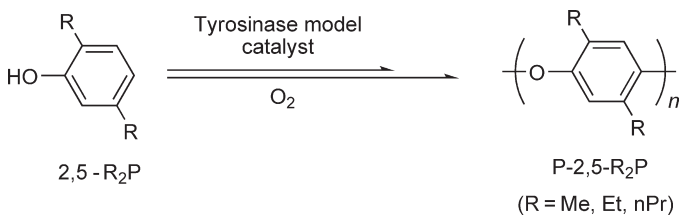

Figure 24 Oxidative polymerization of 2,5-R_2P by tyrosinase model catalyst.

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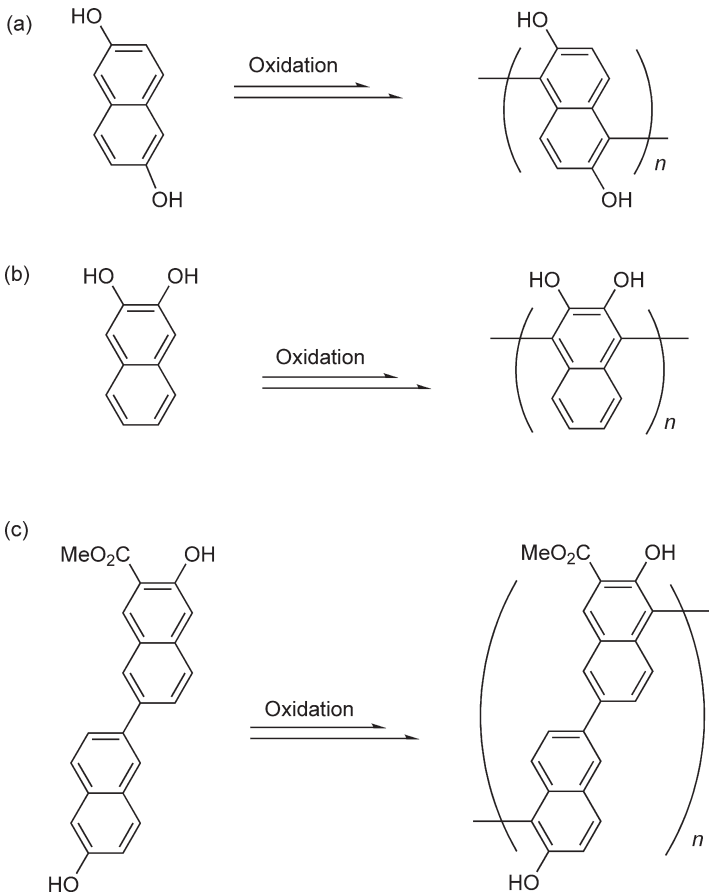

Figure 25 Oxidative polymerization of various naphthol derivatives.

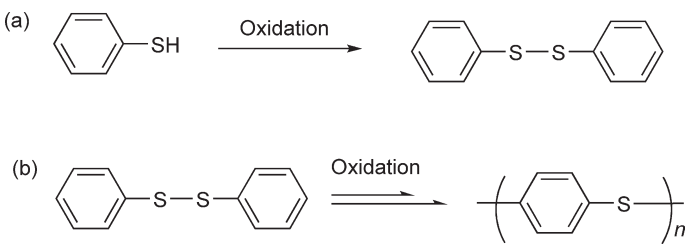

Figure 26 (a) Oxidative dimerization of thiophenol, and (b) oxidative polymerization of diphenyl disulfide.

oxidation of diphenyl disulfide (Figure 26(b)). The polymerization of diphenyl disulfide was performed in the presence of a strong acid by electrochemical oxidation[87] and by reaction with oxidants such as $SbCl_5$[88] and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.[89]

Vanadyl catalysts, such as vanadyl acetylacetonate, with O_2 were also used for oxidative polymerization of diphenyl disulfide under strongly acidic conditions.[90,91] The reaction mechanism is explained as follows:[92,93] a V=O complex is deoxygenized by two molecules of protons to form a V complex, which reacts with another V=O complex to generate a V–O–V dinuclear complex. This active species oxidizes the substrate and is reoxidized by dioxygen (Figure 27).

The chain extension mechanism is speculated in Figure 28.[94] First, diphenyl disulfide is one-electron-oxidized to a cation radical, which reacts with diphenyl disulfide to give a phenylbis(phenylthio)sulfonium cation. Next, the cation undergoes electrophilic attack on another diphenyl sulfide molecule to produce 4-(phenylthio)phenyl phenyl disulfide. Similar reactions follow finally producing PPS, which contains one unit of disulfide per polymer chain.

Oxidative polymerization of some diaryl disulfides produced PPSs substituted with 2- or 3-methyl groups; 2,3-, 2,5-, or 2,6-dimethyl groups; and 2-methoxy groups, among others.[91,95] Terminally functionalized oligomers[96] and block polymers containing alkylene groups[97] were also prepared. In addition, cyclic hexakis(1,4-phenylene sulfide) was synthesized,[98] and the subsequent ring-opening polymerization of such cyclic oligomers was performed.[99] The synthesis of PPS through a poly(sulfonium cation) as a soluble precursor was discovered via oxidative

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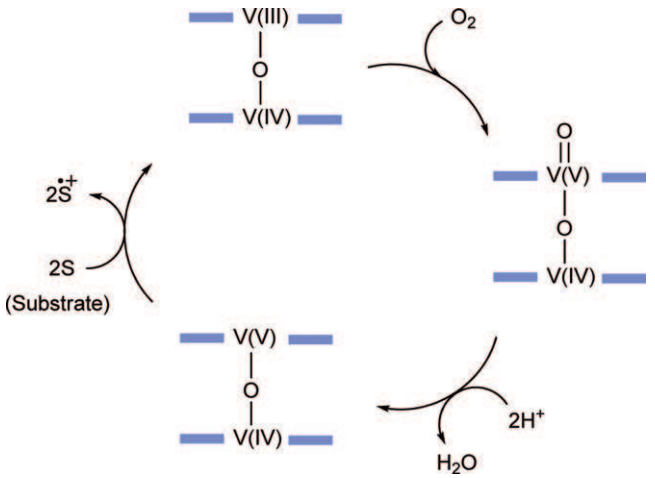

Figure 27 Proposed catalytic cycle of vanadyl complex in oxidative polymerization.

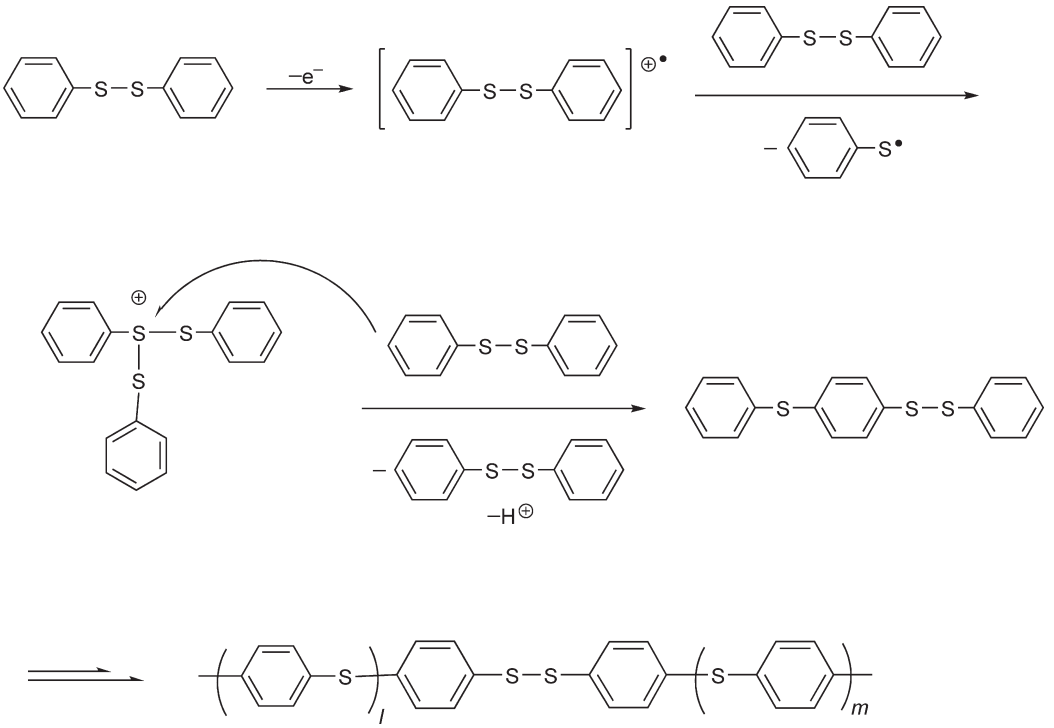

Figure 28 Proposed reaction mechanism for oxidative polymerization of diphenyl disulfide.

polymerization of methyl 4-(phenylthio)phenyl sulfide, followed by dealkylation to produce PPS.[100]

5.07.4 Anilines

Oxidative polymerization of aniline was conceptually reported in 1909, as expressed in Figure 29,[101] although polyaniline (PAN), poly(1,4-phenylene imine), was originally known as aniline black in the nineteenth century. PAN is one of the most studied conducting polymers because of its electronic conductivity (~10 S cm^{-1}), environmental stability, easy preparation, and intrinsic nanostructure formation[102,103] (*see* Chapter 1.14).

5.07.4.1 Aniline

Oxidative polymerization of aniline leading to PAN is typically performed via the electrochemical method[104] and usually in the presence of a strong oxidant, such as ammonium persulfate.[105] Strongly acidic conditions (pH < 2) are generally needed for synthesizing highly conductive PAN (>1 S cm^{-1}), because couplings other than C–N at the *p*-position can occur in nonacidic conditions and proton-doped emeraldine salt (Figure 30) is metallically conductive.[106,108]

Metal-catalyzed oxidative polymerization of aniline has been studied, such as in iron salt catalysis[109] and HRP enzyme catalysis with hydrogen peroxide,[110] iron salt catalysis with ozone,[111] and copper salt catalysis with dioxygen.[112]

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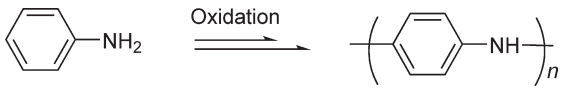

Figure 29 Oxidative polymerization of aniline.

A photo-induced catalytic system[113] and a gas-phase plasma method[114] have also been reported.

5.07.4.1.1 Reaction mechanism

Some reaction mechanisms of oxidative polymerization of aniline have been proposed (**Figure 31**), but the selectivity for C–N coupling under strongly acidic conditions has been unclear. Although a phenazine-type trimer, generated via *ortho* C–N coupling at the early stage (**a**), was assumed to initiate oxidative polymerization,[115] such cyclization to the phenazine structure was reported to be included only in the postpolymerization process.[116] The dimerization step is generally accepted for route (**b**), in which aniline is one-electron-oxidized to a monomeric cation radical, followed by *para* C–N coupling of two molecules of the cation radical to a dimer. For the subsequent steps of the chain extension, three main reaction mechanisms have been proposed. One is that a dimeric cation radical, formed via one-electron oxidation (**c**), would couple with a monomeric cation radical.[117,118] For the others, two-electron oxidation of the dimer could generate a quinodal diiminium ion (**d**) or a nitrenium ion (**e**), leading to electrophilic coupling with neutral aniline.[119,120] The addition of electron-rich arenes did not inhibit polymerization;[118] therefore, routes (**d**) and (**e**) could be ruled out, suggesting that route (**c**) would be the most probable.

5.07.4.1.2 Nanostructure formation

Various nanostructures of PAN, such as nanospheres, nanofibers, nanotubes, and nanosheets, have been obtained. For example, uniform spherical particles of PAN with an average diameter of 150–200 nm were synthesized by oxidative polymerization of aniline in HCl solution with poly(vinyl alcohol coacetate) as a steric stabilizer.[121]

PAN nanofibers are prepared by selecting nanostructure-directing agents during the oxidative polymerization of aniline. Application of sodium dodecyl sulfate as surfactant,[122] poly(acrylic acid) as polyelectrolyte,[123] biological, inorganic, or organic nanofibers as seeds,[124] camphorsulfonic acid/aniline oligomers,[125] and organic solvent for organic/aqueous interfacial polymerization[126] has been previously reported. However, nanofibril morphology does not require such agents and appears to be intrinsic to PAN synthesized in water.[108,127] In the conventional oxidative polymerization of aniline by ammonium persulfate in acidic aqueous solution at 0 °C (**Figure 32**), well-dispersed nanofibers form at the initial stage (0 min). As the oxidant is gradually added to the solution with vigorous stirring, the nanofibers become thicker and coarser (25 min). Finally, the product contains irregularly shaped agglomerates (>100 min).[128] High-quality PAN nanofibers can be readily obtained by rapidly mixing aniline with oxidant in acidic aqueous solution at room temperature or above and allowing the polymerization to proceed to completion in the absence of mechanical agitation.[129] Catalyst-free synthesis of PAN nanofibers with hydrogen peroxide as oxidant has also been reported.[130]

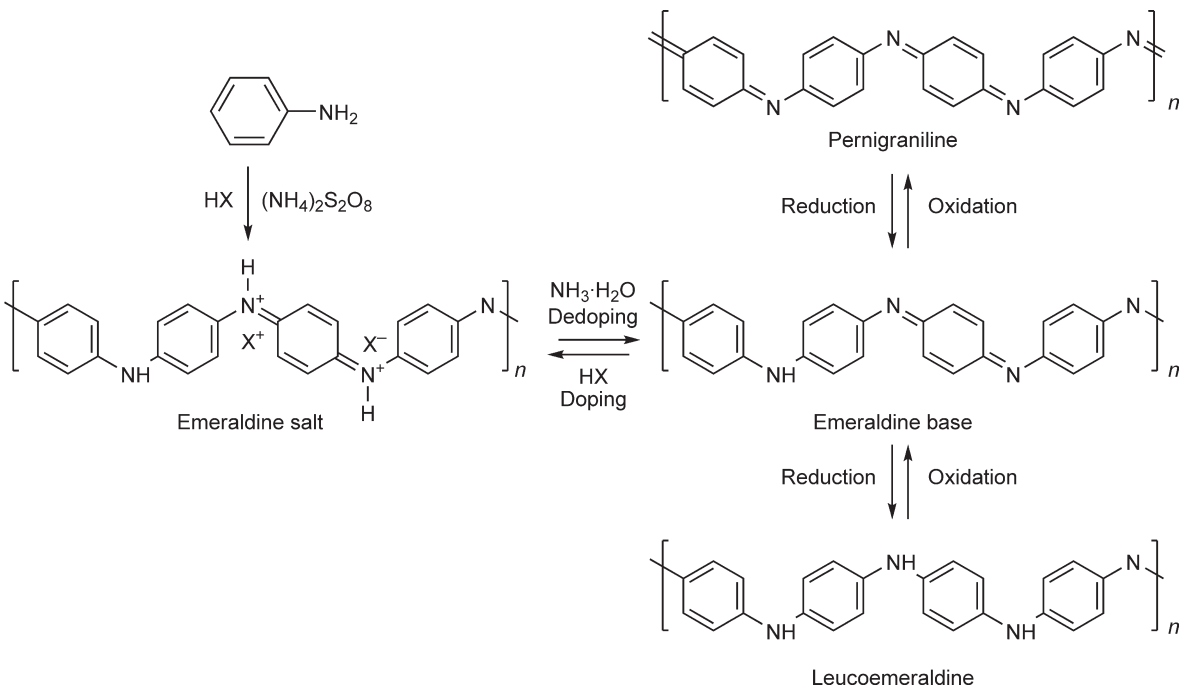

Figure 30 Reversible doping/dedoping and reduction/oxidation chemistry of PAN: Oxidative polymerization produces the emeraldine salt, dedoping of which yields the emeraldine base, followed by reduction and oxidation to afford the leucoemeraldine and the pernigraniline, respectively. Reproduced with permission from Huang, J.; Kaner, R. B. *Chem. Commun.* **2006**, 367. © 2006 The Royal Society of Chemistry.

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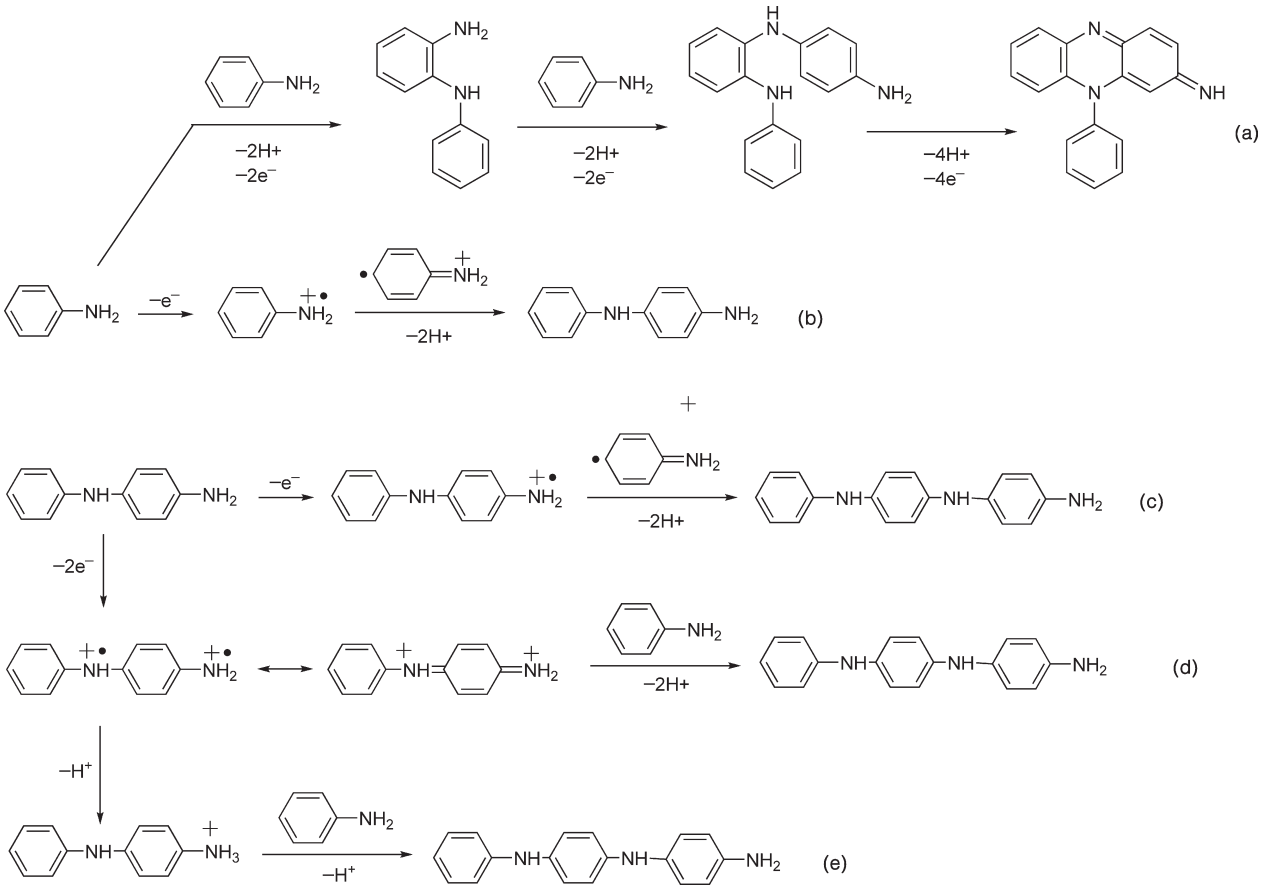

Figure 31 Reaction mechanisms proposed for oxidative polymerization of aniline.

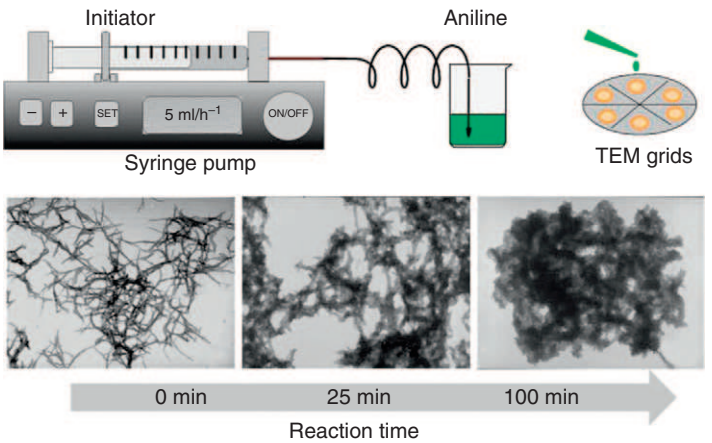

Figure 32 (Top) Schematic illustration of the experimental setup used to explore the morphological change of polyaniline during chemical polymerization. (Bottom) transmission electron microscopy (TEM) images showing the morphological evolution of polyaniline from nanofibers to agglomerates as the reaction proceeds. Reproduced with permission from Huang, J.; Kaner, R. B. *Chem. Commun.* **2006**, 367. © 2006 The Royal Society of Chemistry.

The average diameter of PAN nanofibers can be tuned by the choice of acid, from 30 nm with hydrochloric acid to 120 nm using perchloric acid.[131] Interestingly, nanofibers with diameters of 1–2 nm were observed with doping of D,L-camphorsulfonic acid.[132] The nanofiber diameter can also be controlled by the redox potentials of the oxidants.[133] Furthermore, aqueous colloids of PAN nanofiber were self-stabilized by controlling the pH.[134] Oxidative polymerization of aniline with potassium peroxydisulfate in 1 M HCl at 80 °C and crystal growth at 0 °C produced highly oriented PAN microfiber arrays without any templates or surfactants.[135]

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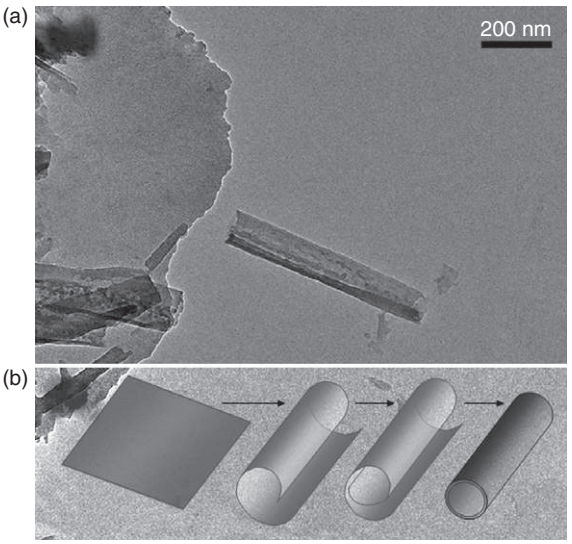

Figure 33 Transmission electron microscope image of (a) the rolled nanotubular polyaniline made of very thin nanosheets, and (b) the corresponding scheme. Reproduced with permission from Zujovic, Z. D.; Laslau, C.; Bowmaker, G. A.; *et al. Macromolecules* **2010**, *43*, 662. © 2010 American Chemical Society.

PAN nanotubes were synthesized by oxidative polymerization of aniline with ammonium persulfate at pH ~7.5 in the presence of an amino acid.[136] During this process, PAN nanosheets are formed in the initial stage, followed by curing or rolling of the nanosheets to generate nonconducting oligomeric nanotubes (Figure 33). These nanotubes then serve in the later stage as templates for the formation of conducting PAN nanotubes when the pH is decreased.[137] PAN nanotubes were also obtained by oxidation-reactive templating of MnO_2 nanowires, followed by removal of the template.[138] PAN microarchitectures, from plate-like to flower-like structures, were generated by the adjustment of the molar ratio of oxidant to monomer in oxidative polymerization in dilute aniline solution.[139]

5.07.4.1.3 Composite preparation

Many dopants and templates have been studied for the further functionalization of PAN composites. For example, the use of optically active camphorsulfonic acid as a dopant produced chiral PAN salts, which were soluble in organic solvents.[140] Poly(styrenesulfonic acid) (PSS) was used in the oxidative polymerization of aniline to yield water-soluble PAN/PSS.[141] In the oxidative polymerization of aniline catalyzed by HRP with hydrogen peroxide, conducting PAN could be obtained even at pH 4.3 in the presence of poly(sodium styrenesulfonate) as the template.[142] Surprisingly, HRP catalysis using poly (acrylic acid) as the template and camphorsulfonic acid as the dopant produced water-soluble and conducting PAN with a helical conformational specificity, which was not induced by the dopants but by the enzyme.[143]

PAN templated with diblock copolymers of acidic block and acrylate showed great flexibility, as well as high conductivity.[144] A thymine-based polymer with phenylsulfonate groups was immobilized on a substrate by photopatterning, which then functioned as a template for the construction of conducting PAN.[145] Furthermore, PAN nanowires were fabricated with a DNA template immobilized on a Si surface, as indicated in Figure 34, showing great promise for sensitive chemical sensor applications.[146]

In addition to fabrication, intercalation of PAN with V_2O_5,[147] $VOPO_4$,[148] MoO_3,[149] FeOCl,[150] and montmorillonite clay[151] has been reported, while the inclusion of PAN in zeolite molecular sieves[152] was also investigated. Furthermore, PAN filaments encapsulated in a mesoporous channel aluminosilicate MCM-41 host were prepared by oxidative polymerization with peroxydisulfate after adsorption of aniline vapor.[153]

5.07.4.2 Other Aniline Derivatives

Oxidative polymerization of some alkylanilines has been performed,[154] and alkyl-substituted PAN nanofibers were obtained.[155] For example, long-chain alkylated anilines were polymerized at an air–water interface by the Langmuir–Blodgett technique.[156] Interestingly, a fluorine-functionalized PAN prepared via a concurrent reduction and substitution method showed higher conductivity (0.1–3 S cm^{-1}) than PAN resulting from oxidative copolymerization of aniline and 2-fluoroaniline.[157] Oxidative polymerization of *o*-phenylenediamine produced nanobelts several hundred nanometers in width and several tens of nanometers in depth, as illustrated in Figure 35.[158] Condensed aromatic monomers with amino groups, such as 1-aminonaphthalene, 1-aminoanthracene,[159] and 8-aminoquinoline,[160] also afforded PAN-like polymers. In addition, an aminothiophene monomer, 2-amino-3-cyano-4-β-naphthylthiophene, also produced C–N coupling polymers.[161]

Self-doping PANs, such as with sulfonic acid substitution,[162] *N*-alkylsulfonic acid substitution,[163] and *N*-phenylsulfonic acid substitution,[164] have been synthesized. PANs with liquid crystalline substituents[165] and redox-active disulfide units[166] have also been prepared. It was reported that oxidative polymerization of 3-aminophenylboronic acid was 4500 times faster in the presence of DNA-functionalized single-wall carbon nanotube as template.[167] PANs having boronic

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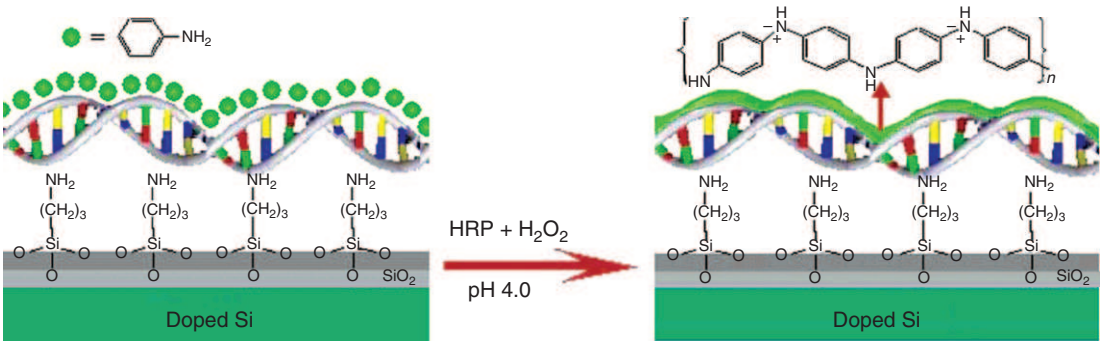

Figure 34 Fabrication of the polyaniline nanowire immobilized on Si surface with stretched double-stranded DNA as a guiding template. Reproduced with permission from Ma, Y.; Zhang, J.; Zhang, G.; He, H. *J. Am. Chem. Soc.* **2004**, *126*, 7097. © 2004 American Chemical Society.

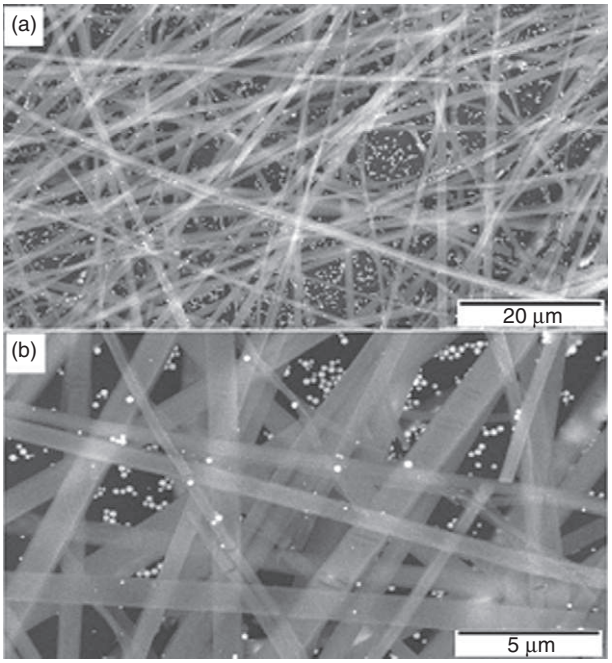

Figure 35 Scanning electron microscope image of poly(*o*-phenylenediamine) nanobelts: scale bars are (a) 20 μm and (b) 5 μm. Reproduced with permission from Sun, X.; Dong, S.; Wang, E. *Chem. Commun.* **2004**, 1182. © 2004 The Royal Society of Chemistry.

acid can be used for detecting sugar and dopamine[168,169] and for controlling self-doped states.[170]

Surface-initiated atom transfer radical polymerization of 4-vinylaniline and oxidative graft copolymerization of aniline produced conductive hollow nanospheres of PAN.[171] A monomer that incorporates both aniline and methacrylamide functional groups was shown to be capable of free radical and oxidative polymerization.[172] Moreover, conjoined conducting PANs carrying the sequence information of DNA were prepared by HRP-catalyzed oxidative polymerization of anilines covalently linked to the nucleobases of duplex DNA.[173]

5.07.5 Pyrroles

Oxidative polymerization of pyrrole to produce, polypyrrole (PPY), poly(2,5-pyrrolylene), as expressed in Figure 36, was performed using hydrogen peroxide in AcOH almost a century ago. The product of this experiment was called pyrrole black.[174] Many studies on oxidative polymerization of pyrrole have since been reported, especially in the past three decades, and have highlighted the high electrical conductivity of PPY (10^2–10^3 S cm^{-1})[175] (*see* Chapter 1.14).

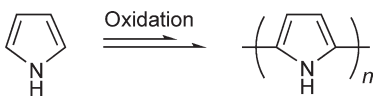

Figure 36 Oxidative polymerization of pyrrole.

5.07.5.1 Pyrrole

PPY is synthesized by chemical oxidative polymerization of pyrrole with a variety of oxidizing agents, such as hydrogen peroxide, nitrous acid, lead dioxide, ferric chloride, persulfates,

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and quinones,[176] as well as by an electrochemical method.[177] Additionally, chemical vapor deposition (CVD) produced PPY doped with iron chloride.[178] For oxidative polymerization of pyrrole under dioxygen, $CuCl/AlCl_3$,[179] $VO(acac)_2/AlCl_3$,[180] and [(salen)VOV(salen)] complex[181] were shown to be effective catalysts. Furthermore, HRP-catalyzed polymerization of pyrrole with hydrogen peroxide in the presence of sulfonated PSt has also been reported.[182]

5.07.5.1.1 Reaction mechanism

Two reaction mechanisms for the oxidative polymerization of pyrrole (Figure 37) are proposed: (a) one-electron oxidation of pyrrole to give its cation radical followed by the coupling of two cation radicals;[183] and (b) coupling of one molecule of cation radical with one molecule of pyrrole.[184] The dimerization step would be the rate-determining step because polymerization of pyrrole in the presence of 2,2′-bipyrrole resulted in a significant increase in the overall reaction rate.[185]

5.07.5.1.2 Nanostructure formation

PPY nanoparticles having average diameters of ~75 nm were obtained by dispersion polymerization with $FeCl_3$ in the presence of poly(vinyl alcohol-*co*-acetate).[186] In addition, core–shell nanomaterials composed of only PPY were fabricated by microemulsion polymerization using two oxidants of different redox potentials in order.[187] Furthermore, one-dimensional microstructures of PPY have been mechanically prepared. For example, microtubules of PPY were produced by polymerization across a micropore membrane,[188] and microcapsule arrays were afforded from polymerization on a micromembrane surface.[189]

Although PAN intrinsically tends to generate the nanofabric structures, it seems that structure-inducing methods or materials are generally needed for PPY to readily form such nanostructures. For example, PPY nanowires with a diameter of ~600 nm were prepared via electrical polymerization from poly(ethyl acrylate)-grafted carbon electrode.[190] Oxidative polymerization of pyrrole/HCl aqueous solution with $(NH_4)_2S_2O_8$, in which small amounts of V_2O_5 nanofibers were added as a seed, produced PPY nanofibers with 60–90 nm in thickness and a few micrometers in length.[191] Moreover, by $FeCl_3$-catalyzed polymerization in the presence of a stoichiometric amount of V_2O_5 nanofibers 10–15 nm in diameter, PPY nanotubes having pores filled with V_2O_5 were obtained.[192] After leaching out the V_2O_5 with 1 M HCl, the nanotubes had 4–8 nm pore diameter and 60–80 nm outer diameter, as shown in Figure 38. In addition, wire/ribbon-like PPY nanostructures were produced when lamellar inorganic/organic mesostructures of cetyltrimethylammonium persulfate were used as a template.[193] In polymerization with $FeCl_3$, adding a small amount of 2,2′-bipyrrole changed the PPY nanostructures from granular particles to nanofibrils.[194]

In addition to one-dimensional structures, two-dimensional structures of PPY have also been fabricated. Oxidative and intercalative polymerization of pyrrole was conducted within the nanoslits of a 0.98-nm-thick layered framework of redox-active coordination polymer. The resulting PPYs were isolated from the framework as stacked sheets, as shown in Figure 39.[195] Additionally, superhydrophobic PPY films showing a static water contact angle of 152° and having double roughness structures on both coarse and fine scales were obtained by $FeCl_3$ oxidation with tetramethylammonium perfluorooctane sulfonate.[196] Vapor-phase oxidative polymerization of pyrrole using colloidal templates with 235 nm diameter was able to fabricate inverse opal patterns of PPY after the templates were removed.[197]

5.07.5.1.3 Composite preparation

Core–shell particles of PSt/PPY with an average diameter of ~250 nm were prepared by one-step polymerization catalyzed by $FeCl_3$ with hydrogen peroxide.[198] Furthermore, oxidative polymerization of pyrrole with DNA as a template gave a higher order superstructure composed of DNA padding and a PPY outer layer.[199]

Copolymerization of aniline and pyrrole assisted by surfactants produced PAN/PPY nanofibers, with spectral characteristics different from those of homopolymers.[200] In addition, coaxial nanocables of PPY/TiO_2 (Figure 40) were obtained by vapor polymerization of pyrrole on the surface of $FeCl_3$-adsorbed TiO_2 nanofibers.[201] Oxidative polymerization of pyrrole encapsulated within the crystalline channels of zeolite Y and mordenite molecular sieves[202] and intercalated within the layer structures of FeOCl[203] was observed.

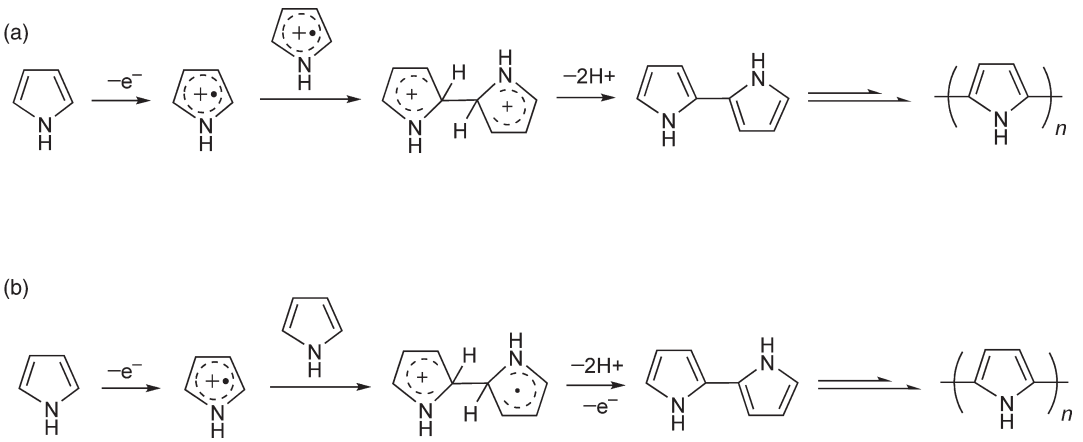

Figure 37 Reaction mechanisms proposed for oxidative polymerization of pyrrole.

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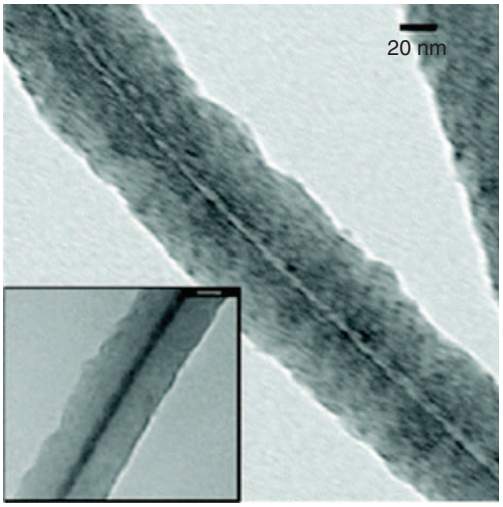

Figure 38 Transmission electron microscope images of narrow pore diameter polypyrrole nanotubes, and in the inset, pore filled with V_2O_5. Reproduced with permission from Zhang, X.; Manohar, S. K. *J. Am. Chem. Soc.* **2005**, *127*, 14156. © 2005 American Chemical Society.

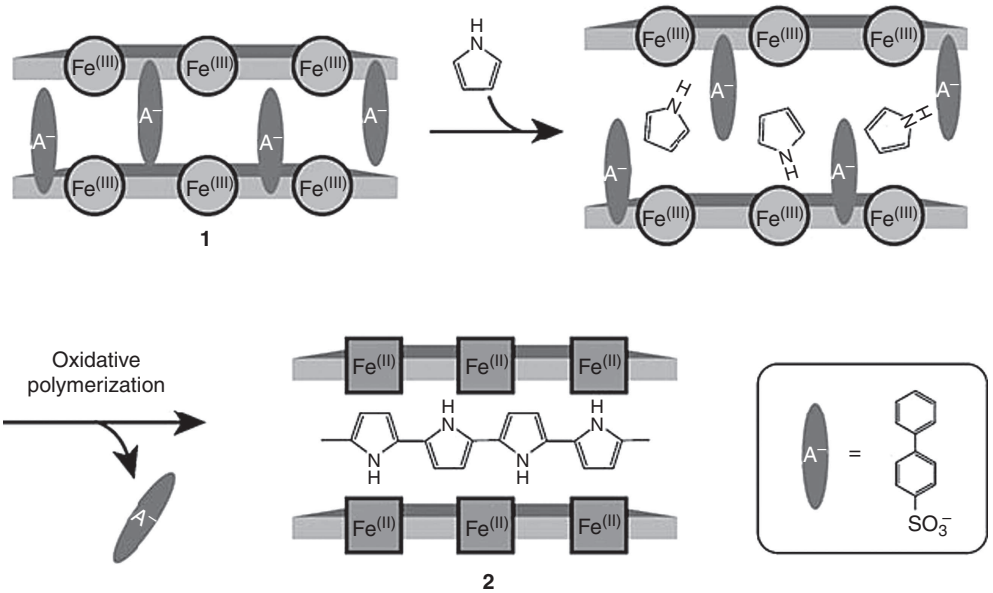

Figure 39 Schematic illustration of intercalation of pyrrole and oxidative polymerization of pyrrole by the Fe(III) ions in the host layers. Reproduced with permission from Yanai, N.; Uemura, T.; Ohba, M.; *et al. Angew. Chem. Int. Ed.* **2008**, *47*, 9883. © 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

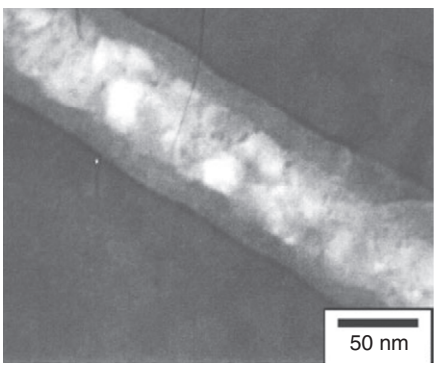

Figure 40 Transmission electron microscope image of polypyrrole/TiO_2 coaxial nanocable. Reproduced with permission from Lu, X.; Zhao, Q.; Liu, X.; *et al. Macromol. Rapid Commun.* **2006**, *27*, 430. © 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

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5.07.5.2 Other Pyrrole Derivatives

Many pyrrole monomers substituted at the N-position,[204] 3-position,[205] and 3,4-positions[206] have found application in oxidative polymerization. Because N-substitution is easy, various PPYs substituted especially at the N-position have been reported. For example, oxidative polymerization of a pyrrole derivative with systinyl groups bound to Fe_4S_4 clusters[207] and a Cu complex with phenanthroline derivatives having two pyrrole moieties[208] were demonstrated. In addition, a graft polymer, poly(sulfonated styrene)-*g*-PPY, resulting from *N*-(4-vinylbenzyl)pyrrole,[209] and a PPY substituted by benzophenone-containing group for photografting proteins[210] were synthesized. For self-assembled monolayers, *N*-(mercaptoalkyl)pyrrole on Au[211] and *N*-(3-aminopropyl) pyrrole on $YBa_2Cu_3O_{7-\delta}$[212] were both electrochemically polymerized. Furthermore, a pyrrole monomer with an ammonium-substituted alkyl group was used as a template for preparing hexagonal silica channels, followed by oxidative polymerization with $FeCl_3$, to produce PPY nanofibers insulated within one-dimensional silicate channels.[213]

Other types of PPY have been synthesized, such as a canopied PPY from a pyrrole with sterically hindered polycyclic substituents at the 3,4-positions,[214] a PPY-convertible polymer from 2,5-bis(2-pyrrolyl)pyrrolidine,[215] and a low band gap polymer from N-substituted dithieno[3,2-*b*:2′,3′-*d*]pyrrole.[216]

5.07.6 Thiophenes

Although addition-type polymerization of thiophene has been performed with phosphoric acid, montmorillonite, and silica-alumina,[217] oxidative polymerization of thiophene to produce polythiophene (PTH), poly(2,5-thiophenylene), as shown in Figure 41, was realized by an electrochemical method almost three decades ago.[218] For PTH, 3-substituted and 3,4-disubstituted PTH have been especially well studied because of their balance between conductivity and processability[219,220] (*see* Chapter 1.14).

5.07.6.1 Thiophene

Thiophene is oxidatively polymerized by electrochemical methods; by equivalent oxidation methods with AsF_5,[221] NO salts,[222] and $FeCl_3$;[223] and by catalytic oxidation methods using $VO(acac)_2$ and $FeCl_3$ with dioxygen.[224] In these polymerizations, two reaction mechanisms for thiophene were proposed, similar to pyrrole, indicating either (a) coupling of two cation radicals[225] or (b) coupling of one cation radical with one neutral molecule.[226]

5.07.6.2 2-Substituted Thiophenes

Oxidative polymerization of a monomer containing a functional unit substituted by two (or more) 2-thienyl groups can produce an alternating copolymer composed of functional units and 2,5-thienylene units. Various monomers containing units such as (a) π-stack,[227] (b) pore-generating,[228] (c) fullerene-backbone,[229] (d) tetrathiafulvalene-bound,[230] (e) Ni/bis(dithiolate) complex,[231] (f) *N*-heterocyclic carbene–Au complex,[232] (g) redox-switchable Ru complex,[233] and (h) Pd–C bonding[234] are shown in Figure 42.

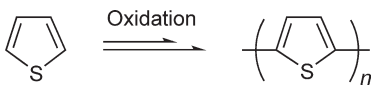

Figure 41 Oxidative polymerization of thiophene.

5.07.6.3 3-Substituted Thiophenes

3-Substituted PTHs, in which the substituents increase the solubility of the resulting polymers, possess three bonding patterns of head-to-tail, head-to-head, and tail-to-tail (Figure 43). High regioselectivity, with 91–98% head-to-tail (HT), was achieved by Kumada–Tamao-type[235] and Negishi-type[236] organometallic cross-couplings, greatly affecting the conjugation length and the electronic properties. HT-regioregular poly(3-hexylthiophene), which is widely used for thin-film transistors and photovoltaics, showed mobility as high as 0.2 $cm^2\ V^{-1}\ s^{-1}$, while regioirregular ones had mobility values of $\sim 10^5\ cm^2\ V^{-1}\ s^{-1}$.[237]

Some 3-alkylthiophenes are readily oxidatively polymerized,[238] but the regioregularity is difficult to control. However, in oxidative polymerization of 3-alkylthiophene with $FeCl_3$, the low reaction temperature and the dilute monomer concentration improved the HT regularity up to 89%.[239] For 3-(4-alkylphenyl)thiophenes,[240,241] 3-(4-acetoxy-3,5-dialkylphenyl)thiophenes,[242] and 3-alkoxy-4-methylthiophenes,[243] 94–96% selectivity for HT content has been achieved. This regioselectivity can be explained by computational studies on the spin density of the radical cations.[244,245]

Electrochemical polymerization of 3-methylthiophene using a capillary flow cell yielded single fibers with uniform diameters of 0.1–0.7 mm and lengths greater than 10 cm.[246] Additionally, electrically independent connections between pairs of wires in an array were fabricated in the polymerization of 3-methylthiophene.[247] Adsorption of 3-methylthiophene into the channel of transition metal-containing zeolites Y resulted in oxidative polymerization to encapsulated PTH derivatives.[248]

A variety of thiophenes substituted by functional groups at the 3-position have also been polymerized, leading to multifunctionalized PTHs. For example, an initiator-bonding monomer, 3-[1-ethyl-2-(2-bromoisobutylate)]thiophene, was polymerized with $FeCl_3$, followed by graft polymerization of *N*-isopropylacrylamide to produce a highly water-soluble and thermally responsive PTH graft polymer.[249] Diblock polymers consisting of hydrophobic rod units and hydrophilic coil units with thiophene moieties formed vesicles in both organic solvents and water, followed by oxidative polymerization.[250] In addition, 12-armed terthiophene-terminated starburst poly(*n*-butyl acrylate) was polymerized with $FeCl_3$ to produce core–shell nanostructures.[251] After the fabrication of thiophenes substituted with an alkyl group containing a trimethylammonium salt in a mesoporous silica matrix, the polymerization of the thiophene moiety by $FeCl_3$ and the removal of silica with HF resulted in the formation of PTH-based nanowires with diameters of 3 nm.[252] Furthermore, PTH nanoline widths of 45 nm, described in Figure 44, were obtained using scanning probe lithography on a polymer containing terthiophene pendant units at high speed.[253]

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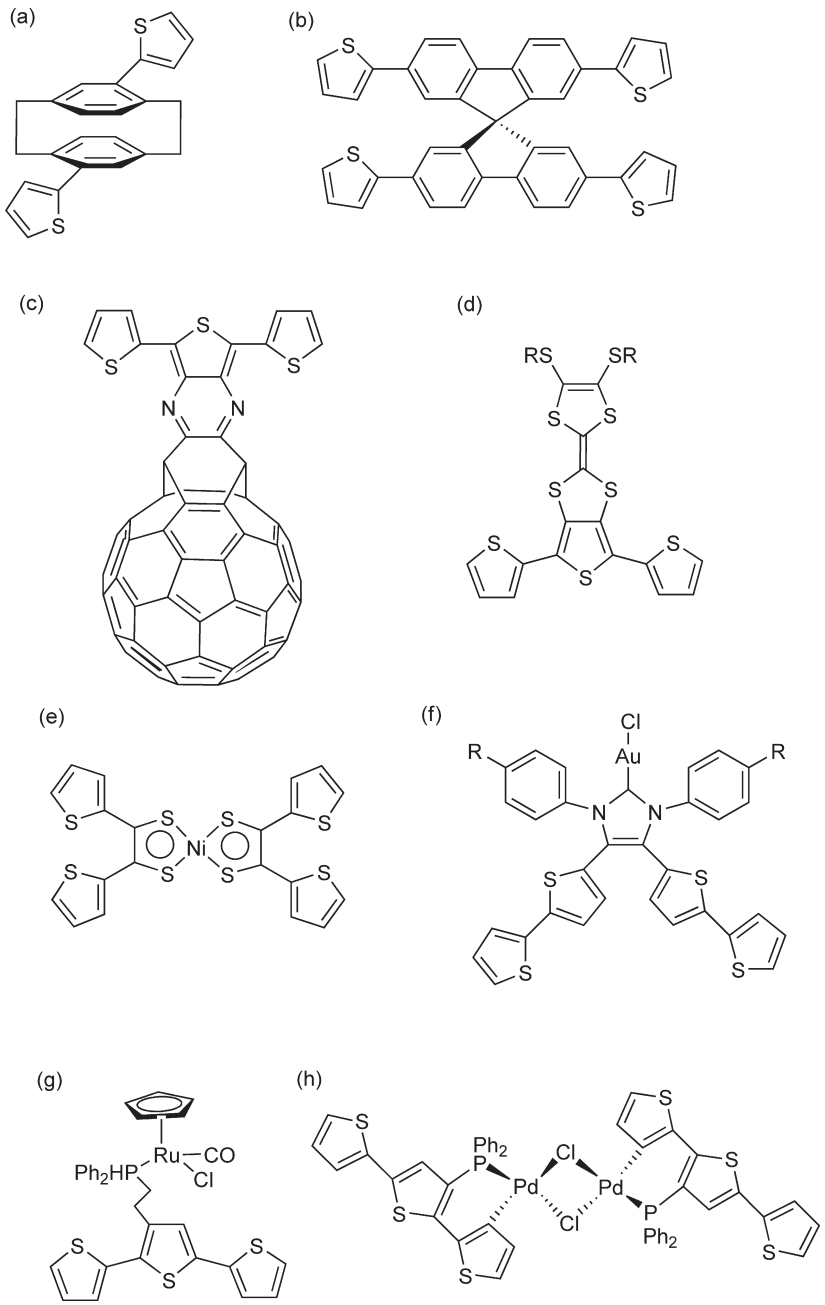

Figure 42 Various monomers containing 2-thienyl groups as bonding sites.

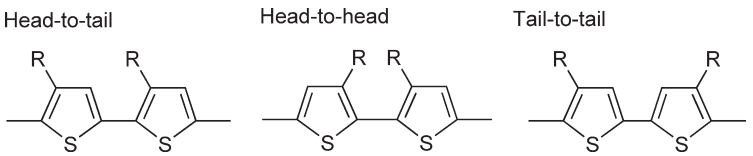

Figure 43 Regioisomers for coupling of 3-substituted thiophenes.

5.07.6.4 3,4-Ethylenedioxythiophenes

Poly(3,4-ethylenedioxythiophene) (PEDOT) was synthesized by oxidative polymerization of 3,4-ethylenedioxythiophene (EDOT) and initially showed insolubility but very high conductivity (~300 S cm^{-1}).[254] Using PSS as a dopant in aqueous solution, PEDOT/PSS (Figure 45) was developed[255] and is now one of the most successful conductive polymers because of its high water solubility, high conductivity (~10 S cm^{-1}), high

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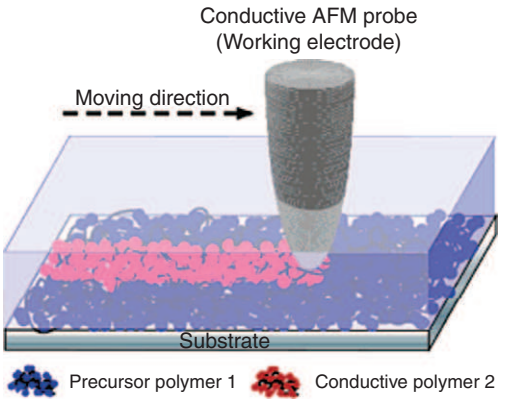

Figure 44 Electrochemical oxidative nanolithography process. AFM, atomic force microscopy. Reproduced with permission from Jang, S.-Y.; Marquez, M.; Sotzing, G. A. *J. Am. Chem. Soc.* **2004**, *126*, 9476. © 2004 American Chemical Society.

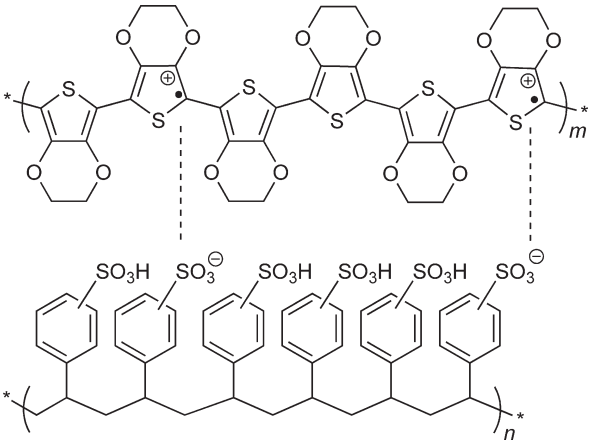

Figure 45 PEDOT/PSS.

transparency to visible light, and excellent stability. Surprisingly, PEDOT/PSS film can be heated to 100 °C for over 1000 h with only a minimal change in conductivity.[256]

Oxidative polymerization of EDOT in aqueous PSS solution with $Na_2S_2O_8$ was generally performed to produce a dark-blue aqueous PEDOT/PSS dispersion, and electrochemical polymerization was then useful in producing highly transmissive, sky-blue doped PEDOT film.[257] PEDOT/PSS can be obtained by enzyme-catalyzed oxidative polymerization of EDOT with H_2O_2 using terthiophene as the radical mediator.[258] Vapor-phase polymerization of EDOT on ferric tosylate was also reported.[259]

Different nanostructures and composites of PEDOT have been reported. Nanostructured PEDOTs, such as tubes, rods, thimbles, and belts, were prepared by oxidative polymerization of EDOT using an Al_2O_3 membrane with 250 nm pore size as the template.[260] A helical superstructure of a PEDOT composite was synthesized using a helix-forming lipid with a sulfonate group as template.[261] Furthermore, a PEDOT/mesoporous silica colloidal crystal with monodispersity was obtained via an inclusive and oxidative polymerization method, as expressed in Figure 46.[262] Fullerene-encapsulated anionic calixarenes were readily deposited by electrochemical polymerization of EDOT.[263] Moreover, PAN nanofibers were prepared in toluenesulfonic acid solution with ammonium persulfate, and PEDOT was subsequently coated onto the PAN nanofibers by oxidative polymerization.[264]

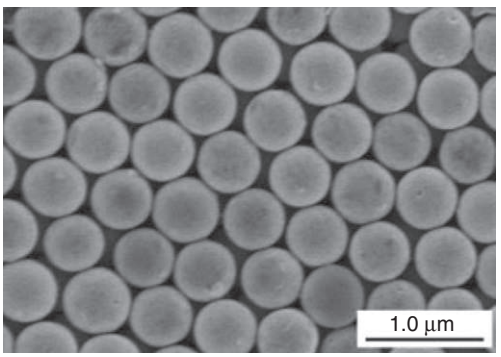

Figure 46 Field emission scanning electron microscope image of PEDOT/mesoporous silica colloidal crystal deposited as an opaline film. Reproduced with permission from Kelly, T. L.; Yamada, Y.; Che, S. P. Y.; *et al. Adv. Mater.* **2008**, *20*, 2616. © 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

EDOT is easier to oxidize than thiophene, so it is utilized as a binding unit much more frequently. As shown in Figure 47, various monomers sandwiching such a functional unit between two EDOT units have been synthesized, including (a) a low band gap-inducing unit,[265] (b) a green polymer-producing unit,[266] (c) a calixarene-capping tungsten complex unit,[267] (d) a metal–salen complex unit,[268] (e) a photoluminescent europium complex unit,[269] (f) a

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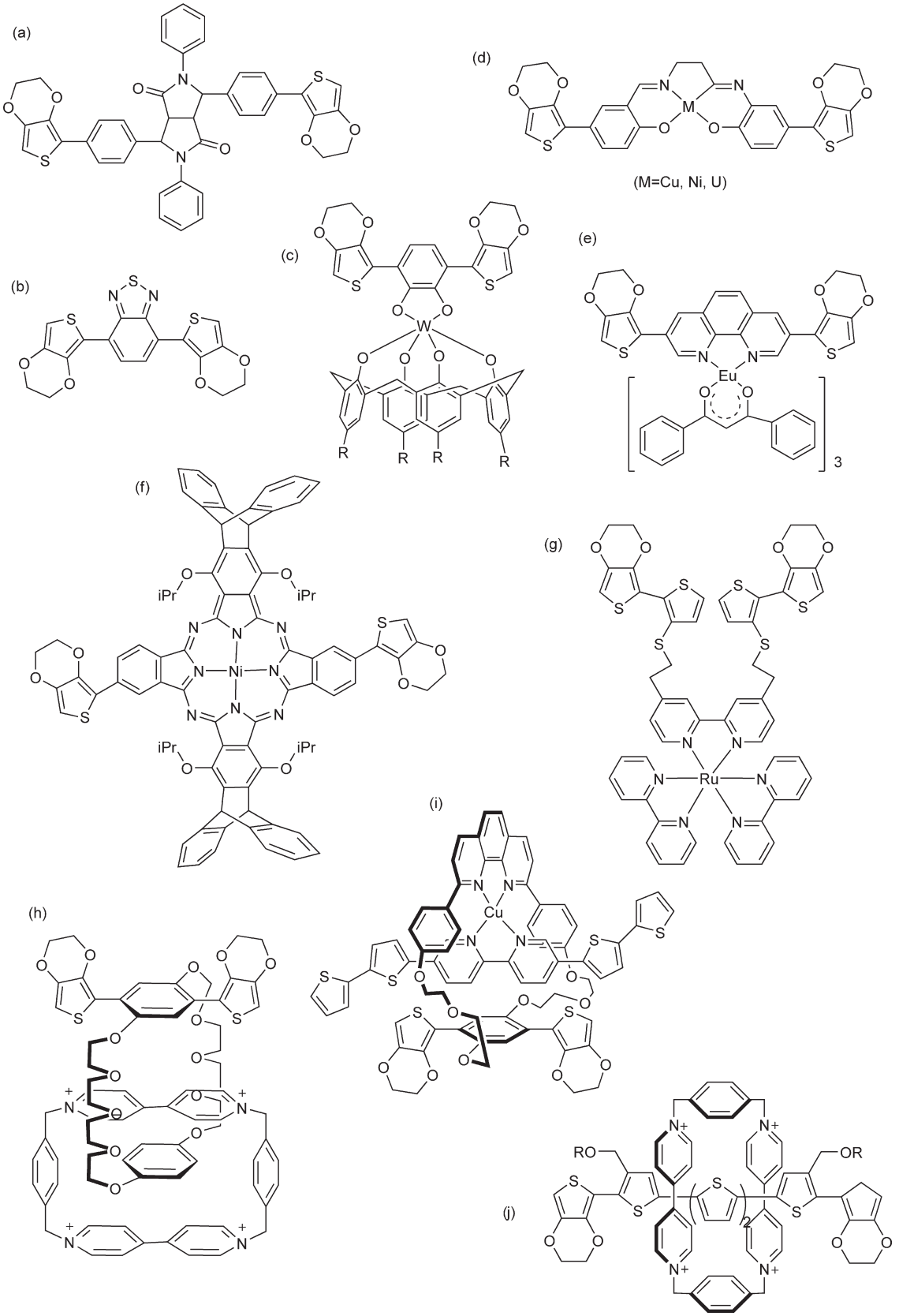

Figure 47 Various bis(3,4-ethylenedioxythien-2-yl) derivatives for oxidative polymerization monomers.

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metallophthalocyanine unit,[270] and (g) a tris(2,2′-bipyridine) ruthenium complex unit.[271] Interlocked molecules are also obtained from EDOT-containing monomers, including (h) a monomer for poly([2]-catenane),[272] (i) a monomer for two-step electropolymerization to produce ladder metallorotaxane,[273] and (j) a monomer for polyrotaxane.[274]

Some substituted EDOTs have been oxidatively polymerized. For example, a vapor-polymerizable and photo-cross-linkable EDOT having a methacryl group led to flexible, conductive PEDOT patterns.[275] PEDOTs with azide groups were also prepared, and via click chemistry, diverse functional groups can then be introduced.[276] This click chemistry is catalyzed by Cu(I), not by Cu(II), so electrochemical Cu(I)/Cu(II) switching resulted in spatially selective functionalization.[277]

5.07.6.5 Other Thiophene Derivatives

Oxidative polymerization of 3,4-propylenedioxythiophene derivatives has been perfomed,[278] including water-soluble sulfonated units[279] and functional unit-sandwiching units.[280] In addition, colorimetric or fluorometric chemosensor PTHs were obtained from 3-alkoxy-4-methylthiophenes with *N*-hydroxysuccinimide ester as a precursor of detecting groups[281] or with a cationic group for detecting iodide ion.[282]

Fused ring systems, such as thienothiophenes, thienopyrroles, isothianaphthalenes, dithienothiophenes, and dithienobenzenes, were successfully applied to oxidative polymerization.[238] Regioselectivity in polymers resulting from 3-alkyl-thieno[3,2-*b*] thiophenes was studied,[283] and step-growth polymerization of 3,5-diphenyldithieno[3,2-*b*:2,3-*d*]thiophene by photoinduced electron transfer[284] was reported.

5.07.7 Other Aromatic Heterocycles

In addition to thiophene, oxidative polymerization of furan[285] and selenophene[286] is also possible. Poly(3,4-ethylenedioxyselenophene) was obtained by oxidative polymerization; it possessed high conductivity and stability and showed a lower band gap (1.4 eV) than PEDOT (1.6 eV).[287] Poly(3,4-ethylenedithioselenophene) was also synthesized.[288]

5.07.8 Aromatic Hydrocarbons

Oxidative polymerization of benzene with $CuCl_2$–$AlCl_3$ to produce polyphenylene was reported in the 1960s.[289] Oxidants such as $AlCl_3$–MnO_2, $FeCl_3$, and $MoCl_5$ can be used, and various aromatic hydrocarbons, such as toluene, chlorobenzene, diphenyl, naphthalene, and phenanthrene,[290] can be used for oxidative polymerization (*see* Chapter 5.22).

Three reaction mechanisms for oxidative polymerization of benzene monomers have been proposed (Figure 48). The first step of each mechanism is one-electron oxidation of benzene to give its cation radical, but then the following steps are different: (a) coupling of two cation radicals;[291] (b) coupling of one cation radical with one neutral molecule[289] ((a) and (b) are similar as for pyrrole and thiophene); and (c) coupling of one cation radical with some neutral molecules, called a stair-step mechanism.[292]

Utilizing the Scholl reaction, bis(1-naphthoxy) monomers were oxidatively polymerized with coupling at the 4-position, as shown in Figure 49(a).[293] Thereby, poly (binaphthyl ether)s containing a 2,2′-binaphthyl unit[294] and a 2,2′-bis(trifluoromethyl)biphenyl unit[295] with low dielectric constants were obtained. The polymerization of 1,4-dialkoxybenzenes was performed by using $FeCl_3$[296] and by oxovanadium catalyst with dioxygen[297] to produce poly (2,5-dialkoxy-1,4-phenylene)s (Figure 49(b)). Poly(4,6-di-*n*-butyl-1,4-phenylene) was similarly produced.[298] In addition, the PEDOT analog, poly(3,4-methylenedioxy-1,2-phenylene), was synthesized as shown in Figure 49(c).[299] Oxidative polymerization of 9,9′-dialkylfluorene with $FeCl_3$ produced soluble polyfluorene,[300] which is used as a light-emitting polymer.

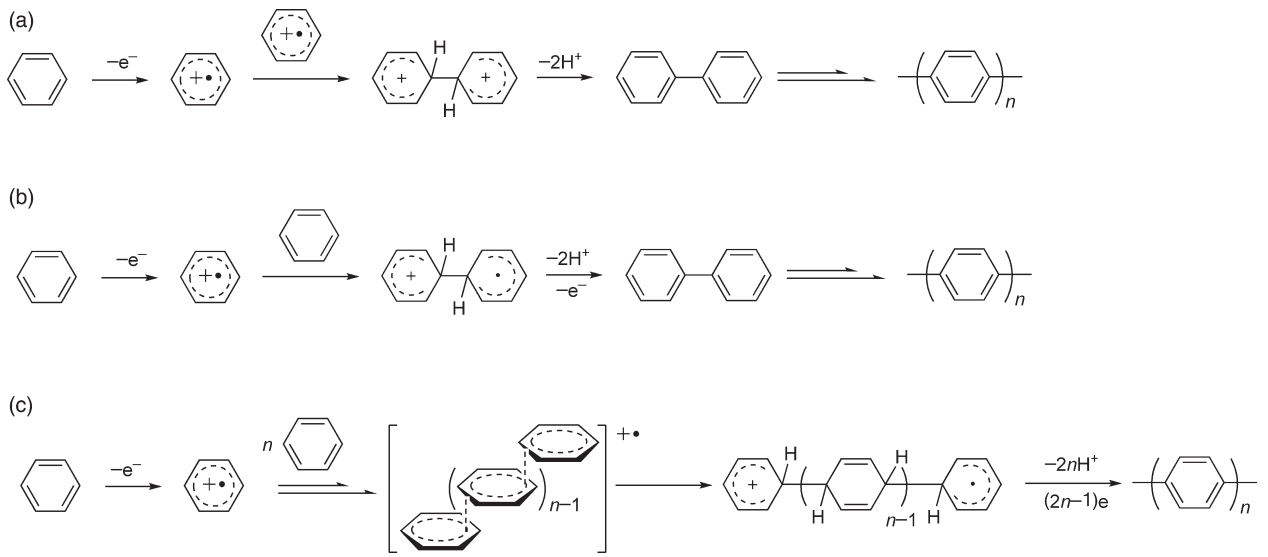

Figure 48 Reaction mechanisms proposed for oxidative coupling of benzene.

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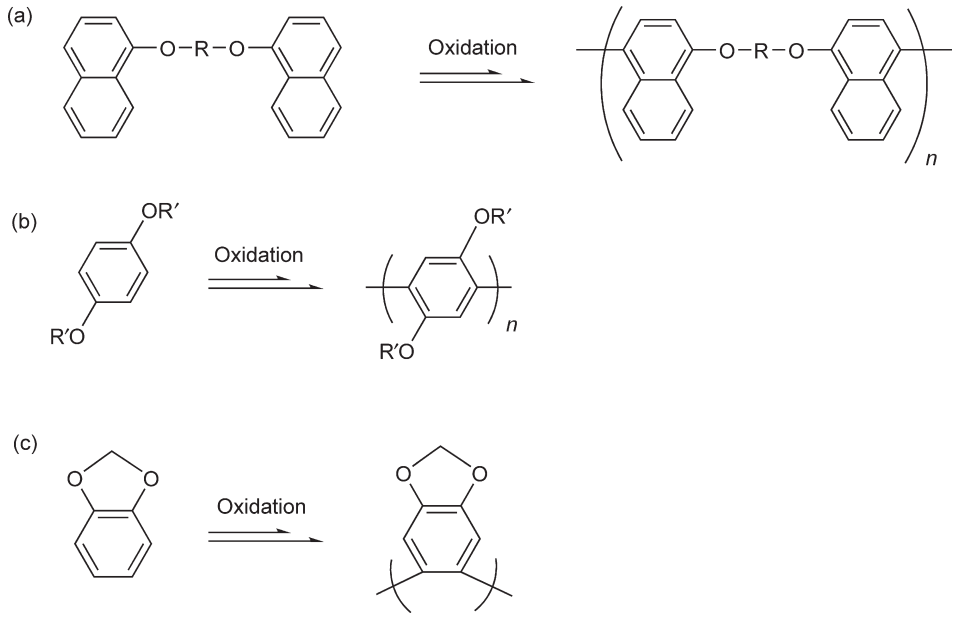

Figure 49 Oxidative polymerization of naphthalene and benzene derivatives.

5.07.9 Other Monomers

Oxidative coupling of an ethynyl group to readily give a butadiynylene group has also been applied to oxidative polymerization. For example, the polymerization of *m*-diethynylbenzene by a copper catalyst with dioxygen yielded poly(phenylene butadiynylene).[301] Using Cu-incorporated mesoporous materials as the oxidative polymerization catalyst for 1,4-diethynylbenzene, highly conjugated poly(1,4-phenylene-1,4-butadiynylene) was successfully obtained.[302] Additionally, stepwise synthesis by oxidative coupling of 1,4-diethynyl-2,5-di-*n*-hexylbenzene using the 3-cyanopropyldimethyl group as the protecting group produced a defined oligo(1,4-phenylene-1,4-butadiynylene) rod.[303]

Activated methyne groups in bifunctional *p*-tolylcyanoacetic esters[304] and monofunctional phenylcyanoacetic esters[305] can lead to oxidative polymerization; hydrogens of the activated methynes are abstracted by the copper catalyst with dioxygen to give radicals that undergo coupling. Oxidative coupling of phenyl acetonitrile using an alkoxide base and iodine was reported in the nineteenth century, and further application of this technology in anionic oxidative polymerization of a 1,4-bis(cyanomethyl)benzene derivative was found to yield poly(1,4-phenylene-dicyanovinylene).[306]

A silylmolybdenum complex catalyst was prepared for dehydropolymerization of arylsilanes leading to the production of polysilanes with high molecular weights.[307] In addition, hexagonal mesoporous germanium was obtained via oxidative polymerization of deltahedral $(Ge_9)^{4-}$ clusters.[308]

5.07.10 Conclusion

Oxidative (coupling) polymerization of various aromatic monomers, such as phenols, naphthol derivatives, diphenyl disulfides, anilines, pyrroles, thiophenes, benzenes, and other monomers, has been developed for the synthesis of a variety of aromatic polymers including PPOS, polyphenols, PPSs, PANs, PPYs, PTHs, polyphenylenes, and other polymers.

Oxidative polymerization of 2,6-Me_2P by a copper/amine catalyst was a pioneering work in this field in the 1950s, but the selectivity for C–O/C–C coupling in this reaction has not been completely defined. However, the resulting P-2,6-Me_2P has become one of the five major engineering plastics. Enzyme catalysts made the polymerization of diverse phenolic monomers possible and allowed control over the solubility and chemoselectivity of the resulting polyphenols. Furthermore, the regioselective polymerization of 2- and/or 6-unsubstituted phenols was a challenging problem, which was solved by enzyme model catalysts through their ability to generate only controlled radicals to produce linear PPOs. Moreover, asymmetric oxidative polymerization of 2-naphthol derivatives was achieved with optically active catalysts.

Thiophenol is oxidized to give diphenyl disulfide, which can be polymerized via further oxidation to produce PPS, referred to as a super engineering plastic. A vanadyl catalyst with dioxygen was used in this reaction and then found use in other polymerizations as well.

Although aniline black has been known for over a century, PAN has been one of the most studied conductive polymers since the 1980s because of its electronic conductivity ($\sim$10 S cm^{-1}), environmental stability, and ease of synthesis. In the oxidative polymerization of aniline, reaction at a pH below 2 leads to electronic conductivity greater than 1 S cm^{-1}, but the reaction mechanism for the observed C–N coupling has remained unclear. Interestingly, PAN nanofibers intrinsically form in water without any surfactants or templates.

PPY, resulting from the oxidative polymerization of pyrrole, is attractive in terms of its high electronic conductivity (100–1000 S cm^{-1}). For PPY, however, structure-inducing

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agents or systems are needed for synthesizing nanostructures such as nanoparticles, nanowires, nanotubes, nanosheets, and lotus leaf-like materials.

The introduction of substituents to PTHs provides some practically useful polymers with a balance between conductivity and processability. HT-poly(3-alkylthiophene)s synthesized by organometallic cross-coupling polymerization possess high mobilities of ~0.1 $cm^2 V^{-1} s^{-1}$, and HT regioregularity has also increased in oxidative polymerization. PEDOT/PSS is produced via oxidative polymerization and shows a high conductivity of ~10 S cm^{-1}, water solubility, high transparency, and excellent stability. Various copolymers, nanostructures, and composites of PTHs have been reported in the literature. Other aromatic heterocycles such as furan and selenophene, aromatic hydrocarbons including benzenes and naphthalenes, and other monomers, such as diethynyl compounds, have also been successfully employed in oxidative polymerization.

The advantage of oxidative polymerization is that the reaction temperatures are moderate, halogenated monomers are not necessary, and the use of catalysts with oxygen or hydrogen peroxide, if possible, produces only water as the by-product. Therefore, catalytic oxidative polymerization in particular can provide an environmentally benign and low-loading method for producing highly sophisticated aromatic polymers, and then control of radical reaction intermediates by the catalysts will be necessary.

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5.08 Condensation Polymers via Metal-Catalyzed Coupling Reactions

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5.08.1 Introduction

Over the past few decades, the discovery and evolution of metal-catalyzed coupling reactions has revolutionized the field of synthetic chemistry, enabling the development of processes that have greatly simplified or made possible new and useful chemical transformations. These transformations have been especially relevant to synthetic polymer chemistry,[1] providing milder and more efficient pathways to known polymeric materials and creating routes to new classes of polymers that show improved or, in many cases, novel physical and/or electronic properties. Herein, we introduce metal-catalyzed coupling reactions that are commonly used to access a wide range of polymeric materials, particularly conjugated polymers (representative examples are shown in **Figure 1**), and describe the significance of many of these polymers within a broader context.

The metal-catalyzed processes that will be discussed can be divided into three major categories: (1) palladium- and nickel-catalyzed coupling reactions that enable coupling between sp^2-hybridized organic halides with nucleophilic species to form C–C bonds; (2) palladium-catalyzed processes that form C–N bonds; and (3) ruthenium-, tungsten-, and molybdenum-catalyzed metathesis reactions that form C–C double and triple bonds. In cases where different metal-catalyzed polycondensation methods have been employed to access the same polymer, a comparison between the different methods will be offered. In addition, the general scope of each reaction discussed and selected examples of the breakthroughs in gaining access to new polymeric materials will be presented.

5.08.2 An Overview of Conjugated Polymers

Interest in conjugated polymers largely began with the discovery of polyacetylene (**1**) in 1958.[2] Upon doping with iodine, this material was subsequently found to exhibit electrical conductivity on apar with some metals, an important discovery that served as the basis of the 2000 Nobel Prize in chemistry.[3] The instability and insolubility of this material however rendered it unsuitable for use in many applications[4] and considerable research efforts over the past several decades have been directed toward the synthesis of other conjugated polymers that have the desirable electrical properties of polyacetylene but are also stable and soluble. Representative examples of the other major classes of π-conjugated polymers are poly(arylene)s, poly(arylenevinylene)s, and poly(aryleneethynylene)s. The poly(arylene) class, represented by poly(*p*-phenylene) (PPP) (**2**), consists of rigid-rod-type polymeric structures that often function as semiconductors upon doping.[5] An important subdivision of this class of polymers includes polythiophenes (**3**), which are being extensively developed for use in bulk heterojunction solar cells,[6] polymer light-emitting diodes (PLEDs),[6] hole-transporting layers

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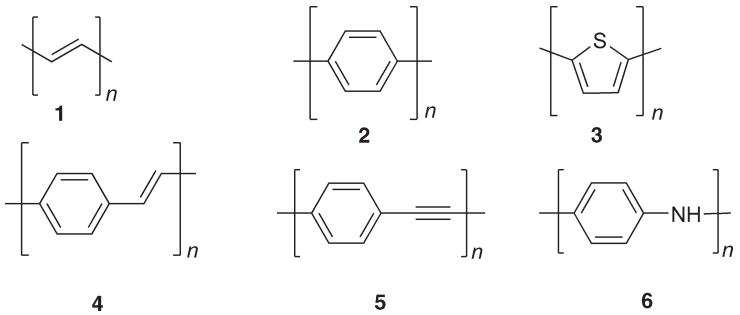

Figure 1 Representative polymers that have been prepared through metal-mediated reactions: **1**, polyacetylene; **2**, poly(*p*-phenylene); **3**, polythiophene; **4**, poly(*p*-phenylenevinylene); **5**, poly(*p*-phenyleneethynylene); and **6**, polyaniline.

for electroluminescent devices,[7] and thin-layer transistors.[6,8] Poly (arylenevinylene)s, represented by poly(*p*-phenylenevinylene) (PPV) (**4**), also have useful characteristics, such as high charge mobilities,[9] nonlinear optical properties,[10] and electroluminescence.[11] Poly(*p*-aryleneethynylene)s (PAEs) such as poly(*p*-phenyleneethynylene) (PPE) (**5**) are similar to PPVs and have been extensively developed for use in PLEDs,[12] field effect transistors, and sensors for a variety of analyses.[13] In contrast to the previously mentioned polymers, which are generally prepared through C–C forming reactions, polyanilines (**6**) are typically synthesized through the catalytic formation of C–N bonds. These polymers have found use as hole-conducting layers in organic light-emitting diodes (OLEDs), among other applications.[14]

As illustrated in the retrosynthetic analysis shown in Figure 2, the primary difficulty in preparing conjugated polymers lies in the formation of sp^2–sp^2 or sp–sp C–C bonds. In contrast, methods for the preparation of polymers formed via the formation of sp^3–sp^3 carbon–carbon bonds (polyesters, polyamides, etc.) are well established. Indeed, a facile method that provided access to well-defined, π-conjugated polymers was unknown until the development of metal-catalyzed coupling reactions. In general, such metal-catalyzed cross-coupling reactions effectively condense a molecule of HX to form a sigma bond between sp^2-hybridized carbons and other sp^2- or sp-hybridized carbons. An alternative route to these methods has been provided by metathesis reactions which form C–C double bonds and triple bonds.

Considering the growing interest in applications where the electronic and optical properties inherent to conjugated polymers are desired, there is a need to develop new synthetic routes to access to such materials. However, many conjugated polymers exhibit rigid-rod-like structures, including poly(phenylene), poly(phenylenevinylene), polythiophene, and poly (phenyleneethynylene), and therefore are often insoluble and difficult to process. It was subsequently shown that the solubility issues could be overcome through the incorporation of solubilizing alkyl or alkyloxy groups into the monomer, which often enables access to polymers with relatively high molecular weight. However, the introduction of such side groups can disrupt planarity along the polymer backbone, as bulky groups increase the torsion angle between aromatic rings along the main chain to relieve the resulting steric congestion.[15] Some planarity is critical for orbital overlap and for enabling electronic communication.[16] Therefore, as will be discussed in more detail below, care must be taken in choosing side groups that solubilize the polymer without diminishing conjugation.

5.08.3 Metal-Catalyzed Carbon–Carbon Bond Forming Reactions

5.08.3.1 Kumada and Negishi Coupling Reactions

As depicted in Figure 3, the Kumada coupling reaction[17] is typically performed by first forming a Grignard reagent from an aryl halide and then adding a Ni(II) catalyst to couple this activated species to another aryl halide. The reaction is usually conducted in refluxing tetrahydrofuran (THF). Mechanistically, the Kumada coupling reaction proceeds through the following series of steps:[18] (1) a nickel(II) species is reduced by an organomagnesium (Grignard) or organozinc reagent to give a nickel(0) species, which is usually the active catalyst. (2) The nickel(0) then oxidatively inserts into an aryl halogen bond. The aryl substituent of the (3) Grignard reagent is transmetallated to Ni catalyst to give a diaryl nickel species, which (4) undergoes reductive elimination to form an aryl–aryl bond and regenerate the active catalyst. Interestingly, it was this Ni-mediated C–C coupling chemistry that introduced the idea of 'reductive elimination', which has become an important concept in organometallic chemistry and was found to be intrinsic to many metal-mediated reactions.[19]

The Kumada coupling reaction was the first cross-coupling reaction to be applied to the synthesis of conjugated polymers and has been widely applied to the preparation of many poly (arylene)s and other conjugated polymers.[20] Limitations of the Kumada coupling stem from the functional group intolerance intrinsic to the highly nucleophilic and proton-intolerant Grignard reagents. Another major drawback of using the Kumada coupling reaction to generate polymer is the low molecular weight of the polymer that is often obtained by this route. Typically, polymers with more than 15 repeat units (for poly (phenylene)) cannot be prepared by this method due to a variety of termination pathways that are challenging to avoid.[21]

Organozinc reagents and palladium catalysts have also been utilized to carry out this transformation.[22] When the organometallic coupling partner is an organozinc reagent, the reaction is called the Negishi coupling.[23] Mechanistically, the reaction proceeds in a similar manner as the Kumada coupling, with the key difference being that the organometallic reagent is an organozinc species rather than a Grignard reagent. Organozinc reagents have a few advantages over Grignard reagents;[24] in particular, they tolerate a larger range of functional groups such as carbonyl and

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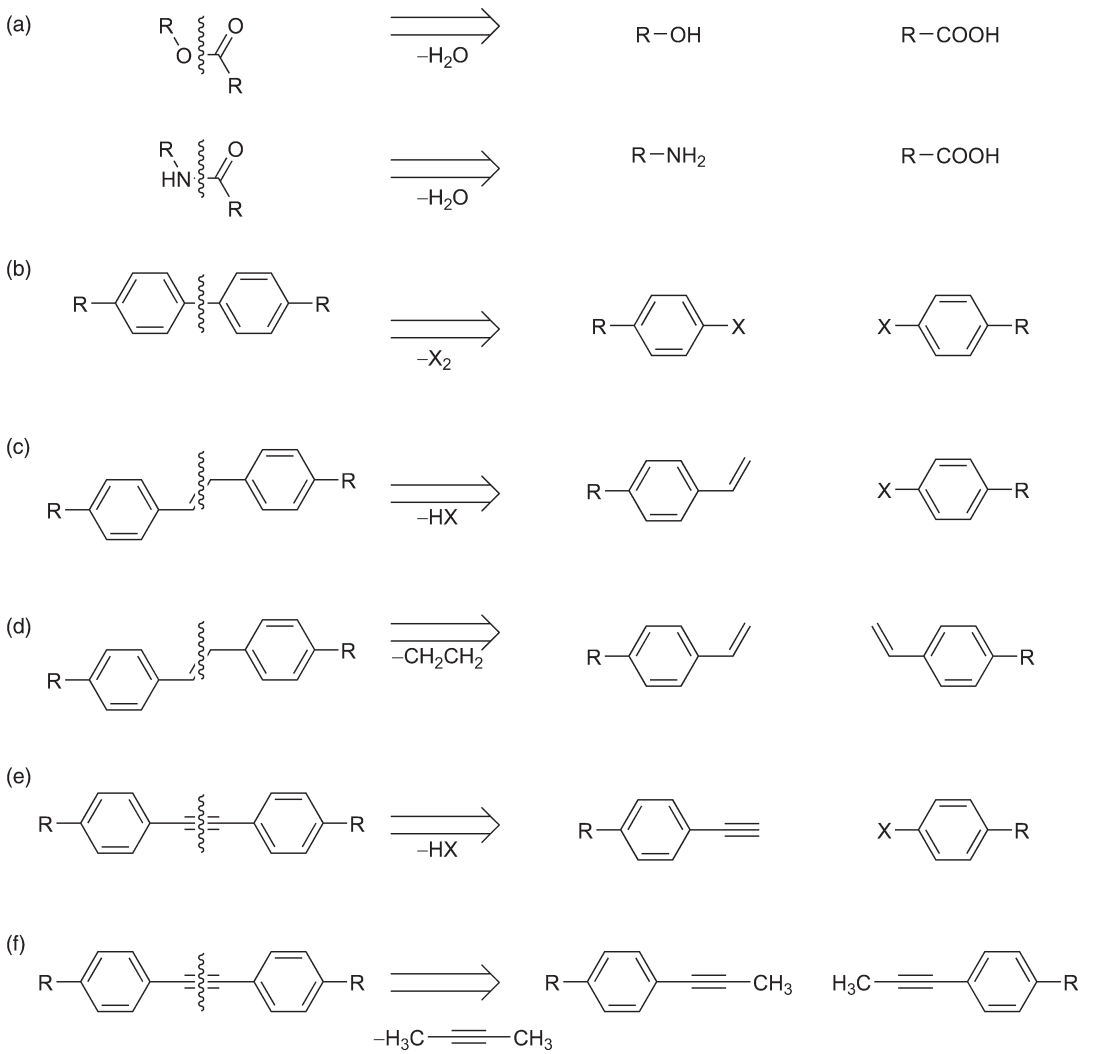

Figure 2 Retrosynthetic analyses of various condensation reactions: (a) esterification and amidation; (b) poly(phenylene); (c) poly(phenylenevinylene) (d) poly(phenylenevinylene); (e) poly(phenyleneethynylene); (f) poly(phenyleneethynylene). X = halogen.

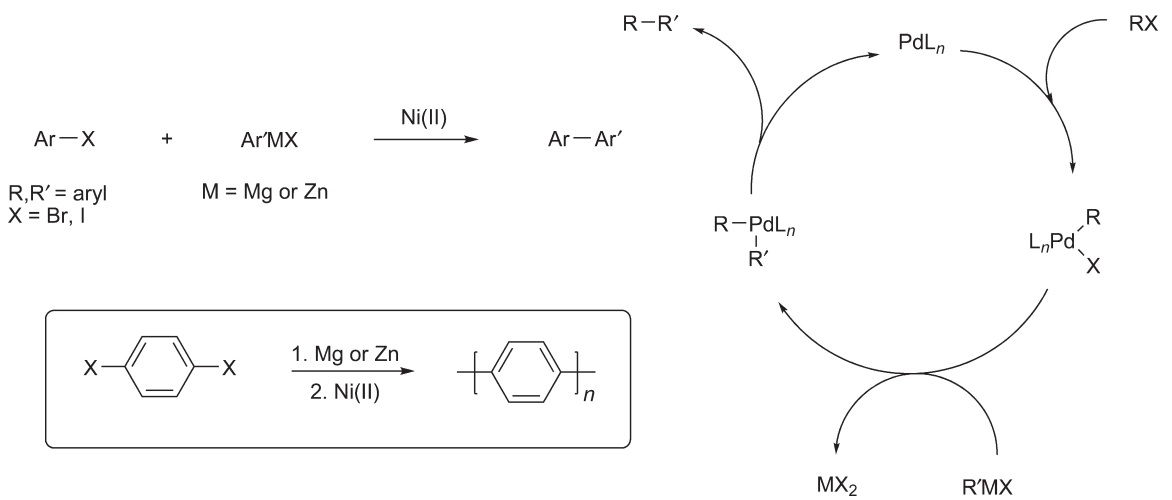

Figure 3 A general example of the Kumada coupling reaction (top left), an example of using the Kumada coupling reaction in polymer synthesis (bottom left), and the mechanism of the Kumada coupling reaction (right).

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cyano groups. In addition, an organozinc reagent can be used in organic solvents such as dimethylformamide (DMF), benzene, or hexamethylphosphoramide (HMPA); Grignard reagents generally require the use of ethereal solvents.

Under certain conditions for selected monomer classes, both the Kumada and Negishi couplings have been shown to operate by a chain-growth rather than a step-growth mechanism.[25] This advancement has facilitated the preparation of polythiophenes[26] and poly(*p*-phenylene)s with controlled molecular weights and low polydispersities.[27] In these cases, a catalyst-transfer mechanism operates and the metal is believed to 'walk' across the π-system of the most recently added monomer to oxidatively insert into a C–X bond on the end of the growing chain rather than dissociating and then reacting with another monomer in solution. In these cases, the molecular weight can be controlled by the initial ratio of the monomer to the nickel catalyst.

5.08.3.2 Nickel Homocoupling Reaction

Nickel(0) has been found to mediate the coupling of aryl halides to form carbon–carbon bonds between sp^2 centers.[28] This process has the drawback of being stoichiometric in nickel (0), which is generally sensitive to oxygen. However, it was later determined that this process could also be carried out with stoichiometric zinc(0) and catalytic nickel(0)[29–31] in which case the zinc(0) is the terminal reductant. Aryl iodides, bromides, tosylates, and even chlorides (which are typically the least reactive) can be coupled by this method.

As summarized in **Figure 4**, there are different possible mechanisms for this reaction. When the reaction is mediated by stoichiometric nickel(0), the reaction begins with nickel(0) undergoing oxidative addition to the aryl halide bond. The nickel(II) intermediate then disproportionates to give a nickel(II) halide and a diaryl nickel intermediate. Upon reductive elimination, a biaryl is formed and nickel(0) is regenerated.[32] When zinc is involved, a nickel(I) to nickel(III) catalytic cycle has also been suggested as a possible mechanism.[33] In this case, nickel(0) oxidatively inserts into an aryl halide bond. Zinc then reduces the intermediate to an aryl nickel(I) species. Subsequent oxidative addition into an aryl halide gives a diaryl nickel(III) intermediate, which, upon reductive elimination, forms a biaryl compound and affords nickel(I), which can then repeat the cycle.

5.08.3.3 The Stille Reaction

The Stille reaction is the palladium(0)-catalyzed cross-coupling of aryl or alkenyl halides with aryl, alkenyl, or alkynyl tin compounds and it results in C–C bond formation.[34] As organotin are typically not nucleophilic and often even stable to oxygen and water, they have an advantage over harsher methods as they exhibit good functional group tolerance (amines, aldehydes, esters, ethers, and nitro groups).[35] A disadvantage is the high toxicity associated with tin reagents and the stoichiometric tin waste that is generated as a by-product. Since aryl or alkenyl halide fragments can be coupled to aryl, alkenyl, or alkynyl stannanes, the Stille reaction has great versatility and can be employed in the synthesis of PPP- and PPV-type polymers.[36]

As shown in **Figure 5**, the mechanism of the Stille reaction is as follows: first the palladium(0) catalyst undergoes oxidative addition into the aryl halide bond. The organic fragment bound to tin is then transmetallated to palladium. Ultimately, the two organic fragments are reductively

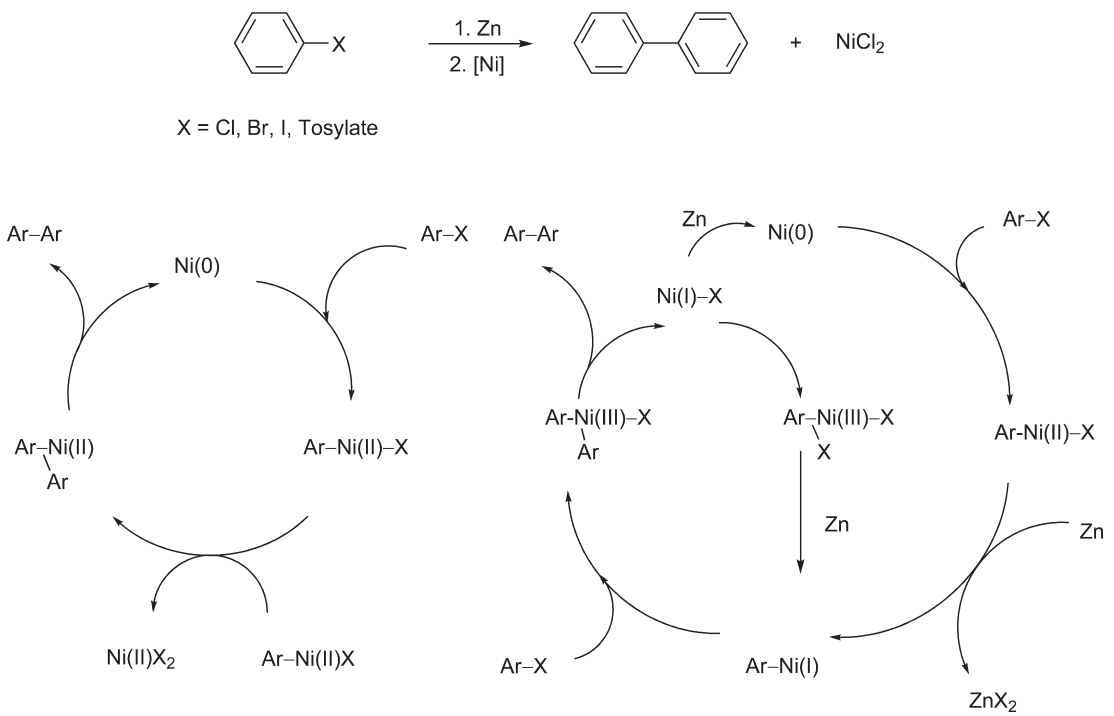

Figure 4 The nickel catalyzed homocoupling reaction (top); proposed mechanisms for nickel homocoupling: mediated by Ni(0) (bottom left) and catalyzed by Ni(0) and mediated by Zn (bottom right).

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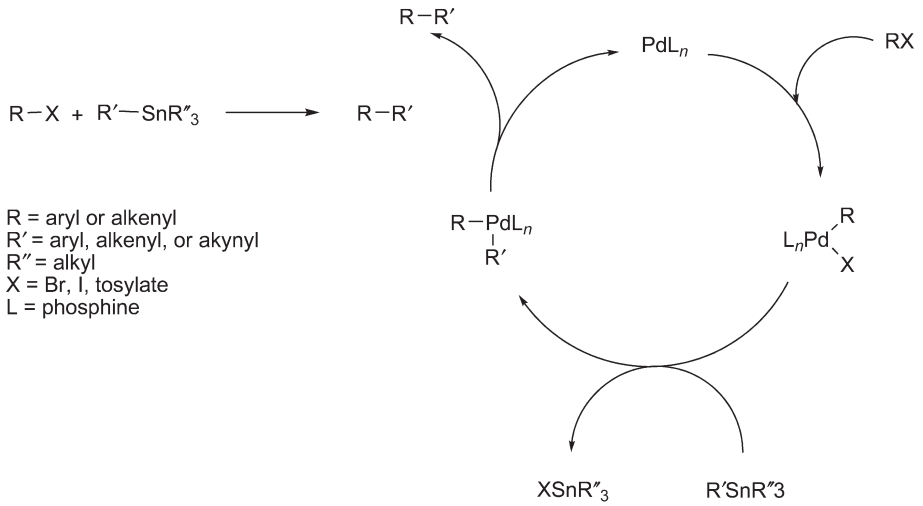

Figure 5 The Stille reaction (left) and the general mechanism of the Stille reaction (right).

eliminated from palladium species to give a C–C coupled product, which reforms a palladium(0) species in the process.

An early example of applying the Stille reaction to polycondensation chemistry was by Bochmann, who used the reaction to couple nBu$_3$Sn–R–Sn(nBu)$_3$ (R = p-Ph$_2$O and p-C$_6$H$_4$(C≡C)$_2$) fragments with a series of dihalo compounds to prepare a series of polymers.[37] These polymerizations were catalyzed by PdCl$_2$(PPh$_3$)$_2$ (PPh3 = triphenylphosphine) with added triphenylphosphine at elevated temperatures (130–165 °C) to afford polymers with a degree of polymerization that ranged between 5 and 22 units.

Subsequent improvements in Stille coupling methodology have provided access to polymers of increased molecular weight. For example, Moreau optimized the conditions required to prepare poly(3-octylthiophene) from an AB-type monomer, 2-bromo-3-octyl-5-tributylstannylthiophene.[38] The outcome of this polymerization reaction was shown to be sensitive to solvent effects as well as the catalyst's ligand:metal ratio. For example, a Pd(II) precursor, Pd$_2$(dba)$_3$ (dba = dibenzylideneacetone), and triphenylphosphine in a 1:4 ratio in 1:1 THF:DMF (v/v) were demonstrated to afford a 90% yield of poly(3-octylthiophene) with a high molecular weight (number average molecular weight (M_n) = 14 000 Da (Dalton); polydispersity index (PDI) = 1.5), whereas other solvents, ligands, or palladium:ligand ratios afforded oligomers or relatively low-molecular-weight polymers.

In addition to C–C bond forming processes, Lo Sterzo discovered that the Stille reaction can also be applied to the formation of carbon–metal bonds providing access to organometallic polymers (see **Figure 6** for examples).[39] Cyclopentadienyl iron dicarbonyl iodides were used rather than the typical aryl halides and were reacted with a variety of dialkynyl stannanes to form carbon–iron bonds. These polymers, which are analogous to PAE derivatives, had limited solubility. Moreover, the lower molecular weight fractions that were soluble in THF had a degree of polymerization that ranged from 5 to 9 repeat units. Regardless, these examples illustrate the versatility inherent in the Stille reaction and the diverse range of materials that can be prepared using this chemistry.

5.08.3.4 The Suzuki Reaction

The Suzuki reaction, in which boronic acids or boronic esters are coupled with aryl or alkenyl halides to afford new sp^2–sp^2-hybridized centers, is catalyzed by various palladium (0) species and requires a stoichiometric base.[40] The catalyst precursor commonly used in Suzuki polycondensations is

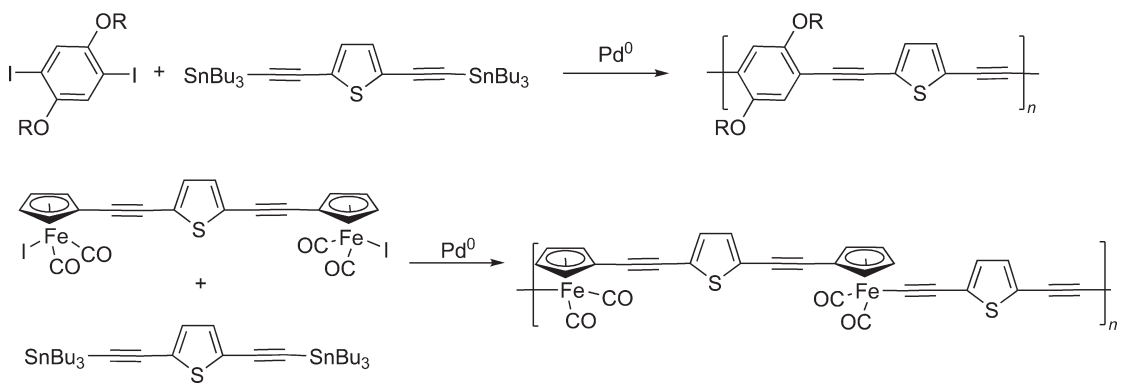

Figure 6 Selected examples of the application of the Stille reaction to form poly(aryleneethynylene)s and organometallic analogues.

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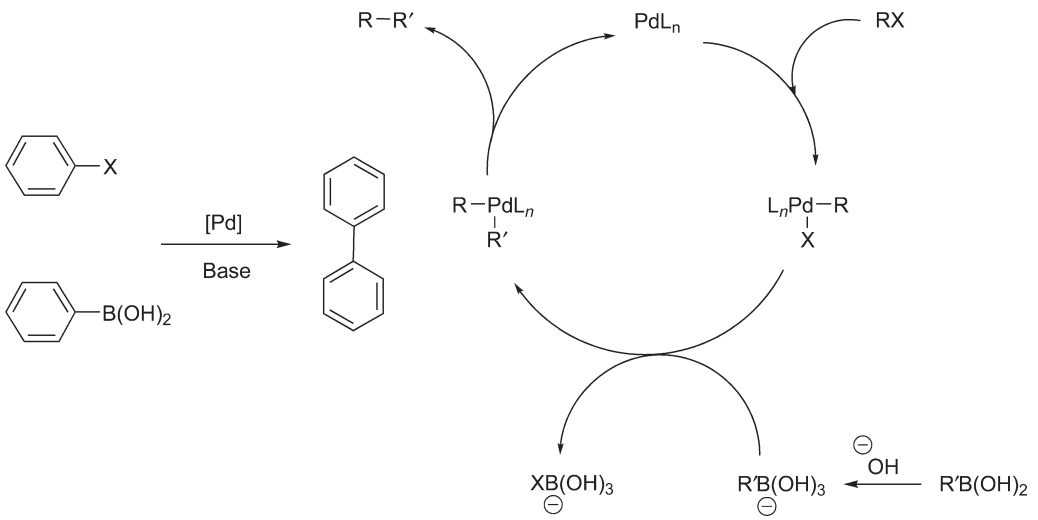

Figure 7 The Suzuki reaction (left) and the mechanism of the Suzuki reaction (right).

tetrakis(triphenylphosphine)palladium(0). An advantage of the Suzuki coupling reaction is that it can be used to form similar species as the Kumada coupling, but does so under relatively mild conditions. In addition, boronic acids have been found to be easier to handle than the Grignard reagents used in the Kumada coupling reaction because they are stable to air and water. The Suzuki reaction also exhibits good functional group compatibility due to the relatively poor nucleophilicity of boronic acids and tolerates substrates containing aldehydes, amides, cyanides, esters, ethers, and nitro groups.

Mechanistically, the Suzuki coupling reaction begins with the oxidative addition of palladium into an aryl halide bond (see **Figure 7**). In parallel, an aryl boronic acid reacts with a base to form a borate, which is then transmetallated onto the aforementioned palladium species. Finally, reductive elimination results in C–C coupling and regenerates a palladium(0) species that can facilitate another catalytic cycle.

When applied to polycondensation chemistry, the Suzuki reaction has been used to prepare poly(*p*-phenylene)s, polythiophenes, and PPVs. Monomers with flexible side chains are typically employed because the enhanced solubility imparted by them allows the chains to keep growing in solution to achieve higher molecular weight polymer.[41] There are limitations to this method and these primarily stem from side reactions. For example, electron-rich aromatic boronic acid compounds have a propensity to undergo deborylation under cross-coupling conditions.[42] Such side reactions cause stoichiometric imbalance, which, when applied toward a step-growth polymerization reaction, will result in reduced molecular weight. For this reason, when electron-rich aromatic units such as thiophenes are used as coupling partners in the Suzuki reaction, they are incorporated into the polymer via dihalide monomers rather than diboronic acid monomers.[41] Another side reaction is the exchange of aryl groups between the substrate aryl groups and the triphenylphosphine, which results in the formation of polymers with triphenylphosphonium end groups and cross-linked materials.[43] Regardless of this, the Suzuki reaction is one of the most common methods for preparing a variety of polymers such as PPPs,[44] for which a higher degree of polymerization can be obtained than with other methods such as the Kumada coupling reaction.[45]

5.08.3.5 The Heck Reaction

The Heck reaction couples a vinyl group to a haloarene.[46] This palladium-catalyzed reaction proceeds with the formal loss of a molecule of hydrogen halide and results in the formation of a C–C bond between an olefin and the aryl group. The Heck reaction proceeds under relatively mild conditions, tolerates a variety of functional groups such as aldehydes, amines, esters, and nitro groups,[47] and often affords high yields of desired products.

The mechanism of the Heck reaction (see **Figure 8**) begins with the oxidative addition of palladium into the aryl halogen bond. After coordinating to palladium, the olefin inserts into the palladium–carbon bond to give an alkyl-palladium intermediate. Appropriate structural reorganization often occurs to eliminate steric congestion so that *syn*-β-hydride elimination affords the thermodynamically favored *trans*-olefin. The base then reacts with the hydrogen halide, which ultimately regenerates Pd(0).

The Heck reaction has been broadly utilized in the synthesis of poly(arylenevinylene)s. The experimental parameters pertaining to the Heck reaction as applied to polymer synthesis were explored in detail by Heitz.[48] Stoichiometric base (often triethylamine) is generally needed to react with the acid that is produced to regenerate the active catalyst. While phosphines are not required when iodoarenes are used, they are needed when bromoarenes are employed[49] because palladium does not generally insert into C–Br bonds as readily as it does into C–I bonds. The σ-donating phosphine ligands provide the palladium center with sufficient electron density to oxidatively insert into the former.

A broad range of functionalized PPVs have been synthesized via the Heck reaction and many of these materials are not accessible through any other route. PPVs obtained through the Heck polycondensation feature almost exclusively *trans*-olefin linkages, although a minor side reaction results in a small percentage of exocyclic olefin defects, which renders the

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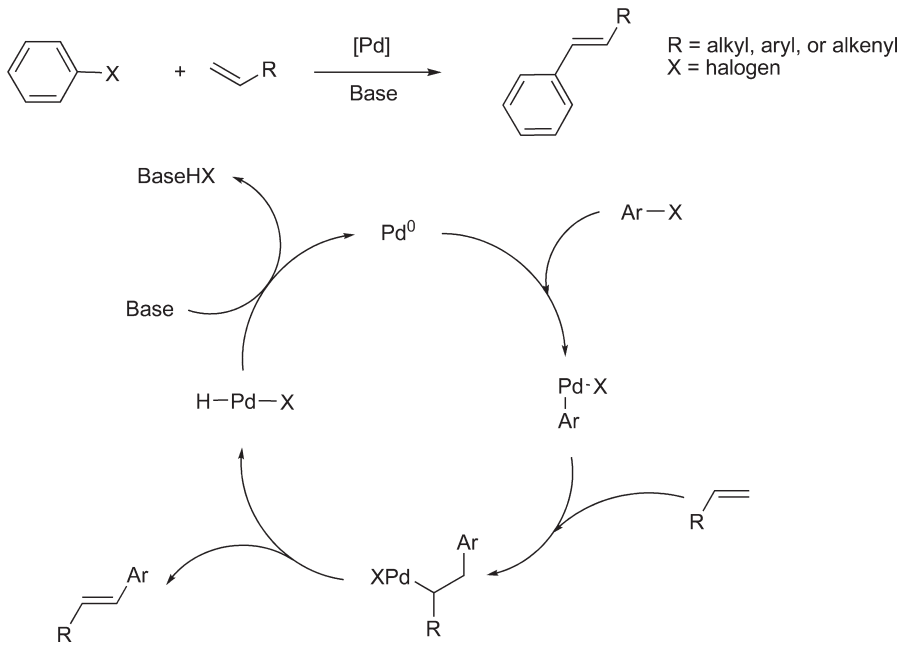

Figure 8 The Heck reaction (top) and the mechanism of the Heck reaction (bottom).

reaction less than 100% regioselective and is a drawback of using the Heck reaction. However, there are advantages to using the Heck reaction over conventional synthetic methods for the synthesis of PPVs. For example, the Wittig, McMurry, Gilche, and sulfonyl routes are incompatible with many functional groups and often result in defects along the polymer backbone, diminishing the desirable optoelectronic properties of these materials.[50]

5.08.3.6 The Sonogashira Reaction

The Sonogashira reaction couples aryl or alkenyl halides to terminal alkynes to give disubstituted alkynes.[51] Several excellent reviews that describe the chemistry of the Sonogashira reaction are available.[52] Both $Pd(PPh_3)_4$ and $(PPh_3)_2PdCl_2$ catalysts are frequently employed along with a copper(I) cocatalyst; a stoichiometric base is also required to deprotonate the terminal alkyne (see below). Typically, amine bases such as triethylamine, diisopropylamine, or piperidine are used and sometimes even serve as the solvent. Otherwise, THF is usually selected as the solvent of choice because it enhances catalytic activity and reduces sensitivity toward oxygen and water.[53] The reaction conditions employed are typically mild, being conducted at room temperature, and the reaction tolerates functional groups such as esters, polypeptides, and even sugars. However, there are some drawbacks to using this reaction to synthesize polymers: diyne defects cannot be prevented, polymer end groups are poorly defined,[54] and polymers with high molecular weights are challenging to obtain.[55]

As shown in Figure 9, the active catalyst, a Pd(0) species, undergoes oxidative addition into an aryl halide bond. The terminal acetylide is subsequently deprotonated and then metallated to give a copper acetylide, which is transmetallated to palladium. Reductive elimination ultimately yields the disubstituted acetylene and regenerates a Pd(0) species, which can facilitate another catalytic cycle.

5.08.3.7 Buchwald–Hartwig Amination

The palladium-catalyzed aryl amination reaction developed by Hartwig and Buchwald[56] couples aromatic amines to aromatic or aliphatic halides under basic conditions, effectively condensing hydrogen halides to form carbon–nitrogen bonds. Palladium complexes derived from $Pd(OAc)_2$ with bulky phosphines, chelating bisphosphines,[57] biphenyl systems,[58] or *N*-heterocyclic carbene (NHC) ligands[59] are commonly used to catalyze this reaction.

The exact details of the mechanism of this reaction are not universally agreed upon and may vary to some extent depending on the substrates and ligands employed but, in general, the reaction is thought to proceed as shown in Figure 10.[60] The reaction begins with the oxidative addition of palladium into an aryl halide bond. An amine then coordinates to the metal either before or after deprotonation. Subsequent reductive elimination then gives the coupled product and regenerates the active catalyst. When applied to polycondensation chemistry, the aryl amination reaction has provided an excellent route to polyanilines (see below).

5.08.4 Metathesis Reactions – Acyclic Diene and Acyclic Diyne Metathesis

Alkene and alkyne metathesis are different from the palladium- and nickel-catalyzed cross-coupling processes in that new C–C double bonds and triple bonds are formed, and small molecules such as ethylene (acyclic diene metathesis (ADMET)) or 2-butyne (acyclic diyne metathesis (ADIMET)) are evolved.

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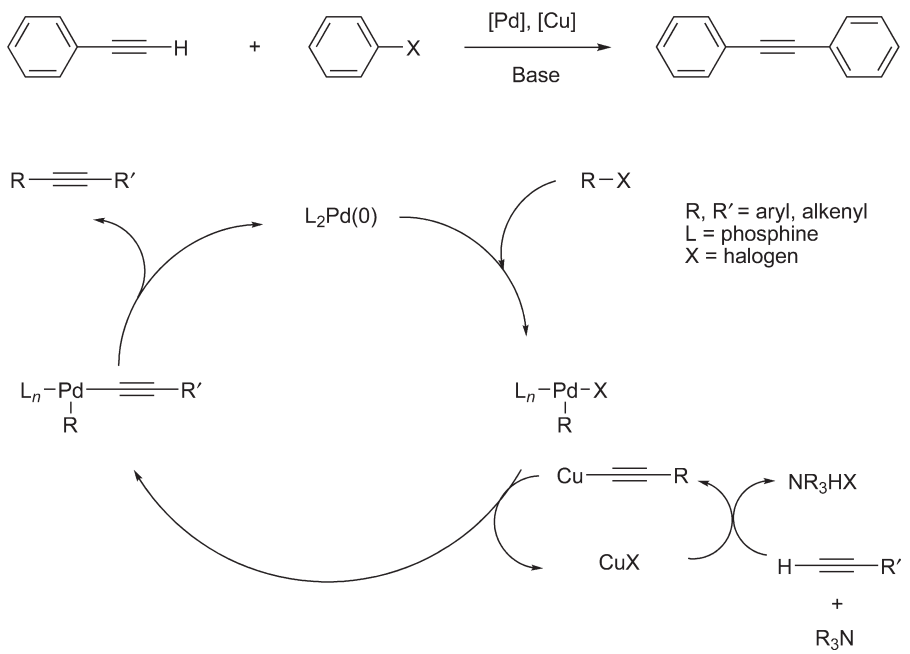

Figure 9 The Sonogashira reaction (top) and the mechanism of the Sonogashira reaction (bottom).

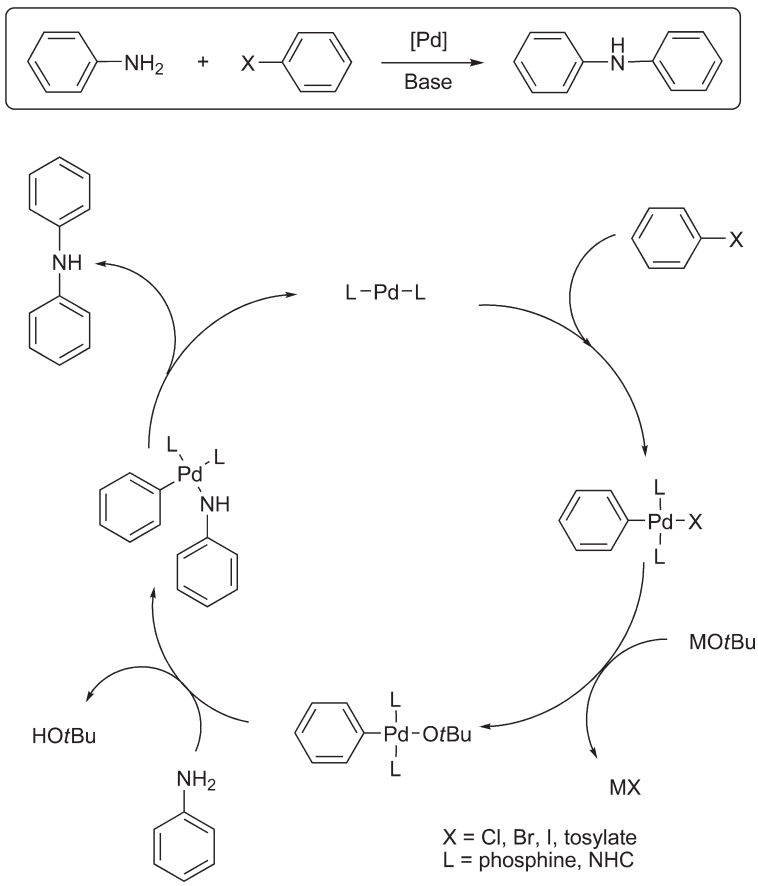

Figure 10 The aryl amination reaction (top) and its mechanism (bottom). NHC, *N*-heterocyclic carbene.

5.08.4.1 Acyclic Diene Metathesis

The term 'olefin metathesis' was coined in 1967 by Calderon[61] and refers to several mechanistically related processes that involve a redistribution of olefinic bonds: ring-opening metathesis (ROM), ring-closing metathesis (RCM), ring-opening metathesis polymerization (ROMP), cross-metathesis, and

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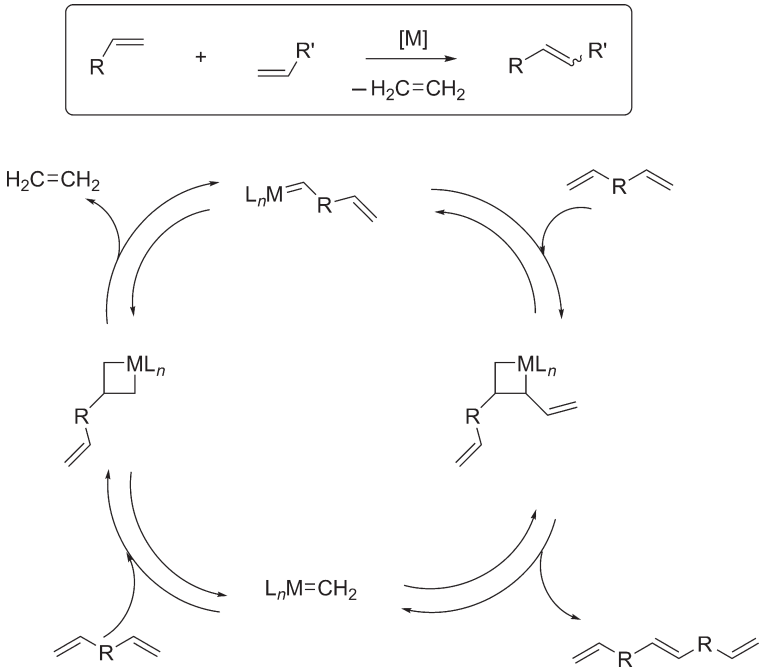

Figure 11 The ADMET process (top) and its mechanism (bottom).

ADMET. ROMP and ADMET are both applicable to polymer synthesis, but only ADMET is a condensation process and will be discussed here. ADMET couples cyclic α,ω-dienes and condenses ethylene. This polymerization reaction greatly differs from the nickel- and palladium-catalyzed processes previously discussed, and it involves coordination of an olefin to the metal center, followed by the formation of a metallocyclobutane by a formal (2 + 2) cycloaddition, and finally cycloreversion along the alternate bonds to release an olefin.[62] This mechanism was expanded upon by Wagener *et al.* [63] and is shown in **Figure 11**. Each mechanistic step is reversible but the process is driven irreversibly to polymer formation through removal of ethylene.

5.08.4.1.1 Early systems

The earliest catalyst systems were multicomponent Ziegler–Natta-type catalysts consisting of an early transition metal halide and an alkylating agent.[64] These classical systems suffered from many limitations. For example, the catalysts were not well defined and therefore the active catalyst-to-monomer ratio could not be finely controlled. Also, reactivity was hard to predict and side reactions were observed due to the harsh conditions employed. Despite these drawbacks, related multicomponent systems have found some commercial success, such as the Shell higher olefin process (SHOP).[65]

A significant development that allowed ADMET chemistry to develop into well-known and viable polymerization methodology was the discovery of single-site well-defined tungsten and molybdenum alkylidene catalysts by Schrock (**Figure 12**).[66] Wagener capitalized on this breakthrough by successfully employing the Schrock catalyst to perform the ADMET reaction on 1,9-decadiene, which was the beginning of ADMET.[67] Limitations of the Schrock catalysts stem from their high oxophilicity. These catalysts are susceptible to poisoning by air or water and therefore dry and air-free conditions are required. In addition, they are incompatible with many functional groups (including alcohols, aldehydes, and carboxylic acids) which narrows the range of monomers that can be polymerized. However, the Schrock catalyst is more tolerant of functional groups that contain sulfur than many other metathesis catalysts.

The Grubbs first-generation catalyst (G1)[68] discovered in the 1990s overcame many limitations of the Schrock catalyst. It contained a late transition metal, ruthenium, and was found to react with olefins more readily than other functional

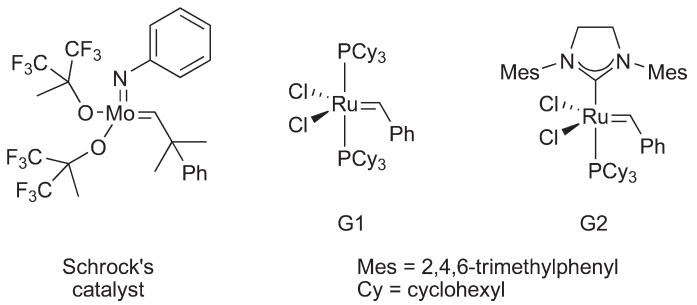

Figure 12 Metathesis catalysts: Schrock's molybdenum alkylidene (left); Grubbs' 'first-generation' (middle) and 'second-generation' (right) benzylidene catalysts.

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groups.[68b] In general, the Grubbs catalysts are more air-stable and functional group tolerant (alcohols, esters, and ketones are tolerated) but less reactive than the Schrock catalyst. Herrmann found that replacing a phosphine with an NHC enhanced catalytic activity without sacrificing functional group tolerance.[69] This development paved the way to the Grubbs second-generation catalyst, G2.

5.08.4.1.2 Considerations for monomer choice

The range of polymers accessible through ADMET is primarily limited by the availability of the monomer. For the most part, if an α,ω-diene can be synthesized and is 10 atoms or greater in length, it can be polymerized via ADMET. The 10 atom monomer length requirement for the α,ω-diene is to suppress a competing reaction: monomer cyclization via ring-closing metathesis. Cyclization frequently competes with polymerization when a 5-, 6-, or 7-membered ring can be generated.[70] Under ADMET conditions, the product distribution is determined by thermodynamics and a shorter monomer will preferentially yield the RCM product rather than polymer.[71] This is a significant limitation of the ADMET method that cannot be overcome except by choosing a monomer that contains more atoms (i.e., a longer monomer).

5.08.4.1.3 Materials accessible through ADMET

ADMET has been used to generate linear polyoctenamer, which upon hydrogenation yields perfectly linear polyethylene (Figure 13).[72] Similarly, conducting ADMET on a monomer with a pendant alkyl branch or other functional group exactly in the middle of the two terminal olefins yields polymers in which the pendant groups are perfectly spaced from each other along the polymer backbone. ADMET demonstrates exceptional utility with regard to precision placement of pendant groups.[73] This allows access to polymers with a pure microstructure and much sharper melting points than those generated by other means.[74] This technique has also provided model systems that proved fruitful in providing detailed understanding of structure–property relationships applicable to commercial polyethylene and related polymers.[72,75]

The versatility of ADMET has been demonstrated by the diverse array of polymers that are prepared by this technique: hybrid organic/inorganic polymers[76] such as polycarbosilanes[77] and siloxanes;[78] liquid crystalline polymers;[79] graft copolymers with 'perfect comb' architectures;[80] conjugated polymers including polyacetylenes;[81] poly(thiophene)ethylene;[82] and biopolymers containing chiral amino acid moieties[83] such as lysine residues.[84] Representative examples are shown in Figure 14. For further details on ADMET, see the reviews by Wagener and co-workers.[71]

5.08.4.2 Acyclic Diyne Metathesis Polymerization

Alkyne metathesis is a process in which alkylidyne units undergo a mutual exchange, and is analogous to the olefin metathesis reaction.[85] When alkyne metathesis is conducted on acyclic diynes to form polymer, the process is known as ADIMET polymerization. ADIMET holds much promise as a polymerization method, but has not yet been developed as extensively as olefin metathesis-based methods. The first alkyne metathesis catalyst consisted of tungsten oxides on silica.[86] This early system had little preparative value because elevated temperatures (200–450 °C) were required to facilitate the reaction. The alkyne metathesis reaction was then explored by Mortreux, who found that a mixture of $Mo(CO)_6$ and phenol additives in a high-boiling solvent such as decalin brought about the scrambling of internal alkynes.[87] In contrast to the earlier systems, the Mortreux catalyst had the advantage of being homogeneous. The mechanism of this reaction was something of a mystery until Katz and McGinnis[88] proposed that metal carbynes are the catalytically active species and that the reaction proceeded through a formal (2 + 2) cycloaddition to form metallocyclobutadiene followed by cycloreversion as depicted in Figure 15. This hypothesized mechanism was later confirmed by Schrock, who isolated and characterized catalytically active intermediates.[89] Schrock also made a major contribution to the field through the development of well-defined catalytically active tungsten carbyne complexes,[90] which facilitate alkyne metathesis under milder conditions than previously developed catalysts.[91,92]

Schrock was also the first to use alkyne metathesis for ADIMET polymerization. For example, 2,10-dodecadiyne was polymerized with the tungsten catalyst $[(t\mathrm{BuO})_3\mathrm{W{\equiv}C}t\mathrm{Bu}]$ to give a polyoctenamer. This material was insoluble, rendering the polymerization nonliving, and therefore it was not

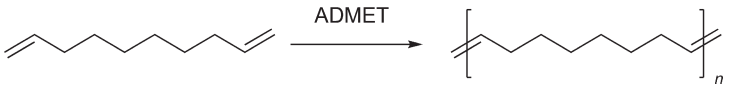

Figure 13 A representative example of ADMET.

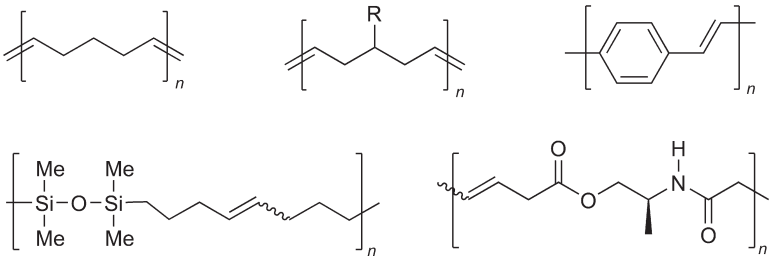

Figure 14 Selected examples of polymers prepared via ADMET.

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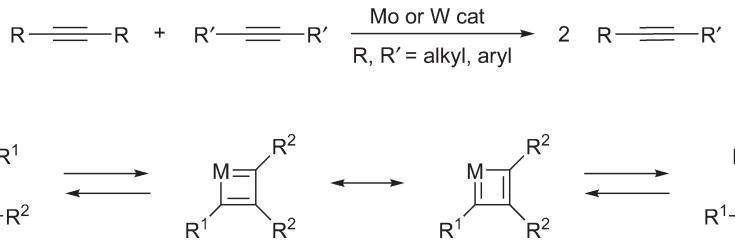

Figure 15 General reaction (top) and the mechanism (bottom) of alkyne metathesis.

examined in greater detail.[91] The ADIMET polymerization was then further explored by Weiss *et al.*[92] in 1997. Since then, several groups have investigated a number of alkyne metathesis catalysts including well-defined tungsten complexes, molybdenum complexes, and Mortreux systems for the preparation of a number of polymers.

5.08.4.2.1 Comparison of catalysts

The tungsten-based catalyst [$(t\text{BuO})_3\text{W}{\equiv}\text{C}t\text{Bu}$], the first homogeneous catalyst explored for ADIMET activity, has the advantage of being active at relatively low temperatures (room temperature for nonconjugated diynes and 80–90 °C for conjugated diynes). Although this catalyst tolerates many functional groups, substrates containing thioethers, amines, and crown ethers are incompatible[93] due to deactivation of the catalyst through coordination to the Lewis-acidic tungsten center.[94] Another disadvantage is the tedious and inconvenient synthesis of the pyrophoric cocatalyst, which requires strict exclusion of air and moisture.

The molybdenum catalysts developed by Fürstner tolerate functional groups that the tungsten catalyst cannot. This has been rationalized in terms of the coordination sphere around molybdenum being more crowded, which prevents deactivation through coordination by donor ligands.[95] In fact, these catalysts are even active in coordinating solvents such as THF and acetonitrile. Incompatibility is encountered, however, with secondary amides, thiophenes, and other species.[96]

The Mo(CO)_6/phenol systems initially discovered by Mortreux have the advantages of the catalyst being benchtop stable and prepared in one step from commercially available starting materials. Higher temperature (130–150 °C) is required for activity. These systems have the disadvantage of rather poor functional group compatibility, severely curtailing their applicability.[97] So far, no ideal catalyst for ADIMET has been developed and there is tremendous opportunity in this area.

5.08.4.2.2 Scope of reaction/outlook

One important application of ADIMET is the provision of an alternative route to PPEs and other PAEs which are free from defects that result from palladium-catalyzed processes.[85b] In some cases, high-molecular-weight PPE has been obtained through ADIMET processes, with degree of polymerization (P_n) values in excess of 1000.[98]

Tungsten carbynes are particularly promising for alkyne metathesis reactions as they have been shown to tolerate olefins.[99] This surprising orthogonality between olefin metathesis and alkyne metathesis allows for the ADIMET polymerization to be performed on monomers that contain olefins. A major limitation of the scope of this reaction is that only internal alkynes can be used;[100] terminal alkynes do not react with the catalyst in a way that facilitates productive alkyne metathesis reactions. The ADIMET reaction is driven toward completion through the removal of the condensate: 2-butyne or 3-hexyne. In general, applicability of alkyne metathesis to condensation polymerization is limited by the availability and stability of metathesis catalysts as well as the harsh conditions required for activity in some cases. The development of catalysts that can be synthesized conveniently and that operate under milder conditions, with improved air/water stabilities and a greater functional group tolerance, should greatly expand the utility of alkyne metathesis as a general synthetic method, particularly for the preparation of condensation polymers.

5.08.5 An Overview of Various Polymers Prepared Using Metal-Mediated Coupling Reactions

5.08.5.1 Poly(*p*-arylene)

The use of transition metal-catalyzed cross-coupling chemistry in general and nickel in particular for the synthesis of condensation polymers was spearheaded in 1977 by Yamamoto and Yamamoto,[101] who applied the Kumada coupling reaction to the synthesis of poly(phenylene) and other poly(arylene)s (**Figure 16**). These investigators were interested in poly(*p*-phenylene) because it is resistant to thermal degradation and therefore could be used as a material for applications that demand resistance to high temperature. Previous methods utilized in the preparation of poly(phenylene)s, including the Ullmann coupling and the Wurtz–Fittig reaction, were found to operate under harsh conditions (>200 °C, via radical pathways) to yield polymers that contained structural irregularity and branches. The Kumada coupling reaction was seen as a good alternative because it operates under relatively mild conditions. Indeed, such reactions are typically conducted by combining the various dihaloarenes with magnesium and the nickel complexes in THF followed by heating to 60 °C. A

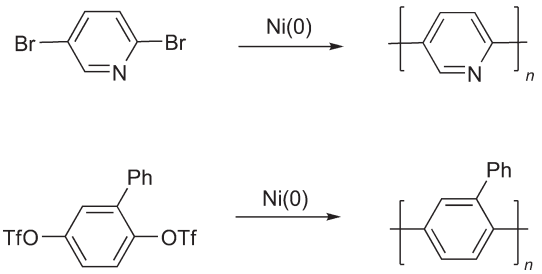

Figure 16 Selected poly(*p*-phenylene) (PPP) derivatives prepared via nickel homocoupling: poly(2,5-pyridinediyl) (top) and phenyl-substituted PPP (bottom).

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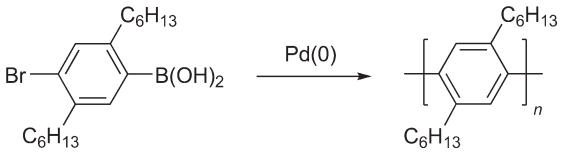

Figure 17 Synthesis of a poly(*p*-phenylene) derivative via Suzuki coupling.

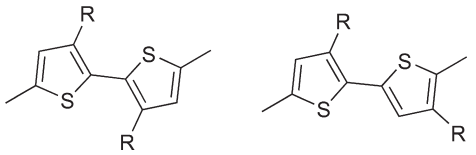

Figure 18 Head-to-head poly(3-alkylthiophene) linkage (left) and head-to-tail linkage (right). R = alkyl.

number of catalysts and ligands were screened to determine the optimal conditions; however, the polymers reported displayed poor solubilities and were of low molecular weight (the degree of polymerization values were found to range between 12 and 46 as determined by halogen content using elemental analysis and based on the assumption that both end groups were halogens). The inability to prepare high-molecular-weight polymers illustrated key challenges of this reaction for accessing polymeric materials, which would be later addressed by others.

Yamamoto *et al.*[28] first reported the Ni(0)-mediated homocoupling of aryl halides via a dehalogenation polycondensation process. Poly(2,5-pyridinediyl)s were prepared in good yields (54–95%) from 2,5-dibromopyridine, although the molecular weights were low (1200–1900 Da corresponding to degree of polymerization values of 16–25, as measured by light-scattering techniques). These reactions were carried out at 60 °C for 16 h in DMF with stoichiometric $Ni(cod)_2$ (cod = 1,5-cyclooctadiene). Percec *et al.*[102] later employed this reaction in the synthesis of functionalized poly(*p*-phenylene)s. Starting from the bistriflates of functionalized hydroquinones, low-molecular-weight polymers (M_n = 500–6300 Da) in variable yields were obtained, depending on substituents and other factors.[102]

Schlüter and co-workers[45] first utilized the Suzuki reaction for the preparation of poly(phenylene)s, achieving soluble polymers with a degree of polymerization of approximately 30, results which exceeded that achievable via the aforementioned Kumada coupling chemistry (**Figure 17**).

5.08.5.2 Polythiophene

By using the Kumada coupling reaction, Yamamoto *et al.*[20] reported the first polythiophene containing a regular structure. The Kumada coupling resulted in only the 2,5-coupled product, whereas techniques that were previously employed to prepare polythiophenes generally afforded some degree of the 2,4-coupled product, which disrupted conjugation. The Grignard reagent was prepared by treating 2,5-dibromothiophene with one equivalent of Mg(0). Upon addition of a catalytic amount of $NiCl_2$bpy (bpy = 2,2-bipyridine) and refluxing for 3 h, a 61% yield of 2,5-polythiophene was obtained. The product was mostly insoluble, although 22 wt.% could be extracted into hot chloroform. This fraction had a low molecular weight of 1370 Da (determined by vapor pressure osmometry (VPO)). The polymer was also not highly conductive (10^{-8} S m^{-1}), but upon doping with iodine, conductivity was found to increase sevenfold.

Yamamoto *et al.*[24] later found that employing an organozinc reagent rather than a Grignard reagent in Kumada polycondensations had several advantages. Organozinc reagents generally exhibit better functional group compatibility and tolerate functional groups such as carbonyl and cyano groups. Also, other organic solvents besides ethers could be used. Optimized conditions were applied to 2,5-dibromothiophene, which afforded polythiophene in 78% yield. Only 25 wt.% was found to be soluble in hot chloroform corresponding to a molecular weight of less than 3000 Da. The insoluble fraction had a degree of polymerization value of 55 and a molecular weight M_n of 4700 Da, as determined by elemental analysis.

Poly(3-alkylthiophene)s (PATs) are important because in addition to having the sought after electronic properties of polythiophene, they are soluble and processable. Unlike polythiophene, however, PATs can have different regioisomeric linkages (**Figure 18**). Regioregular head-to-tail 3-alkylpolythiophene (HT PAT) appears to have superior electronic properties. For example, HT poly(3-hexylthiophene) (P3HT) exhibits an electrical conductivity of 150 S cm^{-1} in contrast to regiorandom P3HT, which exhibits an electrical conductivity of 1 S cm^{-1}.[103] This is due to head-to-head linkages diminish the effective length of conjugation due to steric crowding of the alkyl groups which forces the thiophenes out of planarity. McCullough *et al.*[104] applied the Kumada coupling reaction to achieve the first synthesis of 3-alkyl-substituted head-to-tail regioregular polythiophenes (**Figure 19(a)**). It was found that 3-alkyl-2-bromothiophenes were selectively deprotonated at the 5-position and the lithiated thiophene could then be transmetallated to magnesium. Upon addition of $Ni(dppp)Cl_2$ (dppp = 1,3-bis(diphenylphosphino)propane), these AB-type monomers reacted to give regioregular polythiophene. Yields were moderate (~65%) as were molecular weights (M_w = ~12 000 to ~24 000 Da), but the remarkable accomplishment was the high degree of regioregularity (93–98% head-to-tail microstructure).

The Negishi cross-coupling reaction was utilized by Chen and Rieke[105] to prepare regioregular HT PAT (**Figure 19(b)**). They found that zinc would react quantitatively and regioselectively (9:1) with 2,5-dibromo-3-hexylthiophene to give 2-bromozincio-5-bromo-3-hexylthiophene. Treatment of this organozinc intermediate with $Pd(PPh_3)_4$ yielded regiorandom polythiophene. However, treatment with catalytic Ni(dppe)Cl_2 (dppe = 1,2-bis(diphenylphosphino)ethane) gave regioregular HT PAT (up to 98.5% head-to-tail linkages). The polymers prepared in this manner had M_n of ~5000 Da and PDIs of ~4, and were obtained in high yield. Regioregularity was diminished when a different nickel catalyst ($Ni(PPh_3)_4$) was used. These results demonstrated that the identity of both the metal and the ligands affected the degree of regioregularity, and were rationalized in terms of the difference in the sizes of the ionic radii of Ni(II) versus Pd(II), along with the difference in steric effects. The degree of regioregularity is dictated by the reductive elimination step. A larger metal center and a more sterically demanding ligand generally affords higher regioregularities.

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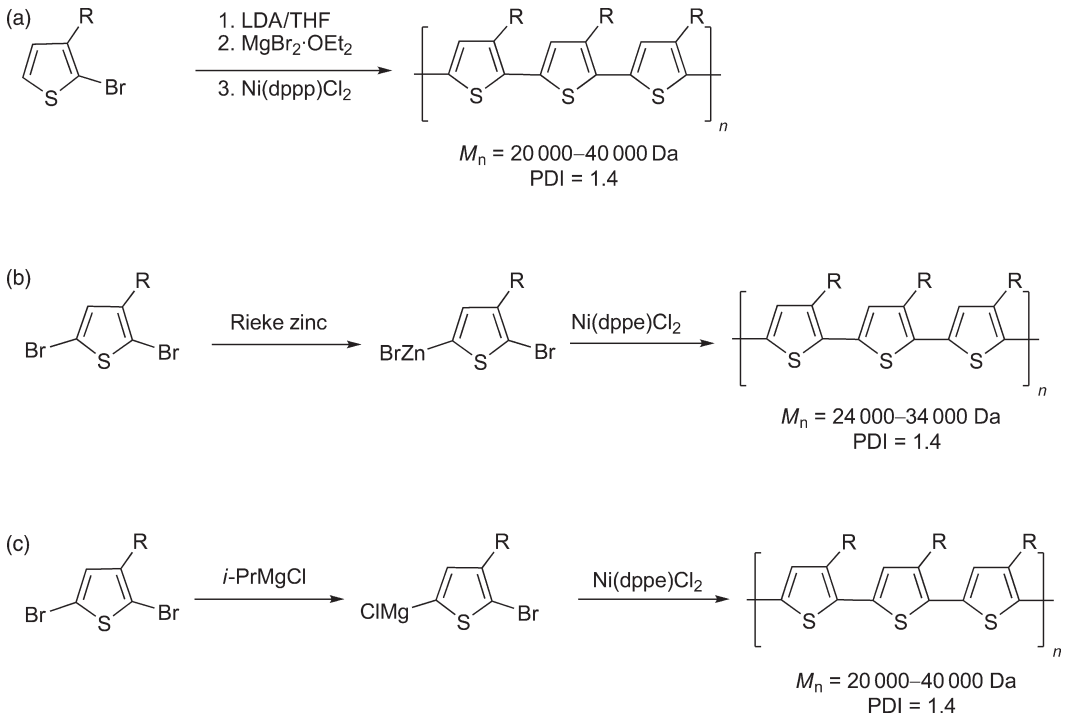

Figure 19 Three different routes to head-to-tail regioregular polythiophene. LDA, lithium diisopropylamide.

McCullough and co-workers[106] later reported the Grignard metathesis (GRIM) method for preparing HT PAT (Figure 19(c)). The Grignard reagent of 2,5-dibromo-3-alkylthiophene was prepared by reacting this monomer with isopropylmagnesium chloride at room temperature. The less substituted Grignard reagent is preferentially generated (85:15), and upon addition of a nickel catalyst, regioregular HT PAT with greater than 99% head-to-tail linkages was obtained. A remarkable advantage of this method is that it allows the synthesis of high-molecular-weight polymer (M_n = 20 000–30 500 Da) with a low polydispersity (PDI = 1.2–1.4). The polymerization has been shown to proceed by a chain-growth mechanism.[26]

Zhang and Tour[107] utilized the Stille reaction in the preparation of a variety of polythiophenes with alternating donor/acceptor repeat units (Figure 20) for the preparation of low band gap polymers. Yields were generally high, giving a molecular weight range of M_n = 5800–17 000 Da. The electron-poor thiophene coupling partners were employed as the distannanes and the electron-rich thiophene coupling partners were employed as the dihalides. Better results were obtained if the halogenated monomers were electron deficient because electron-poor substrates generally undergo oxidative addition more readily. Copper(I) iodide was added to accelerate transmetallation and triphenylarsine was added because this ligand has been found to speed up the reaction in addition to providing polymer of relatively high molecular weight.

5.08.5.3 Poly(*p*-arylenevinylene)

Poly(*p*-arylenevinylene)s (PAVs) have been accessed by a few different metal-catalyzed polycondensation reactions. The first metal-catalyzed route to be utilized was the Heck reaction. In addition, the Suzuki and ADMET reactions have also been applied to the synthesis of PAVs.

Heitz *et al.*[108] utilized the Heck reaction to synthesize PPVs in 1988. Since then, the Heck reaction has found significant use in the synthesis of designer PPVs.[109] Both AB and AA/BB monomer approaches have been utilized (Figure 21). The Heck reaction has also been used to prepare organometallic monomers such as divinyl functionalized metalloporphyrins that can be polymerized to give metalloporphyrin-containing PPVs (Figure 22).[110] These polymers had a molecular weight

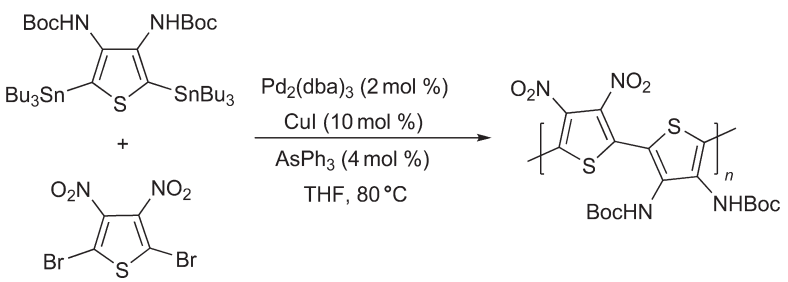

Figure 20 Synthesis of a polythiophene with alternating donor/acceptor groups.

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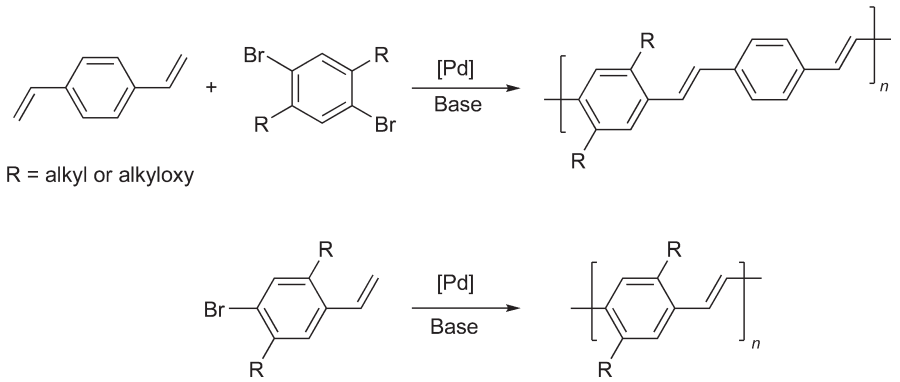

Figure 21 Examples of using the Heck reaction to synthesize PPV.

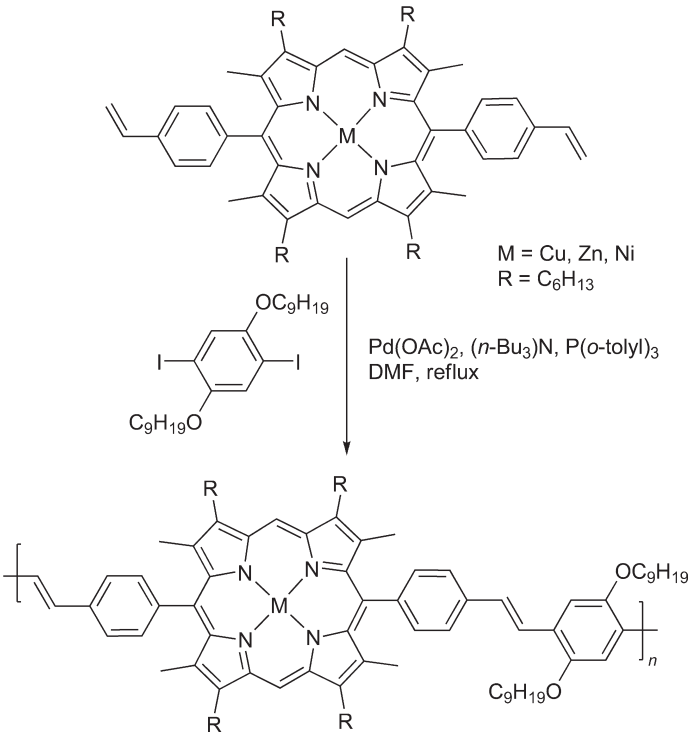

Figure 22 An example of a metalloporphyrin-containing PPV.

ranging from $M_w = 8300–46\,000$ Da and the metal coordinated in the porphyrin was not displaced by palladium during the course of the reaction. Metalloporphyrin-containing PPVs are interesting because they are photoconductive and photorefractive.

Koch and Heitz[111] reported PPV derivatives from *trans*-1,2-dibromoethylene and aryldiboronic acids via the Suzuki polycondensation reaction (Figure 23). Moderate to high yields (up to 82%) and moderate molecular weights (up to $M_n = 12\,310$ Da) were obtained using a biphasic reaction medium at room temperature. The polymer was not defect-free as a small percentage of biphenyl linkages were formed due to homocoupling of the boronic acid groups on the diboronic acid monomer.

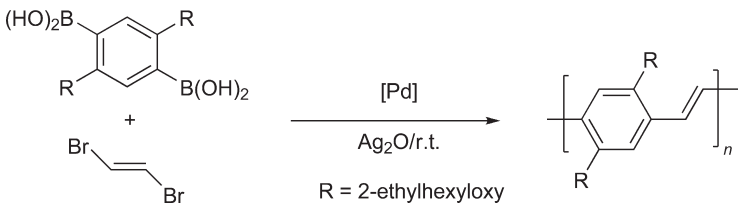

Figure 23 A selected example of using the Suzuki reaction to prepare high-molecular-weight PPV. r.t. = room temperature.

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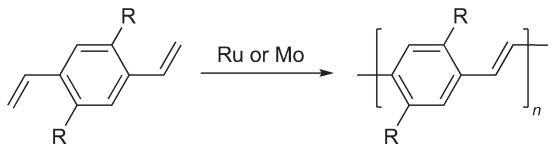

Figure 24 An ADMET approach to PPV.

Wolf and Wagener first reported the use of the ADMET approach to the preparation of PPVs (Figure 24),[112] which has since been explored by other groups.[113] Weychardt and Plenio[114] further developed the ADMET polymerization of divinylarenes with various Grubbs-type catalysts under dynamic vacuum at high temperatures to obtain high-molecular-weight PPVs ($M_n > 100\,000$ Da). The ADMET approach to PPVs has advantages over the palladium-catalyzed methods: (1) ADMET affords vinylidene linkages that are all in the *trans* configuration; and (2) the polymer is defect-free and lacks impurities such as halides or ambiguous end groups. A disadvantage of this approach is that it is limited mainly to the preparation of homopolymers, whereas the Heck and Suzuki reactions can often provide homopolymers as well as alternating copolymers. Likewise, to the best of our knowledge, catalysts for growing PAVs in a chain-growth manner are unknown and remain important targets as they may potentially enable the synthesis of these polymers in a living or controlled fashion.

5.08.5.4 Poly(aryleneethynylene)s

Excellent reviews have been written on the poly(aryleneethynylene)s.[55,115] Like other conjugated polymers, PAEs are rigid rods and, without solubilizing substituents, it is challenging to prepare them in high molecular weights. Moreover, the materials produced are often insoluble and infusible, which prevents their application and utility.

Yamamoto and co-workers[116] were the first to apply the Sonogashira reaction to a polycondensation involving the preparation of poly(aryleneethynylene)s. Dihaloarenes and dialkynylarenes were polymerized to give alternating copolymers (Figure 25) in high yields (64–100%) but relatively low molecular weights (<4000 Da). This reaction has become one of the most commonly used methods for preparing these materials.[115,117] Both dibromides and diiodides have been used as substrates but diiodides generally give better results.[118] The diiodides are more reactive, presumably due to more facile oxidative addition, and give higher yields and fewer defects. However, there are a few drawbacks in the use of the Sonogashira reaction to prepare PAEs. For example, diyne defects resulting from Glaser coupling of the alkynes cannot be completely avoided. Additionally, high-molecular-weight polymer is hard to obtain in most cases and end groups are poorly defined because dehalogenation and phosphonium salt formation occur under the reaction conditions.[54]

In addition to the palladium-catalyzed processes, the ADIMET reaction has also been used to prepare PAEs (Figure 26). The application of ADIMET toward the preparation of PPEs was explored by Weiss *et al.*[92] in 1997. A tungsten catalyst [$(t\mathrm{BuO})_3\mathrm{W}{\equiv}\mathrm{C}t\mathrm{Bu}$] was used to prepare PPEs with M_n values up to 40 000 Da and a PDI of 2. Bunz and co-workers[119] later applied the $\mathrm{Mo(CO)_6}$/phenol Mortreux-type catalyst system to the polymerization of dipropynylbenzenes. The polymerizations were carried out at 150 °C and the butyne condensate was removed by a constant nitrogen purge. No effort was made toward the exclusion of water or oxygen from the system which illustrates a key advantage over the pyrophoric tungsten catalysts. Yields for the PPEs were nearly quantitative, giving degree of polymerization values of up to 150, as determined by nuclear magnetic resonance (NMR) spectroscopy.

The development of the highly active molybdenum catalysts allowed Zhang and Moore[120] to access various poly(2,5-thienyleneethynylene)s (Figure 27) that were inaccessible via previously developed alkyne metathesis catalysts that could not tolerate the thiophene functionality. The active catalyst was generated by combining the trisamidomolybdenum(VI) propylidene precatalyst with three equivalents of *p*-nitrophenol. These polymers, which were generated at room temperature in high yields (93–98%), were defect-free. Moreover, they featured propynyl end groups, and had a degree of polymerization between 20–40, and a molecular weight (M_n) range of 15 000–35 000 Da.

5.08.5.5 Polyaniline

Polyanilines are an important class of organic conducting polymers, which were previously prepared via the chemical

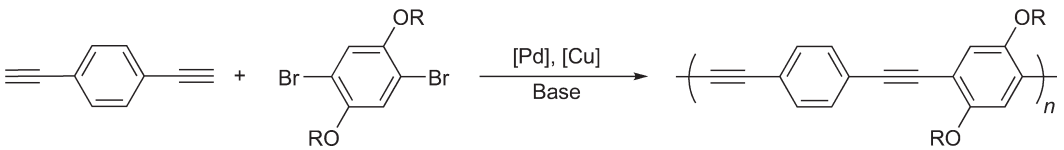

Figure 25 Synthesis of PPE via Sonogashira coupling.

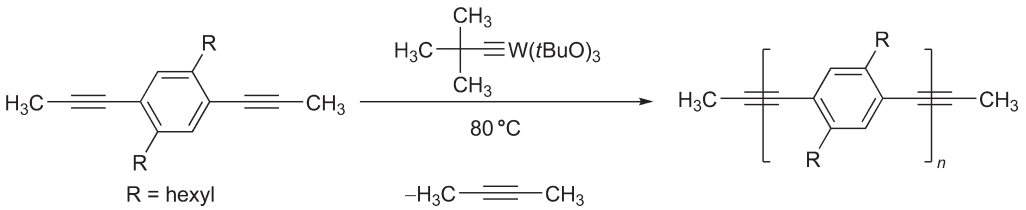

Figure 26 Synthesis of PPEs via ADIMET.

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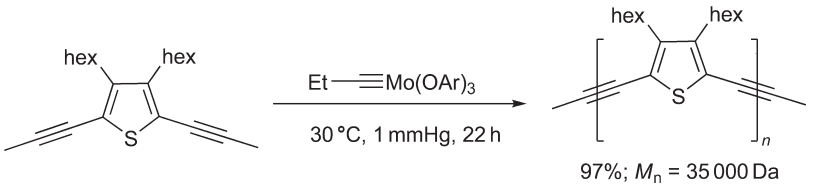

Figure 27 Synthesis of poly(3,4-dihexylthiophene) via ADIMET.

or electrochemical oxidation of aniline.[121] This approach yielded polymers that contained primarily *para* linkages but contained defects resulting from C–C coupling.[122] The Ullmann coupling reaction has been used for the preparation of poly(*m*-aniline),[123] although this approach gives material that contains insoluble fractions, which probably results from cross-linking.[124] The development of the palladium-catalyzed aryl amination reaction provided a new route to polyanilines that held the promise of gaining access to regioregular material, and after the recent discovery of this reaction, several groups spearheaded efforts in this direction.[125–127]

In their initial work on the application of this reaction to polymer synthesis, Kanbara *et al.*[125] prepared poly(imino-1,3-phenylene)s of moderate molecular weight (up to $M_n = 20\,100$ Da, $M_w = 42\,400$ Da) in good yield (**Figure 28**). Relatively optimal results were obtained with an *in situ*-generated Pd–BINAP catalyst (BINAP = 2,2′-bis (diphenylphosphino)-1,1′-binaphthyl). The reaction was performed in toluene with stoichiometric sodium *t*-butoxide as the base at 100 °C. Meyer and co-workers[127] independently reported the synthesis of poly(imino-1,3-phenylene)s using a similar protocol. They found that competing side reactions resulted in the formation of several minor polymer defects: (1) hydrodehalogenation resulted in endcapping, thus reducing molecular weight; (2) aryl transfer with the phosphine ligand resulted in the incorporation of the BINAP ligand and consequently phosphorus into the polymer chain; and (3) trisubstitution resulted in the formation of a cross-linked material.

Buchwald and co-workers[128] developed an improved protocol for obtaining high-molecular-weight polymer via the aryl amination reaction (**Figure 29**). To overcome the problem of *p*-bromoaniline being a poor substrate for the reaction, a boc-protected monomer (boc = *tert*-butoxycarbonyl) was employed. A catalyst was generated *in situ* from $Pd_2(dba)_3$ and the bulky phosphine ligand 2-(di-*tert*-butylphosphino) biphenyl. Optimal results were obtained by performing the reaction at room temperature for 24 h, which afforded a high-molecular-weight boc-protected polyaniline ($M_n = 39\,500$ Da). Thermolysis was then used to deprotect the polymer to afford polyaniline. While isolation under an inert atmosphere yielded the leucoemeraldine base, exposure to air gave the emeraldine base and afforded the emeraldine salt upon exposure to acid.

Polymeric triarylamines have generated interest due to their electronic properties, which are similar to those of the analogous polyanilines (**Figure 30**).[129] Triarylamines can undergo oxidation to give stable radical cations, which makes these materials promising for use as hole transport layers in light-emitting diode (LED) applications. It was envisioned that polymeric triarylamines would have the combined electronic properties of small molecule triaryl amines and the good material properties of a high-molecular-weight polymer. The reaction conditions were optimized to prevent the side reactions, such as ligand arylation, aryl bromide hydrodehalogenation, and exchange of phosphine aryl groups with the aryl bromide. To overcome these problems, a variety of phosphine ligands were screened, and it was found that tri(*t*-butyl)phosphine and tris(*o*-methoxymethylphenyl)phosphine afforded high conversion to defect-free high-molecular-weight polymer

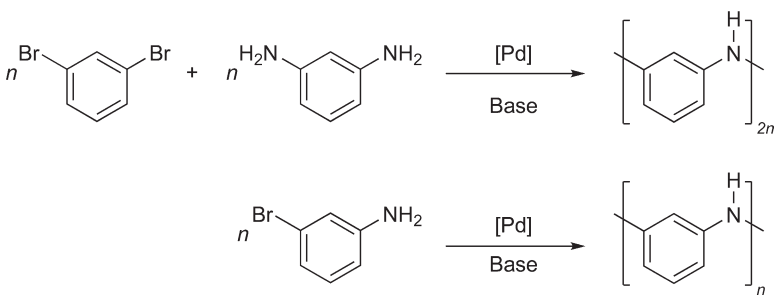

Figure 28 Two approaches to polyaniline via aryl amination: AA/BB monomers (top); and AB monomer (bottom).

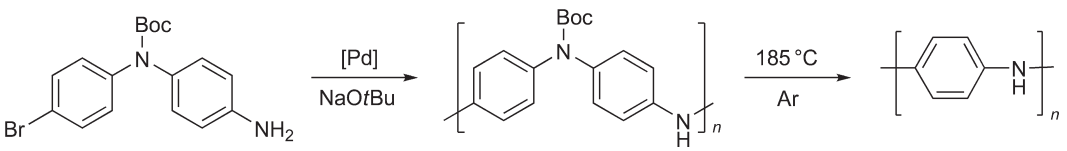

Figure 29 An approach to synthesizing high-molecular-weight polyaniline.

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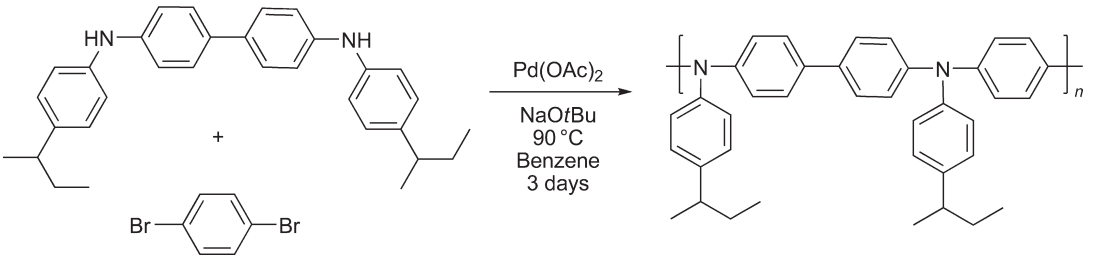

Figure 30 Synthesis of poly(triarylamine)s.

($M_w = 10^5$ Da). Meerholz and co-workers[130] applied the aryl amination reaction to the development of cross-linkable triarylamine-based polymers for use as hole-conducting layers for OLEDs. While the polymers were obtained in high yield (78–85%), they were of low molecular weight (7390–9370 Da) representing degree of polymerization values of approximately 12; regardless, the materials were successfully employed as hole transport layers in OLEDs.

5.08.6 Conclusion

The number of metal-catalyzed coupling reactions applied to the synthesis of condensation polymers have come a long way since their inception in 1977. A broad range of new polymeric materials (e.g., regioregular polyanilines, polythiophenes, polypyridines, and functionalized PPPs, PPVs, and PPEs) with well-defined structures that were inaccessible a few decades ago are now routinely prepared using transition metal-catalyzed reactions. Many of these materials exhibit useful electronic properties and serve as the basis for growing industries. However, despite the tremendous amount of work that has been done in this area, many significant challenges remain. For example, there is still a great need for catalysts that operate under milder conditions, tolerate more sensitive functional groups, and facilitate the preparation of higher molecular weight material. However, looking back at the history of this field, it is clear that its future hinges on the development of new metal-mediated bond formation reactions, as such discoveries are likely to enable access to unprecedented classes of condensation polymers.

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5.09 Advances in Acyclic Diene Metathesis Polymerization

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5.09.1 Introduction

5.09.1.1 Acyclic Diene Metathesis: Metathesis Polycondensation Chemistry

Acyclic diene metathesis (ADMET) polymerization is the step growth polycondensation reaction of a linear diolefin (Figure 1), which provides an efficient route to polyolefins with precise distribution of an exactly defined functional group, either within or pendant to the polymer backbone.[1–4] The mechanism of this polymerization (Figure 1) begins with a single turnover of the olefin metathesis catalyst, which eliminates a small molecule condensate to yield an active metal alkylidene and begin the catalytic cycle. The catalytic cycle continues with the addition of a second diene monomer to form a dimer and release an active metal methylidene. This species then reacts with another diene of any size (monomer, dimer, trimer, etc.) releasing ethylene to reform the active metal alkylidene and restart the catalytic cycle. Like all step growth polymerizations, ADMET is an equilibrium that is driven to completion by the removal of the condensate (ethylene in this case) and requires conversions greater than 99% for the formation of high-molecular-weight polymer. Being a gas at room temperature and atmospheric pressure, ethylene is easily removed using mild conditions (i.e., gentle heating and reduced pressure). This reaction has been used to create a vast library of functionalized materials, including most recently amino acid-functionalized polymers,[5,6] silicon-containing elastomers,[7–11] supramolecular graft copolymers,[12] metal-containing polymers,[13–20] sequenced copolymers of ethylene and vinyl comonomers,[21–39] *p*-conjugated polymers,[40–43] hyperbranched polymers,[44,45] liquid crystalline polymers,[46] nanoparticles,[47] mechanically interlocked daisy chains,[48] templated macrocycle synthesis,[49] and even artificial muscle mimics.[50]

5.09.1.2 The Evolution of ADMET

By the mid-1980s, considerable advancements had been made in the field of olefin metathesis chemistry.[51] This mild carbon bond-forming reaction was discovered by accident in the late 1960s when researchers at Goodyear exposed a mixture of α-olefins to a combination of tungsten hexachloride and a Lewis acid with the intent to find a new catalyst for the polymerization of vinyl olefins.[52,53] Instead of high polymer, the

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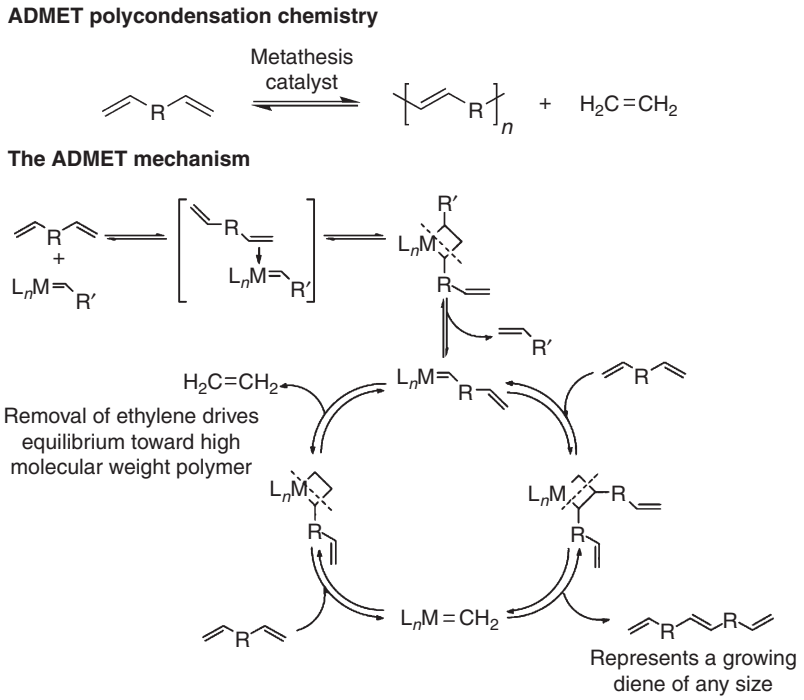

Figure 1 ADMET chemistry and mechanism.

research team observed a complex mixture of scrambled olefin products. The mechanism of this reaction, first proposed by Chauvin[54] in 1971 and later confirmed by Katz[55] in 1975, involves the 2+2 cycloaddition of an olefin to a metal carbene to form a metallocyclobutane, followed by a 2+2 cycloreversion to yield a new olefin and metal carbene. A majority of the research in the years to follow involved the development of stable metal carbenes that could facilitate this useful transformation, which has become an indispensable tool to the synthetic organic chemist.[51,56]

This reaction was used from its inception in the synthesis of polymers. Despite the lack of well-defined catalyst systems, a large volume of work had been produced by the mid-1980s on the ring-opening polymerization of strained cyclic olefins.[56] This reaction, coined ring-opening metathesis polymerization (ROMP), has become one of the most useful methods in the fabrication of functionalized polymers for use in every imaginable application. Although it was proposed early on that this reaction could also be used in the polycondensation of a linear diolefin, it was not until 1987 when the first study proving the feasibility of this concept appeared.[57] In this report, the Wagener group at the University of Florida attempted the polymerization of 1,9-decadiene using an ill-defined tungsten hexachloride/Lewis acid mixture, resulting in viscous oil and an intractable solid. Monitoring the disappearance of terminal olefin signal via ^{13}C-nuclear magnetic resonance (NMR) and infrared (IR) spectroscopy confirmed that the polymerization had occurred. Since any polycondensation requires that the reaction involved proceeds quantitatively, the self-metathesis of styrene to stilbene was attempted as a test reaction. The isolated product in this case was polystyrene (PS), rather than stilbene, due to the cationic polymerization of styrene initiated by the Lewis acid present in the ill-defined catalyst system. The authors were quick to realize that while the concept was feasible, a well-defined metal carbene catalyst would be necessary to prevent this detrimental side reaction.[57]

Fortunately, excellent progress was made in catalyst design at this time. By utilizing well-defined metal carbene catalysts developed independently by the Grubbs and Schrock groups, researchers in the Wagener group successfully synthesized stilbene from styrene in quantitative yields and reported the first viable ADMET of 1,9-decadiene to polyoctenamer.[58]

It was obvious even in the initial ADMET report that this reaction could have utility in the fabrication of unique structures.[57,58] Virtually, any compound that can be functionalized with two olefins could potentially become an ADMET monomer. Not surprisingly, early efforts in this area involved the synthesis of a wide variety of functionalized polymers using this chemistry. As metathesis catalysts became increasingly robust and tolerant of functional groups, the number of moieties that could be used in this reaction increased and the library of ADMET polymers grew considerably. Several recent review articles cover this topic.[1–4]

5.09.2 Functional Polymers and Materials via ADMET

5.09.2.1 'Latent Reactive' Polycarbosilane and Polycarbosiloxane Elastomers

Silicon-containing organic copolymers, that is, polycarbosilanes and polycarbosiloxanes, are a useful class of materials due to their improved mechanical response relative to purely silicon-based polymers, high thermal and oxidative stability, electrical resistance, antiadhesive properties, and so on.[7,9–11] Traditionally, synthesis of such materials is not trivial. ADMET however provides a convenient means to produce both polycarbosilanes and polycarbodisiloxanes efficiently via the polymerization of a carbosilane of carbosiloxane-containing

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diene (both readily accessible synthetically). Recently, 'latent reactive' copolymers of carbosilane and oligo(ethylene oxide) were prepared[7] and tested to evaluate the effect of polyether incorporation on the properties of the resultant materials, the end goal being development of a high-performance elastomer. The latent reactivity, installed via chain-end or chain-internal dimethoxy silyl moieties, is inert to the mild ADMET polymerization conditions, however, it is susceptible to cross-linking when exposed to moisture. Cross-linking in this fashion produces thermoset materials with improved strength over the uncross-linked counterparts.

The synthesis of these copolymers is shown to be rather straightforward. By simply altering the number of polyether repeating units, static ethylene run lengths, cross-linking density, and the incorporation of chain-end cross-links, the characteristics of the material can be tuned over a wide range of responses. This chapter highlights the effectiveness and efficiency of ADMET in fabricating polymers with fine-tuned properties, as the modifications are accomplished facilely by varying the ratios of a small number of easily prepared monomers. The morphology of polymers reported ranges from semicrystalline to completely amorphous with melting temperatures ranging from −35 to 57 °C and glass transition temperatures ranging from −79 to −50 °C. The properties of these materials range from purely elastic to flexible plastics; some materials in this series show elongations up to 700% and tensile strengths up to 10 MPa.

In an extension of this work, the authors also examined the use of thermally activated, latent, reactive chain ends[11] as well as chain-end/chain-internally cross-linked polycarbosilane and polycarbosiloxanes lacking the polyether soft phase.[10] These methods proved successful, however without significant improvement in properties over the previous examples.

5.09.2.2 Conjugated Polymers via ADMET

Conjugated polymers remain prime candidates for use as semiconductors in the emergent field of organic electronics.[40–43] Such materials are typically synthesized via polycondensation reactions using various aryl cross-coupling reactions. These methods are subject to problems that relate to, for example, the elimination of precursor functional groups. The polymers produced from these methods often contain defects and unwanted branching, which can have deleterious effects on the conductive properties of the resultant material.

Given that ADMET produces linear, defect-free polymers with high *trans*-olefin content, it is only logical that this method would have utility in the fabrication of *p*-conjugated materials. As it turns out, issues with catalyst stability, removal of ethylene, and polymer solubility complicate this matter; prior to 2005, only a few reports of *p*-conjugated polymers synthesized via ADMET exist.[1] The materials reported therein suffered from low molecular weights and less than ideal physical properties.

The advent of more robust metathesis catalyst, however, recently permitted the synthesis of well-defined, high-molecular-weight poly(arylene vinylenes) using a clever approach. While typical ADMET polymerizations are conducted in the bulk under high vacuum, Weychardt and Plenio[43] reasoned that by running the ADMET polymerization of such monomers in high-boiling organic solvents, the previously discussed impediments to high polymer could be circumvented. In this report, several defect-free poly(arylene vinylenes), poly(vinyl ferrocenes), and copolymers thereof were reported with excellent relative molecular weights (above 100 000 in some cases). This methodology was subsequently applied to a series of poly(*N*-alkyl carbozole vinylenes) and related poly(alkyl fluorenes) by Yamamoto *et al.*[41] The defect-free materials described in this report likewise possess high molecular weights and superb photophysical properties.

More recently, Qin and Hillmyer[40] used similar methodology to produce well-defined poly(3-hexylthiophene vinylene), a material attractive due to its stability, high conductivity on doping, and low bandgap. The synthesis of this material via ADMET had been attempted previously;[40] however, the instability of the requisite 2,5-divinyl-3-hexylthiophene monomer precluded these efforts. By synthesizing 2,5-dipropenyl-3-hexylthiophene, these stability issues could be resolved. The condensate produced during the ADMET of this monomer, 2-butene, is much less volatile than ethylene; hence, polymerization of this monomer in the bulk proved difficult. Polymerization in a high-boiling solvent at reflux facilitated the removal of 2-butene, albeit with reduced low molecule weights, which the authors attributed to rapid catalyst death due to elevated temperature. Despite the low molecular weights, these well-defined poly(3-hexylthiophene vinylenes) exhibited properties in agreement with other examples in the literature.

The synthesis of poly(phenylene vinylene) (PPV) nanoparticles using ADMET has also been reported.[47] Here, the authors utilized an aqueous emulsion polymerization. Particle sizes ranging from 200 to 300 nm were observed. The molecular weights of the PPVs in this case are rather low, on the order of 1 kDa. This has been attributed to slow reaction times, rather than sensitivity of the catalyst species to aqueous conditions. Despite having low molecular weights, these polymers show absorption and photoluminescence data consistent with previously reported PPVs. Examples of conjugated polymers synthesized via ADMET are shown in **Figure 2**.

5.09.3 Exotic Polymer Structures

5.09.3.1 Hyperbranched Architectures via ADMET

Hyperbranched polymers,[44,45] highly branched polymers with a globular structure, feature many of the appealing properties of dendrimers without the tedious synthesis: high solubility, low solution viscosity, and high end-group concentration to name a few. These materials are typically synthesized in one pot using $AB_{n\geq 2}$ functional monomers. These monomers are designed such that A and B functionalities react with one another but not with themselves. Recently a clever strategy (shown in **Figure 3**) to hyperbranched polymers via ADMET has been developed.[45] By using a terminal alkene as the A functionality and an acrylate as the B moiety, the authors were able to demonstrate the feasibility of this approach: the electron-poor acrylic olefin will not homometathesize but will metathesize with the terminal alkenes or their dimers. In a follow-up report,[44] the authors demonstrated that the acrylate end-groups at the periphery of the hyperbranched polymer could be readily functionalized via cross-metathesis with a

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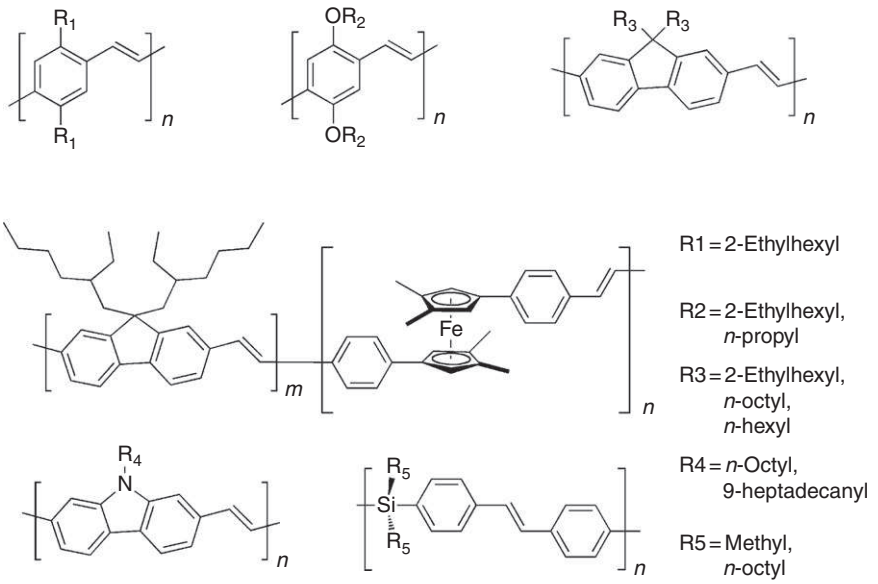

Figure 2 Examples of conjugated polymer structures accessible using ADMET.

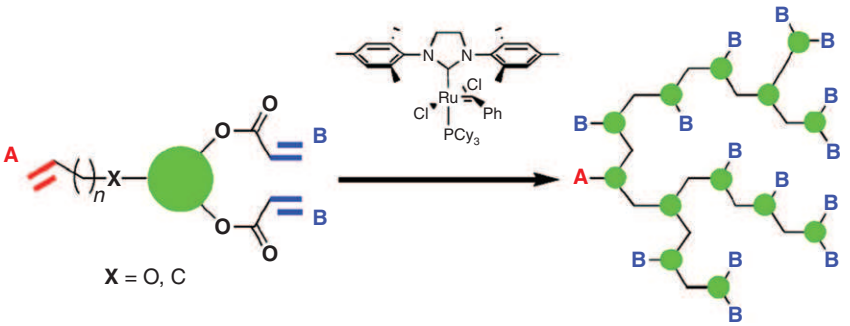

Figure 3 ADMET synthesis of hyperbranched polymer architectures. Reprinted from Gorodetskaya, I. A.; Choi, T. -L.; Grubbs, R. H. *J. Am. Chem. Soc.* **2007**, *129*, 12672,[45] with permission.

terminal alkene and intimate drug delivery as a likely application for this chemistry.

5.09.3.2 Supramolecular Graft Copolymers

Supramolecular polymers[59,60] make use of directional and reversible secondary interactions between monomers to yield materials that display bulk properties like conventional covalent polymers. This subject has been explored in depth for a wide variety of both secondary interactions and monomer motifs. ADMET, again chosen for its ability to produce defect-free linear polymers, was recently employed[12] in an interesting spin on the traditional work in this area: supramolecular graft copolymers. To create this exotic material, the authors synthesized a diene containing 2,7-diamido-1,8-naphthyridine, a donor–acceptor–acceptor–donor quadruple hydrogen bonding array. After polymerization of this monomer, supramolecular grafting with a linear polymer end functionalized with the complimentary 2-ureido-4-pyrimidinone acceptor–donor–donor–acceptor quadruple hydrogen bonding array affords the final structure. In order to prevent unwanted interaction between the 2,7-diamido-1,8-naphthyridine within the diene and the metathesis catalyst, a supramolecular protecting group was required to permit high molecular weights. The authors demonstrated the dynamic nature of the supramolecular grafting and reasoned that this chemistry could be adapted for reversible immobilizations in solution-phase combinatorial chemistry.

5.09.3.3 'Daisy Chain' Polymers

Mechanically interlocked polymers (referred to as 'daisy chains') remain an elusive target synthetically.[48] These rotaxane-based macromolecules, which feature host/guest sites, covalently bound in a single molecule garner interest for their unique solid-state and solution properties, as well as the synthetic challenge involved in their fabrication. In a recent report,[48] ADMET was adopted to polymerize a mechanically interlocked monomer to afford a daisy chain polymer (Figure 4). The synthesis was accomplished using ring-closing metathesis to create the mechanically interlocked daisy chain premonomer. This structure was then functionalized with terminal olefins and polymerized. In this case, ADMET was chosen for the mild reaction conditions and functional group

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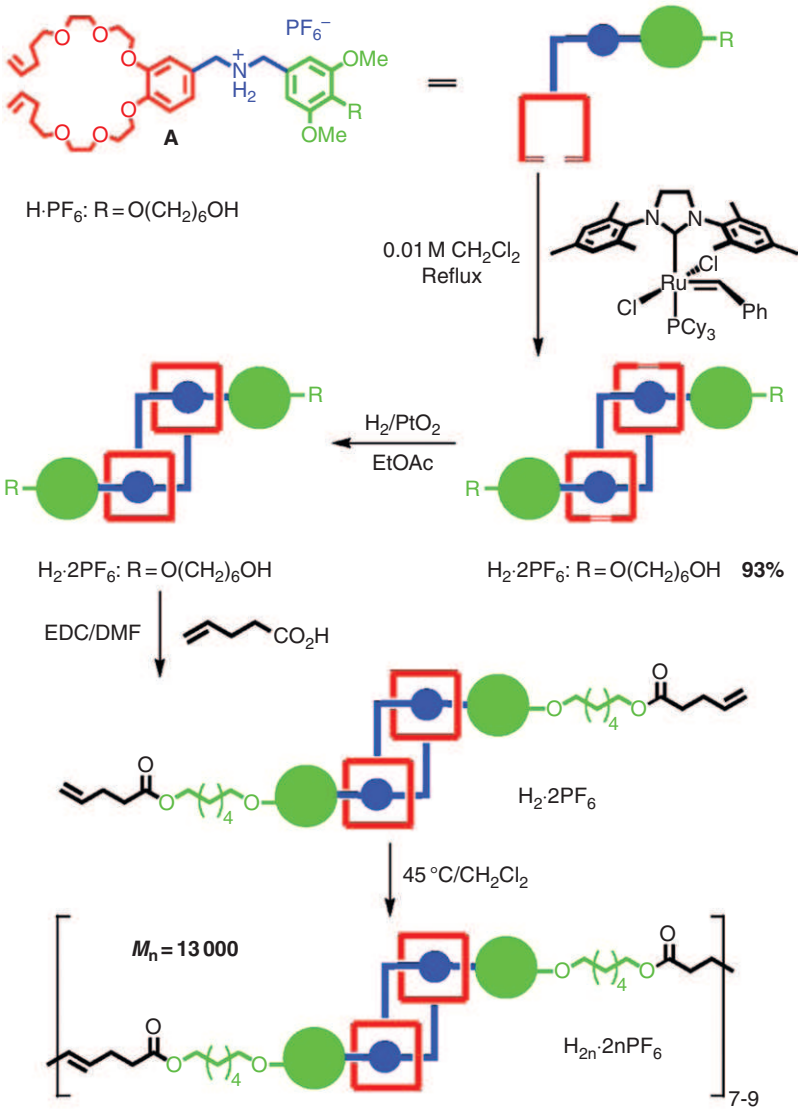

Figure 4 ADMET synthesis of 'daisy chain' polymers. Reprinted from Guidry, E. N.; Li, J.; Stoddart, J. F.; Grubbs, R. H. *J. Am. Chem. Soc.* **2007**, *129*, 8944,[48] with permission.

tolerance of ruthenium metathesis catalyst. This report highlights the utility of the many forms of olefin metathesis in the fabrication of complex structures that were previously synthetically unobtainable.

5.09.4 Precision Polyolefins

Polyolefins, and in particular polyethylene (PE), represent the largest production volume material in the world.[61] This is due in large part to its wide range of material responses, structural simplicity, and ease of production. Because of this, PE, its copolymers, and its many end-use products have made their way into every facet of daily life. The range of properties available in polyolefins is staggering. Simply altering comonomer identity, concentration, and distribution can change the morphology of a material from completely amorphous to highly crystalline and thus change the properties from a low-melting rubber to a high-impact-strength engineering material.[2]

Chain propagation chemistry is generally used to produce these materials, during which undesirable chain transfer or chain-walking side reactions incorporate small fractions of structural imperfections, like undesired branches, into the polymer microstructure. These irrepressible side reactions lead to random distribution of defects throughout almost every chain polymerization, leading to imperfect microstructure for many industrial materials. Furthermore, mismatches in reactivity ratios between comonomers can result in poor levels of incorporation coupled with poor control over comonomer distribution, which makes characterization of primary structure tedious and complicates the interpretation of structure/property relationships. Modeling unwanted branching and the effects of comonomer distribution is a topic of great interest since branch and comonomer content, distribution, and identity ultimately determine the material properties of the final

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polymer. The variability of these features results in the myriad of properties polyolefins exhibit in many end-use products. While many polymer-modeling studies have been conducted on materials made by chain propagation chemistries, to accurately study the effects of these structural attributes, model polymers of known chemical microstructure and no unwanted branching are necessary.[61]

Step growth polycondensation chemistry is not subject to the inherent side reactions and random comonomer incorporation associated with chain propagation mechanisms; these materials are perfectly linear and possess pristine microstructures that mirror the structure of the monomers used during polymerization. ADMET offers a unique method to create perfectly linear, defect-free model polyolefins in precisely this fashion. The 'comonomer' content and distribution is perfectly controlled *a priori* by controlling the monomer structure. Polymerization of a symmetric diene containing a pendant functional group (in essence, mimicking an oligomer of ethylene and a vinyl comonomer), followed by exhaustive saturation of the resulting unsaturated backbone, results in polyolefins with some exactly known functionality at perfectly regular intervals along a linear polymer backbone that contains no structural defects or irregularities (**Figure 5**). This is the meaning of 'precision polyolefins'.

Precisely knowing the identity, content, and distribution of a pendant functional group allows for specific structural features to be isolated in polyolefins and their effects on material behavior and property to be precisely understood. This chapter describes this intensive investigation of structure and property by examining several separate studies on precision polyolefins and presenting the results in a systematic fashion. Beginning with perfectly linear defect-free PE, we show that even though these materials are not made the same way as the commercial materials they model, their behaviors are nonetheless identical. We then discuss the effects of introducing regularly spaced defects, systematically increasing in size and bulk, to fully understand the role of pendant functional group size and placement on the behavior of these materials. We delineate the requirements for a pendant group's inclusion or exclusion from the polymer unit cell. We address the roll interactions between these pendant groups and the properties these materials possess, and demonstrate how this knowledge can be used to impart specific properties in a highly controllable fashion using a simple concept: precise structure manifests in precise properties.

For simplicity of discussion, the polymers described in this section will follow a systematic nomenclature based on the identity and distribution of the pendant functional group they contain. The name (or abbreviation) of this pendant group is named first, followed by a number corresponding to how often it regularly appears along the polymer backbone. For example, Br21 would correspond to PE with a bromine atom appearing on every 21st backbone carbon, $COOH_9$ indicates a carboxylic acid group on every ninth backbone carbon, and so on.

5.09.5 Meeting the Benchmark: Linear Acyclic Diene Metathesis Polyethylene

Unbranched or perfectly linear PE is of considerable interest, particularly for studying the behavior of this homopolymer during crystallization. Much of this work has been conducted on large *n*-paraffins (monodisperse PE oligomers) up to 390

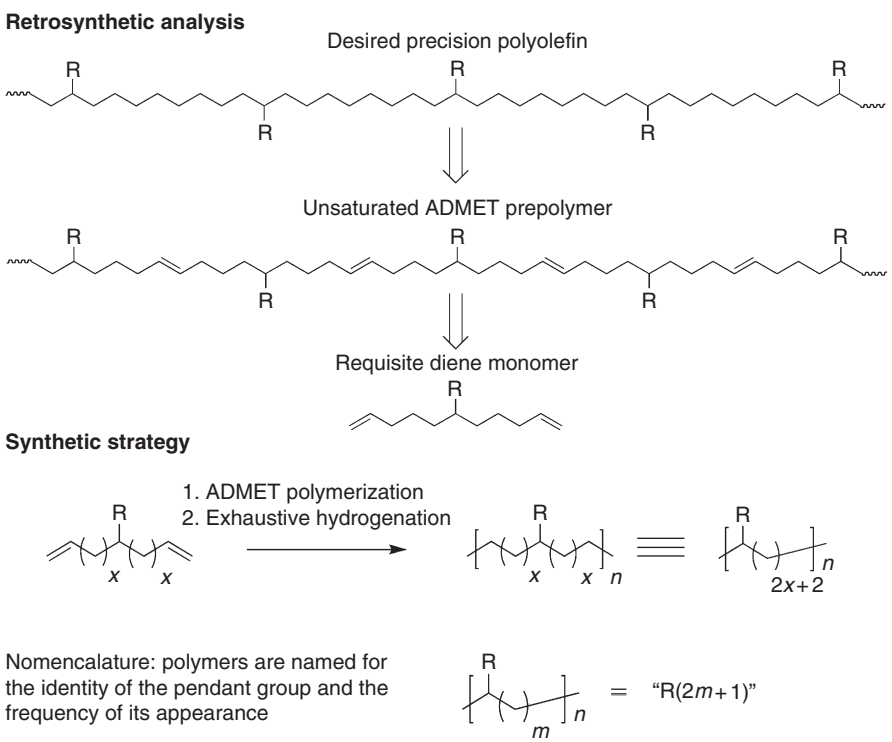

Figure 5 Well-defined polyolefins via ADMET polymerization followed by exhaustive hydrogenation.

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carbons long,[62] since defect-free, high-molecular-weight PE is an elusive goal. While small molecule paraffin compounds allow in-depth study of structurally perfect model materials,[62,63] end-group concentration becomes a problem and leads to irregularities when trying to extrapolate morphological behavior to a macromolecular system. The methyl end-groups present in *n*-paraffins are regarded as defects that hinder crystallization. Polymer chains up to millions of grams per mole, on the other hand, possess an infinitesimal number of methyl end-groups relative to backbone carbons, thus comparisons between these two systems can lead to ambiguous results.[61] The synthesis of perfectly linear, defect-free PE via ADMET is therefore a choice model system for studying the behavior of high-density polyethylene (HDPE).[64] One possible drawback in this reasoning is the staggering differences in molecular weight between these step growth models and the commercial materials. Commercial PE samples can have molecular weights in the millions, orders of magnitude higher than those of polymers made using metathesis polycondensation chemistry. To prove these ADMET polymers can truly measure up, a family of linear PE with various molecular weights was synthesized to find the molecular weight required in these materials to meet the benchmark melting temperature possessed by HDPE: 134 °C.

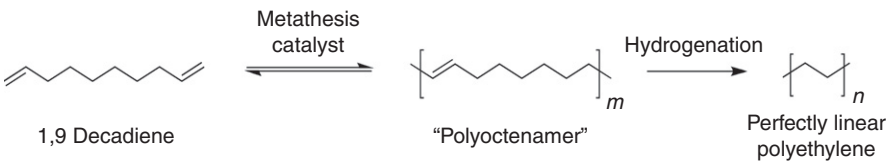
Perfectly linear ADMET PE (**Figure 6**) is easily prepared via the polymerization of 1,9-decadiene, followed by saturation of the product polyoctenamer with hydrogen. Molecular weights of products can be controlled by regulating reaction time, temperature, and the monomer/catalyst ratio, affording a family of ADMET PE polymers with varied thermal responses. All the samples exhibit thermal behavior similar to that of HDPE; despite the relatively low molecular weights (between 2000 and 15 000 g mol^{-1}), these polymers all display sharp differential scanning calorimetry (DSC) melting transitions above 130 °C. While the peak melting points increase slightly with increasing molecular weight, the polymer of $M_n = 15\,000$ shows a peak melt of 134 °C, exactly that of HDPE. It is evident based on this work that beyond the molecular weight threshold of roughly $M_n = 15\,000$, ADMET polymers can effectively model analogous materials of higher molecular weight made via chain propagation chemistry.[64]

5.09.6 Precision Halogenated Polyolefins

ADMET polyolefins with precisely placed halogen atoms provide an excellent system for studying crystallization and melting behavior of precision polyolefins. By synthesizing polymers decorated with fluorine, chlorine, and bromine, the effect of this systematic increase in pendant defect size can be probed. Four separate studies[28–31] were conducted on this class of precision polyolefins. In the first, the static methylene sequence length between defects was held constant (18 backbone carbons) and the defect identity altered.[31] In the other three, the defect identity was held constant (fluorine, chlorine, or bromine) and the distance between defects altered.[28–30] In the first study, it was found, not surprisingly, that with the increased defect size came a decrease in melting temperature and enthalpy.[31] When the defect identity was held constant, melting temperature and enthalpy decreased with decreasing distance between defects,[28,29] the notable exception being the fluorine-containing polymers all of which have approximately the same melting temperature despite differences in defect distribution.[30]

5.09.6.1 Synthesis of Precision Halogenated Polyolefins

The synthesis of the precision halogenated polyolefins is relatively straightforward.[31] Regardless of the identity of the halogen atom being incorporated, synthesis begins with the preparation of a secondary diene alcohol via a double Grignard reaction using an alkenyl bromide and ethyl formate. The halogen distribution in the final polymer is controlled by the size of the alkenyl bromide used in the Grignard reaction. This alcohol is converted to the desired halogen atom following simple transformations. In the case of the fluorine- and bromine-containing polymers, a single reaction is required: diethylaminosulfur trifluoride and catalytic pyridine for the fluorine-containing polymers or carbon tetrabromide and triphenylphosphine for the bromine-containing polymers. The chlorine-containing monomers are synthesized in two steps from the diene alcohol: tosylation of the alcohol followed by nucleophilic substitution using lithium chloride. Polymerization of these monomers via first-generation



DSC data for linear ADMET polyethylenes

M_n	T_m (°C) (peak)	Δh_m (J g^{-1})
2400	130.7	252
7600	131.3	213
11 000	132.0	221
15 000	133.9*	204

*Melting temperature of commercial PE = 134 °C

Figure 6 Synthesis and behavior of linear ADMET PE. Beyond a molecular weight threshold of $M_n = 15$ kg mol^{-1}, ADMET of PE exhibits thermal behavior analogous to that of commercial HDPE.

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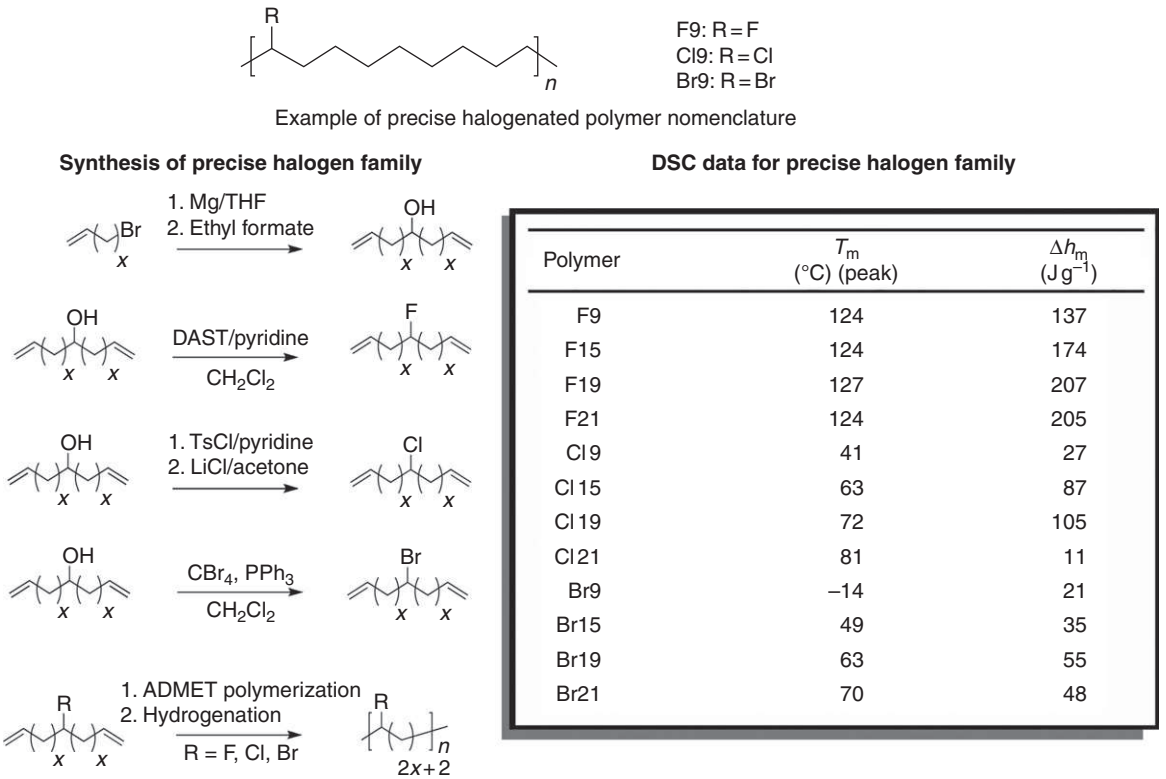

Polymer	T_m (°C) (peak)	Δh_m (J g^{-1})
F9	124	137
F15	124	174
F19	127	207
F21	124	205
Cl9	41	27
Cl15	63	87
Cl19	72	105
Cl21	81	11
Br9	–14	21
Br15	49	35
Br19	63	55
Br21	70	48

Figure 7 Synthesis and properties of precision halogenated polyolefins (for nomenclature, see **Figure 5**).

Grubb's catalyst, followed by exhaustive hydrogenation using toluene sulfonyl hydrazide, affords the final precision halogenated polyolefins. Careful NMR characterization confirmed the precise nature of the structures. The precise composition of these polymers in terms of halogen incorporation was confirmed via thermogravimetric analysis by monitoring the loss of HF, HCl, or HBr during the decomposition of the sample. In all cases, the experimental results perfectly match the theoretically predicted values. **Figure 7** outlines the synthetic route to precision halogenated polyolefins and their thermal behavior (discussed below).

5.09.6.2 Behavior of Precision Halogenated Polyolefins

Precise fluorine placement. Regardless of branch distribution, the melting temperatures of ADMET polymers containing precisely placed fluorine atoms are consistent with what is witnessed for linear ADMET PE, evidencing that the orthorhombic crystal structure of HDPE is not significantly affected by the addition of the fluorine atom.[30] Wide-angle X-ray scattering (WAXS) measurements confirm this; only small shifts in the reflections for the orthorhombic unit cell are witnessed, indicating only a minor lattice expansion due to fluorine incorporation. This is not surprising; considering the similarity in size between hydrogen and fluorine, the steric requirements for housing this defect in the crystal should not be significantly different. The melting enthalpy of this family of copolymers does however decrease with increasing fluorine content. This is much more significant in the cases of F15 and F9 than in the cases of F19 and F21. The decrease in enthalpy for the higher defect concentrations is evidence that electronic repulsions and bond polarity, as well as sterics, play an important role in the crystallization behavior for precision polyolefins.[30,31] Polymers containing the same fluorine content, however with a random rather than precise distribution, are not expected to show behavior significantly different from the precision versions.[65] However, a slightly higher melting temperature was witnessed for these random copolymers, hinting at a different crystallization mechanism in which long methylene sequences without fluorine atoms are able to crystallize first, creating populations of crystallites less affected by fluorine incorporation.

Precise chlorine placement. The consequences for the incorporation of chlorine atoms at precise intervals along PE's backbone are much more severe.[29] There is a marked decrease in melting temperature compared with both ADMET PE and the precise fluorine family. There is also a change in crystal structure, from orthorhombic to triclinic. Solid-state ^{13}C data show that the distribution of chlorine atoms in the crystalline and amorphous regions is uniform. Further, the lamellar thickness (estimated using atomic force microscopy (AFM)) far exceeds the distance between defects on the backbone. This confirms that the chlorine atoms are without a doubt included within the crystal. The steric requirements, however, are too severe for the orthorhombic crystal structure to remain intact. There is also a clear relationship between the distribution of chlorine atoms and the melting behavior. As the chlorine content increases, a decrease in melting temperature and enthalpy is witnessed. This is not surprising; although the chlorine atom is small enough to reside in a triclinic crystal, the ability of the polymer to crystallize becomes strained as higher amounts of defects become incorporated. In the case of Cl9, which has the

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highest amount of chlorine incorporation, a complex melting and recrystallization process is observed, highlighting the stress increased chlorine content imparts on the crystallization of this polymer. This behavior is solely a result of the uniform defect distribution, as random analogs with similar branch content possess slightly broadened melting profiles with higher peak melting temperatures.[65] This difference in behavior is easily explained by the difference in defect distribution between the random and precise samples. Long, chlorine-free ethylene sequences in the random samples crystallize first. This results in populations of lamella of various thicknesses, which manifest in the broadened melting behavior. This is quite unlike the sharp melting endotherm and homopolymer-like crystallization witnessed in the precise samples that possess uniform lamellar thickness.

Precise bromine placement. ADMET models with precise bromine placement represent the upper size limit for the study of halogen-containing polymers (iodine-containing samples proved too unstable for use in these studies). The increase in size in moving from a precisely spaced chlorine atom to a precisely spaced bromine atom results in a decrease in both melting temperature and melting enthalpy.[28] Like the precision chlorine polymers, a triclinic crystal structure was assigned for the bromine-containing polymers. Again, solid-state ^{13}C data confirmed that the distribution of the bromine atoms was uniform in both crystalline and amorphous regions like the chlorine polymers. Based on AFM measurements, as is the case for chlorine, the bromine atom must reside within the crystal. In this light, it is clear that the detrimental effects on thermal behavior here are a direct result of the increased steric requirements of the bromine atom, which more severely perturb the PE crystal than do the smaller chlorine atoms.

The difference in thermal behavior between the precision brominated polyolefins and their random counterparts is much more pronounced than in the previous chlorinated examples. Here, no sharp melting peak is witnessed for the random samples, rather a very broad ill-defined endotherm is observed.[65] As is the case with the random chlorinated samples, a sequence selection-type crystallization mechanism is in operation, resulting in a broad distribution of lamellar thicknesses. The precise versions, similar to the precise chlorine family, all possess sharp, well-defined melting peaks attributed again to uniform lamellar thickness. Perhaps the most interesting feature of the precision bromine polymers is their similarity in thermal response to ADMET polymers with precise methyl branch placement (discussed in the following section). This similarity is based on the similarity in size between a methyl group and a bromine atom. In conjunction with the data for the precision fluorinated polymers, that is, negligible relationship between fluorine content and behavior, it appears that defect steric requirements are perhaps the most important factor in dictating the crystallization and melting behavior of the resulting ADMET polymer crystal. Or more simply put, a defect is a defect, regardless of its identity.[28]

5.09.7 Precision Polyolefins with Alkyl Branches

For more than half a century, studies on structure and morphology have been central to polyolefin research.[61] Discoveries in this area have allowed for the synthesis of materials with wide range of properties and behaviors. This is exemplified particularly in the case of linear low-density PEs (LLDPEs), which are synthesized industrially by the copolymerization of ethylene and α-olefins. Here, the behavior of the polymer can be greatly altered by simply varying the content and the identity of the comonomer chosen. In typical industrial polymerizations, both interchain and intrachain structural heterogeneities exist, which in turn lead to a broad lamellar thickness distribution and result in decreased mechanical performance. The pristine polymers available via ADMET, free from intrachain and interchain heterogeneities, can serve the dual purpose of elucidating the effects of specific structural features and providing precise control over properties.

5.09.7.1 Synthesis of Precision Polyolefins with Alkyl Branches

Although relatively straightforward, the synthesis of the polymers used in modeling studies described here is rather tedious. This is in large part because the synthesis of symmetric alkyl-branched dienes requires several steps, often with dismal overall yields. In addition, a different synthetic scheme was necessary for each type of branch studied. The synthesis of these materials has been discussed in detail in a number of recent reviews.[1–4]

Recently, a new synthetic route (**Figure 8**) to symmetric alkyl-branched diene monomers has been presented and utilized in the synthesis of a whole family of precision alkyl-branched polyolefins.[66] This general route, which can be used to create dienes with virtually any branch, involves only two steps with quantitative yields. The first step is the dialkylation of a primary nitrile using freshly prepared lithium diisopropylamide (LDA). Alkylation in this fashion affords a symmetric diene premonomer with the desired alkyl branch and a nitrile group on the central carbon. In the next step, this nitrile is removed by reductive elimination in the presence of potassium metal, hexamethylphosphoramide (HMPA), and *t*-butanol. The mechanism of this reaction[67] proceeds first with the insertion of an electron from the metal surface into the nitrile forming a radical anion. The nitrile then cleaves, liberating a cyanide anion and leaving a tertiary radical on the diene monomer. The diene radical then quickly abstracts a proton from *t*-butanol, resulting in the final ADMET monomer. HMPA is present simply to help solvate the radical species.

The only drawback associated with this method, from a synthetic standpoint, is the inability to create monomers that space branches every ninth backbone carbon in the resulting polymer. This is because the rapid radical cyclization of the diene is favored at this particular spacing (five- and six-membered rings are formed). For dienes with longer spacing between the branch and the terminal olefin, this cyclization is not favored; however, olefin isomerization was observed when other decyanation conditions were employed. Although this method provides a high-yielding, efficient route to a variety of ADMET monomers, it does involve the use of highly toxic and carcinogenic reagents with an extremely reactive alkali metal in highly flammable solvents. Extreme caution is necessary when conducting such reactions, and small reaction scales should be employed to minimize personal risk.

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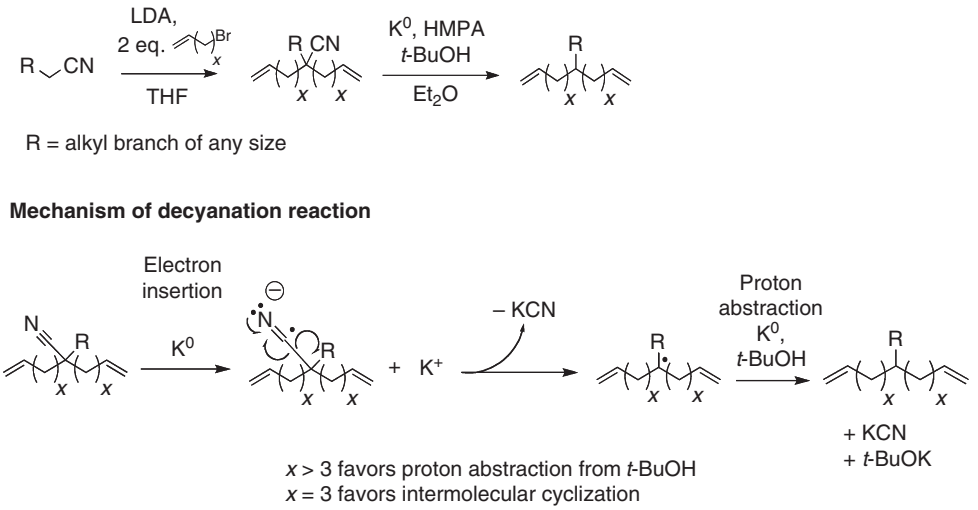

Figure 8 Two-step synthetic route to precision alkyl-branched monomers of any size.

5.09.7.2 Behavior of Precision Polyolefins with Alkyl Branches

Precise methyl placement. Besides being commercially significant, ethylene/propylene (EP) copolymers can provide a general insight into the structure–property relationship when viewed as model systems. Consider polypropylene: it is highly crystalline when the orientation of the pendant methyl group is highly regular (syndiotactic or isotactic); however, it is completely amorphous when backbone methyl groups are randomly oriented (atactic), a simple structural difference resulting in significantly altered behavior. Linear defect-free PE, the other extreme, is highly crystalline. However, this crystallinity can be disrupted by the incorporation of defects, clearly evident in the aforementioned halogen work. Between the extremes of amorphous atactic polypropylene and highly crystalline, defect-free PE lie EP copolymers. Simply varying the amount and placement of the incorporated methyl defect allows the response of the final material to be significantly altered and ultimately controlled.[2]

Although numerous methods are available for producing model polymeric systems, ADMET modeling controls comonomer content and distribution, therefore, leading to fewer ambiguities relative to other model systems when relating structure at the molecular level to macroscopic properties.[2,22,68,69] Polymerization of symmetrical, methyl-branched terminal dienes, followed by exhaustive saturation of the resultant polymer, affords these precise EP models.[69] To date, Me5, Me7, Me9, Me11, Me15, Me19, and Me21 have been investigated. The synthesis of Me9 through Me21 is rather straightforward using this simple yet elegant polymerization/hydrogenation approach.[69] Placing branches every fifth or seventh backbone carbon requires the synthesis of a symmetrical diene dimer, as the corresponding diene monomers undergo ring-closing metathesis rather than ADMET.[22] Attempts to place methyl groups every third backbone carbon, using a diene trimer, were unsuccessful due to the placement of the methyl group in the allylic position. This allylic methyl decreases the yield of the cross-metathesis reaction, allowing for only the partial oligomerization of the diene rather than polymerization.[70]

The effects of branch distribution are clear when examining the thermal behavior of the precision EP copolymer family.[69] As defect content increases, melting temperature and enthalpy decrease. These precise models are semicrystalline even at branch contents high enough to render random EP copolymers completely amorphous. Not until methyl groups are placed on every fifth carbon do these precise ADMET EP copolymers lose the ability to crystallize.[22] By precisely controlling the sequence of EP copolymers in this fashion, it is possible to control the melting temperature of PE over a range of $\sim 200\ ^{\circ}C$.

Copolymerization of ADMET EP monomers with 1,9-decadiene, thereby forming linear EP copolymers with random branch distribution, has also been accomplished.[68] In this study, it was again found that as the branch content increased, overall crystallinity as well as the melting temperatures and enthalpies decreased. In the cases of the highest amount of branch incorporation, the random materials exhibited a broad, ill-defined melting behavior in contrast to the sharp melting endotherm observed for the precise models with similar branch content. This drastic difference in the behavior between precise and random models punctuates the effect of precise branch placement.[68,69]

Me21 and Me15 have been further characterized by using X-ray diffraction, transmission electron microscopy (TEM), and Raman spectroscopy to further understand their structure and morphology.[71] TEM results indicate a lamellar thickness far exceeding the inter branch distance along the backbone, proving that like chlorine and bromine atoms, the methyl group must be included within the crystal. The diffraction work elucidated crystal structure: this data showed that the chains pack into a triclinic lattice, which allows inclusion of methyl branches as lattice defects. Further, it was found that methylene sequences between defects participate in a hexagonal sublattice. In order for the chains to pack in this way, the defects must be contained within plains oblique to the chain stems. This is more prevalent in the case of Me15 than in Me21 due to the greater defect content, a result confirmed by Raman spectroscopy. The melting point depression witnessed as methyl content increases is no surprise, given these observations. Further scattering experiments and exhaustive DSC

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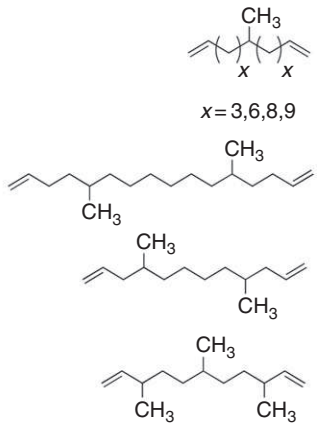

Diene monomers with $x \geq 3$ polymerize under ADMET conditions, monomers with $x < 3$ ring-close

Diene ADMET 'dimers' are required to place groups 5 or 7 backbone carbons apart

Allylic functional groups decrease the yield of the cross metathesis reaction, preventing the placement of groups 3 backbone carbons apart

DSC data for precise methyl family

Polymer	T_m (°C)	Δh_m ($J g^{-1}$)
Me5	Amorphous	–
Me7	–60	19
Me9	–14	28
Me11	11	66
Me15	39	82
Me19	57	96
Me21	63	103

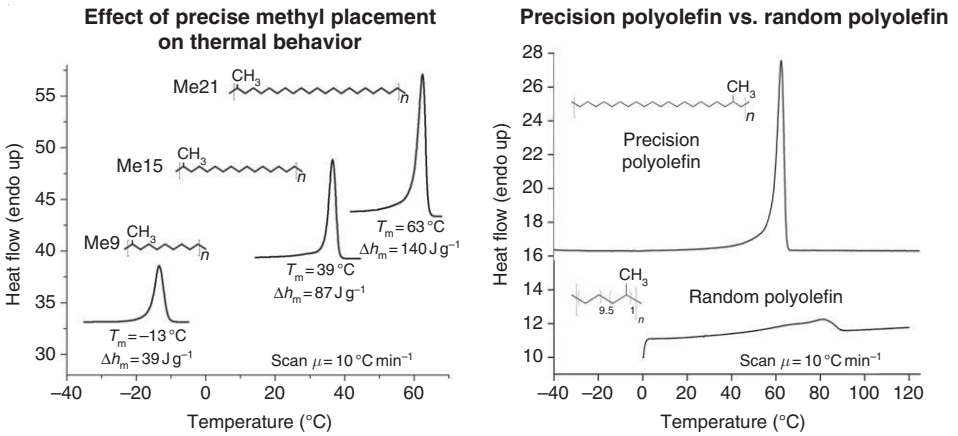

Figure 9 Diene monomers for ADMET polymerization to polyolefins with precise methyl branch placement and thermal properties of the resulting polymers.

experiments performed on Me21 lead to the same conclusion involving defects concentrated in planes between stacks of hexagonally packed methylene sequences; however, a monoclinic rather than triclinic lattice was used by the authors to describe the main unit cell within which the defect planes and hexagonal sublattice resides.[72,73] The effects of precise methyl branching are summarized in Figure 9.

Precise geminal dimethyl placement. Precision geminal dimethyl ADMET models display the effect increasing steric bulk has on the polymer's thermal behavior.[74] The addition of the second methyl group when moving from Me9 to 2Me9 disrupts the polymer's ability to pack into crystals, resulting in an amorphous material for 2Me9. Extending the interdefect sequence length to 14 or 20 carbons renders the polymer semicrystalline with a depressed melting temperature when compared to the analogous EP models. Interestingly, 2Me15 shows much less melting point depression from Me15 than does 2Me21 from Me21. Further, 2Me21 shows thermal behavior unlike either 2Me15 or any of the EP family. Exhaustive DSC studies on this material reveal that much of this behavior is dependent on thermal history. WAXS studies show reflections associated with hexagonal, monoclinic, and triclinic packing, pointing toward polymorphism as a possible cause of this complex behavior. The melting temperature in this instance is incident with that of eicosane (a 20-carbon *n*-paraffin), implying that crystallization behavior of 2Me21 is

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strongly related to the branch-to-branch distance. It has been suggested that placing two methyl branches on the chain in this fashion creates a favorable place to induce a fold in the chain stem, resulting in the similarity between the melting point of this polymer and that of eicosane.[73]

Precise ethyl branch placement. Ethylene/butene (EB) copolymers featuring precisely placed ethyl branches was the next logical step in this study, moving from two single-carbon defects to a single two-carbon defect.[75] These are of particular interest as EB copolymers are important materials commercially. Like 2Me9, Et9 is fully amorphous. Again, extending the space between defects allows for crystallization in both Et15 and Et21. Like the geminal dimethyl models, the EB models show greatly depressed melting temperatures when compared to the EP models. Another point of interest is the difference in the observed thermal behavior from both the geminal dimethyl family and the EP family. Et21 and Et15 exhibit bimodal melting profiles very much unlike the sharp, uniform melt exhibited by the EP family.[75]

WAXS investigations,[75] as well as exhaustive DSC analysis,[73] have helped in explaining this behavior. Like 2Me21, the melting behavior of Et21 can be correlated with that of eicosane and is therefore very much dependent on the branch-to-branch distance. The WAXS results show some lattice expansion, implying the partial inclusion of ethyl groups into the crystal, however to a lesser extent than in EP21. Comparing these results for 2Me21 and Et21 implies that much of the melting behavior is attributed to crystallization of methylene sequences between defects. The bimodal melt could therefore be a result of polymorphism involving the inclusion and exclusion of these defects, or a melting and simultaneous crystallization mechanism.

A second study on the morphology of Et21 using WAXS, small-angle X-ray scattering (SAXS), DSC, and TEM has further helped in understanding the behavior of this system.[76] The data collected using this variety of techniques indicated the formation of lamella of uniform thickness for this polymer. The measured thickness of the lamella, about 55 Å, is approximately double the distance between branches along the backbone, indicating on average that about one ethyl branch will be included in the lamella stem. In this case, scattering experiments point toward a pseudohexagonal unit cell for this polymer. The unusual melting behavior witnessed, then, is likely due to crystal forms that both partially include and exclude this branch. Samples of EB copolymers made using chain propagation techniques with similar branch content displayed a much broader distribution of lamellar thicknesses, again highlighting the ability of precise defect placement to create materials with precise morphology.

Precise butyl branch placement. ADMET ethylene/hexene (EH) copolymers provide an interesting system to model commercial LLDPE materials containing butyl branches (synthesized by the copolymerization of ethylene with 1-hexene) and industrial low-density polyethylene (LDPE) synthesized via radical chemistry (where the short-chain branch identity is primarily butyl due to backbiting during polymerization). These industrial materials typically show broad ill-defined melting behavior due to selective crystallization of long defect-free ethylene run lengths. The precision butyl polymers prepared by ADMET, however, show the sharp, well-defined melting and crystallization transition typical of other ADMET polymers. The melting temperature for Butyl21 is 14 °C, significantly depressed from that of Et21 (see **Figure 11**). This is not surprising considering the increased steric requirements of a four-carbon branch compared with a two-carbon branch. The low melting temperature likely indicates very small or very distorted crystals. Even Butyl15 is semicrystalline (albeit with an extremely low melting temperature of −33 °C). This is far above the branch concentration required to render similar polymers with random branch placement completely amorphous. When comparing the precise butyl polymer to a random sample with similar branch content, the effects of precise placement once again become perfectly clear: the precise material displays a sharp, well-defined melt in contrast to a broad, ill-defined melting behavior of the random versions.

Precise hexyl branch placement. ADMET ethylene/octene (EO) copolymers serve as LLDPE models with precise hexyl branch placement.[37] These precise EO models follow a similar trend in behavior as the previously discussed families; that is, with increasing branch content, decreasing melting temperature and enthalpy are observed. It is no surprise that Hexyl9 is totally amorphous, as the much smaller ethyl branch is able to completely disrupt crystallinity at this branch concentration. A semicrystalline morphology is observed for Hexyl15, an interesting result considering all other known EO copolymers with similar branch content are completely amorphous.[37] Hexyl21 is also semicrystalline. The very low melting temperature (16 °C) is indicative of very small crystallites. Interestingly, the melting enthalpy of Hexyl21 is similar to that of Et21, which is likewise surprising considering the notable decreases in enthalpy from Me21 to 2Me21 to Et21. The melting profile of the Hexyl21 closely mimics that of Me21 with a single sharp melting endotherm, rather than the complex endotherms displayed by 2Me21 and Et21.

Like Et21, Hexyl21 was thoroughly characterized in a separate study via WAXS, SAXS, DSC, and TEM.[76] The result in this case showed again that the precision sample contained uniform lamellar thickness. The scattering data support monoclinic packing, although with much less lattice expansion than either the ethyl- or the methyl-branched ADMET polymers. In fact, these data agreed quite well with monoclinic homo PE reflections, implying that the hexyl branch does not significantly affect the lattice dimensions. The measured lamellar thickness in this case was 26 Å, which correlates precisely with the distance between hexyl branches along the backbone. These results prove, beyond any doubt, that the hexyl branch must be completely excluded from the crystal. **Figure 10** compares the TEM images of commercial random polyolefin Et21 and Hexyl21.

Branch inclusion versus exclusion. There is an interesting correlation between the melting behavior of Butyl21 and Hexyl21: the thermal profiles are nearly identical. Considering that the hexyl branch is completely excluded from the crystalline lamella in Hexyl21, it is likely that the same is true for Butyl21. This prompts an interesting question: if an ethyl group is partially included but butyl or hexyl groups are excluded, what is the limit on branch length for inclusion in or exclusion from the crystal? Also, is crystallization with branch exclusion limited to *n*-alkane branches or can polyolefins retain the ability to crystallize even with bulkier pendant groups such as isopropyl or *t*-butyl? To probe this behavior, an entire family of precision alkyl-branched polyolefins with

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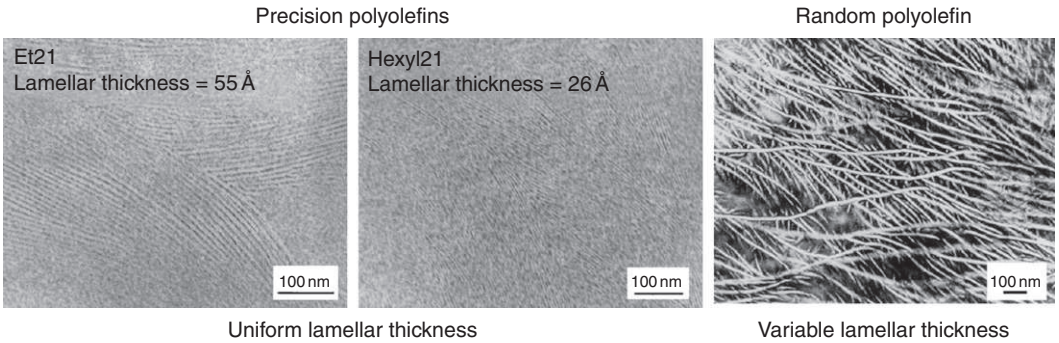

Figure 10 TEM images illustrating the effect of precise branch placement in comparison to random polyolefins, revealing a broad distribution of lamellar thicknesses; precision polyolefins Et21 and Hexyl21 feature lamella of uniform thickness.

increasing branch length (methyl, ethyl, propyl, butyl, pentyl, and hexyl), and increasing steric bulk (isopropyl, *sec*-butyl, *t*-butyl, cyclohexyl, and adamantyl), were examined (or reexamined) by DSC and WAXS in an attempt to find these limits.[35]

The thermal behavior (Figure 11) exhibited a clear result: all branches longer than ethyl display nearly identical behavior. When increasing steric bulk, even the polymer decorated with an enormous adamantyl group is able to crystallize. Although there is a slight depression in peak melting temperature, the behavior of the bulky substitutes closely resembles that of the linear branched analogs. The scattering data show clear lattice expansion when going from Me21 to Et21, as discussed above. Beyond Et21, however, the reflections show a contraction in the lattice dimensions that remain constant even as branches get larger and bulkier. This is a clear proof that the ethyl branch is the size limit for alkyl branch inclusion in PE; anything larger in terms of branch length or steric bulk will be excluded to amorphous regions.[35]

5.09.7.3 Increasing the Spacing Between Alkyl Branches in Precision Polyolefins

The results in this section bring up an extremely important point about the structure–property relationship in PE: by

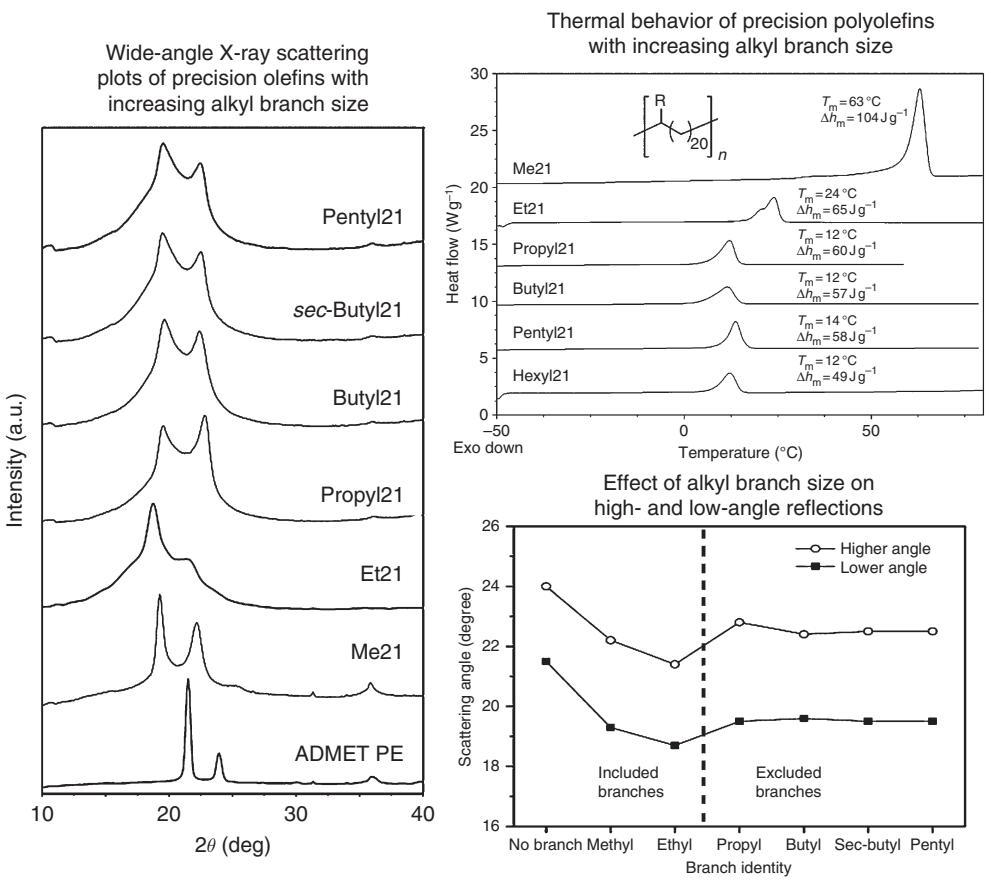

Figure 11 Probing the limits of branch inclusion: alkyl branches larger than an ethyl group are completely excluded to amorphous regions.

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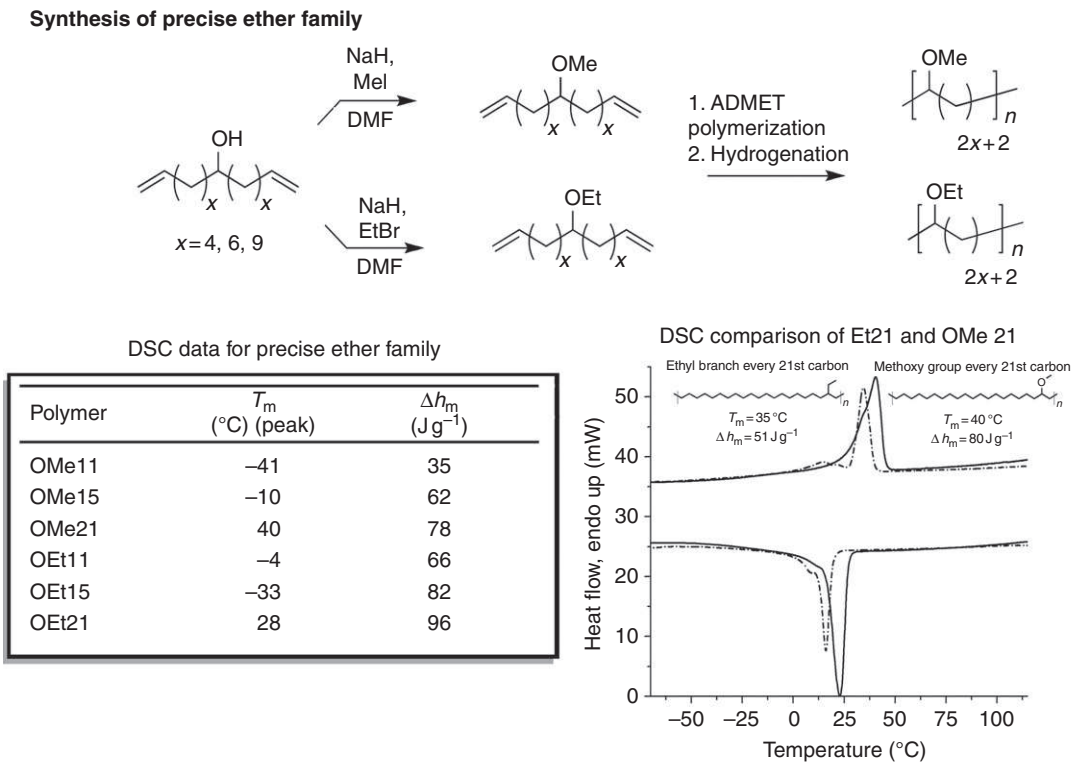
perfectly controlling branch placement and ensuring that this branch possesses sufficient steric bulk to be excluded from crystalline lamella (i.e., the branch dictates where a chain stem will fold), it is possible to precisely control the secondary structure and thus the physical properties of these polymers. Although this is intellectually interesting, it is of little practical value if these materials melt below room temperature. For this reason, a synthetic route was developed to reduce the branching frequency and ultimately increase the melting point.[38] As a proof-of-concept study, Butyl39 was synthesized using the quantitative nitrile alkylation/decyanation route. The alkenyl bromides used in this case are not commercially available but can be easily made by coupling 11-bromo-undecene via cross-metathesis, hydrogenating the olefin, and performing a mono elimination on the resulting terminal dibromide. This method, although demonstrated for spacing branches every 39th backbone carbon, could be adopted to space them even further. DSC and WAXS measurements on the polymer prove that this concept works perfectly: scattering reflections indicate that the orthorhombic crystal structure of PE remains intact at this branch spacing. The melting behavior, similar to other polymers in this family, is very sharp and well defined, consistent with uniform lamellar thickness. The melting temperature (75 °C) is incident with that of a 40-carbon *n*-paraffin molecule, suggesting that the thickness of the lamella is consistent with the branch-to-branch distance. This method shows great promise for the synthesis of high-melting precision polyolefins with mechanical properties superior to any current commercial material.

5.09.8 Precision Polyolefins with Ether Branches

Precision polyolefins with the regular placement of ether groups represent the first examples of linear ethylene-*co*-vinyl ether (EVE) copolymers ever made;[23,24] the difference in reactivity ratios between ethylene and vinyl ethers prevented the synthesis of this type of material via chain propagation chemistry until very recently.[77] Although they do not model a commercially important industrial copolymer, this class of precision polyolefins is closely related to the alkyl-branched precision polyolefin family, the only difference being the exchange of a methylene group for an oxygen atom directly off the PE backbone. While this slight change in sterics and bond polarity seems subtle, comparisons between the two provide a great deal of information concerning the consequences of this type of structural manipulation and its effect on the behavior of precision polyolefins.

5.09.8.1 Synthesis of Precision Polyolefins with Ether Branches

The diene monomer required to make polyolefins with precisely placed ether groups is synthesized in one step from a symmetric secondary diene alcohol (the synthesis of which is discussed in Section 5.09.6.1) using the classic Williamson ether synthesis (see **Figure 12**). Polymerization followed by hydrogenation results in a defect-free, linear-sequenced copolymer of ethylene and either methyl vinyl ether or ethyl vinyl ether as confirmed by careful NMR characterization.



DSC data for precise ether family

Polymer	T_m (°C) (peak)	Δh_m (J g^{-1})
OMe11	–41	35
OMe15	–10	62
OMe21	40	78
OEt11	–4	66
OEt15	–33	82
OEt21	28	96

Figure 12 Synthesis and thermal behavior of polyolefins with precise ether branch placement.

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5.09.8.2 Behavior of Precision Polyolefins with Ether Branches

Similar to other ADMET precision polyolefin families, the precision EVE family shows a clear relationship between branch size and placement and the observed thermal behavior. As branch content increases, melting temperature and enthalpy decrease. Likewise, increasing sterics from a pendant methyl ether group to a pendant ethyl ether group generally results in a decrease in peak melting temperature. There is a notable exception in this case: OMe11 and OEt11, where the polymer with the larger pendant group has a higher peak melting temperature and exhibits a very complex thermal profile.

The most useful information provided by this family of precision polyolefins comes when comparing their behavior to that of the corresponding alkyl-branched polymers, that is, OMe21 with Et21 and OEt21 with Propyl21. The substitution of an oxygen atom for a methylene group results in only a slight increase in the peak melting temperature and melting enthalpy for OMe21 when compared to Et21. As is the case in several of the previous examples, this melting point is incident with that of eicosane, suggesting a strong relationship to the branch-to-branch distance. The Fourier transform infrared spectroscopy (FTIR) data on this polymer indicate a significant amount of kink defects, similar to Et21. As the steric requirements are roughly the same for these two polymers, it is reasonable that this group could be included, at least partially, within the unit cell.

The effect of this slight structural change is much more pronounced when the size of the ether branch is increased by one methylene unit. When compared to Propyl21, OEt21 has an increase in melting temperature of 12 °C and in melting enthalpy of 19 J g^{-1}. Based on the alkyl branching data, it seems unlikely that a defect of this size is included within the unit cell, as the smaller ethyl group delineates this boundary when placing defects every 21st backbone carbon. In this case, it can be reasonably concluded that the polarity of the bond and the electronics of the oxygen create a favorable place to initiate a fold in the polymer backbone, allowing for a more complete crystallization of the interdefect paraffin unit cell, resulting in the increased melting temperature and enthalpy.

Comparing the behaviors of OMe15, OEt15, and Et15 leads to another rather interesting observation. The thermal profile of Et15 shows two distinct melting endotherms, likely due to two populations of lamella that partially include or completely exclude the ethyl branch defect at this branch content. Both OMe15 and OEt15 show a single melting endotherm, closely matching the two melting points of Et15. It appears that at this branch concentration, the addition of the oxygen atom allows the material to prefer a single crystal form at each of these defect sizes.

5.09.9 Precision Polyolefins with Pendant Acid Groups

5.09.9.1 Precise Carboxylic Acid Placement

Ethylene/acrylic acid copolymers are a commercially important class of materials due to ease and low cost of production and multiple end-use applications.[21] By simply varying the acid content in the polymer, the properties of the resultant material can be tuned over a wide range of responses. The combination of PE's crystallinity and hydrogen bonding between carboxylic acid groups provides these materials with improved mechanical performance over homo PE. The synthesis of these materials industrially requires chain propagation techniques that again result in materials subject to intrachain and interchain heterogeneities. By utilizing ADMET chemistry to synthesize precision carboxylic acid-containing polyolefins, these irregularities can be minimized and the effects of specific structural features probed. This study also compared the behavior of the precision carboxylic acid-containing polymers to that of linear, defect-free polymers prepared using ROMP that feature random acid placement.

Synthesis of precision carboxylic acid-functionalized polyolefins. The symmetrical diene acid (**Figure 13**) is easily prepared in three steps beginning with diethyl malonate and the appropriate alkenyl bromides. To ensure that the acid moiety does not poison the ruthenium catalyst during polymerization, hemiacetal ester protection chemistry was employed. This protecting group is easily cleaved during the hydrogenation step or thermally to afford the final material. Careful ^{1}H- and ^{13}C-NMR experiments confirm the precise structure. IR spectroscopy revealed, interestingly, that all carboxylic acids are dimerized in the final material.

Behavior of precision carboxylic acid-functionalized polyolefins. The effect of incorporating a functional group capable of supramolecular interactions is evident in the behavior of these materials relative to the precision alkyl-branched polyolefins[21] (**Figure 13**). In the case of $COOH_{21}$, the melting temperature is ~20 °C higher than that of Et21. $COOH_{15}$, however, is completely amorphous. This is clearly an effect of the carboxylic acid dimerization. In the case of the lower acid content, this interaction between acid groups has a positive effect on the polymer's crystallization, serving to produce more stable, higher melting crystals than analogous precision polyolefins with pendant groups of similar steric requirements. However, as acid content increases, these interactions overwhelm the system preventing the interacid methylene sequences from organizing into lamella. $COOH_9$ has a higher T_g compared to $COOH_{15}$, attributed again to dimerized carboxylic acids, essential physical cross-links, and restricting mobility to a greater extent at higher concentrations. The materials with random acid placement made by ROMP possess much broader melting and crystallization profiles with higher peak melting temperatures compared to the precision materials, again attributed to the selection of long ethylene run lengths during crystallization. At the highest amount of acid incorporation studied, equivalent to that of $COOH_9$, the random materials become amorphous as well, although with a significantly depressed T_g compared to the precision material, displaying again the effect precise placement has on these materials.

Despite the fact that no crystallinity is observed in DSC experiments on $COOH_9$ and $COOH_{15}$, there is still evidence that these systems possess order. Scattering data show reflections corresponding exactly to the interacid distance along the backbone for all three polymers in this family. In $COOH_{21}$, this is very pronounced and multiple orders of diffractions corresponding to 2.53 nm are present, indicating a high degree of ordering based on the interacid distance along the backbone.

To better understand this phenomenon, thermal and scattering experiments were conducted on drawn samples, a

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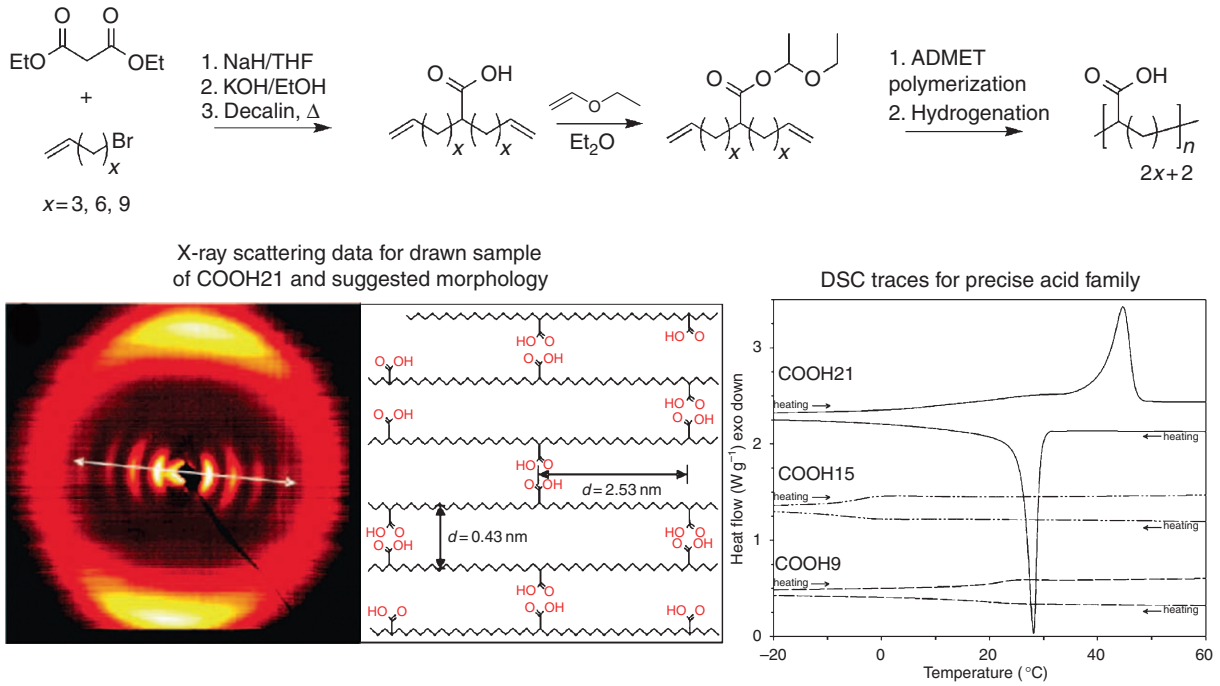

Figure 13 Synthesis, thermal behavior, and scattering data of precision carboxylic acid-functionalized polyolefins suggesting a layered morphology.

well-known method for inducing anisotropy in polymer samples. For $COOH_9$ and $COOH_{15}$, no anisotropy was observed upon drawing. Drawing $COOH_{21}$, however, produced noticeable changes in both the thermal and scattering behaviors. The melting profile of the drawn sample is bimodal, suggesting two populations of crystallites. The scattering data (Figure 13) showed several reflections perpendicular to the draw axis that again perfectly correspond to the acid–acid distance along the backbone and multiples thereof. The authors speculate that in the case of the drawn sample, dimerized carboxylic acids are able to lie within the orthorhombic unit cell perpendicular to the chain stems. This unique behavior is likely responsible for this polymer's excellent mechanical strength. This system is a superb example demonstrating the ability of using precise primary structure to control and improve the properties of traditional ill-defined, chain-made materials.

5.09.9.2 Precise Phosphonic Acid and Sulfonic Acid Ester Placement

PE-containing sulfonic and phosphonic acids are attractive for a wide range of applications, particularly in the realm of biomaterials and membrane technologies.[33,34] These materials are difficult to make industrially: reactivity ratios prevent efficient comonomer incorporation. Postfunctionalization, for example, via phosphorylation of PE or sulfonation of PS, results in materials with no microstructural control. Homopolymers of vinyl sulfonic, styrene sulfonic, and vinyl phosphonic acids are well studied, but again these materials are made using chain propagation techniques that are again subject to interchain and intrachain heterogeneities as well as structural defects. Studying precision polyolefins containing these groups can simultaneously probe the effects of efficient incorporation of these groups into PE and the effects of regular spacing and controlled composition.

Synthesis of precision phosphonic acid- and sulfonic acid ester-functionalized polyolefins. The synthesis of symmetric dienes utilized in the fabrication of these polymers begins with the sequential dialkylation of ethyl methane sulfonate, ethyl toluene sulfonate,[34] or ethyl methane phosphonate[33] using freshly prepared LDA and an alkenyl bromide. Standard ADMET polymerization/hydrogenation techniques are used to convert the protected acid-containing dienes to the corresponding protected acid-functionalized precision polyolefins. Deprotection of the phosphonic acid esters proceeds quantitatively upon treatment with trimethylsilyl bromide in methanol; the deprotection of the sulfonic acid ester-containing precision polyolefins has not been reported as of yet. Thorough ^{1}H, ^{13}C, and ^{31}P (in the case of the phosphonic acid polymers) NMR characterization confirm the pristine structure of these materials.

Behavior of precision phosphonic acid and sulfonic acid ester-functionalized polyolefins. Thermal characterization using DSC reveals very different behavior for the two precision sulfonic acid ester polyolefins.[34] SO_3Et21 is semicrystalline, exhibiting a sharp melting endotherm and a crystallization exotherm typical of ADMET precision polyolefins. The melting temperature in this case is 29 °C, very similar to the behavior of OEt21, albeit with a decreased melting enthalpy (not surprising considering the increased steric requirements of this bulkier defect). These data suggest, as is the case for the precise ether family, that this group is likely excluded from the crystal. Here again, the polarity of this group creates favorable conditions for the crystallization of the interdefect ethylene run length. Scattering data are not yet available for this polymer, so drawing absolute conclusions about the morphology of this system becomes difficult.

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The placement of a phenyl group spacer between the polyolefin backbone and the sulfonic acid ester moiety induces a significant change in behavior.[33] $PhSO_3Et21$ is completely amorphous with a glass transition temperature at 24 °C. Apparently, the sterics of the phenyl group are too severe in this case to allow crystallization of the backbone. It is also possible that interactions between pendant functional groups (e.g., the relatively electron-deficient phenyl ring on one pendant pairing with the relatively electron-rich SO_3Et group on another) in essence create supramolecular physical cross-links, similar to the precise carboxylic acid family, which impedes the ability of the backbone to organize into lamella.

Although no thermal data were reported on the precision phosphonic acid-functionalized polymer, solid-state NMR experiments can provide insight into the morphology and behavior of this system. The ^{13}C cross-polarization magic angle spinning (CPMAS) spectrum for this polymer shows peaks consistent with all transcrystalline PEs, indicating some degree of order for this polymer. Temperature-dependent NMR experiments reveal that the motion of the phosphonic acid groups is minimal even at elevated temperatures. This suggests strong hydrogen bonding interactions between acid groups; the authors attribute the toughness of this polymer and its poor solubility to these supramolecular interactions. Chemical cross-linking (via anhydride formation) can be ruled out as the cause of this behavior based on ^{31}P-NMR data.

5.09.10 Precision Amphiphilic Copolymers

We have discussed in the previous sections how increasing the size of a pendant branch and its concentration leads to perturbations in the preferred crystal structure of PE until, at a certain point, the branch is entirely excluded from the crystal or the material itself is rendered completely amorphous. We have likewise discussed how properties can further be affected by noncovalent interactions between these pendant branches. The studies presented here on precision amphiphilic copolymers combine these principles to show how such information could be used to design materials with a specific behavior or application in mind. The concept is relatively straightforward: placing an oligo polyethylene glycol (PEG) branch at regular intervals along a PE backbone takes advantage of the branch's size (large enough to be excluded) and the incompatibility of the branch with the backbone to afford materials with two distinct phases, one phase of crystalline PE and one phase of amorphous PEG.[25,27] Then, by altering the identity of the PEG branch end-group, the interaction of the PEG phase can be adjusted to separately tune its properties without significantly affecting the PE segments.[26] Results indicate that this is indeed feasible and that it is even possible to 'trick' the backbone into crystallizing with the excluded pendant group.

5.09.10.1 Synthesis of Precision Amphiphilic Copolymers

Synthesizing these intricate materials involves only a few simple organic transformations[25–27] (Figure 14). Reduction of the symmetric carboxylic acid diene described in Section 5.09.9.1 using lithium aluminum hydride affords a symmetric diene primary alcohol, which serves as the basis for all of the monomers described here. This alcohol can be deprotonated and used as the nucleophile in a Williamson ether synthesis to attach the desired branch,[26,27] or it can be tosylated and used as an electrophile.[25] Standard ADMET polymerization/hydrogenation techniques are employed to yield the final precision amphiphilic copolymers.

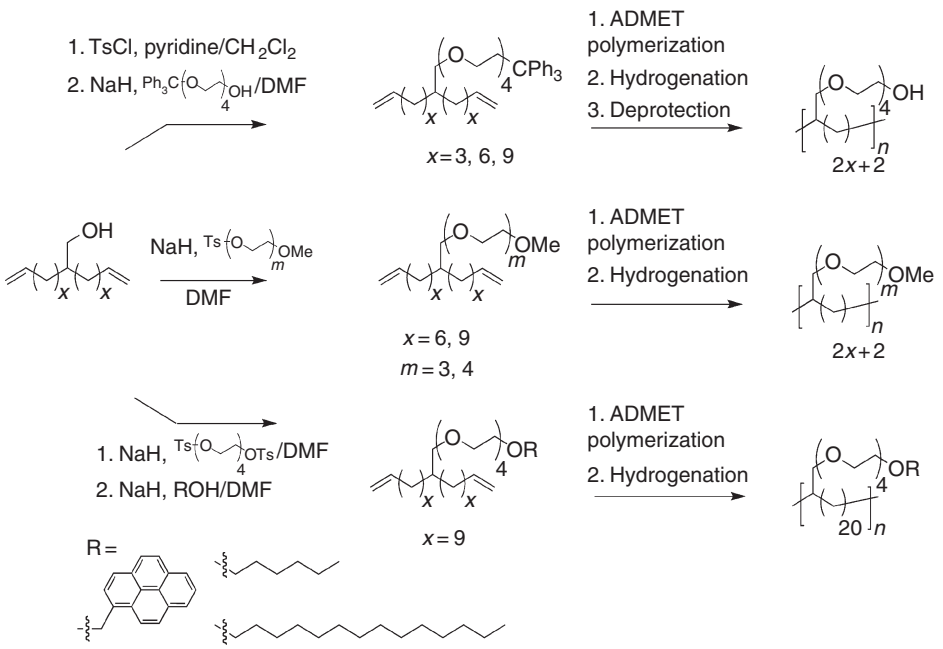

Figure 14 Synthetic route of a variety of precision amphiphilic copolymers.

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5.09.10.2 Behavior of Precision Amphiphilic Copolymers

Precise methoxy-terminated PEG branch placement. To ensure the concept works and the branches are indeed excluded from the crystal, a set of polymers with methoxy-terminated PEG branches of two different sizes (three or four oxyethylene repeating units) were synthesized and their behaviors compared.[27] Evaluating the thermal profiles for 3EGOMe-branched and 4EGOMe-branched materials shows that indeed the size of the PEG branch has no effect on the behavior of the material. As shown in Figure 15, these polymers all display a T_g at about −75 °C, regardless of pendant branch size or distribution, which corresponds to a fully amorphous, primarily polyether phase. These polymers also exhibit the sharp crystalline melting endotherms characteristic of ADMET polyolefins. The melting temperatures, as is the case for other precision polyolefins, decrease with increasing branch content. The temperature of the melt in the cases of 3EGOMe21 and 4EGOMe21 is very similar to that of the Hexyl21 (and its relatives), indicating that this endotherm is surely an effect of the PE backbone crystallizing to exclude the PEG branch. This is punctuated when examining the thermal profile of the corresponding polymers with unsaturated backbone: this behavior is severely disrupted (for branches every 21st backbone carbon) or completely destroyed (for branches every 15th backbone carbon).

Precise hydroxy-terminated PEG branch placement. To evaluate the effect interactions of the pendant branches could have on the behavior of these precision amphiphilic copolymers, a family of similar polymers with hydroxy-terminated PEG branches was synthesized.[25] In this study, the typical full ADMET series with branches placed every 9th, 15th, and 21st backbone carbon atom was examined. The DSC traces for these polymers are shown in Figure 16. 4EGOH9 is completely amorphous, unsurprisingly, with a T_g at −65 °C. Increasing the branch spacing, 4EGOH15 is semicrystalline with complex melting behavior (peak melting temperature of −3 °C) that is very much dependent on thermal history. The T_g for the polyether phase is −63 °C in this case. Again increasing the distance between branches to 4EGOH21 does not affect the T_g of the excluded polyether phase but, as expected, results in an increase in melting temperature to 29 °C. WAXS experiments conducted on this sample show reflections indicative of a slightly contracted hexagonal unit cell for this polymer and absolutely confirm that the polyether branch is excluded from the crystal in these materials (Figure 16).

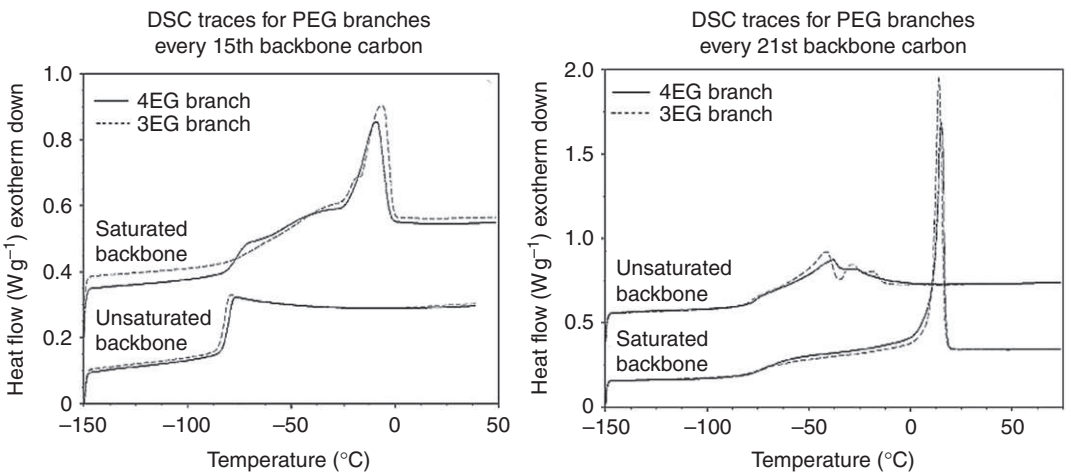

Figure 15 Thermal behavior of precision amphiphilic copolymers featuring precise placement of methoxy-terminated PEG branches.

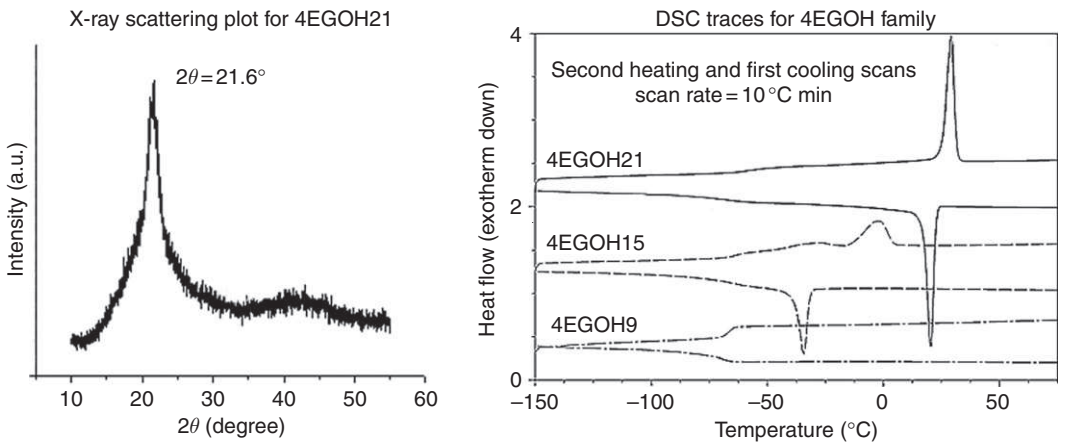

Figure 16 WAXS diffractogram (left) and DSC traces (right) of precision amphiphilic copolymers featuring precisely placed hydroxy-terminated PEG branches.

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Comparing the behavior of 4EGOMe21 and 4EGOH21 shows the role that the branch end-group interactions play in the thermal behavior of precision amphiphilic copolymers. The peak melting temperature of 4EGOH21 is 13 °C higher than that of 4EGOMe21. IR spectroscopy confirms the hydrogen bonding between the free –OH groups, and the increase in T_g for the 4EGOH family compared to the 4EGOMe family reflects this. The more restricted motion of amorphous PEG phase, due to the interaction between branch end-groups, apparently imparts a bit more order to this system. This ultimately allows for a more complete crystallization of the methylene sequences between PEG branches, resulting in the increase in melting temperature.

Precise amphiphilic branch placement. Given the noticeable effect of this structural manipulation in the previous example, three polymers with different PEG branch end-groups were synthesized to probe the limits of this behavior[26] (see **Figure 17**). In this study, the distance between the branches was held constant (branches every 21st carbon) to maximize the propensity of the backbone to crystallize in order to isolate the effects of the branches. For the same reasoning, the behavior of the unsaturated version of these polymers was investigated as well. The three polymers exhibit remarkably different thermal behavior (**Figure 17**), a clear indication that changing the graft end-group moiety has significant effects on the morphology of these systems. The difference in behavior

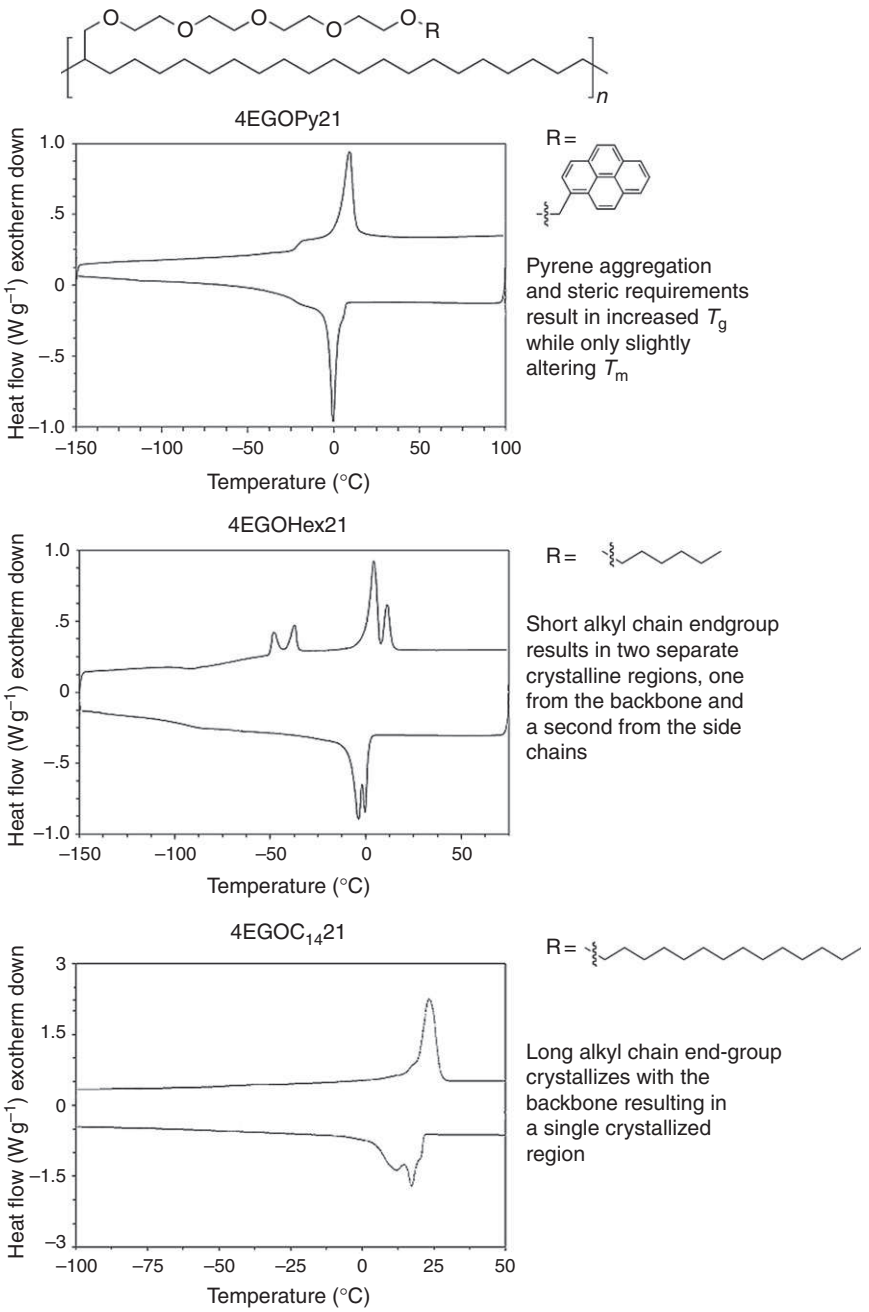

Figure 17 Thermal behavior of precision amphiphilic copolymers: small structural modifications at the PEG branch terminus result in significant changes in behavior and morphology.

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between the saturated and unsaturated polymers is also significant, emphasizing the role of backbone crystallization in these materials.

The heating and cooling curves for 4EGOPy21 (both saturated and unsaturated) reveal that the saturation of the backbone allows for crystallization to occur, while the unsaturated polymer remains completely amorphous. This suggests that the pendant defect does not contribute to the crystallization as expected. The T_g of the saturated polymer is also slightly increased compared to the unsaturated analog, an indication that segmental motion of the grafts is restricted by the crystallinity of the PE backbone. The completely amorphous behavior of unsaturated 4EGOPy21 is an interesting result, considering that previous reported unsaturated ADMET polymers with the same distribution of pendant functionality are semicrystalline.[1–3] The lack of crystallinity in the unsaturated 4EGOPy21, as well as the depressed melting point for 4EGOPy21 compared to other polymers in this family, is most likely a result of pyrene aggregation (confirmed by fluorescence spectroscopy), which impedes backbone crystallization, similar to the effect of carboxylic acid dimers in the precise COOH family.

The difference between saturated and unsaturated 4EGOHex21 in terms of thermal response is especially interesting. The unsaturated polymer is semicrystalline with a melting endotherm at −13 °C. There is significant amorphous content to this material as well, indicated by the distinct T_g at −76 °C. The thermal behavior of the saturated analog is completely different, however. A single, bimodal crystallization at −4 °C is witnessed on cooling. Upon heating, a small exotherm is barely observed at −91 °C, followed by a bimodal melting endotherm with peaks at −48 and −37 °C. A second bimodal melting endotherm occurs with peaks at 4 and 11 °C. This complex behavior of 4EGOHex21 was further investigated by modulated differential scanning calorimetry (MDSC), which provides increased sensitivity compared to traditional DSC and allows for resolution of overlapping transitions.[78–81] The MDSC data indicate a melting and annealing process is at work in these two endotherms. Because the melting enthalpy of this higher temperature peak matches the enthalpy of crystallization, and also because its melting temperature and enthalpy (4 °C and 27 J g^{-1}) are in good agreement with those of 4EGOPy21 (9 °C and 24 J g^{-1}), it can be concluded that this behavior is a result of crystallization of the backbone excluding the pendant branch during cooling. During subsequent heating, the excluded branches gain sufficient mobility to self-crystallize, noted by the exotherm at −100 °C. The pendant crystals then melt at about −50 °C, followed by the melting of the backbone crystals.

The thermal behavior of unsaturated and saturated 4EGOC$_{14}$21 differs significantly from that of the previous two examples. Both polymers exhibit extremely sharp melting transitions at temperatures much higher than those of the other polymers in this family. This deviates from the well-known trend discussed in this chapter for ADMET polymers, which typically show a decrease in melting temperature and enthalpy as the pendant group size increases. For the 4EGOC$_{14}$21-substituted polymers, the increase in pendant group length results in marked increases in both melting temperature and enthalpy. Further, no T_g is observed in either the saturated or unsaturated analogs, indicating the absence of appreciable amorphous content for these polymers. Thus, the long alkyl chains at the termini of the PEG branches must also be crystallizable. Since there is only one melting peak, the C$_{14}$ chain must be long enough to extend back into the crystallizing PE backbone, forming a single crystallized region. By cleverly playing with structure, the authors in this case were able to completely exclude the branch from the crystal at the point of attachment but 'trick' the backbone into reincluding the terminus of the excluded branch, effectively bringing this study of structure and property full circle.

5.09.11 Summary and Outlook

ADMET polymerization is a versatile technique for the synthesis of unique, complex, and functional polymer structures. ADMET is a step growth polycondensation reaction that proceeds under mild conditions. Any molecule that can be functionalized with two terminal olefin groups has the potential to be an ADMET monomer, allowing an almost limitless possibility for the creation of interesting and useful polymer structures.

This chapter has described the synthesis of a wide variety of polymers using this versatile technique. From potentially useful materials such as organic semiconductors, thermoplastic elastomers, and engineering plastics to exotic structures that push the boundaries of conventional polymer chemistry, ADMET provides a tool to facilitate even the most complex polymer designs.

We have also discussed in great detail the behavior of precision polyolefins and their synthesis via metathesis polycondensation chemistry. The term 'precision polyolefin' used here refers to a class of linear, defect-free polymers that mimic perfectly sequenced copolymers of ethylene and a vinyl comonomer. These materials, which are available only through ADMET polymerization/hydrogenation chemistry, allow for the systematic study of structure and its relationship to property in ethylene-based materials. The effects of both the size and the identity of the 'comonomer' (i.e., pendant functional group) have been evaluated, as well as the effects of changing the frequency of its appearance.

Perfectly linear PE synthesized by ADMET, although of lower molecular weight, behaves similarly to the commercial materials it mimics, indicating the effectiveness of this method in creating reliable model systems. Introducing a regularly spaced defect with small steric will cause predictable perturbations in the crystal structure. Most notably, an expansion of the lattice with shift from an orthorhombic to a triclinic structure occurs, resulting in a decrease in melting temperature and melting enthalpy as the size of the defect increases. Eventually, as the size of this defect increases, a point is reached where the steric requirements for housing such a defect within the crystal become too great. When this happens, the defect is completely excluded from the crystal and a contraction of the unit cell back to an orthorhombic structure is witnessed. The melting behavior remains largely consistent across a range of polymers, indicating that the regular spacing of large branches is responsible for this unique behavior.

It is evident through this volume of work how important structural control is when attempting to fine-tune behavior in ethylene-based materials. The model polymers available through ADMET have helped isolate the effects of very specific

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structural features. Applying this knowledge to the design of new materials will allow for the synthesis of polymers with exactly predictable behavior. Creatively tailoring materials with such controllable behavior for useful applicability represents a promising topic for future work. Clearly this area of research is by no means exhausted; the simple and elegant reaction will continue to provide a facile way to explore both basic structure–property relationships and complex functional materials.

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Biographical Sketches

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5.10 Enzymatic Polymerization

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5.10.1 Introduction

Enzymatic polymerization has been extensively developed over the past two decades. It is defined as "the *in vitro* polymerization of artificial substrate monomers catalyzed by an isolated enzyme via nonbiosynthetic (nonmetabolic) pathways".[1] This chapter deals with two reaction categories: polycondensation and polyaddition. Almost all enzymatic polymerizations ever developed fall within these categories.

From a historical point of view, the first stage of polymer synthesis, which began in the1920s, utilized classical catalysts such as acids (Brønsted acids, Lewis acids, and various cations), bases (Lewis bases and various anions), and radical-generating compounds. In the following second stage of synthesis, which began in the 1950s, Ziegler–Natta catalysts and metathesis catalysts based on transition metals, and also rare earth metal-based catalysts, were developed. These catalysts still play major roles in polymer synthesis. The use of enzymes as polymerization catalysts can be regarded as the third stage of polymer synthesis, which was aided by the availability of unique biocatalysts. It is to be noted that *in vitro* enzymatic catalysis has been extensively used in the organic synthesis area as a convenient and powerful tool.[2]

According to the Enzyme Commission, all the enzymes are classified into six main groups. Of the six groups, only three groups of enzymes have been utilized so far in enzymatic polymerization. **Table 1** presents the six main groups, key members of these groups as well as some of the polymers synthesized.

The characteristics of enzymatic functions are as follows. In living cells, all biopolymers (biomacromolecules) are produced by enzymatic catalysis. Such biopolymers include nucleic acids (DNA, RNA), proteins, polysaccharides, polyesters, polyaromatics, natural rubber, and so forth.

There are two fundamental characteristics of enzymatic reactions. (1) A 'key and lock' theory proposed by E. Fischer in 1894 pointed out the relationship between an enzyme and a natural substrate.[3] The theory implies that there exists a key and lock relationship between the enzyme and the substrate and the enzyme catalyzes the reaction of a substrate that is recognized by it due to this relationship. The substrate is to be recognized first and activated with the formation of the enzyme–substrate complex in which the substrate (key) binds the enzyme (lock) with geometrical adaptation to lead to the reaction to take place. (2) L. Pauling explained the reason why an enzymatic reaction proceeds under mild reaction conditions. It is because the activation energy is much lowered due to stabilization of the 'transition state' involving an enzyme–substrate complex when compared to no-enzyme reaction. The rate acceleration is normally 10^6–10^{12}-fold; however, in specific cases, it can even reach 10^{20}-fold![4]

Based on the above views, it has been proposed that for the *in vitro* enzymatic polymerization to occur the monomer has to be designed according to the new concept of 'transition-state analog substrate' (TSAS), the structure of which should be close to the transition-state structure of the *in vivo* enzymatic reaction.[1c,1d,1f–1j] This is due to the fact that the enzyme stabilizes the transition state via complex formation with the

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Table 1 Classification of enzymes, examples of enzymes, and typical polymers synthesized

Enzymes	*Examples of enzymes*	*Polymers synthesized*
1. Oxidoreductases	Peroxidase, laccase, tyrosinase, glucose oxidase	Polyphenols, polyanilines, vinyl polymers
2. Transferases	Phosphorylase, glycosyltransferase, acyltransferase	Polysaccharides, cyclic oligosaccharides, polyesters
3. Hydrolases	Glycosidase (cellulase, amylase, chitinase, hyaluronidase), lipase, peptidase, protease	Polysaccharides, polyesters, polycarbonates, polyamides, polyphosphates
4. Lyases	Decarboxylase, aldolase, dehydratase	
5. Isomerases	Racemase, epimerase, isomerase	
6. Ligases	Ligase, synthase, acyl CoA synthetase	

substrate. An appropriately designed artificial monomer thus readily forms an enzyme–substrate complex and the reaction is induced to give the product. It is stressed that in both *in vivo* and *in vitro* reactions structurally resembling transition-state analogs must be involved.

In vivo enzymatic reactions involve the following characteristics: (1) high catalytic activity (high turnover number); (2) reactions under mild conditions with respect to temperature, pressure, solvent, pH of the medium, and so on, bringing about energetic efficiency; and (3) reactions with high regio-, enantio-, chemo-, and stereoselectivity, giving rise to perfectly structure-controlled products. If these *in vivo* characteristics could be realized for *in vitro* enzymatic polymer synthesis, we may expect the following outcomes: (1) perfect control of polymer structures; (2) creation of polymers with a new structure; (3) a clean, selective process without by-product formation, (4) a low loading process with energy saving; and (5) product polymers with biodegradable properties in many cases. These are indicative of the 'green' nature of the *in vitro* enzymatic reactions for developing new polymeric materials. Actually, many of the expectations have been realized in numerous reactions. Therefore, enzymatic polymerization provides a good opportunity for conducting 'green polymer chemistry'.[1d,1j]

5.10.2 Enzymatic Polycondensation

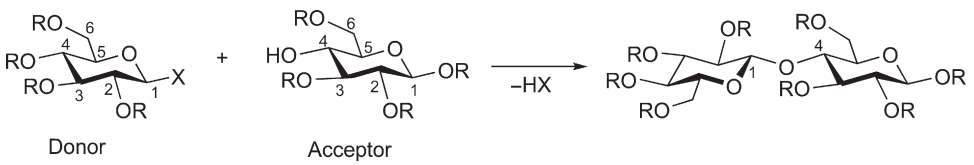
5.10.2.1 Polysaccharide Synthesis

Polysaccharides are among the most important biomacromolecules together with nucleic acids (DNA, RNA) and proteins. They are polymers in which the monomeric units are linked with a glycosidic linkage. Since the formation of glycosidic linkage involves control of regio- and stereoselectivities, which is difficult to achieve with the conventional organic chemistry, *in vitro* synthesis of polysaccharides had not been successful. The first synthesis was, however, accomplished via enzymatic polymerization.[5]

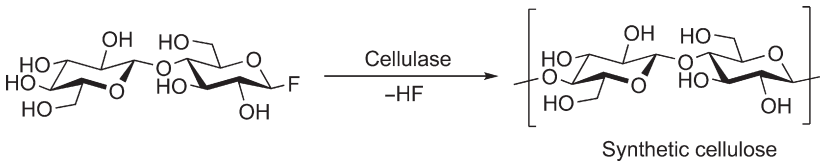
The formation of glycosidic linkage is a basic reaction, and has been extensively studied over the centuries and still it is one of the most important subjects in the sugar chemistry. The polysaccharide synthesis needs a highly selective glycosylation reaction between a donor molecule and an acceptor molecule to form a β(1→4) linkage, for example, (Scheme 1). For producing a higher-molecular-weight polysaccharide, this type of glycosylation reaction has to take place repeatedly many times.

5.10.2.1.1 Cellulose synthesis

Cellulose is by far the most abundant biochemical compound. It is estimated that around 20 billion tons of cellulose is photosynthesized in nature annually. In 1991, the first successful *in vitro* synthesis of cellulose was reported, utilizing cellulase as catalyst for the polymerization of β-cellobiosyl fluoride (β-CF) monomer (Scheme 2).[6] Cellulase is a hydrolase enzyme and it catalyzes the hydrolysis reaction of β(1→4) glycosidic linkage between two glucose units *in vivo*. In a mixed solvent of acetonitrile/acetate buffer (pH 5.0) (5:1, v/v), cellulase catalyzed the bond formation reaction, and hence, formally cellulase catalyzed the reverse reaction of the inherent reaction. The reaction produced 'synthetic cellulose' having a perfectly controlled β(1→4) glycosidic structure with the degree of



Scheme 1 A typical condensation reaction of glycosylation between a donor molecule and an acceptor molecule.



Scheme 2 Cellulase-catalyzed polycondensation of β-cellobiosyl fluoride to 'synthetic cellulose'.

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polymerization (DP) value around 22. During the reaction, hydrogen fluoride (HF) was liberated and hence the reaction is of typical polycondensation.

β-CF is considered a TSAS monomer, and is recognized readily by cellulase catalyst and activated for continuing the polymerization. During the reaction, the glycosidic linkage formation reaction is repeated. β-CF is considered an excellent TSAS monomer due to the following factors: (1) a disaccharide structure of cellobiose is the smallest unit of the cellulose repeating unit structure to be recognized by cellulase; (2) the size of fluorine atom (covalent radius 0.64 Å) is close to that of oxygen (0.66 Å), which enables β-CF to be recognized by cellulase; this was speculated by previous observations that the hydrolysis of fluoride compounds was promoted by cellulase catalysis;[7a] and (3) fluoride anion is the best leaving group. These characteristics were fully utilized later for the synthesis of various cellulose oligomers.[7b]

Figure 1 shows postulated reaction mechanisms for the cellulase-catalyzed hydrolysis of cellulose (A) and for the cellulase-catalyzed synthesis of cellulose via polycondensation of β-CF (B). Two carboxylic acid residues are present at the active site of cellulase. After the glycosidic linkage of cellulose is cleaved in the hydrolysis (stage a), then at the transition (or intermediate) state an α-glycosidic-carboxylate structure is involved (stage b). In the polymerization of β-CF, with the cleavage of the fluoride anion, a similar α-glycosidic-carboxylate structure (stage b′) is formed as a transition (or intermediate) state and this serves as an activated monomer form. Thus, a close resemblance of structures between stages b and b′ is a key for the polymerization to occur, and hence stage b′ is brought about owing to β-CF functioning as the TSAS monomer. Water or the 4-OH group of monomer and/or the growing chain attacks the structure at stage b or b′ to give with inversion a hydrolysis product (stage c) or a two-glucose-units-elongated product (stage c′) with β-configuration. During the polymerization, the glycosidic linkage formation reaction is repeated; the monomer serves as a glycosyl donor as well as a glycosyl acceptor.[5]

By utilizing the advantages of this polymerization, which produces synthetic cellulose via a one-step *in situ* reaction, high-order self-assembly of synthetic cellulose was investigated by means of transmission electron microscopy (TEM) and scanning electron microscopy (SEM). There are typically two types of allomorphs of high-ordered molecular structure in cellulose. One is thermodynamically metastable cellulose I, in which cellulose chains are aligned in parallel. The other is

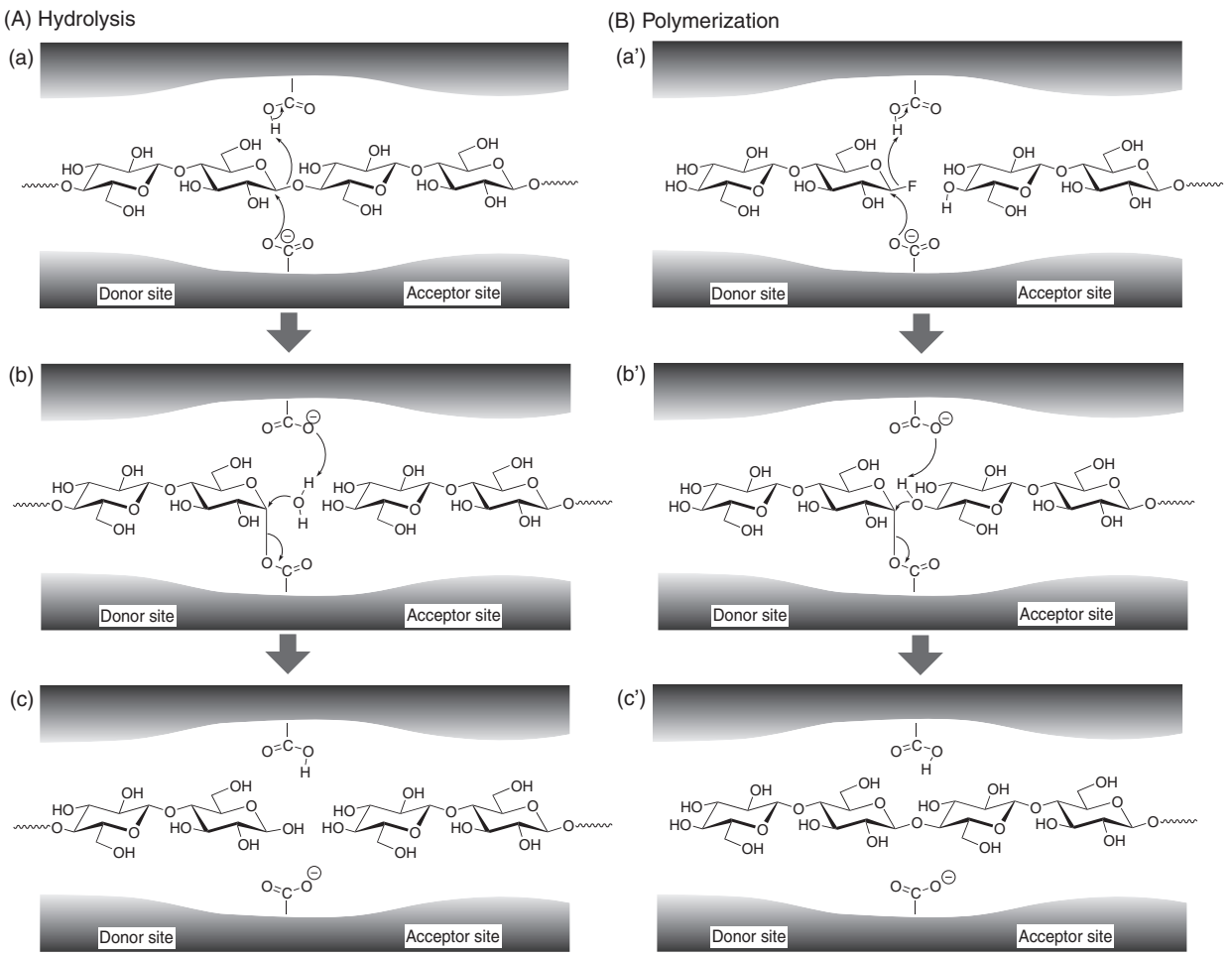

Figure 1 Postulated reaction mechanisms of cellulase catalysis for hydrolysis of cellulose (A) and for polycondensation of β-CF to synthetic cellulose (B). Reprinted with permission from Kobayashi, S. *Proc. Jpn. Acad. B* **2007**, *83*, 215. © Copyright 2007 The Japan Academy.[5]

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thermodynamically stable antiparallel cellulose II. Interestingly, naturally occurring cellulose exhibits less stable cellulose I crystalline structure.

Crystalline structures of cellulose synthesized via crude cellulase-catalyzed polymerization were cellulose II as shown by SEM measurements.[8a] On the other hand, cellulose I formation with purified cellulase catalyst was confirmed by TEM measurements.[8b] The thermodynamically metastable crystalline I formation was the first successful example of *in vitro* polymerization via nonbiosynthetic pathways. Based on this type of new control in high-order molecular assembly during polymerization, a new concept of 'choroselective polymerization' was advanced.[9]

Furthermore, a self-assembling process of synthetic cellulose during cellulase-catalyzed polymerization was investigated at real time and *in situ* by a combined small-angle scattering (SAS) method.[10] It was disclosed that cellulase enzymes aggregate themselves into associations with characteristic lengths larger than 200 nm in an aqueous reaction medium. On the other hand, cellulose molecules created at each active site of enzymes associate themselves around the enzyme associations into cellulose aggregates having surface fractal dimensions (D_s) increasing from 2 (smooth surface) to 2.3 (rough surface with fractal structure) with the progress in reaction time. The fractal structure formed at the end of the reaction extends over a wide length scale ranging from ~30 nm to ~30 μm (three orders of magnitude).

The cellulase-catalyzed cellulose synthesis involves a problem that the product cellulose might be hydrolyzed *in situ* by cellulase catalysis. In order to suppress hydrolysis, a mutant cellulase, that is, a cellulose-binding domain (CBD)-deleted cellulase, was prepared and used as catalyst. The mutated enzyme of cellulase (endoglucanase II, EG II) was expressed in yeast (Figure 2). The mutant enzyme, EG $II_{(core)}$, catalyzed the polymerization of β-CF to form synthetic cellulose with β(1→4) glycosidic linkage. As expected, the resulting crystalline product was hardly hydrolyzed by the mutant enzyme. This result indicates that CBD is not important for inducing polymerization.[11]

Another approach for the synthesis of cellulose was recently reported, extending the above method in principle which utilized a disaccharide monomer of cellobiose and a cellulase/surfactant (CS) complex as catalyst.[12] The CS complex consisted of a mixture of cellulase and a specific nonionic surfactant of dioleyl-*N*-D-glucono-L-glutamate ($2C_{18}\Delta^9GE$). In the nonaqueous medium of dimethylacetamide (DMAc)/LiCl, a cellulose-solubilizing solvent, polymerization took place at 37 °C to form synthetic cellulose as a white powder. The DP value was high (over 100) and the product yield was low (up to 5%). The reaction was of dehydration polycondensation and led to controlled regioselectivity and stereochemistry, involving an extensive transglycosylation of the product with a statistical even- and odd-numbered chain length.

Cellulose derivatives were synthesized by cellulase-catalyzed polycondensation of 6-*O*-methyl- and 6′-*O*-methyl-cellobiosyl fluorides.[13] The former fluoride was recognized by cellulase as a TSAS, giving rise to the corresponding alternatingly C-6 methylated cellulose derivative with number average molecular weight (M_n) equal to 3.9×10^3. Cellooligosaccharides were prepared using β-lactosyl fluoride (β-LF) as a donor via a step-by-step chain elongation by combined use of cellulase and β-galactosidase.[14] First, cellulase catalyzes the glycosidation of β-LF to the nonreducing 4-OH of the acceptor glucose unit. Second, β-LF does not act as an acceptor; therefore, β-galactosidase cuts off a β-galactoside unit to give a new nonreducing end of 4-OH of glucose unit. These two steps give a one-glucose-unit-elongated oligomer. Repetition of the set reactions produces cellooligomers.

5.10.2.1.2 Xylan synthesis

Xylan is a polysaccharide of xylose having a β(1→4) glycosidic linkage and is one of the most important components of hemicellulose in plant cell walls. Based on the TSAS concept, β-xylobiosyl fluoride was used as monomer for polycondensation catalyzed by cellulase (Scheme 3). Synthetic xylan has a β(1→4) glycosidic linkage structure, a well-defined structure compared with that of naturally occurring xylan, with an M_n of 6.7×10^3 and a DP value of around 23.[15]

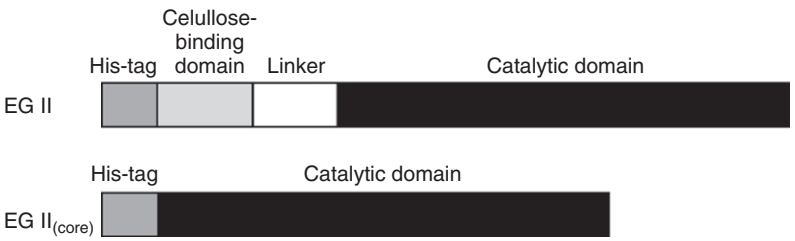
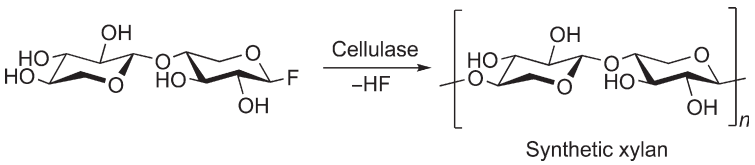


Figure 2 Schematic representation of EG II expressed by *Saccharomyces cerevisiae* and that of the mutant EG $II_{(core)}$. Reprinted with permission from Kobayashi, S. *Proc. Jpn. Acad. B* **2007**, *83*, 215. © Copyright 2007 The Japan Academy.[5]



Scheme 3 Cellulase-catalysed polycondensation of β-xylobiosyl fluoride to 'synthetic xylan'.

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5.10.2.1.3 Amylose synthesis

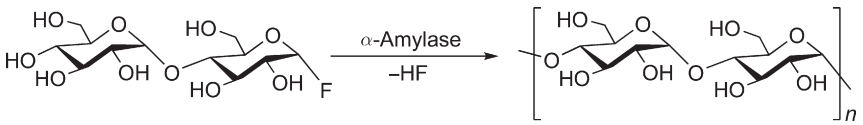
Amylose is a glucose polymer linked through α(1→4) glycosidic linkages. In analogy to cellulose synthesis, α-amylase-catalyzed polycondensation of α-D-maltosyl fluoride in a methanol–phosphate buffer (pH 7.0) was conducted and this yielded amylose oligomers with up to seven glucose units (Scheme 4).[16] Oligomer formation may be due to a steric barrier caused by the helical structure of amylase to give longer chains.

Phosphorylase is an exo-type enzyme that catalyzes *in vivo* phosphorolysis at the nonreducing end of the glycosidic linkage. It is a transferase enzyme. It forms part of metabolic pathways, but its *in vitro* catalysis is regarded within the scope of the present enzymatic polymerization.

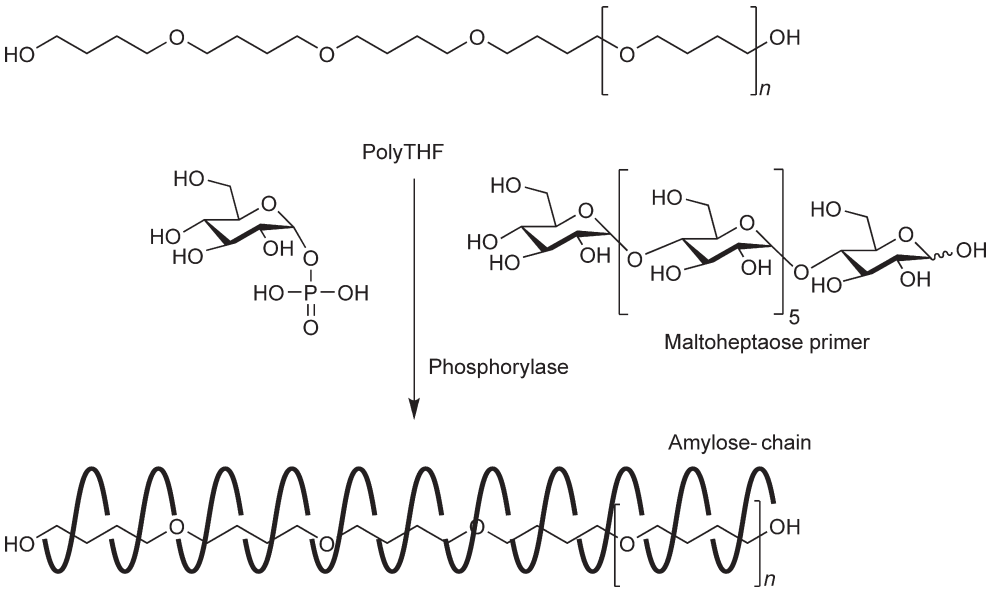
Amylose was synthesized *in vitro* by the phosphorylase-catalyzed polycondensation of α-D-glucose 1-phosphate (Glc-1-P) monomer, which was initiated from a primer of maltoheptaose.[17] When polycondensation was carried out in the presence of polytetrahydrofuran (polyTHF) as a hydrophobic polymer, polymerization proceeded with the formation of amylose–polyTHF inclusion complex (Scheme 5).[18] Formation of amylose–polymer inclusion complexes was studied using various axle hydrophobic polymers. This unique polymerization to produce amylose–polymer inclusion complexes was termed 'vine-twining polymerization'.[19] Phosphorylase-catalyzed polymerization was applied for the synthesis of various polymers like amylose-grafted chitin and chitosan as well as amylose-grafted cellulose.[20]

5.10.2.1.4 (1→3)-β-D-Glucan synthesis

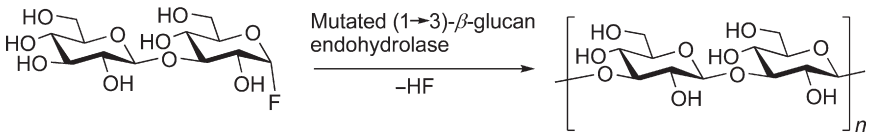
Polysaccharides such as curdlan, laminarin, and sizofiran are β(1→3)-linked D-glucose polysaccharides and are generically called (1→3)-β-D-glucans. (1→3)-β-D-Glucans possess high immunostimulatory and anticancer activities. (1→3)-β-D-Glucan endohydrolase is an enzyme that hydrolyzes the β(1→3) glycosidic linkage of (1→3)-β-D-glucans. A wild-type endohydrolase isoenzyme showed a low catalytic activity for the polymerization of a β-laminaribiosyl fluoride monomer (Scheme 6). However, a mutant E231G enzyme, whose catalytic nucleophile Glu (E) residue at 231 is replaced by Gly (G), showed high catalytic efficiency and DP values of the resulting polysaccharides ranged from 28 to 44.[21]



Scheme 4 α-Amylase-catalyzed polycondensation of α-D-maltosyl fluoride to amylose oligomers.



Scheme 5 Phosphorylase-catalyzed polycondensation of α-D-glucose 1-phosphate initiated by maltoheptaose primer in the presence of polyTHF to form amylose-polyTHF inclusion complexes.



Scheme 6 Mutated endohydrolase-catalyzed polycondensation of β-laminaribiosyl fluoride to a (1®3)-β-D-glucan.

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5.10.2.1.5 Unnatural polysaccharide synthesis

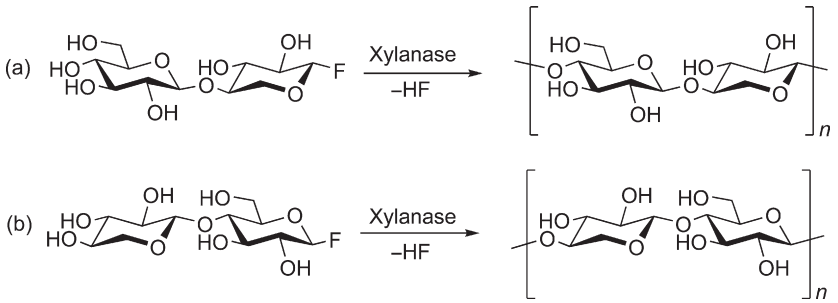
Unnatural polysaccharides of hybrid type were prepared via polycondensations. The first example is a cellulose–xylan hybrid polysaccharide. Two monomers were designed on the basis of the TSAS concept: Glcβ(1→4)Xyl-β-fluoride (a) and Xylβ(1→4)Glc-β-fluoride (b) (Scheme 7).[22] Both monomers were polymerized by xylanase from *Trichoderma viride*, giving rise to the corresponding hybrid polysaccharide in an acetonitrile–buffer solution.

A cellulose–chitin hybrid polysaccharide was successfully prepared via polycondensation of GlcNAcβ(1→4)Glc-β-fluoride (GlcNA, *N*-acetyl-D-glucosamine) designed on the basis of the TSAS concept for cellulase catalysis (Scheme 8). The polycondensation resulted in a cellulose–chitin hybrid polysaccharide as a white precipitate, with an M_n value of 2800.[23] It is noticeable that a bulky 2′-acetamido group in the monomer did not deactivate the cellulase catalyst activity.

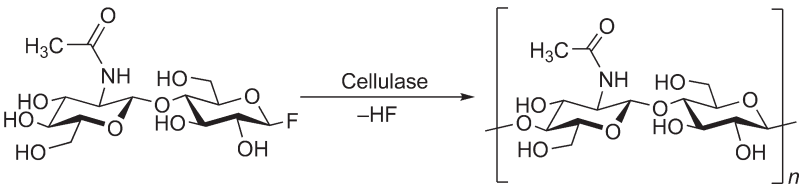
5.10.2.2 Polyester Synthesis

The major enzyme catalyst used for polyester synthesis is lipase (triacylglycerol acylhydrolase), and it catalyzes the hydrolysis of fatty acid glycerol esters *in vivo* with an ester bond cleavage. Similar to hydrolase enzymes, which induce polymerization to yield polysaccharides, lipase catalyzes polymerization reactions to give polyesters *in vitro* with an ester bond formation. Actually, various synthesis reactions have been developed in the past two decades.[1,24] The lipase-catalyzed polyester synthesis via polycondensation proceeds between a carboxyl group and an alcohol group, being divided into two modes a and b (Scheme 9). Polyesters can also be synthesized by ring-opening polymerization (ROP) of cyclic ester monomers.

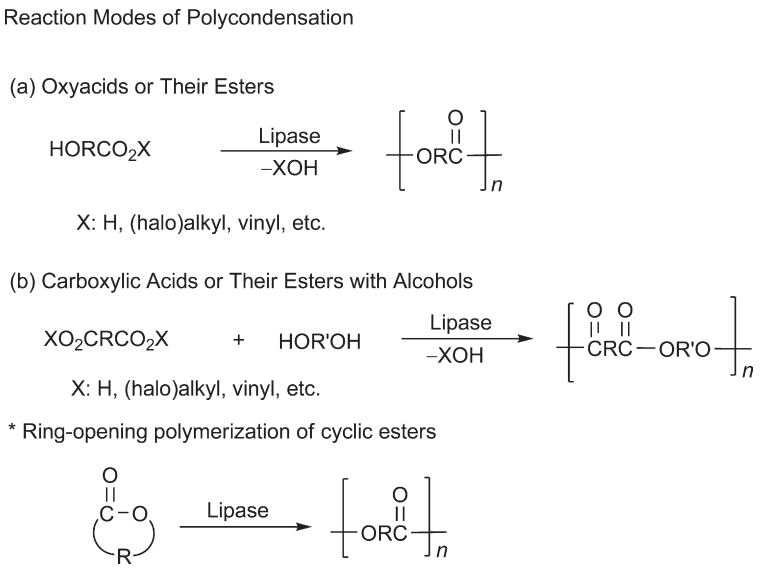
The merits of using lipases as catalysts are as follows: (1) High regioselectivity of the reaction produces polyesters in which only a primary OH group reacted with $-CO_2H$ or $-CO_2R$



Scheme 7 Unnatural polysaccharide synthesis of a cellulose–xylan hybrid via polycondensation of Glcβ(1→4)Xyl-β-fluoride monomer (a) and Xyl β(1→4)Glc-β-fluoride monomer (b).



Scheme 8 Cellulase-catalyzed polycondensation of GlcNAcβ(1→4)Glc-β-fluoride to a celluose–chitin hybrid polysaccharide.



Scheme 9 Lipase-catalyzed polyester synthesis via polycondensation is divided into two modes (a) and (b).

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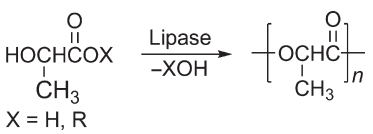
group without involving the reaction of a secondary OH group. (2) Optically active polyesters can be readily obtained. (3) Reactions can be carried out in a green solvent like water, supercritical CO_2, or an ionic liquid. (4) ROP, which is only briefly explained in this chapter, involving lipases allows new methods such as chemoenzymatic polymerization and enantioselective polymerization. These merits are often very difficult to be realized by conventional chemical catalysts. Thus, the merits enable the production of various functionalized polyesters, and contribute to conduct green polymer chemistry.[24e,24f]

5.10.2.2.1 Oxyacids or their esters

Dehydration polycondensation is the simplest polycondensation mode. The first paper appeared in 1985, reporting a lipase-catalyzed polycondensation of an oxyacid monomer, 10-hydroxydecanoic acid, in benzene using poly(ethylene glycol) (PEG)-modified lipase soluble in the medium. The DP value of the product was more than 5. The PEG-modified esterase also induced the oligomerization of glycolic acid, the shortest oxyacid.[25a] A lipase-catalyzed polymerization of lactic acid (LA, X = H) gave a low-molecular-weight poly(lactic acid) (PLA) (Scheme 10).[25b]

The general scheme of a lipase-catalyzed transesterification to form an ester bond via condensation reaction is discussed here. Scheme 11 indicates an accepted mechanism for the reaction $R^1C(=O)OX + R^2OH \rightarrow R^1C(=O)OR^2 + XOH$. The active site of lipase is the $-CH_2OH$ group of the serine residue, and an acyl-enzyme intermediate (EM) formation is a key for the reaction to be catalyzed. The enzyme and $R^1C(=O)OX$ form the intermediate (acylation of lipase); thus $R^1C(=O)OX$ acts as an acyl donor. Then, R^2OH nucleophilically attacks the acyl carbon to form an ester bond (deacylation of lipase); thus R^2OH acts as a nucleophile.[24f]

A very recent paper reported that lipase (Novozym 435)-catalyzed polycondensation of alkyl esters of LA as monomer produces oligoLAs (X = alkyl, n = 2–7 in Scheme 10).[26] The reaction is perfectly enantioselective; only an alkyl D-lactate (RDLa) monomer produced the oligomers. Figure 3 demonstrates the reaction pathways of only the dimer formation for simplicity. An EM formation (acylation of lipase) is achieved from both D- and L-monomers as shown by the hydrolysis results of alkyl lactate (RLa) monomers given as steps a and e, while the subsequent ester bond formation (deacylation of lipase) by the reaction of OH group of RLa or oligoLAs with EM is achieved only by the reaction between the EM from D-monomer and OH group having (R) configuration of step b, namely, "the enantioselection is governed by the deacylation step!" These results provide the first direct evidence for the important step in the lipase-catalyzed reaction mechanism. The rate of step a is a couple of times faster than that of step e.



Scheme 10 Lipase-catalyzed polycondensation of lactic acid and lactate to low-molecular weight poly(lactic acid).

Ricinoleic acid was polymerized via dehydration with immobilized lipase PC (*Pseudomonas cepacia*) catalyst to give a polymer with M_w up to 8500.[27] Immobilized *Candida antarctica* lipase B (CALB, Novozym 435) was efficient as catalyst for the dehydration polycondensation of an oxyacid, *cis*-9,10-epoxy-18-hydroxyoctadecanoic acid, isolated from the outer birch bark to give a polyester with the highest M_w of 2.0×10^4 (polydispersity index (PDI) = 2.2) after 68 h; the reaction was performed in toluene in the presence of molecular sieves at 75 °C.[28] Copolymerization of 12-hydroxydodecanoic acid with methyl 12-hydroxystearate (both from seed oil) was catalyzed by Novozym 435 in toluene in the presence of molecular sieves at 90 °C. During the reaction, water and methanol were liberated. After several days, the copolymer was obtained in good yield, having $M_w \sim 1.0 \times 10^5$, showing elasticity and biodegradable properties.[29]

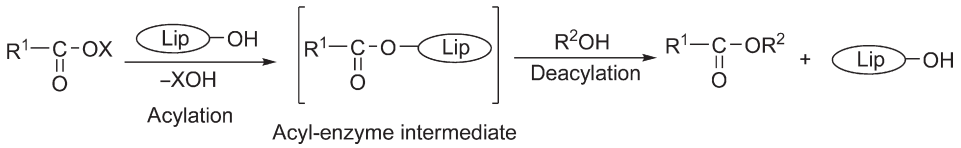
A regioselective polycondensation of isopropyl aleuriteate was achieved with Novozym 435 catalyst, where the only primary alcohol was reacted at 90 °C (Scheme 12). The polymer of M_n 5600 was obtained in 43% yield. Copolymerization of isopropyl aleuriteate with ε-caprolactone(ε-CL) gave a random copolymer having M_n up to 1.06×10^4 in ~70% yield.[30]

An enantioselective transesterification polycondensation of racemic AB-type monomers having a secondary hydroxy group and a methyl ester moiety led to chiral polyesters by iterative tandem catalysis. The concurrent actions of an enantioselective acylation catalyst (Novozym 435) and a racemization catalyst (Ru catalyst) brought about the high conversion of the racemic monomers to enantio-enriched polymers. AB-type monomers used were typically methyl 6-hydroxyheptanoate, methyl 8-hydroxynonanoate, and methyl 13-hydroxytetradecanoate. The polycondensation at 70 °C in toluene gave a polyester in high yield having M_n around several thousands with ee higher than 74%.[31]

5.10.2.2.2 Carboxylic acids or their esters with alcohols

The general scheme of dehydration polycondensation mode is given in Scheme 13.

It was in 1984 that the first paper on lipase-catalyzed polymerization reported an *Aspergillus niger* lipase (lipase A)-catalyzed dehydration polycondensation of several free dicarboxylic acids in the presence of an excess amount of a diol to give oligomeric polyesters.[32] A high-boiling diphenyl ether was the preferred solvent for the polycondensation of adipic acid (p = 4) and 1,8-octanediol (q = 8) giving a product with M_n of 28 500 (48 h, 70 °C). The reactions involving monomers having longer alkylene chain lengths of diacids



Scheme 11 Accepted mechanism for a lipase-catalyzed reaction $R^1C(=O)OX + R^2OH \rightarrow R^1C(=O)OR^2 + XOH$.

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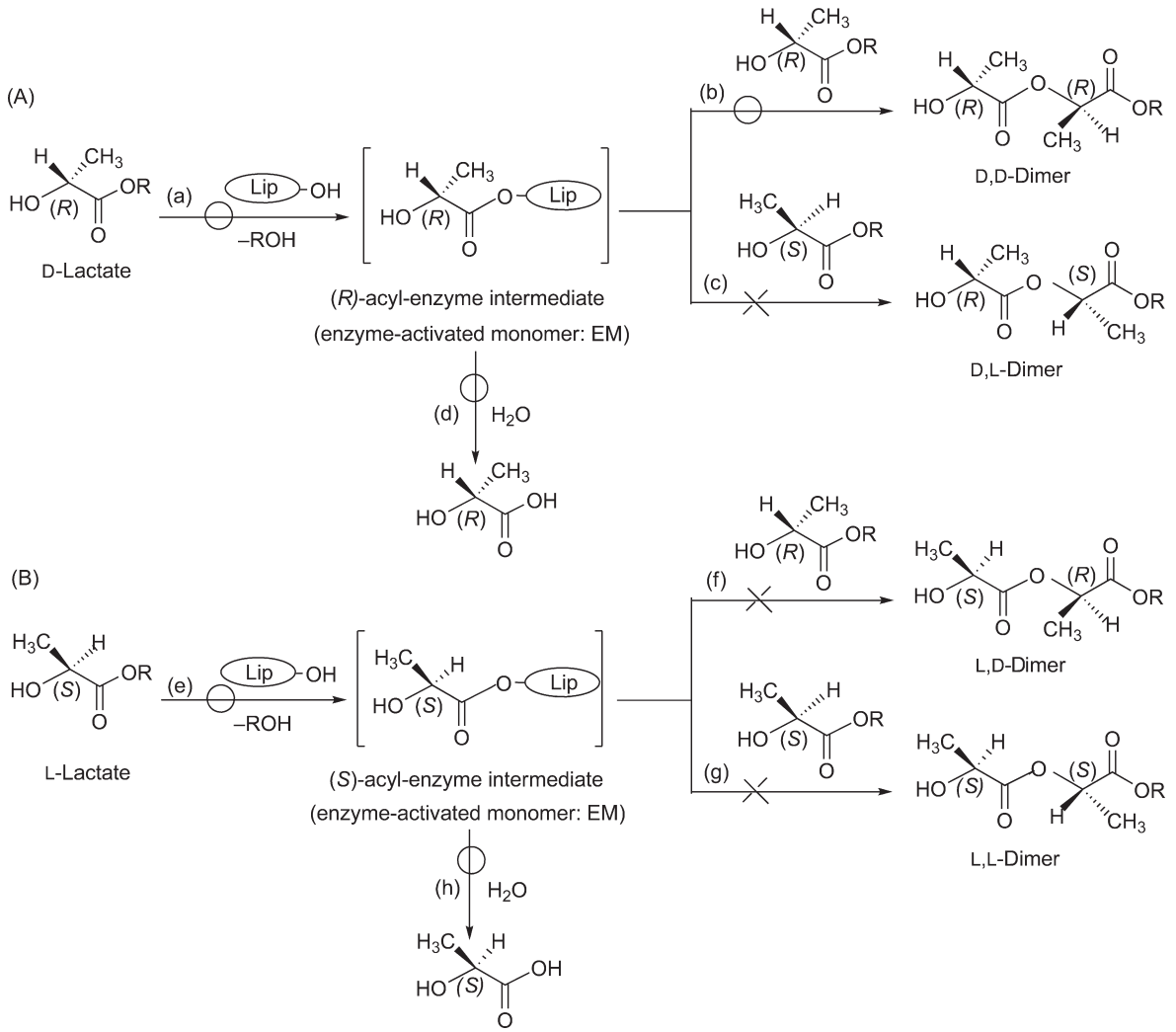
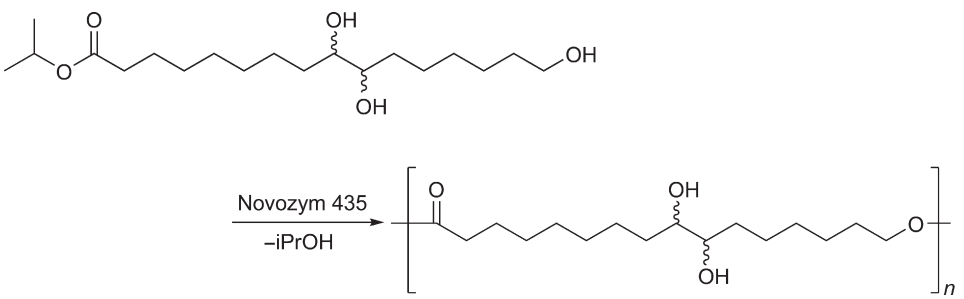
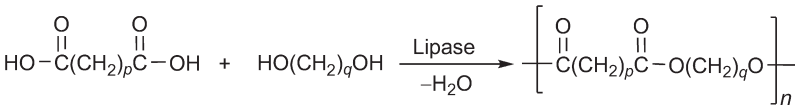


Figure 3 Lipase-catalyzed reaction pathways of D-lactates (A) and L-lactates (B): acyl-enzyme intermediate formation steps (a and e), subsequent dimer formation steps (b, c, f, and g), and hydrolysis steps (d and h). The symbol ○ denotes that the step takes place, whereas the symbol × denotes that the step does not take place. Reprinted with permission from Ohara, H.; Onogi, A.; Yamamoto, M.; Kobayashi, S. *Biomacromolecules* **2010**, *11*, 2008. © Copyright 2010 The American Chemical Society.[26]



Scheme 12 Lipase-catalyzed regioselective polycondensation of isopropyl aleuriteate to polyester.



Scheme 13 Lipase-catalyzed dehydration polycondensation of a dicarboxylic acid and a diol to a polyester.

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(sebacic and adipic acids) and diols (1,8-octanediol and 1,6-hexanediol) showed a higher reactivity than those involving monomers of shorter chain lengths.[33]

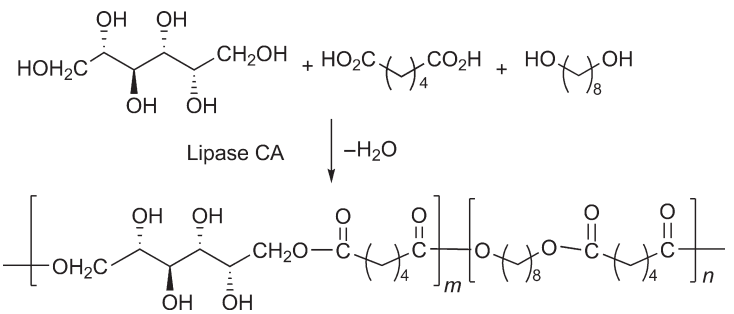
A dehydration reaction was found possible in an aqueous medium. Dehydration reactions are normally conducted in nonaqueous media because water, which is a product of dehydration and which is in equilibrium with starting materials, disfavors the dehydration to proceed in an aqueous medium due to the 'law of mass action'. Nevertheless, lipase catalysis enabled dehydration polycondensation of a dicarboxylic acid and a glycol in water at 45 °C, to afford a polyester in good yield.[34a,34b] In the polymerization of an α,ω-dicarboxylic acid and a glycol, the polymerization behavior largely depended on the methylene chain length of the monomers. Hydrophobicity of monomers is a key factor for the production of polymers. Dehydration polycondensation in water is a new finding in organic chemistry, and the principle was later utilized for organic synthesis by other chemists.[34c]

A regioselective direct dehydration polycondensation between a polyol sugar component sorbitol and adipic acid was carried out with lipase CA (*C. antarctica*) catalyst at 90 °C for 48 h. The product poly(sorbityl adipate) was water soluble. The M_n and M_w values were 10 880 and 17 030, respectively. Sorbitol was esterified at the primary alcohol group of 1- and 6-positions with high regioselectivity (85 ± 5%). To obtain a water-insoluble sorbitol polyester, sorbitol, adipic acid, and 1,8-octanediol (molar ratio 15:50:35) were terpolymerized at 90 °C for 42 h (**Scheme 14**). The methanol-insoluble part (80%) had M_w of 1.17×10^5.[35]

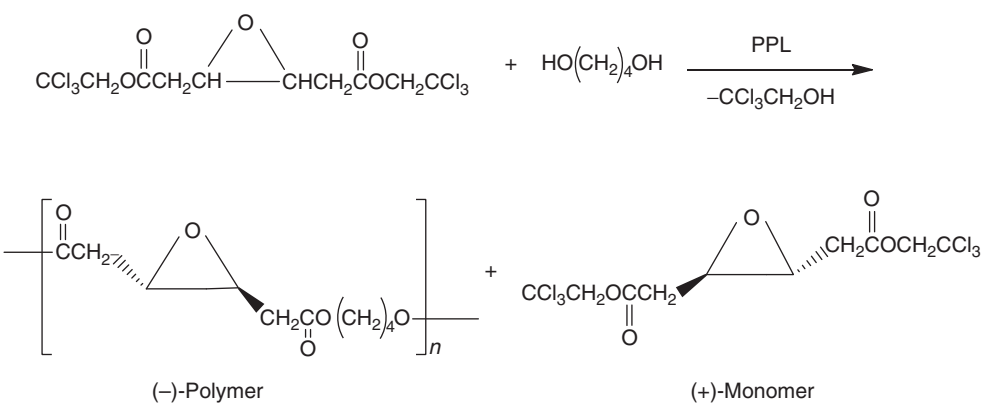
Cutinase (1 wt.%) catalyzed a dehydration polycondensation between a glycol and a diacid at 70 °C for 48 h under vacuum.[36] With the adipic acid component fixed, polyesters with M_n values up to 12 000 were obtained from diols. With the 1,4-cyclohexanedimethanol component fixed, polyesters obtained from succinic acid, adipic acid, suberic acid, and sebacic acid had M_n values of 900, 4000, 5000, and 19 000, respectively.

An efficient enantioselective transesterification polymerization with lipase catalyst was reported in 1989; the reaction of bis(2,2,2-trichloroethyl) *trans*-3,4-epoxyadipate with 1,4-butanediol using porcine pancreas lipase (PPL) catalyst gave a highly optically active polyester (**Scheme 15**). The enantiomeric purity of the (−)-polymer that resulted was >96%, and the unchanged (+)-monomer had a purity >95%.[37]

For the synthesis of an optically active polyester from a racemic monomer, a new method of dynamic kinetic resolution (DKR) was used. A mixture of stereoisomers of a secondary diol, α,α′-dimethyl-1,4-benzenedimethanol, were enzymatically polymerized with dimethyl adipate (**Scheme 16**).[38] Due to the enantioselectivity of lipase CA, only the hydroxyl groups at the (*R*) center are preferentially reacted to form the ester bond with the liberation of methanol. The reactivity ratio was estimated as $(R)/(S) = \sim 1 \times 10^6$. *In situ* racemization from the (*S*) to the (*R*) configuration by Ru catalysis allowed the polymerization to high conversion, that is, the enzymatic polymerization and the Ru-catalyzed racemization occurred concurrently. During the reaction, molecular weight increased to 3000–4000 and the optical rotation of the reaction mixture increased from −0.6° to 128°.



Scheme 14 Lipase-catalyzed dehydration ter-polycondensation of sorbitol, adipic acid, and 1,8-octanediol to polyester.



Scheme 15 Enantioselective transesterification polymerization with lipase catalyst to optically active polyester.

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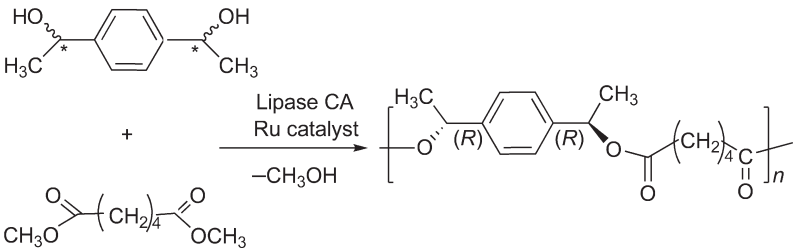


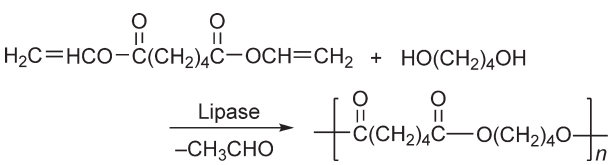
Scheme 16 Dynamic kinetic resolution method for optically active polyester synthesis from a racemic diol monomer.

Transesterifications are inherently reversible reactions. To shift the equilibrium toward the product polymer more effectively, activation of esters was carried out using a halogenated alcohol such as 2-chloroethanol, 2,2,2-trifluoroethanol, and 2,2,2-trichloroethanol instead of using methanol or ethanol for increasing the electrophilicity of the acyl carbonyl. This activation helps to avoid significant alcoholysis of the products by decreasing the nucleophilicity of the leaving alkoxy group.

In 1994, an irreversible process was developed using a vinyl ester for the lipase-catalyzed acylation, where the product of vinyl alcohol tautomerizes to acetaldehyde. A divinyl ester was employed for the first time as the activated acid form in the enzyme-catalyzed polyester synthesis. The lipase PF-catalyzed polycondensation of divinyl adipate and 1,4-butanediol was performed at 45 °C in diisopropyl ether for 48 h to afford a polyester with M_n of 6.7×10^3 (Scheme 17), whereas the use of adipic acid and diethyl adipate did not produce the polymer. Later, the same polycondensation of divinyl adipate and 1,4-butanediol with lipase PC catalyst produced a polyester with M_n of 2.1×10^4.[39]

A lipase-catalyzed terpolymerization of monomers, ω-pentadecalactone, diethyl succinate, and 1,4-butanediol, was carried out by CALB catalyst desirably at 95 °C via a two-stage vacuum technique. The polymerization involving two types, polycondensation and ROP, was examined under various reaction conditions and the product terpolyester reached M_w 77 000 with M_w/M_n ~1.7–4.0.[40]

A new cross-linkable polyester was prepared by lipase-catalyzed polycondensation of divinyl sebacate with glycerol in the presence of an unsaturated higher fatty acid (i) such as linoleic acid and linolenic acid obtained from renewable plant oils (route A, Scheme 18). Curing of product (iii) accomplished by oxidation or thermal treatment gave a cross-linked transparent film (iv). Biodegradability of the film obtained was verified by biochemical oxygen demand (BOD) measurement.[41] Furthermore, epoxide-containing polyesters were enzymatically synthesized via two routes using unsaturated fatty acids (routes A and B, Scheme 18). In route A, product (iii) was enzymatically epoxidized to give (iv), and in route B the epoxidization of the fatty acid was first conducted and lipase-catalyzed polycondensation of product (ii) was performed to produce (iv). Curing of (iv) proceeded thermally, yielding transparent polymeric films with high gloss surface.[42]



Scheme 17 Irreversible process of lipase-catalyzed polycondensation between divinyl adipate and 1,4-butanediol to the polyester.

Mercapto group can be a cross-linking group. Direct lipase CA-catalyzed polycondensation of 1,6-hexanediol and dimethyl 2-mercaptosuccinate at 70 °C in bulk gave an aliphatic polyester having free pendant mercapto groups with M_w 14 000 in good yield.[43]

5.10.2.2.3 Cyclic esters (lactones)

With reference to polycondensation, the mechanism of ROP of lactones to give polyesters is described here, since the key steps are condensation reactions (Scheme 19). Both initiation and propagation reactions involve nucleophilic attack of OH groups on the EM to cleave off a lipase leaving group, which is similar to reaction type of the deacylation in Scheme 11 and Figure 3.

5.10.2.3 Polyaromatics Synthesis

Oxidoreductase enzymes employed for oxidative polymerization of aromatic compounds are typically peroxidase containing Fe at the active site (a), and laccase (b), tyrosinase, and bilirubin oxidase containing Cu at the active site(s) (Scheme 20).[1j] Their catalysis needs an oxidant, which is often hydrogen peroxide or oxygen gas (air).

5.10.2.3.1 Oxidative polymerization of phenolic compounds

Currently, two polymers are commercially produced from phenolic compounds: phenol/formaldehyde resin (Bakelite) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), both via polycondensation. So far, various phenolic compounds have been oxidatively polymerized using enzyme catalysts.[44] Peroxidase-catalyzed polymerization of phenol was induced to proceed under mild reaction conditions, giving rise to a soluble polyphenol having C–C and C–O coupling units with M_n of 3000–6000 (Scheme 21). The catalysts include horseradish peroxidase (HRP) and soybean peroxidase (SBP), the reaction of which involves one-electron oxidation of phenol in the presence of H_2O_2 via oxy or carbon radical intermediate. The reaction liberates H_2O and hence it is of polycondensation type. It was important to select the reaction solvent using an aqueous buffer alcohol (methanol or ethanol). The content of oxyphenylene unit (32–59%) was controlled by varying the methanol amount. The polymer solubility increased with the increase in the oxyphenylene unit content.[45]

By using PEG monododecyl ether as a template for the HRP-catalyzed polymerization of phenol in water, the regioselectivity for the phenylene unit was much increased to 90% content.[45] The polymerization using Pluronic F68 (EG_{76}-PG_{29}-EG_{76}) template gave a homogeneous reaction

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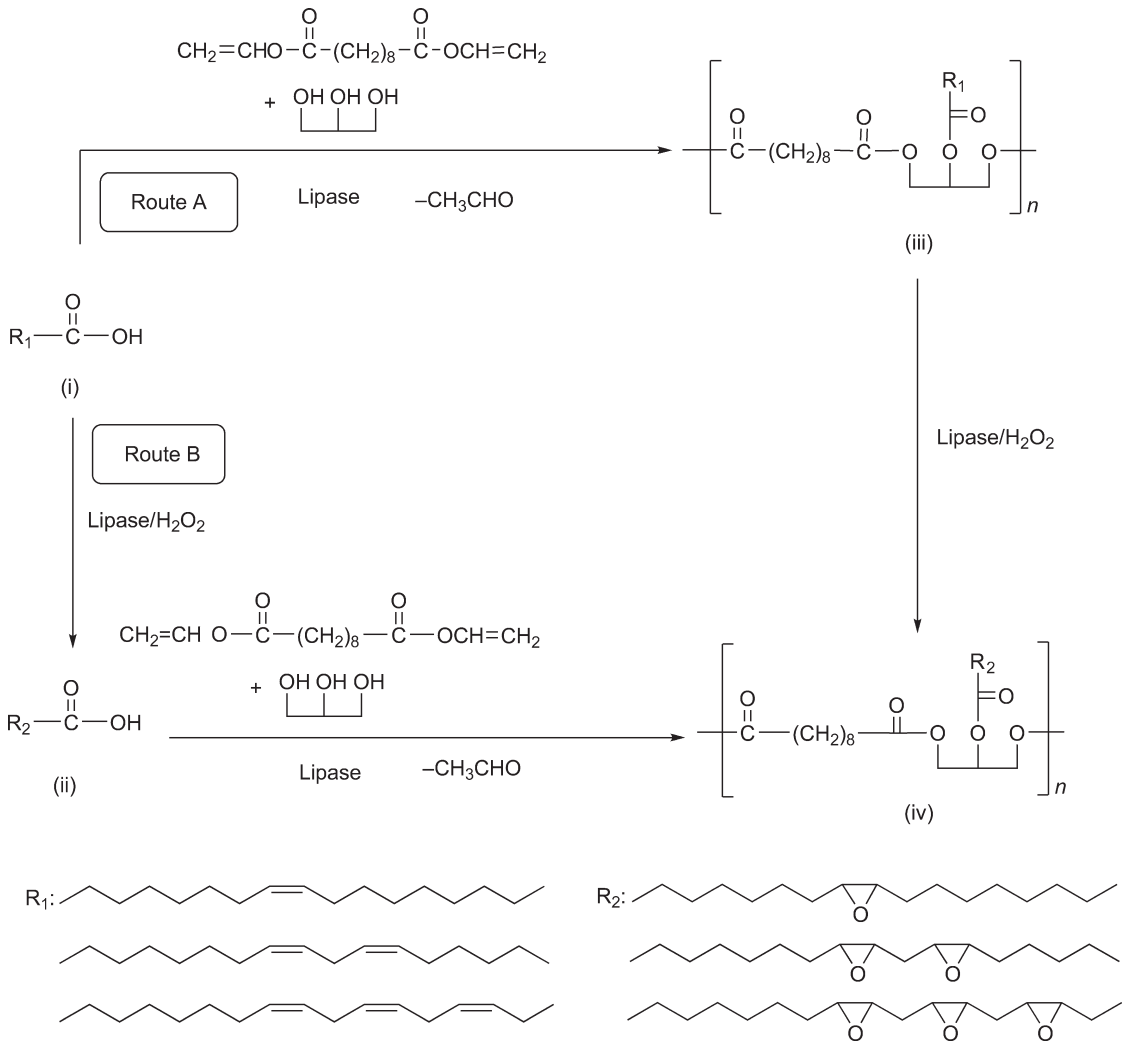
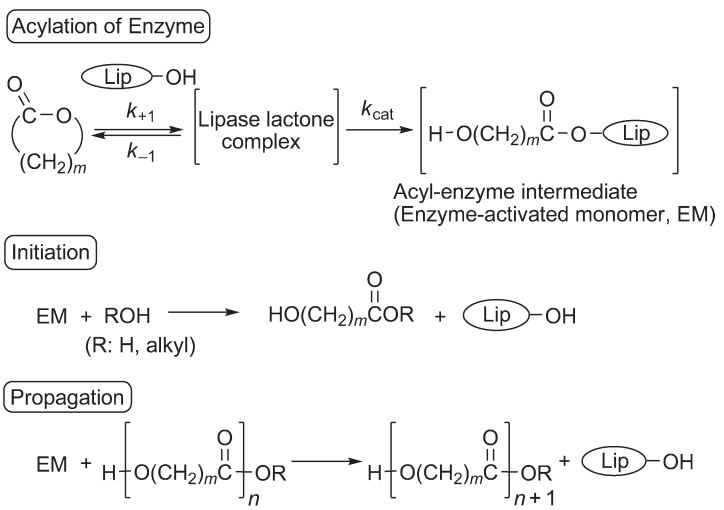


Scheme 18 Synthesis of crosslinkable and crosslinked polyestesrs by lipase-catalyzed polycondensation of divinyl sebacate and glycerol.



Scheme 19 Mechanism of ring-opening polymerization of lactones to give polyesters.

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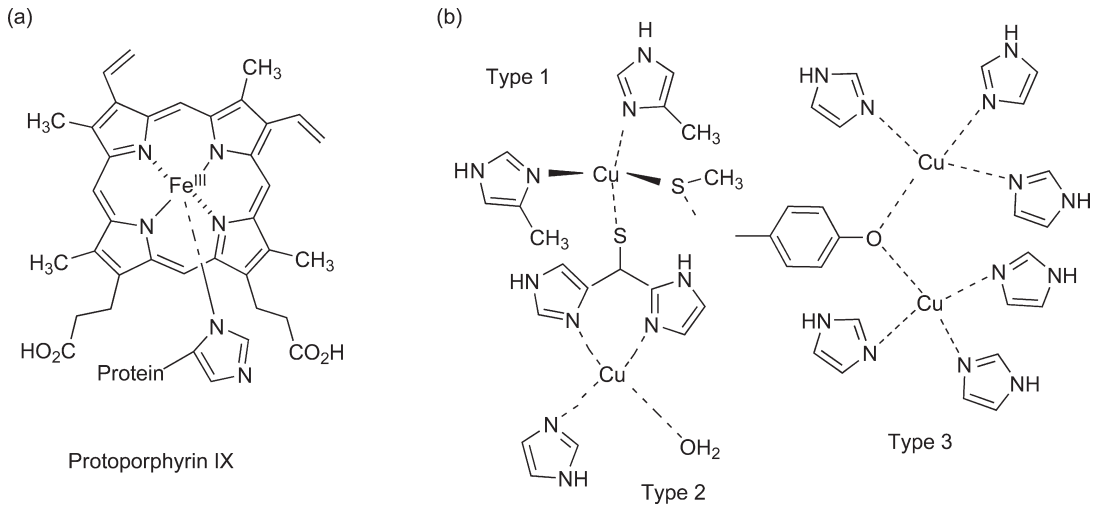
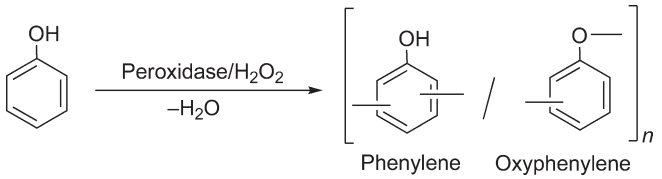


Scheme 20 Active sites of peroxidase containing Fe (a) and laccase containing Cu (b).

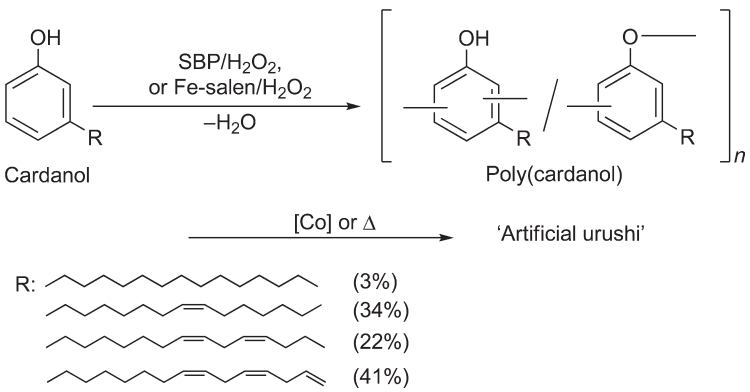


Scheme 21 Peroxidase-catalyzed polymerization of phenol to a soluble polyphenol.

mixture and produced ultrahigh-molecular-weight polyphenol (M_w value reaching 3.2×10^6), which was complexed with the template molecules.[46]

From ancient times, a traditional Japanese lacquer has long been known, called 'urushi', displaying excellent toughness and brilliance over many hundreds of years, but it is expensive. It is a natural cross-linked material of 'urushiol' catalyzed by laccase in air. A main component of urushiol is a catechol derivative directly linked at 3- or 4-position to unsaturated hydrocarbon chains (mainly C-15) constituted from a mixture of monoenes, dienes, and trienes. To prepare cheaper lacquer, an artificial urushi was derived from cardanol. Cardanol is the main component derived from cashew nut shell liquid; it is a phenol derivative having a meta-substituent of a C-15 unsaturated hydrocarbon chain mainly with 1–3 double bonds. A new cross-linkable polymer was synthesized by the SBP- or Fe-salen (Fe(II)-*N*,*N*′-ethylenebis(salicylideneamine))-catalyzed polymerization of cardanol (Scheme 22), where Fe-salen was regarded as a model complex of the peroxidase. The product poly(cardanol) with molecular weight 2000–4000 was soluble in a polar organic solvent. The polymer was further cross-linked by thermal treatment or by cobalt naphthenate-catalyzed oxidation, which involves a radical reaction of double bonds. The cross-linked poly(cardanol) showed a tough and hard property as a film with high gloss surface and is regarded as 'artificial urushi' due to a close structural resemblance with natural urushi.[47]

Syringic acid (3,5-dimethoxy-4-hydroxybenzoic acid), an *o*-disubstituted phenol derived from plants, was polymerized



Scheme 22 SBP and Fe-salen catalyzed oxidative polymerization of cardanol to 'artificial urushi'.

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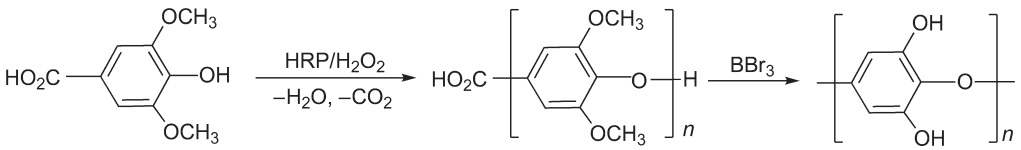


Scheme 23 Oxidative polymerization of syringic acid to poly(1,4-oxyphenylene)s.

by HRP or SBP catalyst to produce poly(2,6-dimethoxy-1,4-oxyphenylene) having a carboxyl group at one end and a hydroxy group at the other end. Carbon dioxide and water were liberated during the polymerization. The molecular weight reached 1.5×10^4 with SBP catalyst. Demethylation of the product polymer by boron tribromide catalyst gave a new polymer, poly(2,6-dihydroxy-1,4-oxyphenylene), which is thermally stable below 300 °C under nitrogen (**Scheme 23**).[48]

Lignin-related polymers were synthesized. Coniferyl alcohol (4-hydroxy-3-methoxycinnamyl alcohol, CoA), a phenolic lignin monomer (monolignol) contained in plant cell walls, was polymerized by HRP/H_2O_2 in pectin solution in order to mimic lignification, which is the final step of biosynthesis of plant cell wall.[49a] CoA was also polymerized in the presence of α-cyclodextrin (α-CD) with HRP/H_2O_2 system. The presence of α-CD led to the product polymer with 8-O-4′-richer linkages, compared with the no-additive case. This is probably due to the inclusion complex formation between CoA and α-CD, which suppresses the other linkages such as 8–5′ and 8–8′ linkages, due to steric hindrance of the complex.[49b] A lignin-based macromonomer, lignocatechol, was prepared from wood components and oxidatively polymerized by laccase catalyst to produce cross-linked polymers in good yield. Laccase-catalyzed copolymerization of lignophenol with urushiol was also performed to afford the corresponding copolymers in high yield. The thermal stability of these polymers was excellent.[49c]

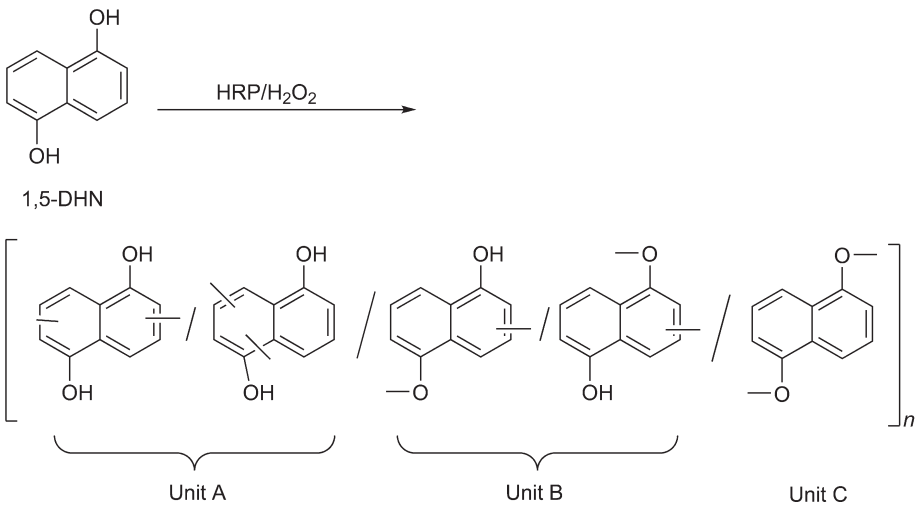
2-Naphthol was oxidatively polymerized in a reverse micelle system to give a polymer as single and interconnected microspheres, which demonstrated the fluorescence characteristics of the 2-naphthol chromophore.[50a] Polymerization of 1,5-dihydronaphthalene (1,5-DHN) with HRP catalyst produced poly(1,5-DHN) as a dark-brown solid consisting of 1,5-dihydroxynaphthalene unit (A), 1(or 5)-hydroxy-5(or 1)-oxynaphthalene unit (B), and 1,5-dioxynaphthalene unit (C) (**Scheme 24**). HRP-catalyzed polymerization of 2,6-DHN proceeded selectively at the aromatic ring to give poly(2,6-DHN) consisting of only the 2,6-dihydroxynaphthalene unit. Optical, electrochemical, and thermal properties of these polymers were investigated.[50b]

Polymerization of polyphenols, compounds with more than two hydroxyl groups in the aromatic ring(s), analogously took place. Natural urushiol from urushi trees belongs to catechols, a family of polyphenols, leading to 'natural urushi' by laccase catalysis in air (**Scheme 25**, also see **Scheme 22**).[47]

Nanometer-scale surface patterning of caffeic acid (3,4-dihydroxycinnamic acid) was achieved on 4-aminothiophenol (*p*-ATP)-modified gold surfaces by a dip pen nanolithography (DPN) method. HRP-catalyzed polymerization was applied on the patterned caffeic acid features (**Scheme 26**).[51] The product polymer contained the exclusive C–C ring coupling unit.

Flavonoids, a few examples of which are given in **Scheme 27**, are contained in green tea: (+)-catechin, (−)-epicatechin, (−)-epigallocatechin, (−)-epicatechin gallate, and (−)-epigallocatechin gallate (EGCG) are the typical flavonoids present in tea. Green tea is known to possess many biological functions, with anticancer effects being one among them.[52]

The HRP-catalyzed polymerization of catechin was carried out in an equivolume mixture of 1,4-dioxane and buffer (pH 7) to give the polymer with a molecular weight of 3.0×10^3 in 30% yield.[53a] In the laccase-catalyzed polymerization of catechin, a mixture of acetone and acetate buffer (pH 5) was suitable for the efficient synthesis of soluble poly(catechin) with higher



Scheme 24 HRP-catalyzed polymerization of 1,5-dihydronaphtahalene (1,5-DHN).

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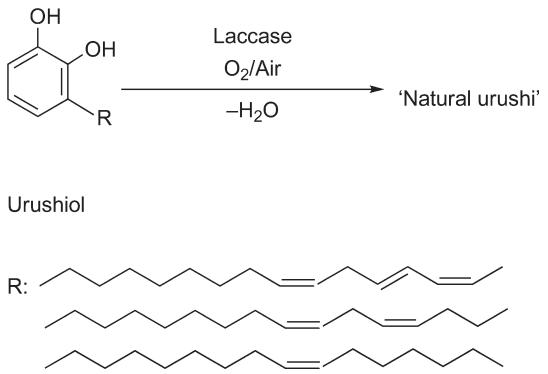
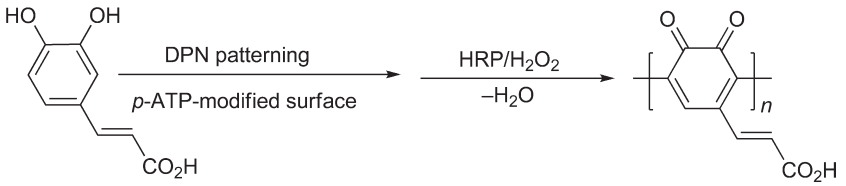
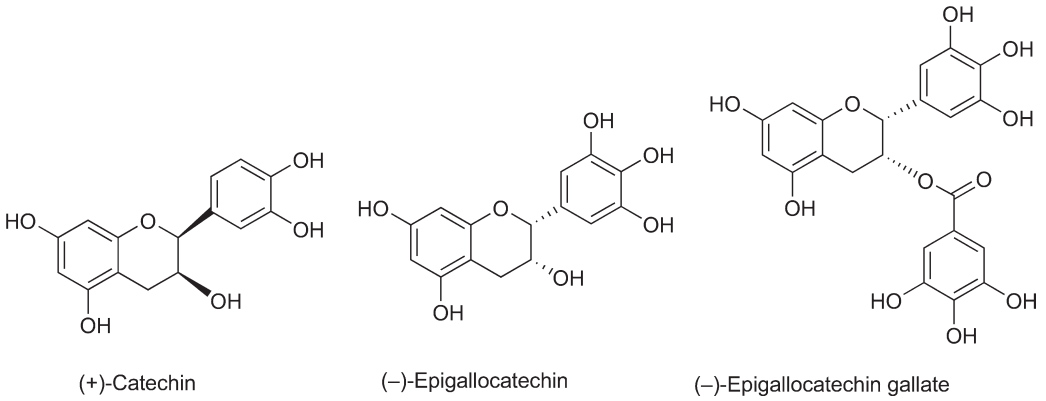


Scheme 25 Laccase-catalyzed oxidative polymerization of urushiol to 'naturel urushi'.



Scheme 26 Oxidative polymerization of caffeic acid (3,4-dihydroxycinnamic acid) for surface patterning involved in a dip pen nanolithography (DPN) method.



Scheme 27 Example compounds of flavonoids.

molecular weight around several thousands. In the UV–vis spectrum of poly(catechin) in methanol, a broad peak centered at 370 nm was observed. In alkaline solution, this peak was red-shifted and the peak intensity became larger than that in methanol. In the electron spin resonance (ESR) spectrum of the enzymatically synthesized poly(catechin), a singlet peak at $g = 1.982$ was detected, whereas the catechin monomer possessed no ESR peak.[53b] The HRP-catalyzed polymerization of catechin greatly enhanced the antioxidant property. For example, the enzymatically prepared poly(catechin) exhibited a much enhanced superoxide anion scavenging activity compared with catechin monomer. Likewise, polyEGCG with a molecular weight of 1×10^3 showed excellent inhibition of xanthine oxidase (XO), which was about 20 times higher than that achieved with EGCG monomer.[53c]

5.10.2.3.2 Oxidative polymerization of aniline compounds

Polyaniline (PANI) has been known over a century. Currently, PANI is one of the most popular conducting polymers because of its stability and good electrical and optical properties, which are attractive for technological applications in lightweight batteries, microelectronics, electrochromic displays, light-emitting diodes, electromagnetic shielding, sensors, and so forth. The well-known methods for the synthesis of PANI are either chemical or electrochemical oxidation polymerization of aniline monomer. However, the reaction conditions are harsh involving extreme pH, high temperature, strong oxidants, and highly toxic solvents.

On the contrary, enzymatic polymerization of aniline, its derivatives, and other aromatic compounds provides an alternative method of a 'green process' toward the formation of soluble and processable conducting polymers. These reactions are usually carried out at room temperature and in aqueous organic solvents at neutral pH. The reaction condition is greatly improved and the purification process of the final products is simplified when compared to traditional methods (Scheme 28).[54]

Water-soluble conducting PANI was obtained by HRP-catalyzed polymerization of aniline using H_2O_2 oxidant,

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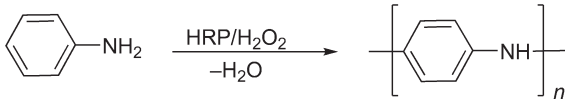


Scheme 28 HRP-catalyzed oxidative polymerization of aniline.

in the presence of sulfonated polystyrene (SPS), which acted as a polyanionic template. The resulting polymer was complexed to the SPS and exhibited electroactivity. The conductivity of the PANI/SPS complex was measured to be $0.005\,S\,cm^{-1}$. The values increased to $0.15\,S\,cm^{-1}$ after HCl doping and could be increased further with an increase in the aniline to SPS molar ratio. The enzymatic approach is claimed to offer unsurpassed ease of synthesis, processability, stability (electrical and chemical), and environmental compatibility.[55]

Enzymatic polymerization of aniline in the presence of a template like SPS produced PANI having a linear structure, due to the electrostatic alignment of the monomer and SPS to promote a para-directed coupling. Without the template, the PANI structure became branched, which is not a desirable property of conducting materials.[56] Enzymatically synthesized PANI is normally in the protonated form, which can be converted to the unprotonated base form by treatment with aqueous ammonia solution or other suitable bases. The unprotonated base form of PANI consists of reduced base units 'A' and oxidized base units 'B' as repeat units, where the oxidation state of the polymer increases with decreasing values of y ($0 \le y \le 1$). The three extreme possibilities for values of y are 1, 0.5, and 0, corresponding to fully reduced PANI (leucoemeraldine), the half-oxidized PANI (emeraldine), and fully oxidized PANI (pernigraniline), respectively (Scheme 29).[57]

PANI colloid particles were prepared by HRP- or SBP-catalyzed oxidative polymerization of aniline in a dispersed medium together with toluenesulfonic acid using poly(vinyl alcohol), poly(*N*-isopropylacrylamide), or chitosan as the steric stabilizer. The colloidal particles are pH- and thermosensitive, and are claimed to have potential applications in smart devices such as thermochromic windows, temperature-responsive electrorheological fluids, actuators, and colloids for separation technologies.[58]

5.10.2.3.3 Oxidative polymerization of other aromatic compounds

Other aromatic compounds that can be polymerized are pyrrole and 3,4-ethylenedioxythiophene (EDOT). A biomimetic polymerization of them in the presence of SPS produced polyEDOT/SPS and polypyrrole/SPS complexes, where a PEG-modified hematin (PEG-hematin) was used to catalyze the polymerization in water at 25 °C at pH 1–2 using H_2O_2 oxidant. The electronic conductivities of the products polyEDOT and polypyrrole were 1×10^{-3} and $1 \times 10^{-4}\,S\,cm^{-1}$, respectively. Copolymer of EDOT and pyrrole was also synthesized to give the copolymer/SPS complex, whose conductivity ($0.1–1.0\,S\,cm^{-1}$) was much higher than that of the homopolymers.[59] An HRP-catalyzed polymerization of EDOT gave a two-phase reaction system. The enzyme HRP and EDOT form droplets in the solution to trigger polymerization in the interface, giving rise to water-soluble conducting polyEDOT. Toward the end of the polymerization, the polymer aqueous phase and the HRP/EDOT phase were separated. The latter phase acted as a biocatalyst, which can be recycled and reused, giving a simpler and easier encapsulation method than the conventional encapsulation of HRP into solid supports.[60]

5.10.3 Enzymatic Polyaddition

5.10.3.1 Enzymatic Ring-Opening Polyaddition

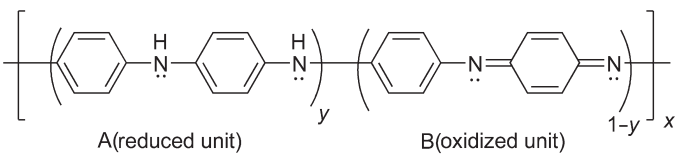
In the category of polyaddition, enzymatic ring-opening polyaddition is within the context of the enzymatic polymerization area.

5.10.3.1.1 Chitin synthesis

Chitin is a β(1→4)-linked GlcNAc polysaccharide, which is synthesized *in vivo* by the catalysis of chitin synthase with UDP-GlcNAc as a substrate. Chitosan is an N-deacetylated product of chitin. They are one of the most abundant and widely found polysaccharides in animals as a structural material.

The first *in vitro* synthesis of chitin was accomplished in 1995 via ring-opening polyaddition of a chitobiose oxazoline derivative monomer (a disaccharide) catalyzed by chitinase, and was published in 1996 (Scheme 30) (*see* Chapter 4.15 for a review on ring-opening polymerization of oxazolines).[61,62] The reaction is of ring-opening polyaddition mode, and was promoted under weak alkaline conditions (pH 9.0–11.0), where the hydrolysis of the product chitin was much suppressed. The DP value of 'synthetic chitin' was evaluated as 10–20 under the reaction conditions employed.[5]

The mechanism of chitinase catalysis involves two carboxylic acid residues (Figure 4). In the *in vivo* hydrolysis of chitin (A), the oxygen atom of glycosidic linkage is protonated by one of the carboxylic residues immediately after the recognition of chitin (stage a). Carbonyl oxygen atom of



y = 1 Leucoemeraldine base
y = 0.5 Emeraldine base
y = 0 Pernigraniline base

Scheme 29 Three extreme possibilities of the oxidation state of polyaniline.

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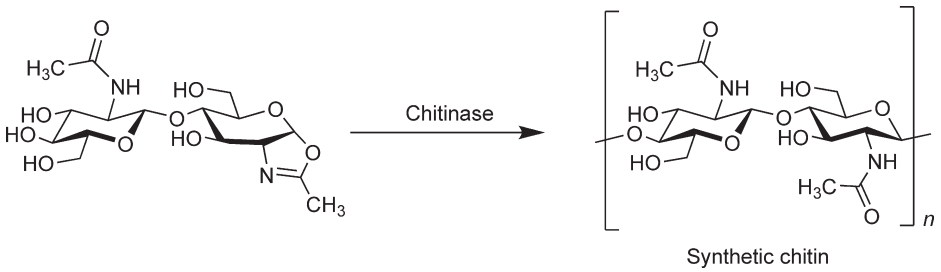

Scheme 30 Chitinase-catalyzed ring-opening polyaddition of a chitobiose oxazoline monomer to 'synthetic chitin'.

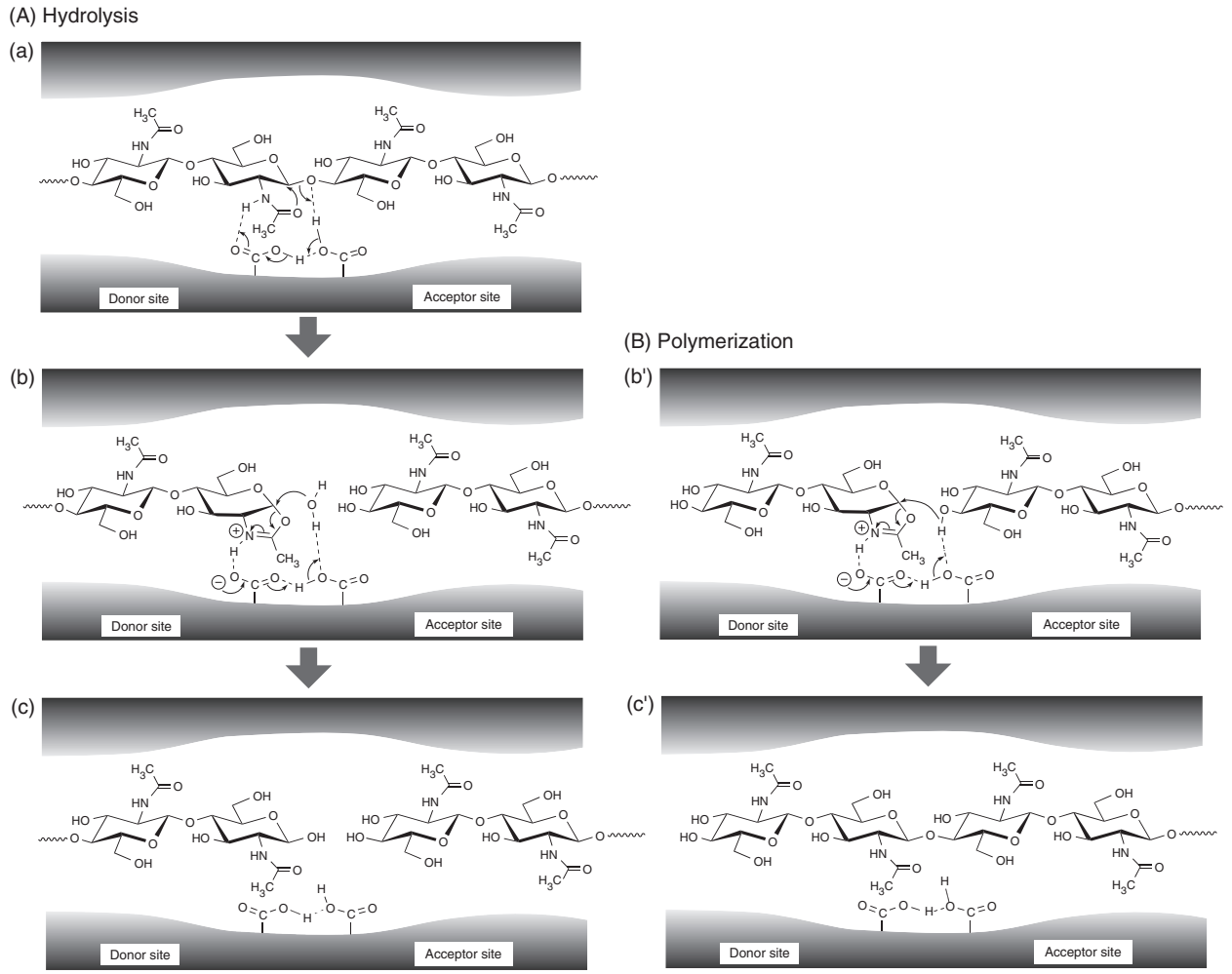

Figure 4 Postulated mechanisms of chitinase catalysis for *in vivo* hydrolysis of chitin (A) and for *in vitro* ring-opening polyaddition of the chitobiose oxazoline monomer to form synthetic chitin (B). Reprinted with permission from Kobayashi, S. *Proc. Jpn. Acad. B* **2007**, *83*, 215. © Copyright 2007 The Japan Academy.[5]

C-2 acetamide group is attacked by the neighboring anomeric carbon from the α-side to form an oxazolinium stabilized by another carboxylic residue, and the C-1–O bond cleavage is completed (stage b). Therefore, the reaction is of 'substrate-assisted mechanism'. Ring opening of the oxazolinium ring occurs by nucleophilic attack of water molecule from the β-side, giving rise to hydrolysate in a retaining manner (stage c). It is considered that the oxazolinium ion formation is a transition (or intermediate) state in the hydrolysis. In the *in vitro* polymerization (B), the monomer is first recognized and at the same time the nitrogen atom is protonated by the carboxylic acid residue at the donor site of chitinase, forming the corresponding oxazolinium ion (stage b′). This is because the monomer already has an oxazoline structure. Instead of the water molecule in the hydrolysis, C-4 hydroxyl group of sugar unit located at the acceptor site attacks nucleophilically the anomeric carbon from the β-side to open the ring, providing a new glycosidic linkage with β-configuration (stage c′). Thus,

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the monomer acts as a glycosyl donor as well as a glycosyl acceptor, and this glycosidic linkage formation reaction is repeated during the polymerization. The most important point is the resemblance of the structure at transition (or intermediate) state involved in both reactions at stage b and stage b′. From these considerations a new concept of TSAS was first proposed,[61] and afterward a mechanism involving an oxazolinium ion intermediate in the chitin hydrolysis by family 18 chitinase was reported.[63]

Extension of the polymerization to a stepwise elongation of GlcNAc unit via combined use of chitinase and β-galactosidase brought about a new synthesis of chitooligosaccharides, where a disaccharide of galactose, (Gal)β(1→4)GlcNAc, was used as a building block monomer.[64]

Chitin derivatives were prepared from new TSAS monomers. 6-*O*- or 6′-*O*-carboxylmethylated (CM) chitobiose oxazoline derivatives were polymerized as monomers by chitinase catalyst, indicating that both monomers were recognized by the donor site of chitinase. However, the resulting product was a dimer (tetrasaccharide) from the reaction of 6′-*O*-CM chitobiose oxazoline derivative.[65] A TSAS monomer bearing a bulky *N*-sulfonate group at the C-2′ position was designed. Chitinase-catalyzed polymerization proceeded homogeneously, due to the good solubility of the resulting polysaccharide. By selecting appropriate chitinase enzymes, molecular weight was controlled to some extent. For example, chitinase from *Serratia marcescens* provided a polysaccharide of M_n 4180.[66] The copolymerization of *N*-acetylchitobiose oxazoline monomer with *N*,*N*′-diacetylchitobiose oxazoline monomer provided a tailor-made chitin derivative with controlled deacetylation ranging from 0% to 50%.[67]

5.10.3.1.2 Glycosaminoglycans synthesis

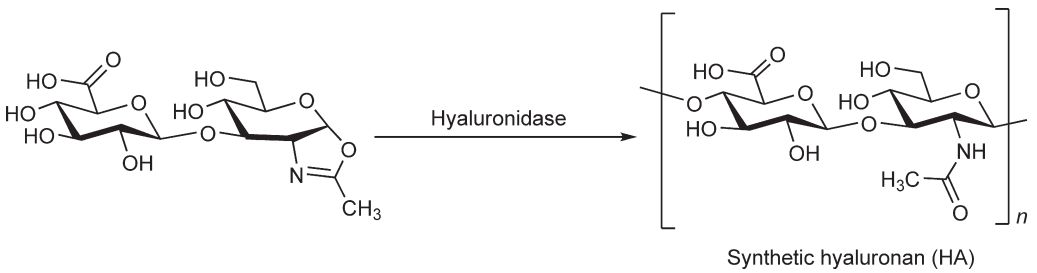
Glycosaminoglycans (GAGs) are heteropolysaccharides containing hexosamine and uronic acid. GAGs are usually attached to various proteins to form proteoglycans. Proteoglycans, collagens, and fibronectins fill the interstitial space between living cells, named the extracellular matrix (ECM), and act as a compression buffer against the stress placed in the ECMs. GAGs play important roles in living organisms, and are frequently used as therapeutic materials and food supplements.[5]

Hyaluronan (hyaluronic acid, HA) is a nonsulfated GAG and one of the major components of ECMs. HA has a disaccharide repeated structure of D-glucuronic acid (GlcA) and GlcNAc, GlcAβ(1→3)GlcNAc, connected through a β(1→4) glycosidic linkage. Hyaluronidase (HAase) is an endo-type glycoside hydrolase, which hydrolyzes β(1→4) glycosidic linkage between GlcNAc and GlcA. A novel GlcAβ(1→3)GlcNAc oxazoline derivative was designed as a TSAS monomer and its HAase-catalyzed polymerization induced the polymerization of the monomer, giving rise to HA with M_n value 1.74×10^4 in 52% yield. Regio- and stereochemistry of the resulting HA were perfectly controlled ('synthetic HA') (Scheme 31).[68] Synthetic HA is an example polymer having one of the most complicated structures ever prepared *in vitro*.

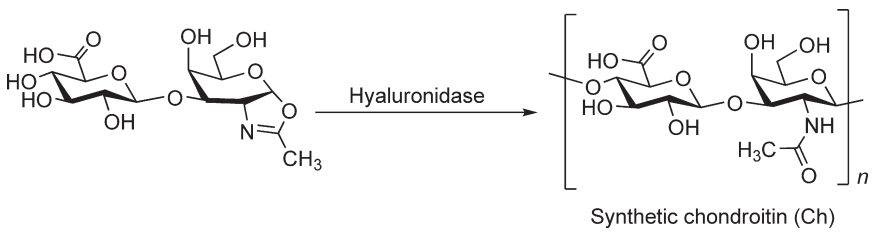
HA derivatives having ethyl, *n*-propyl, and vinyl groups instead of methyl group have been derived. The HA derivative having *N*-acryloyl group has a reactive vinyl group, and hence, functions as a macromonomer, leading eventually to telechelics and graft copolymers.[69]

Chondroitin (Ch) is a sulfated GAG composed of alternatingly aligned *N*-acetyl-D-galactosamine (GalNAc) and GlcA. There are four types of chondroitin sulfate (ChS) in nature according to the site of sulfation. ChSs sulfated at C-4 of GalNAc, C-6 of GalNAc, C-2 of GlcA and C-6 of GalNAc, and C-4 and C-6 of GalNAc are known as ChS-A, ChS-C, ChS-D, and ChS-E, respectively. Many papers have been published, describing the functions of ChS at a molecular level and how the various sulfation patterns confer specific biological activities.

New oxazoline derivatives, 2-methyl (for Ch) as well as 2-ethyl, 2-*n*-propyl, 2-isopropyl, 2-phenyl, and 2-vinyl oxazoline derivatives, were designed as new TSAS monomers for HAase (Scheme 32).[70] The polymerization of GlcAβ(1→3) GalNAc oxazoline monomer catalyzed by HAase produced



Scheme 31 Hyaluronidase-catalyzed ring-opening polyaddition of GlcAβ(1→3)GlcNAc oxazoline monomer to 'synthetic hyaluronan'.



Scheme 32 Hyaluronidase-catalyzed ring-opening polyaddition of GlcAβ(1→3)GalNAc oxazoline monomer to 'synthetic chondroitin'.

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the corresponding nonsulfated Ch. The M_n value of 'synthetic Ch' reached 5.0×10^3, corresponding to that of naturally occurring Ch. Unnatural *N*-propionyl and *N*-acryloyl derivatives of Ch were obtained, with M_n of 2700 and 3400, respectively.

Structurally well-defined ChS was prepared using HAase catalyst. Three oxazoline monomers sulfated at C-4 of GalNAc, C-6 of GalNAc, and C-4, 6 of GalNAc were synthesized. Among them, a TSAS monomer sulfated at C-4 gave rise to the ChS in good yield. The resulting ChS had sulfonate group exclusively at C-4 of GalNAc unit and was a pure ChS-A. The M_n value ranged from 4.0×10^3 to 1.8×10^4.[71]

5.10.3.1.3 Unnatural polysaccharide synthesis

By extending the wide spectrum of substrate recognition of glycoside hydrolases, synthesis of unnatural polysaccharides composed of two different polysaccharide components was achieved. Such polysaccharides (hybrid polysaccharides) are very difficult to synthesize via conventional chemical synthesis.

A cellulose–chitin hybrid polysaccharide was synthesized from Glcβ(1→4)GlcNAc oxazoline monomer based on the TSAS concept for chitinase catalysis via ring-opening polyaddition (**Scheme 33**).[23] The polymerization afforded the cellulose–chitin hybrid polysaccharide as a white precipitate. The M_n values of the products reached 4.0×10^3.

The synthesis of a chitin–xylan hybrid polysaccharide was performed using a Xylβ(1→4)GlcNAc oxazoline TSAS monomer with chitinase catalyst.[72] The resulting polysaccharide showed good solubility in water and no precipitate was observed during the polymerization. The highest peak detectable was the sugar unit of 60, with a mass weight $>1.0 \times 10^4$.

A chitin–chitosan hybrid polysaccharide was prepared via ring-opening polyaddition of a new *N*-acetylchitobiose oxazoline derivative by chitinase catalyst, producing the corresponding polysaccharide having alternatingly aligned N-deacetylated group (**Scheme 34**). With the catalyst from *S. marcescens*, a chitin–chitosan hybrid polysaccharide with M_n 2020 was obtained in 75% yield.[73]

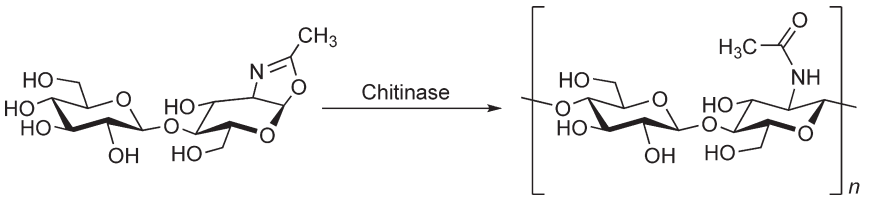
GAG hybrid polysaccharides were synthesized via HAase-catalyzed polymerization. Via the copolymerization of GlcAβ(1→3)GlcNAc oxazoline monomer with GlcAβ(1→3) GalNAc oxazoline monomer, a copolymer with M_n 7.4×10^3 was obtained in 50% yield. In a similar way, a copolymer with M_n 1.4×10^4 was produced in 60% yield from the copolymerization with the oxazoline monomer sulfated at C-4 of GalNAc. Copolymer composition was controlled by changing the monomer feed ratio.[74]

5.10.4 Summary

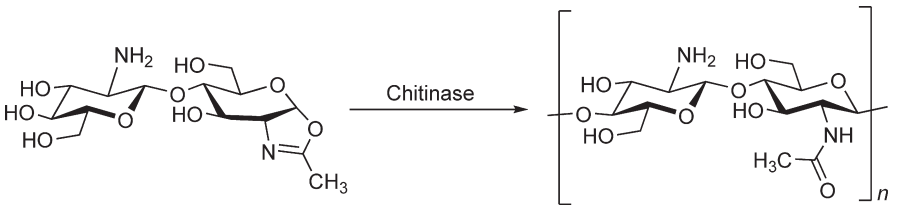
Enzymatic polycondensations and polyadditions are described in a short comprehensive way. Hydrolase enzymes are used as polymerization catalysts; glycosidases and lipases are used for the synthesis of polysaccharides and polyesters, respectively. Oxidoreductase enzymes are employed as catalysts for the polymerization of aromatic compounds. It is to be emphasized particularly that the hydrolase (glycosidase) catalysis enabled for the first time the *in vitro* synthesis of natural biomacromolecules such as cellulose, chitin, HA, and Ch. The synthesis of these compounds is very difficult via conventional methods. They have one of the most complicated structures ever synthesized *in vitro*. Phosphorylase-catalyzed synthesis of amylose derivatives was also developed.

Catalysis of the enzymes is highly selective in all respects, that is, it shows enantio-, regio-, and chemoselectivities, and can be achieved under mild reaction conditions. The catalyst activity of lipase is achieved not only in naturally occurring solvent conditions, mainly in water, but also in pure organic media, in supercritical carbon dioxide, and even in ionic liquids, at a wide range of temperature. Among others, it is a nontoxic biocatalyst, which is renewable. Furthermore, it is relatively cheap.

Because of these characteristics, enzymatic catalysis involving lipases and also oxidoreductases has the potential to serve as a basis for 'green polymer chemistry', thereby contributing toward solving environmental problems.[1c,1d,1f–1j] Some of the enzyme-catalyzed polymerizations have already provided good examples of green polymer chemistry from the viewpoint of clean process, energy savings, natural resources, carbon dioxide emission, and so on.



Scheme 33 Chitinase-catalyzed synthesis of a cellulose–chitin hybrid polysaccharide from Glcβ(1→4)GlcNAc oxazoline monomer.



Scheme 34 Chitinase-catalyzed synthesis of a chitin-chitosan hybrid polysaccharide from *N*-acetylchitobiose oxazoline monomer.

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Biographical Sketch

Shiro Kobayashi studied organic chemistry and polymer chemistry in Kyoto University. After the PhD course, he worked at Case Western Reserve University as a postdoctoral fellow for 2 years and investigated cationic reaction mechanisms. He joined Kyoto University and restarted polymer synthesis studies. He worked at Mainz University as a Humboldt fellow in 1976. Then, he was appointed as a full professor of Tohoku University in 1986 and started research on enzymatic polymerization. He moved to Kyoto University in 1997 and officially retired in 2005 to become a professor emeritus. Thereafter, he became a distinguished professor at Kyoto Institute of Technology. His research interests include polymer synthesis, organic reactions, materials chemistry, and in particular, enzymatic polymerization. He has received the Award of the Chemical Society of Japan for Young Chemists (1976), the Award of the Society of Polymer Science Japan (1987), the Humboldt Research Award (1999), the Chemical Society of Japan Award (2001), the John Stauffer Distinguished Lecture Award (2002), the Medal with Purple Ribbon (2007), and others. He is a foreign member of the Northrhine-Westfalian Academy of Science since 1999. Currently, he serves as a member of the (executive) advisory board and editorial (advisory) board of 14 international journals.

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5.11 Nonlinear Polycondensates

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5.11.1 Introduction

There are many commercially available nonlinear polycondensates, which include thermosetting resins, epoxy resins, phenol resins, elastomers, gels, and cross-linked resins. The properties of nonlinear polycondensates are highly dependent on the cross-linking density. Highly cross-linked materials are usually insoluble and infusible. They are also called gel when the materials are swollen by solvents. Since 1990, soluble nonlinear polycondensates have attracted considerable attention as hyperbranched polymers. Hyperbranched polymers usually show good solubility in solvents although the main chains have a consecutive branching architecture.

Nonlinear polycondensates can be prepared by polymerization of multifunctional monomers or condensation of linear polymers by cross-linking agents. Phenol resins are historically important polymers in which phenol acts as a trifunctional monomer and is condensed with formaldehyde. Natural rubber is prepared by vulcanization of raw materials (latexes), which imparts unique elastic properties. Flory and Stockmayer have developed the statistical theory for infinite network formation.[1–7] The critical conversion for infinite network formation is practically important to predict or avoid gelation. There are many attempts to modify the classical theory to fit the experimental data. Reactivity change during polymerization is considered by Gordon[8,9] and Dusék.[10,11] Ring-forming parameters are introduced by several researchers to discuss intramolecular cyclization.[12–14] Percolation models are also used to discuss the critical gel conversion.[15] Although the modified theory and models are successfully applied for some polymerization systems, there is no universal and accurate theory to predict gelation applicable for a broad range of polymerizations. The classical theory developed by Flory and Stockmayer is simple and valid for many polymerization systems. Therefore, this chapter mainly deals with the classical theory. Critical conversion for gelation (infinite network formation) for polymerization of multifunctional monomers and condensation of linear polymers by cross-linking agents are separately described in the next section. The molecular weight distribution of nonlinear polycondensates is also discussed.

The classical theory also involves polymerization of AB_x-type monomers to form soluble polymers, which are recently called hyperbranched polymers.[16] The statistical theory for the formation of hyperbranched polymers and the typical examples are also described in Section 5.11.3.

5.11.2 Insoluble Cross-Linked Polymers

When polymerization proceeds to form an infinite network, the polymerization mixture often becomes gel. The gel is composed of a three-dimensional structure and is insoluble in solvents. Flory and Stockmayer reported the statistical theory for gelation more than 50 years ago.[1–7] Intramolecular condensations and reactivity changes during the reaction are neglected in the consideration. Although the theory is classical, the basic concept is still valid and gives useful information on critical gel conversion and molecular weight distribution. The following sections describe the critical gel conversion for gelation in two typical cases by the statistical theory. Molecular weight distribution of three-dimensional polymers is briefly discussed.

5.11.2.1 Polymerization of Multifunctional Monomers

In the following sections, A and B represent the different functional groups which can react to form the linkage. Polymerization of A-A (A_2) and B-B (B_2) monomers gives a linear polymer. The branched polymer can be formed when the polymerization mixture contains A_3- or B_3-type monomers. The possible polymer structure prepared from A_2, A_3, and B_2 monomers is described in Figure 1. When the resulting polymer has a limited molecular weight, a soluble polymer can be isolated from the polymerization mixture. On the other hand, an insoluble polymer is formed if the molecular weight of the resulting polymer is infinite. The resulting insoluble polymer becomes a swollen gel when the linear segment is dissolved in a solvent. This section describes polymerization of A_2 and B_2 monomers in the presence of multifunctional monomers, such as A_3 and B_3. Critical conversion for gelation is of prime interest because conversion is practically important.

The relationship between the conversion of functional groups and the probability of gel formation is discussed for the following reaction:

[1]

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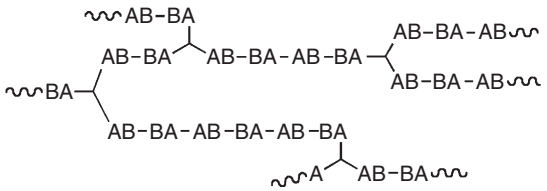

Figure 1 Three-dimensional polymer prepared from A_2, A_3, and B_2 monomers.

The 'i' in eqn [1] may have any value from 0 to infinity. The probability of the formation of molecule shown in eqn [1] can be related to the probability of the functional groups and the ratio of A_3 monomer:

$$p_A[p_B(1-\rho)p_A]^i p_B\rho \qquad [2]$$

In eqn [2], 'p_A' and 'p_B' represent the probability of A and B functional groups being reacted. 'ρ' represents the ratio of A functional group in the A_3 molecule to the total number of A functional group. '$p_B(1-\rho)$' implies the probability of B functional group to be reacted with A-A. '$p_B\rho$' implies the probability of B functional group to be reacted with the A_3 molecule. The branching coefficient, α, is defined as the probability that a given functional group of a branch unit leads via a chain of bifunctional units to another branch unit. Therefore, the sum of the probability shown in eqn [2] from $i=0$ to infinity is equal to the branching coefficient:

$$\alpha = \sum_{i=0}^{\infty}[p_A p_B(1-\rho)]^i\, p_A p_B\rho \qquad [3]$$

Evaluation of this summation result yields the following equation:

$$\alpha = \frac{p_A p_B \rho}{[1-p_A p_B(1-\rho)]} \qquad [4]$$

When the initial ratio of A functional group to B functional group ([A]/[B]) is 'r', the branching coefficient can be calculated by r and p_A or p_B:

$$\alpha = \frac{r p_A^2 \rho}{[1-r p_A^2(1-\rho)]} = \frac{p_B^2\rho}{[r-p_B^2(1-\rho)]} \qquad [5]$$

When there is no A-A molecule, ρ is equal to 1 and eqn [5] is simplified to

$$\alpha = r p_A^2 = \frac{p_B^2}{r} \qquad [6]$$

When the number of a and b functional groups is equal, r becomes 1 and p_A is equal to p_B. Then, eqn [5] is simplified to

$$\alpha = \frac{p^2\rho}{[1-p^2(1-\rho)]} \qquad [7]$$

The critical value of α for gelation can be deduced as follows.[1] Assume that the linear segment is connected with an A_3 branching unit. The two unreacted A functional groups can connect with both linear and branching units. When the unreacted A functional group connects with another branching unit, the propagation direction increases. Therefore, if α is greater than 0.5, the propagation direction increases infinitely. On the other hand, when α is less than 0.5, more than half of the chains end in linear segments. The infinite network formation is inhibited in this case. Therefore, the critical value of α for gelation is 0.5. More generally, when the branching units have n functional groups, the critical value of α is $1/(n-1)$.

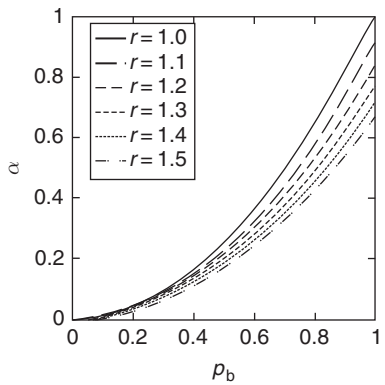

Figure 2 Relationship between p_b and α in eqn [6].

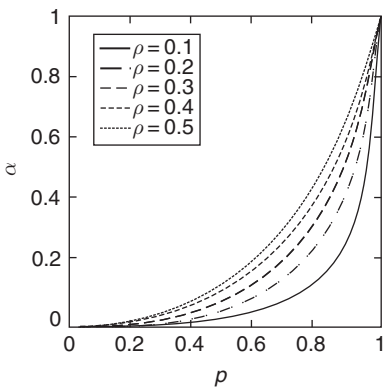

Figure 3 Relationship between p and α in eqn [7].

Figure 2 shows the relationship between p_B and α in the case of polymerization of A_3 and B_2 monomers without A_2 monomer ($\rho=1$). The critical value of α to form an infinite network is 0.5 in this polymerization system. The critical conversion (p_B) for gelation to reach $\alpha=0.5$ increases with the increase in the ratio of A and B functional groups. When the ratio of A and B is equal ($r=1$), the critical conversion is calculated to be 0.70. When an equimolar amount of A_3 and B_2 monomers is used ($r=1.5$), the critical conversion is calculated to be 0.86.

Figure 3 shows the relationship between p and α in the case of polymerization of A_2, A_3, and B_2 monomers with the ratio of A and B set equal ($r=1$). In the presence of small amounts of A_3 monomer ($\rho=0.1$), α increases with the conversion (p) and reaches 0.5 at $p=0.96$. The increase in A_3 monomer strongly affects the critical conversion for gelation. When r is equal to 0.5, the critical conversion is calculated to be 0.81.

5.11.2.2 Cross-Linking Reaction of Polymer Chains

This section describes the cross-linking reaction of polymer chains to form an infinite network. Figure 4 shows the model structure of cross-linked chains. In Figure 4, the primary chains are composed of γ-units (γ-mers). The cross-linkage is formed between randomly selected two units of each γ-mer. When the

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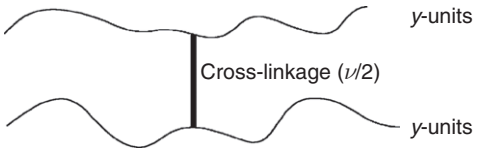

Figure 4 Cross-linkage formed between two *y*-mers.

number of cross-linking points is v, the number of cross-linkage is half of v. The cross-linking density (ρ) is calculated by the following equation, where N_0 is the total number of units:

$$\rho = \frac{v}{N_0} \quad [8]$$

The expectancy (ε) that the cross-linked chain (γ-mer) has another cross-linking unit can be calculated by multiplying ρ by the number of rest of the units (γ – 1), as shown in the following equation:

$$\varepsilon = \rho(\gamma - 1) \quad [9]$$

When ε is lower than 1, a limited number of chains are connected via cross-linking and the formation of an infinite network is impossible. On the other hand, ε greater than 1 implies that an indefinite number of chains are connected via cross-linking. Therefore, the critical value of ε for infinite network formation is 1:

$$\rho_c = \frac{1}{(\gamma - 1)} \approx \frac{1}{\gamma} \quad [10]$$

It is clear that ρ_c becomes very small when the primary molecules (γ-mers) are large.

In synthetic polymers, the primary molecules have molecular weight distribution. Since the expectancy (ε) of γ-mers is described in eqn [9], the integration from $\gamma = 1$ to infinity gives the expectancy for the polymer having molecular weight distribution:

$$\varepsilon = \rho \sum_{\gamma=1}^{\infty} w_\gamma(\gamma - 1) = \rho(\gamma_w - 1) \quad [11]$$

In eqn [11], w_γ is the weight fraction of γ-mers and γ_w is the weight average of degree of polymerization. As discussed for γ-mers, $\varepsilon = 1$ is the critical value for infinite network formation. Therefore, the critical cross-linking density (ρ_c) is described as

$$\rho_c = \frac{1}{(\gamma_w - 1)} \approx \frac{1}{\gamma_w} \quad [12]$$

The number of cross-linked units per primary molecules is equal to $\rho\gamma_n$, which is called the cross-linking index. When γ_w and γ_n are equal, the critical value for the cross-linking index is unity. On the other hand, the critical index for an infinite network falls below unity when the polymer has molecular weight distribution. It is clear that the polymer having a broader molecular weight distribution forms an infinite network easily when γ_n is equal.

5.11.2.3 Molecular Weight Distribution

It is known that the molecular weight distribution of three-dimensional polymers is large. Low-molecular-weight components are often observed after gelation has occurred. Flory and Stockmayer successfully reported the molecular weight distribution by statistical and mathematical methods.[1–7]

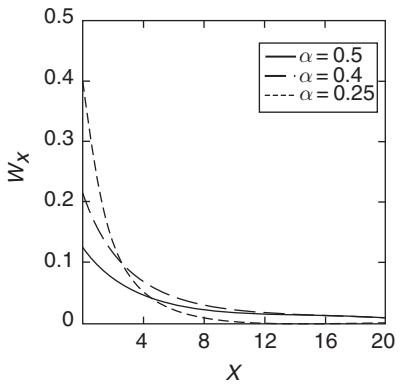

Figure 5 Relationship between x and its weight fraction (w_x) in the polymerization of A_3 and B_3 monomers.

The simplest case is the polymerization of A_f and B_f monomers in which both the number of A and B functional groups are equal. The weight distribution function, w_x, of an x-mer molecule can be described as:

$$w_x = \frac{(1-\alpha)^2}{\alpha}\left[\frac{(fx-x)!f}{(x-1)!(fx-2x+2)!}\right]\beta^x \quad [\beta = \alpha(1-\alpha)^{f-2}] \quad [13]$$

In eqn [13], α is the probability that one branch unit connects to another branch unit and is equal to the extent of reaction, p. The weight distribution by eqn [13] is plotted in **Figure 5** in the case of $f = 3$. The weight fraction of small molecules ($x = 1$–4) decreases with the increase in α. It should be noted that large amounts of small molecules are still present in the polymer when α reaches the critical value of 0.5.

Figure 6 shows the plots of weight fraction (w_x) against α. It is clear that large amounts of small molecules, such as w_1 and w_2, are present when α is small. The maximum of the curve w_x shifts toward larger α when x in w_x increases. **Figure 6** also shows the weight fraction of the gel (w_{gel}), according to eqn [14].[4] After α reaches the critical value of 0.5, w_{gel} increases rapidly and then reaches 1.0.

$$w_{gel} = 1 - (1-\alpha)^3/\alpha^3 \quad [14]$$

The number-average and weight-average values of x are given in eqns [15] and [16], respectively[3]:

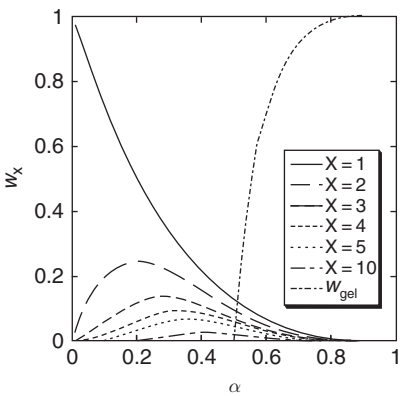

Figure 6 Relationship between α and its weight fraction (w_x) in the polymerization of A_3 and B_3 monomers.

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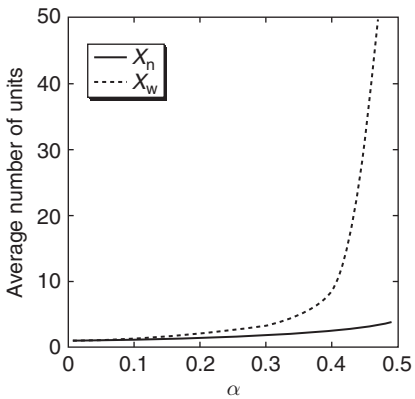

Figure 7 Plots of average degree of polymerization against α in the polymerization of A_3 and B_3 monomers.

$$X_n = \frac{1}{(1-\alpha f/2)} \quad [15]$$

$$X_w = \frac{(1+\alpha)}{[1-(f-1)\alpha]} \quad [16]$$

Figure 7 shows the relationship between X_n, X_w, and α in the case of $f = 3$. The figure clearly demonstrates that X_w increases toward infinity when α approaches the critical value of 0.5, but at the same time, X_n is still small near the critical value.

The more practically important case is the polymerization of A_2 and B_2 monomers in the presence of small amounts of an A_3 molecule:

[17]

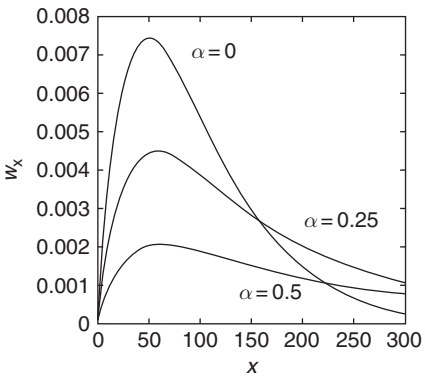

Figure 8 Relationship between x and its weight fraction (w_x) in the polymerization of A_2, B_2, and A_3 monomers.

Flory[2] reported the equation for the weight fraction of x-unit species for the polymerization system:

$$w_x = 2(1-\alpha)^2(1-q)^2 q^{x-1} \sum_{n=0}^{\infty} \frac{h^n x(x-1)\ldots(x-2n)}{(n+2)!n!} \quad [18]$$

where $q = p\,\frac{(G-3Y)}{G}$, where G is total number of functional groups and Y is number of trifunctional branching units; $h = \beta(1-q)^2/q^2$, where $\beta = \alpha(1-\alpha)$; and n is number of branching units in x-mer.

Figure 8 shows the relationship between the weight fraction and x in the case of $q = 0.98$, which implies that the average chain length is equal to 50. The distribution curve becomes flat with increasing α. Especially the curve for $\alpha = 0.5$ implies that the molecular weight distribution is broad and extremely high- and low-molecular–weight components are involved in the polymerization mixture at the critical conversion.

5.11.3 Soluble Branched Polymers

5.11.3.1 Polymerization of AB_x-Type Monomers

As described in the previous section, polymerization of multifunctional A_2 and B_3 monomers results in gelation when the conversion of functional groups exceeds the critical gel point. On the other hand, polymerization of AB_x-type monomers results in the formation of soluble branched polymers when the propagation reaction proceeds only between A and B functional groups (Figure 9).

Over 50 years ago, Flory[16] described a statistical approach for the polymerization of AB_x-type monomers in a systematic study of branched macromolecules. As described in the previous section, the critical value of α for gelation is $1/(n-1)$ when the branching unit has n functional groups. Therefore, in the case of polymerization of AB_x-type monomers, the critical value of α is $1/x$. At the same time, the maximum value of the conversion of B functional group is equal to $1/x$. Therefore, the probability of α never exceeds $1/x$. In other words, the formation of an infinite network is statistically inhibited in the case of polymerization of AB_x monomer.

Despite the statistical discussion by Flory, there are only few reports on the polymerization of AB_x-type monomers until 1990. Kricheldorf *et al.*[17] first reported the preparation of AB_2-type branched polyester copolymers (eqn [19]). Soluble branched polymers were isolated in good yield and the branched structure was confirmed by ^{13}C NMR measurements. It was also reported that the crystallization behavior was highly dependent on the amount of the branching units.

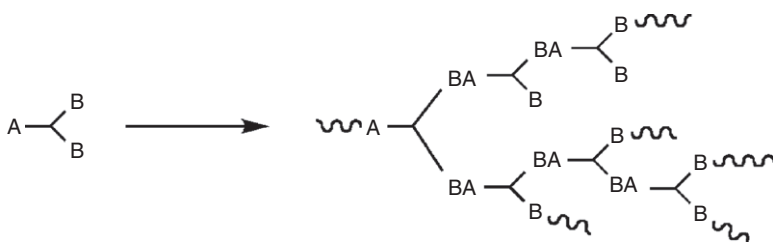

Figure 9 Three-dimensional polymer prepared from AB_2-type monomer.

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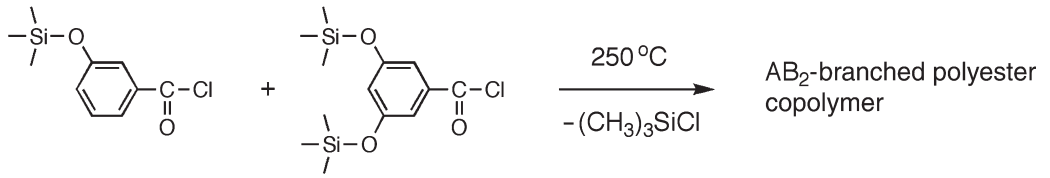

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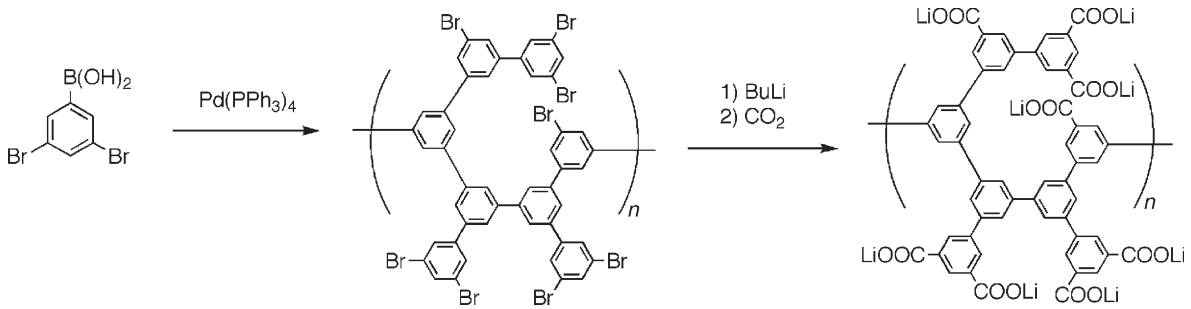


[20]

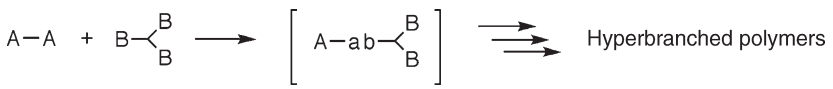
In 1990, Kim and Webster[18] reported soluble branched polyphenylenes prepared from an AB_2-type monomer (eqn [20]). After the reaction with butyl lithium and carbon dioxide, the resulting polymers became soluble in water. In the report, the resulting polymers were first called hyperbranched polymers, which can be recognized as analogues of dendrimers. The soluble branched polyphenylenes were prepared via the C-C coupling reaction catalyzed by tetrakis(triphenylphosphine) palladium (Pd(PPH3)4).

Hyperbranched polymers can be prepared by one-step self-polycondensation, in contrast to multistep reactions required for the preparation of dendrimers. A variety of hyperbranched polymers have been reported in the literature. Experimental data reported in the literature show that the properties of hyperbranched polymers, such as low viscosity, good solubility, and multifunctionality, are similar to those of dendrimers due to consecutive branching structure. It should be mentioned that hyperbranched polymers have an irregular architecture and molecular weight distribution. Hyperbranched polymers have been reviewed in the literature[19–22] and are described in Volume 6 in detail.

5.11.3.2 Polymerization of A_2 and B_3 Monomers

Polymerization of A_2 and B_3 monomers results in gelation when the conversion of the functional group exceeds the critical point for gelation. On the other hand, polymerization of AB_x-type monomers gives soluble hyperbranched polymers. If AB_x-type molecules are formed selectively in the early stage of polymerization, polymerization of A_2 and B_3 monomers will result in the formation of soluble hyperbranched polymers as shown below:

The concept was first proposed in the case of soluble hyperbranched polyamides.[23] The condensation of aromatic diamines (A_2) and trimesic acid (B_3) was carried out in the presence of condensation agents, triphenyl phosphite $(P_9OPh)_3$) and pyridine (Py), in 1-methyl-2-pyrrolidinone (NMP) (eqn [22]). When the amino group of phenylene diamine reacts with trimesic acid, the other amino group would be deactivated due to a decrease in the electron donating effect of the amide group. The deactivation was discussed in terms of proton affinity calculated by *ab initio* molecular orbital calculations. In this polymerization system, the selective formation of AB_2-type monomer was not achieved, and therefore, gelation of the polymerization mixture was observed when the concentration of the monomer was high.



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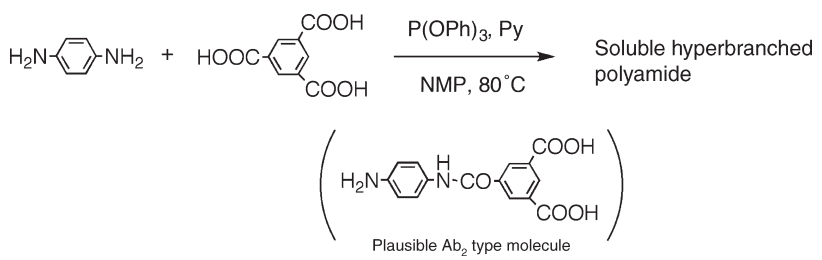

[22]

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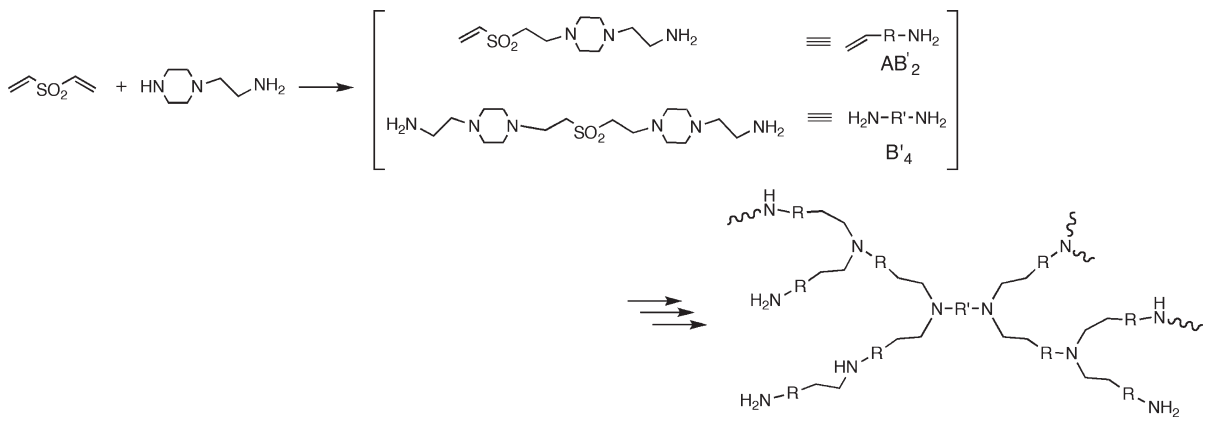
Since A_2 and B_3 monomers are commercially available, many attempts to prepare hyperbranched polymers from A_2 and B_3 monomers have been reported in the literature.[20] When a symmetric monomer is used, the selective formation of AB_2-type monomer cannot be expected. Therefore, optimization of the reaction condition in order to avoid gelation is required to obtain soluble hyperbranched polymers. It is reported that stepwise slow addition of one monomer is effective in avoiding gelation in the case of preparation of hyperbranched aromatic polyimides.[24,25] The resulting polymers have a consecutive branching architecture, similar to hyperbranched polymers prepared from AB_2-type monomers. However, the solution viscosity of soluble polymers prepared from A_2 and B_3 monomers is often high in comparison with that of hyperbranched polymers, which is probably due to the partial cross-linking reactions.

When the monomer has an asymmetric structure and the reactivity of the functional groups is different from each other, the selective formation of AB_2 monomer in the early stage of polymerization can be expected. Yan and Gao[26] reported the preparation of hyperbranched polyamines from divinyl monomers and aliphatic diamines (eqn [23]). In this work, the diamines have primary and secondary amino groups. It is well known that secondary amines are more basic than primary amines. Moreover, the secondary amines formed by the first addition of primary amines with vinyl groups can also react with other vinyl groups. Therefore, the diamines can be recognized as BB'_2 monomers. As shown in eqn [23], the secondary amino group of 1-(2-aminoethyl)piperidine is more reactive and is consumed completely in the early stage of polymerization. Consequently, the selective formation of AB'_2 molecule can be expected. As divinyl sulfone is a symmetric A_2 monomer, B_4'-type molecule can be formed when the concentration of unreacted A_2 monomer becomes low. The B_4'-type molecule may act as a core molecule during polymerization. Soluble hyperbranched poly(sulfone amine)s and poly(ester amine)s have been prepared by the $A_2 + BB'_2$ strategy.[26,27]

Carboxylic anhydrides can react with amines at room temperature without the addition of activating agents to form amide and carboxyl acid groups. The carboxylic acid formed can react with amines in the presence of condensation agents. Chang and Shu[28] reported the synthesis of hyperbranched aromatic poly(amide imide) from phenylene diamine and 4-(3,5-dicarboxyphenoxy)phthalic anhydride (eqn [24]). Condensation of the diamine and the anhydride proceeded rapidly at room temperature. On the other hand, condensation of the amino group and the carboxylic acid did not proceed without the addition of condensation agents. Therefore, selective formation of an AB_2-type molecule was achieved in the early stage of polymerization. After thermal imidization, polymerization of AB_2-type molecule was carried out in the presence of triphenyl phosphite and pyridine as condensation agents to form hyperbranched aromatic poly(amide imide). It was reported that the resulting polymer prepared from the diamine and the anhydride had an almost identical structure to that of the product prepared from the isolated AB_2-type monomer.



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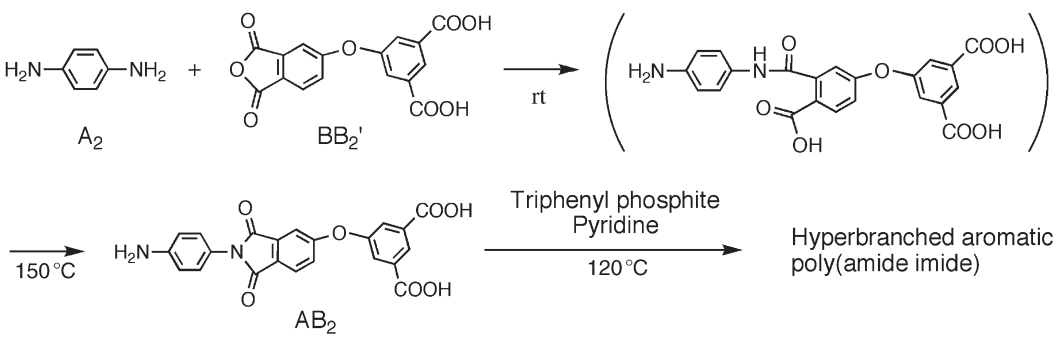

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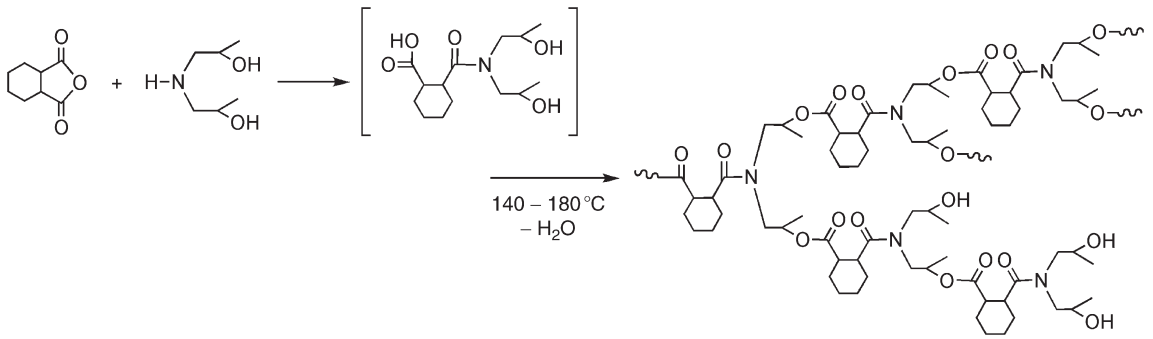

[25]

Hydroxyl groups can act as nucleophiles to carboxylic anhydrides and the nucleophilicity of hydroxyl groups is lower than that of amino groups. Therefore, amino diols can act as BB'_2 molecules. Hyperbranched poly(ester amide)s, commercialized by DSM as Hybrane®, have been synthesized from aliphatic anhydrides and bis(2-hydroxypropyl)amine (eqn [25]).[29,30] It was reported that the secondary hydroxyl group should be used instead of the primary hydroxyl group to avoid side reactions. Moreover, polymerization was carried out in the presence of an excess amount of bis(2-hydroxypropyl)amine. After the initial condensation reaction, the consequent chain extension proceeded efficiently to form ester bonds from the carboxylic acid and the hydroxyl groups. Various grades of hyperbranched poly(ester amide)s are available from DSM Hybrane.

Commercial availability of A_2 and B_3 monomers is advantageous for broadening the field of hyperbranched polymers prepared from A_2 and B_3 monomers. Careful optimization of reaction conditions is required to isolate soluble polymers from symmetric A_2 and B_3 monomers. Since a predominant formation of AB_2-type molecules is expected, the risk of gelation is markedly reduced in the case of polymerization of A_2 and BB'_2 monomers. There are some review articles[20,22] and the topic has been described in Volume 6 in detail.

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Biographical Sketch

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5.12 Post-Polymerization Modification

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5.12.1 Historical Background and Definitions

Chemical modifications of polymers were one of the oldest applications of polymer chemistry. One of the first reactions dates back to 1781 and describes the isomerization of natural rubber in the presence of acids.[1] The first application of synthetic polymers is likely to be the nitration of polystyrene in 1845.[2] However, the most important step forward was driven by Staudinger, who developed the concept of post-polymerization modifications, which he called 'polymer analogous reactions'. He defined those reactions as the "transformation of a polymer into a derivative of equivalent molecular weight", based on his results of hydrogenation of rubber[3] and polystyrene[4] with hardly any chain degradation. Until today, Staudinger has given the best definition. Thus, a polymer analogous reaction would be the transformation of a polymer into a derivative with the same degree of polymerization, as chemical modification of a polymer implies changing its chemical nature while keeping the degree of polymerization constant. It is worthwhile to cite Staudinger's Nobel Prize lecture during which he coined the term 'polymer analogous':

> In many instances a polymeric compound can be transformed into derivatives of a different type without any change in the degree of polymerization of the compound in exactly the same way as small molecules can be transformed. A polymer compound can hence be transformed into polymer analogous derivatives.[5]

The term 'polymer analogous reaction' is often used interchangeably with 'post-polymerization modification' and both terms are used within this chapter. Post-polymerization modifications have an enormous potential, which can be explained by the variety of reactions that can be used in applications. Most early investigations focused on chemical modifications of polymers, that is, fundamental exploration of the chemical possibilities utilizing the variety of organic reactions known at that particular time. However, in recent years polymer chemists have addressed more

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and more the precise attachment of specific functional molecules onto polymer chains. Pioneering work for the synthesis of functional polymeric materials utilizing post-polymerization modifications was done by the group of Ringsdorf.[6] They demonstrated that it is possible to synthesize polymers via post-polymerization modifications that were otherwise very difficult or impossible to synthesize. Also reactions on telechelic polymers and end group modifications can be regarded as polymer analogous reactions, and they have gained recent interest.

In 1983, Carraher and Moore[7] published a monograph on the modification of polymers, and since then the applications of post-polymerization modifications have increased dramatically. However, no thorough update on new developments in the area of post-polymerization modifications has been compiled. This can partly be attributed to the fact that the applications of post-polymerization modifications have become very broad, ranging from materials science to life science. All the same, some specific reviews as well as some textbooks cover a certain area of post-polymerization modifications as a synthetic strategy to prepare functional polymers.[8–16] Besides, there are strong research activities in reactions on cellulose[17] as well as other very specialized functionalization reactions. Those are not covered in this review. This chapter rather tries to a certain extent to cover different post-polymerization modifications without being exhaustive. The intention is to provide the reader with a general overview of the synthetic possibilities that post-polymerization modifications combined with modern polymerization techniques can offer.

5.12.2 General Considerations

5.12.2.1 Classifications

Due to the enormous range of different organic reactions that can be used for post-polymerization modifications, it actually represents a very wide domain of polymer chemistry. The following subsections within this section are intended to provide a general classification of different post-polymerization modifications based on mechanistical aspects with a small number of selected examples. A classification according to functional groups is then given in Section 5.12.3, which covers modern reactions in greater detail.

5.12.2.1.1 Additions

Addition reactions are very useful for the modification of polymers, and practically, many are identical to their small-molecule counterparts. In order to give a flavor of the possible addition reactions, only a small fraction of examples shall be given. In general, in an addition reaction a small molecule reacts with a functional group of the polymer. Various examples have been investigated in the past.

Technologically most important is the hydrogenation of polymers. Recently, the hydrogenation of polystyrene has gained certain technological interest.[18] But also the hydrogenation of polydienes has applications as it has been possible to vary their microstructure.[19] For example, hydrogenation of 1,4-polybutadiene resulted in blocky structures,[20] whereas the degree of hydrogenation of poly(1-pentenylene) could be controlled resulting in materials ranging in structure from amorphous to crystalline.[21] Similar to hydrogenation, halogenation and hydrohalogenation of unsaturated polymers have also been conducted; for example, bromination of polybutadiene resulted in flame-retardant materials.[22]

Another possibility to introduce halogens to polymers following an addition reaction is based on the radiation-induced addition of, for example, carbon tetrachloride onto 1,2-polybutadiene by a radical chain mechanism.[23,24] In a similar radical chain reaction thiols can add to double bonds as well,[25–27] a reaction that has found a revival in recent years.[15,16] Also the radical-induced addition of organic phosphites (dimethyl phosphite) onto poly(1-pentenylene) in the presence of dibenzoyl peroxide has been studied.[28]

Epoxidation of double bonds represents another useful addition reaction for the functionalization of unsaturated polymers, for example, epoxidation of polybutadiene. In this context, Zuchowska[29] found that epoxidation of 1,4-polybutadiene proceeds ~ 1.9 times faster than that of 1,2-polybutadiene.

Concerted addition reactions have also been studied with respect to polymer functionalization. As one example, the ene addition of maleic acid onto unsaturated polymers, such as natural rubber, should be mentioned.[30]

5.12.2.1.2 Substitutions

Substitution reactions are probably the most important class of reactions used within post-polymerization modifications to prepare functionalized polymers. A practical application is chlorination of polyethylene (PE), which proceeds through a free radical substitution mechanism.[31] it is noteworthy that chlorination in the solid state begins predominately in the amorphous areas and on the crystalline surfaces of PE. Also the chlorination of polyvinylchloride (PVC), polypropylene, and fluorinated polymers has been studied. Furthermore, replacing the chlorine atoms in chlorinated polymers, such as PVC, has been investigated.

Esterification and hydrolysis reactions have been the subject of numerous studies. Esterification of poly(methacrylic acid) utilizing carbodiimides as condensing agents is common. During the course of the reaction, a cyclic anhydride is formed first as an intermediate structure, which, in the presence of an alcohol, then reacts to yield the respective ester.[32,33] As such, the intermediate formation of a cyclic anhydride results in a limited conversion of the overall esterification. Esters of cellulose represent a class of commercially produced polymers prepared by esterification of cellulose.[17,34]

Alternating copolymers of maleic anhydride have been studied with respect to hydrolysis of the anhydride moiety.[35] However, the most prominent example of a hydrolysis reaction represents hydrolysis of poly(vinyl acetate) yielding poly(vinyl alcohol), which cannot be synthesized directly because the respective monomer does not exist.

Various examples of reduction and oxidation reactions have been studied as post-polymerization modifications. For example, the synthesis of poly(*N*-alkylethyleneimine)s is best performed through reduction of the corresponding poly(*N*-acetylethyleneimine)s, which are easily accessible through the ring-opening polymerization of oxazolines.[36]

Oxidations are mostly problematic, because they are accompanied by degradation reactions that often result in chain breaking. However, oxidation of poly(vinyl alcohol) with NaOCl and HCl did result in poly(enol-ketone).[7]

Amination and quarternization have been intensively investigated. Most prominent are the substitution reactions of

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chloromethylated polystyrenes.[37–39] In general, modification of polystyrene has been conducted using Friedel–Crafts reactions with the modified units being randomly distributed on the chains.[40–42] Similarly, sulfonation of polystyrene has been studied in great detail since the products find application as ion exchangers.[19,43]

Lithiation of polystyrene by reaction of BuLi with polystyrene had been used for reactive intermediates, for example, to prepare spin-labeled polystyrenes[44–47] or to introduce boronic acid groups.[48]

5.12.2.1.3 Eliminations

Synthetic use of eliminations in post-polymerization modifications has been reviewed by Korshak.[49] His classification has been resummarized in a table in Reference 50, and some examples are given in Scheme 1.

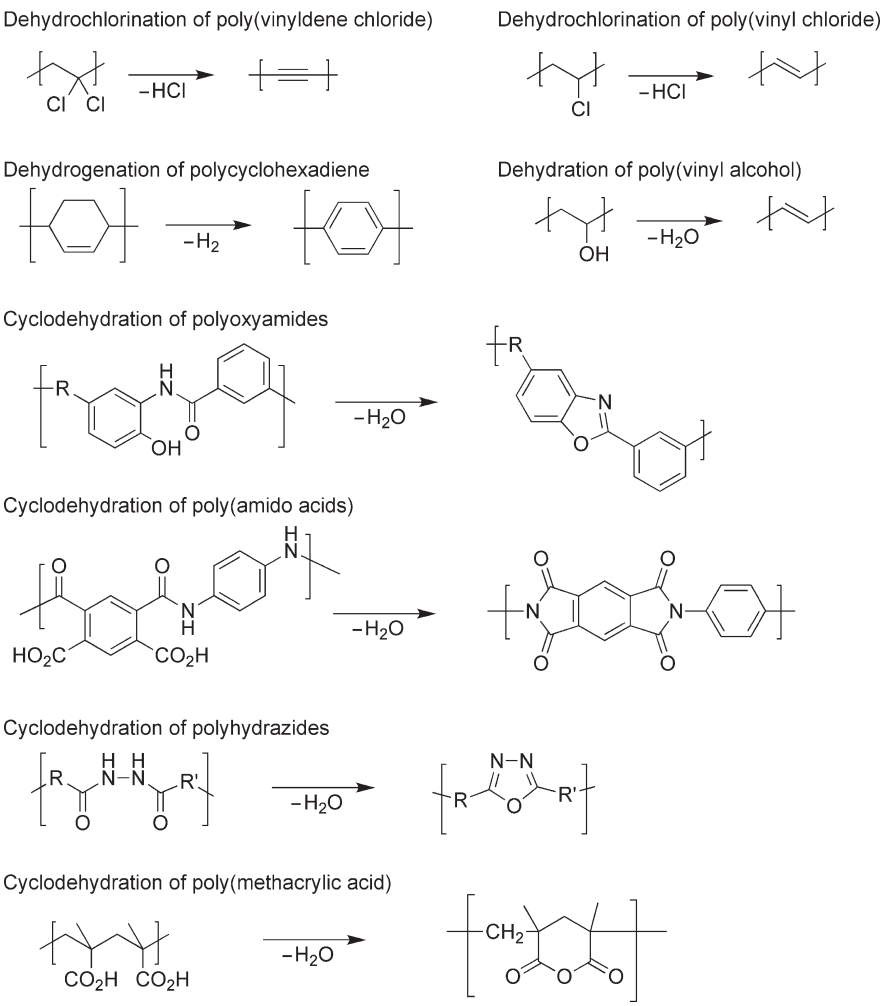
5.12.2.1.4 Isomerizations

In contrast to the previous reaction classes, isomerizations result in a change in the chemical structure; however, the molecular weight of the macromolecules does not change. Even though, according to IUPAC, a configurational change is not usually referred to as a chemical modification, it shall still be mentioned in this context. In principle, one can distinguish between configurational isomerizations, constitutional transformations, and exchange equilibria.

A typical configurational isomerization is the *cis–trans* isomerization of polydienes, often triggered through UV irradiation in the presence of radical transfer agents, such as organosulfides or halogens.[9] An isomerization between tactic polymers has, for example, been described for isotactic poly (isopropyl acrylate) when treated with catalytic amounts of sodium isopropylate yielding atactic poly(isopropyl acrylate).[51] Polymers with chromophoric groups that feature photochromic behavior have been a subject of interest in research as well. Most commonly, azobenzene-containing polymers have been the subject of investigation due to the *cis–trans* isomerization of azobenzene.[52–60]

Among constitutional transformations, cyclizations are the most common. Polyacrylonitrile undergoes cyclization when heated in an inert atmosphere to 200–300 °C.[61] Further heating results in pyrolysis yielding graphene-like structures, which essentially form carbon nanofibers.[62,63]

When segments between two polymer chains can be interchanged, one speaks of an exchange equilibrium. During these exchange reactions, the number of macromolecules and the



Scheme 1 Examples of elimination reactions.

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degree of polymerization remain unchanged. Exchange equilibria have been known for a while; however, they have found profound interest in recent years due to advances in the area of dynamers, which have been promoted by Lehn.[64–66]

5.12.3 Functional Groups Employed in Chemical Modifications

While the previous section focused on a general classification according to reaction types, the following part will highlight certain functional groups that find broad application in polymer analogous reactions.

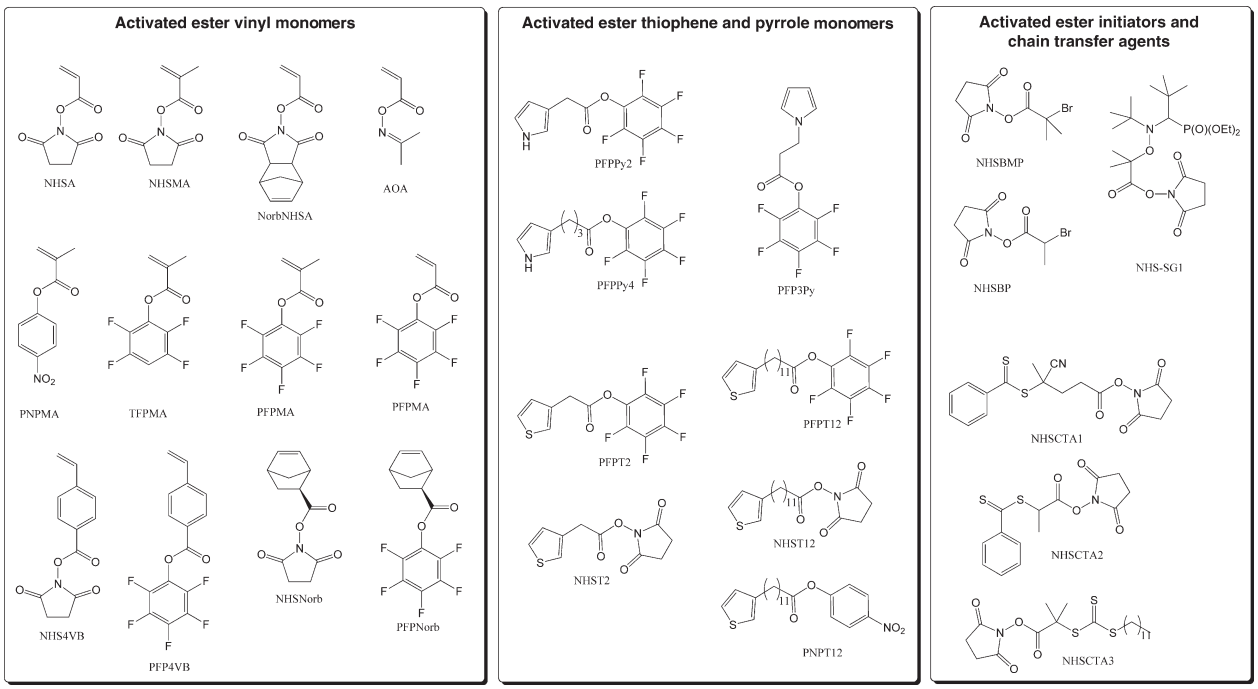
5.12.3.1 Activated Esters

Activated esters have proven to be very useful reactive derivates for covalently linking amines with carboxylic acids to yield the respective amides and thus have found application in organic chemistry, especially in peptide chemistry.[67–71] Pioneering work on reactive polymers based on activated esters was published independently by Ringsdorf and Ferruti.[6,72] Since their first reports, polymeric activated esters have yielded applications reaching into materials science and life science. Scheme 2 summarizes common activated ester monomers as well as chain transfer agents (CTAs) and initiators featuring an activated ester.

N-Hydroxy succinimide acrylate (NHSA) (also called *N*-acryloxysuccinimide) and methacrylate (NHSMA) have found extensive use as reactive monomers in the preparation of reactive polymers. The resulting reactive polymers poly (*N*-hydroxy succinimide acrylate) (PNHSA) and poly (*N*-hydroxy succinimide methacrylate) (PNHSMA) can then be used in a post-polymerization modification with amines under very mild reaction conditions, yielding functionalized polyacrylamide or polymethacrylamide derivates.[73–76] By reaction of reactive polymers with various amines, functional polymers are accessible which cannot be prepared by direct polymerization of the respective acrylamide monomers. Conversions of polymeric activated esters are usually quantitative for small amines and proceed without any side reactions under mild conditions, such as stirring at room temperature. In the classification scheme of Sharpless, the reaction of activated esters with amines represents a prime example of a 'click' reaction. It is noteworthy that in contrast to many other reactions including 1,3-dipolar cycloadditions, the reaction of activated esters with amines proceeds without the need for an auxiliary (metal) catalyst.

Synthesis of polymeric activated esters from the respective activated ester monomers provides several advantages over the transformation of poly(acrylic acid) or its copolymers in a reaction with dicyclohexylcarbodiimide (DCC) or 1-ethyl-3-[3-dimethylaminopropyl]carbodiimide hydrochloride (EDC) and *N*-hydroxysuccinimide or pentafluorophenol into the respective polymeric activated esters. First, the reaction of poly(acrylic acid) with carbodiimides usually proceeds via cyclic anhydrides, which limits the conversion that follows. Second, separation of the formed urea is not always easy. Furthermore, the apparent difference in solubility between the starting polymer, for example, poly(acrylic acid), and the product represents a synthetic challenge. Nevertheless, the concept has been applied to many carboxylic acid-containing polymers including poly(*p*-phenylene vinylene)s (PPVs)[77] and amphiphilic block copolymers.[78]

The high fidelity in functionalization of polymeric activated esters by reaction with functional amines has been employed in many applications.[79] Besides polymerization in solution, various activated ester monomers have also been employed in plasma polymerization. For example, the groups of Förch and



Scheme 2 Chemical structures of activated ester monomers, chain transfer agents, and initiators.

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Gleason investigated the plasma polymerization of pentafluorophenyl methacrylate (PFPMA) resulting in polymeric reactive films.[80,81] Such films enable easy immobilization of various biomolecules exhibiting amine functionality and thereby provide the basis for biological assays and microfluidic biosystems.

Similarly, Lahann *et al.*[82,83] studied the chemical vapor deposition of functionalized [2.2]paracyclophanes resulting in reactive polymer layers.

Recent advances in the area of polymeric activated esters focus on the precise synthesis of defined polymeric structures utilizing controlled polymerization techniques.[10]

Several groups have shown successful atom transfer radical polymerization (ATRP) of NHSMA.[84–86] By dialing in the precise length of the polymer chain, Godwin *et al.*[84] were able to use these reactive precursor polymers for the synthesis of polymer–drug conjugates derived from copolymers of *N*-(2-hydroxypropyl)-methacrylamide (HPMA). Also extension to the synthesis of block copolymers featuring one polymeric activated ester block has been explored. It has been employed for the preparation of (1) metal ligand–containing polymers and block copolymers,[87] (2) charged polymers capable of complexing plasmid DNA,[88] (3) stable core cross-linked micelles,[89] hexa-armed star block copolymers,[90] and (4) thermo- and/or light-responsive polymers.[54,55,91,92] Besides ATRP of NHSMA and NHSA, ATRP of endo-*N*-Hydroxy-5-norbornene-2,3-dicarboxyimidacrylate (NorbNHSA),[93] *p*-nitrophenyl methacrylate,[94] and 2,3,5,6-tetrafluorophenyl methacrylate (TFPMA)[95] has also been described.

Complementary to ATRP, a lot of studies have been conducted on reversible addition–fragmentation chain transfer (RAFT) polymerization of activated ester monomers. Early studies on the polymerization of NHSMA and NHSA under RAFT conditions showed only a moderate control,[96] with slightly better results for copolymerizations with different methacrylamides.[97–100] Nevertheless, these reactive copolymers found versatile applications in, for example, shell cross-linked nanoparticles.[100] RAFT polymerization was also shown for *p*-nitrophenyl methacrylate,[101] which could even extend to the synthesis of reactive block copolymers.[102,103] Alternatively, successful RAFT polymerization of pentafluorophenyl acrylate (PFPA) and PFPMA had been demonstrated[104–106] and found useful applications in areas of gold nanoparticle functionalization[106] and defined reactive diblock copolymers to yield functional HPMA-based self-assembled nanoaggregates for efficient drug delivery.[107]

Besides the popularity of acrylate and methacrylate monomers, there had also been several reports on activated esters based on 4-vinyl benzoic acid. Aamer and Tew[108] described the polymerization of *N*-succinimide activated ester of 4-vinyl benzoic acid (NHS4VB). Simiarly, Nilles and Theato[109,110] had successfully demonstrated that the RAFT polymerization of pentafluorophenyl ester of 4-vinyl benzoic acid (PFP4VB) also leads to a very precise control of the degree of polymerization. Further, poly(PFP4VB) exhibits excellent solubility in a variety of organic solvents and remarkably increased reactivity toward amines. The astonishing difference in reactivity between PFP4VB and PFPMA has been taken advantage of in the synthesis of doubly reactive block copolymers that can provide a selective conversion with amines with varying reactivity.[111]

The *N*-succinimide activated ester of 4-vinyl benzoic acid could also be employed in nitroxide-mediated copolymerization.[112] Successful nitroxide-mediated polymerization of acetonoxime acrylate (AOA) was also demonstrated using *n-tert*-butyl-1-diethylphosphono-2,2-dimethylpropylnitroxide (DEPN) as the stable radical.[113]

In recent years, it turned out that particularly for the synthesis of functional polymers it is of great advantage to activate the moieties that carry the functionality rather than activating the functional groups at the polymer backbone. This is of particular importance if an ester linkage is used. Polymer analogous reactions based on poly(meth)acrylic acid chlorides with hydroxyl derivatives have the disadvantage that the already occurring small traces of hydrolysis reactions may lead to crosslinked and insoluble materials. To overcome this issue, it is advantageous to activate the moieties to be attached to the polymer backbone. Hence, functional polymers featuring hydroxyl functions have been reacted with low-molecular-weight activated acid chloride derivatives.

This approach was successfully used for homopolymers and copolymers as well as for block copolymers, particularly when complex mesogenic side groups had to be attached. For example, Adams and Gronski[114] synthesized homopolymers as well as block copolymers with liquid crystalline side chains by this approach. The corresponding polyalcohol was obtained by quantitatively converting the olefine double bonds of 1,2-polybutadiene via a hydroboration reaction with 9-borabicyclo[3.3.1]nonane and subsequent oxidation with H_2O_2. A further post-polymerization modification was performed with activated cholesteryl derivatives. Arnold *et al.*[115] synthesized block copolymers based on styrene and trimethylsilyl-protected hydroxyethyl methacrylate (HEMA), followed by a cleavage of the protecting groups and subsequent conversion with cholesteryl derivatives. Block copolymers with azobenzene chromophores on the base of hydroxyl functionalized segments were investigated by several research groups[116–124] to obtain polymer materials for advanced complex applications.

5.12.3.2 Anhydrides, Isocyanates, and Ketenes

Side chain functionalization of polymers utilizing anhydrides has been employed through the alternating copolymerization of several monomers with maleic anhydride.[125–127] The inherent high reactivity of anhydrides makes them ideal for reaction with amines.[128] Usually these conversions are performed in a buffer (dimethyl sulfoxide (DMSO)/0.5M $NaHCO_3$) for 3 h and reach almost quantitative conversions.

Similarly, isocyanates have been used as reactive carbonyl groups for a post-polymerization modification. Reactive isocyanate-containing polymers have been prepared by copolymerization of vinyl isocyanate, 1-methyl-vinylisocyanate, or *m*-isproprenyl-α,α′-dimethyl benzyl isocyanate with other vinyl monomers. Conversion of these isocyante groups can be conducted using amines or alcohols. While amines react quantitatively with isocyanates under ambient conditions within minutes, the reaction with alcohols requires either an excess of alcohol or a catalyst.[129]

However, the inherent high reactivity of isocyanate groups demands dry conditions for the polymerization step. To circumvent these problems, poly(4-vinylbenzoyl azide) has been studied as a new isocyanate group generating polymer

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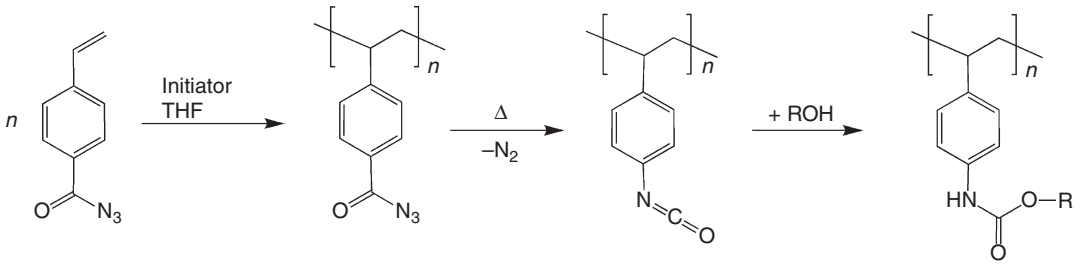

Scheme 3 Poly(4-vinylbenzoyl azide) as a 'dormant' precursor for isocyanate group-containing polymer.

(see Scheme 3). 4-Vinylbenzoyl azide can be polymerized under free radical polymerization conditions at $T = 35\,°C$. Afterward, heating the polymer solution to higher temperatures in the presence of alcohols results in the *in situ* formation of the isocyanate, which then directly reacts with the respective alcohol almost quantitatively.[130]

Further, reactive isocyanates have been used to bind to thiol end groups of polymers, which were readily accessible through RAFT polymerization.[131]

5.12.3.3 Oxazolones and Epoxides

Vinyl-functionalized oxazolones, for example, 2-vinyl-4,4-dimethyl-5-oxazolone, 2-(4′-vinyl)phenyl-4,4-divinylbenzaldehyde, and 2-isopropyl-4,4-dimethyl-5-oxazolone, can be homopolymerized via radical polymerization techniques.[132–135] Poly(2-vinyl-4,4-dimethyl-5-oxazolone) has been shown to react rapidly and quantitatively – even in aqueous solutions – with amines to yield amide-functional polyacrylamides.[135] For the reaction with alcohols, it is necessary to use a catalyst, such as acids, bases, trialkylphosphines, or cyclic amidines.[136]

Epoxide-functionalized monomers, such as glycidyl methacrylate (GMA), 4-epoxystyrene, or glycidyl acrylate, can be homopolymerized by radical polymerization techniques.[137–143] It has been further demonstrated that the epoxide groups can react with carboxylic acids, alcohols, thiols, anhydrides, and amines, even though primary amines lead to ring opening under formation of a secondary amine, which then results in crosslinking or formation of cyclic structures via reaction with another epoxide.

5.12.3.4 Aldehydes and Ketones

The idea to functionalize polymers via carbonyl groups as reactive side groups was already mooted in the 1950s by Schulz and his group, who synthesized acrolein polymers like poly(1,2-acrolein) via free radical polymerization and converted the aldehyde side group in various ways.[144–148] In the last decade, polymers with protected aldehyde side groups, that is, with acetal side groups, gained significant attention[11] when Maynard and co-workers started to polymerize 3,3′-diethoxypropyl methacrylate. First, they used free radical polymerization and applied the resulting polymers to pattern proteins on surfaces.[149,150] Then they used ATRP to produce well-defined reactive polymer scaffolds, which could, after acidic deprotection, be reacted with *O*-(carboxymethyl)hydroxylamine, a potential linker for drugs and peptides, and aminooxy-functionalized tetra(ethylene glycol) and thus are promising candidates for the development of polymeric therapeutics.[151] The combination of this monomer with methacrylates carrying activated ester side groups even allowed for the synthesis of polymers with orthogonally reactive side groups.[102,103]

The reactivity of aldehydes and ketones originates from the positively polarized carbon in the carbonyl group, which can easily react as an electrophile. Nucleophiles frequently used for the conversion of aldehydes or ketones in polymer side chains are, for example, primary and secondary amines, *O*-hydroxylamines, and hydrazines, or hydrazide-yielding imines,[147,148,152,153] enamines,[154] oximes,[145,149–151,155,156] and hydrazones,[147,155,157] respectively. Also, carbon-based nucleophiles can be reacted with a carbonyl group, or they could be oxidized or reduced; however, these reactions are less popular for post-polymerization modifications on aldehydes or ketones, and this chapter will thus focus more on the reactions with nitrogen-based nucleophiles. Among these, the conversion with *O*-hydroxylamines and hydrazines/hydrazides into oximes and hydrazones are usually the favored ones due to the hydrolytic stability of the products between pH values of 2–7 and 5–7, respectively, and their selectivity in the presence of amines.[11,157,158] Conversions with amines result in the less stable imines and, hence, are very often followed by a reduction of the imine to a stable secondary amine linkage with sodium boron hydride ($NaBH_4$) or sodium cyanoborohydride ($NaBH_3CN$). The latter can be used under milder conditions and at neutral pH values and thus is more selective.[159] The combination of these two steps is referred to as 'reductive amination'. However, it should be mentioned that, in contrast to various other amines, *O*-hydroxylamines are rarely available commercially. The possible ways to synthesize them from the corresponding bromide or the corresponding alcohol/amine using *N*-(*tert*-butyloxycarbonyl)hydroxylamine (Boc-hydroxylamine) or Boc-aminooxyacetic acid, respectively, usually involve two steps (Scheme 4).[102,151,160–162]

Instead of the free aldehyde or ketone, which can undergo undesired side reactions during different polymerization processes,[163] very often acetals or ketals are used in monomer structures. These protected analogs of the aldehyde or ketone are hydrolyzed under acidic conditions,[164] very often using trifluoroacetic acid (TFA) or hydrochloric acid, after polymerization in order to obtain the aldehyde- or ketone-functionalized polymers. Depending on the nature of the protective group employed, acetals and ketals with different reactivity can be realized. Dialkyl acetals, for example, are less stable than cyclic acetals like 1,3-dioxolanes under hydrolytic conditions.[160,165] Thus the acid lability of the side group employed can be tuned by the choice of the protective group,

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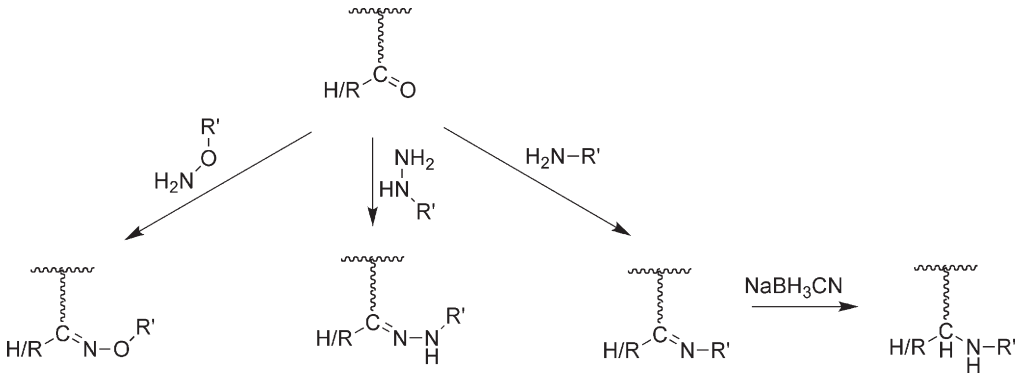

Scheme 4 Functionalization possibilities utilizing carbonyl groups in reaction with *N*-nucleophiles.

or independently functionalizable side groups can be incorporated in a copolymer by using monomers with differently protected carbonyl groups.

Both types, however, are stable under basic conditions and thus suitable candidates for combination with monomers with activated ester groups to copolymers with orthogonally reactive side groups. They can also be copolymerized with azide-functional monomers to yield polymers with orthogonally reactive handles.

5.12.3.4.1 Polymer side chain modifications involving aldehydes and ketones

In this section a variety of monomers and the synthetic pathways by which aldehyde- or ketone-containing polymers can be obtained from these will be presented, as well as examples of post-polymerization modifications on them. Homo- and copolymerization of vinylbenzaldehydes (VBA) have already been studied intensively during the last century; more precisely, free radical polymerization of free VBA as well as several protected derivatives such as (4-vinylphenyl)diethoxymethane and imines of vinylbenzaldehyde have been conducted by several authors.[166–169] Moreover, various protected derivatives have been polymerized by anionic polymerization and afterward been hydrolyzed to yield the reactive polymer precursor poly(vinylbenzaldehyde) (PVBA).[170–175] Heinenberg *et al.*[176] further studied the conversion with *N*-isopropylhydroxylamine. Sun *et al.*[177] developed a straightforward way toward well-defined poly(4-vinylbenzaldehyde) via RAFT polymerization of the unprotected monomer using *S*-1-dodecyl-*S*′-(α,α′-dimethyl-α″-acetic acid)trithiocarbonate as chain transfer agent (CTA) and azobisisobutyronitrile (AIBN) in 2-butanone. The amphiphilic PEG-*b*-PVBA, synthesized with the same method only using a monomethoxy-terminated poly(ethyleneglycol) (PEG)-based macro-CTA, could be assembled into vesicles in aqueous solution and then in a one-pot reaction be labeled with an amine-functionalized dye and crosslinked via reductive amination with a diamine and $NaCNBH_3$.[178] Also a double-functional monomer, namely, 2-formal-4-vinylphenyl ferrocene carboxylate, could be polymerized successfully with AIBN and the CTA 2-cyanopropyl-2-yl dithiobenzoate via the RAFT process in tetrahydrofuran (THF).[179]

Further reactive monomers, which can be polymerized in a free radical process as well as via RAFT polymerization, are the ketone-containing monomers *N*-(1,1-dimethyl-3-oxobutyl) acrylamide,[180] phenylvinylketone, and different alkylvinylketones.[181–183] Among these, methylvinylketone (MVK) is an interesting monomer not only because of its reactivity toward different nucleophiles, but also because PMVK can be oxidized with *m*-chloroperbenzoic acid in a Baeyer–Villiger reaction to yield poly(vinyl acetate).[163] The free radical polymerization of MVK and its conversion with hydroxylamine was already reported in 1938;[181] however, it cannot be homopolymerized via ATRP due to complexation of the copper catalyst by the monomer, although copolymerization with methyl methacrylate is possible via reverse ATRP.[163] This example demonstrates why, in many cases, protected analogs of aldehyde- or ketone-carrying monomers are used.

A very popular monomer, which has been successfully polymerized via free radical polymerization, ATRP, and RAFT polymerization, and subsequently deprotected with diluted trifluoroacetic acid, is 3,3′-diethoxypropyl methacrylate.[102,103,149–151] As observed by several authors, polymers with aldehyde side groups tend to become insoluble upon deprotection due to inter- and intramolecular noncovalent interactions or even covalent crosslinking,[151,184,185] and thus, their deprotection should be conducted *in situ* prior to the desired functionalization step. Due to the stability of acetal under basic alkaline conditions, it is an ideal candidate for the synthesis of copolymers with orthogonally reactive side groups via combination with activated esters, which can be converted with amines under alkaline conditions.[10] So the activated ester moieties can be reacted first, and then, the acetal groups can be deprotected and subsequently reacted with a different type of amines or hydroxylamines, for example, as presented by Maynard and co-workers[102,103] (see **Scheme 5**, right).

Another possible combination of reactive monomers was demonstrated by Yang and Weck,[184] who synthesized statistical copolymers from *exo*-norbornenes with ketones and chloro-substituents in their side groups via ring-opening metathesis polymerization (ROMP). After nucleophilic substitution of the chloride with sodium azide, these copolymers could be functionalized via copper-catalyzed azide–alkyne cycloaddition (CuAAC) and conversion of the ketones in a one-pot synthesis, as shown in **Scheme 5** (left). Different hydrazides were shown to react quantitatively with the ketones forming hydrazones.[184] Comparable experiments were performed on copolymers with aldehyde side groups, which could be converted with hydrazines, but these polymers were insoluble in classical organic solvents before and after conversion.

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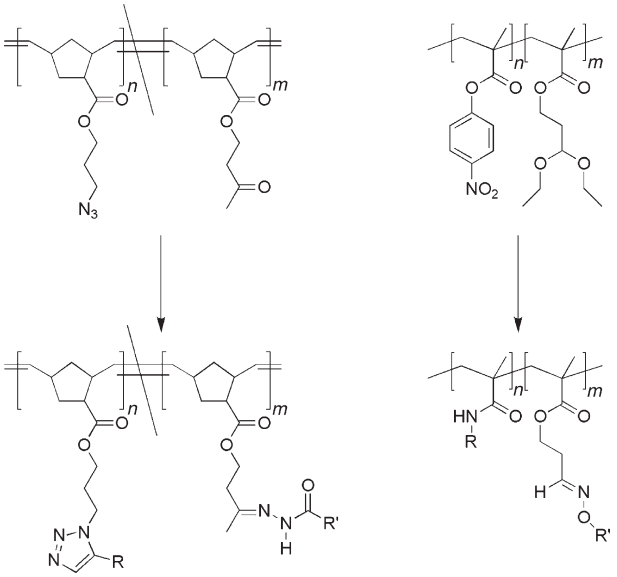

Scheme 5 Orthogonal functionalization of norbornene-based random copolymers and methacrylate-based block copolymers.

Furthermore, the different stabilities of dialkyl acetals and cyclic acetals as protective groups for aldehydes can be utilized to introduce multiple functionalities independently. The higher stability of cyclic acetals toward acids[165] allows for the deprotection and functionalization of dialkyl acetals in the presence of cyclic acetals and thus for independent conversion. Appropriate conditions for the hydrolysis of diethyl acetals, under which cyclic ethylene acetals are stable, were, for example, found for polymer-coated surfaces prepared from inorganic–organic hybrid materials containing poly (2,2-diethoxyethylacrylate) or poly(1,3-dioxolan-2-ylmethyl acrylate) blocks polymerized from functionalized poly(methylsilsesquioxane)s via RAFT.[160] After deprotection, conversion of the aldehyde groups with several amines and hydroxylamines could be used to tune the surface hydrophilicity, and a thermo-responsive surface was obtained after conversion with amino-terminated poly(diethylene glycol methyl ether methacrylate) (PDEGMEMA). The same cyclic acetal groups were also used to protect VBA during anionic polymerization, which, however, resulted in well-defined polymers only in the case of 2-(3-vinylphenyl)-1,3-dioxolane and not of the *ortho*- and *para*-analogs.[172]

In cases where the 1,3-dioxolanes are not linked to the polymer via the methylene bridge but via their ethylene bridge, that is, on position 4 or 5 instead of 2, the acidic deprotection results in 1,2-diols. Monomers of this kind, namely, (2,2-dimethyl-1,3-dioxolane)methyl acrylate and (2,2-dimethyl-1,3-dioxolane) methyl acrylamide, could be copolymerized with DEGMEMA via RAFT polymerization,[185] and after cleavage of the dioxolanes, the obtained 1,2-diols could be oxidized with periodic acid (HIO_4) to form aldehyde groups. Efficiency of this polymer analogous multistep reaction was confirmed via reaction with an amino-functionalized drug, namely, desferrioxamine, which was then used to chelate iron ions (Fe^{3+}) after reduction of the imine linkage with $NaCNBH_3$.[185] The different degradation behaviors of ester and amide bond polymer side chains were demonstrated with respect to applications of polymers such as polymeric therapeutics.

5.12.3.4.2 Polymer end group modifications involving aldehydes and ketones

Besides the functional side groups, polymer analogous reactions can also take place at the end groups of a polymer, which is very often used for end group modification, for example, with a dye, synthesis of linear and nonlinear block copolymers, or bioconjugation. For these purposes, for example, an acetal-containing initiator for ATRP was developed by Mantovani *et al.*[186] With this functional initiator in hand, PEG methacrylate was polymerized and, after deprotection of the resulting acetal end group, the polymer could be conjugated to lysozyme via the amino groups of the protein. The obtained imine linkage was then reduced to a stable secondary amine linkage with $NaCNBH_3$ in phosphate buffer, which also resembles the original amine group in its basicity and thus is supposed not to disturb the native structure of the protein.[186] Anionic polymerization allows to introduce protected aldehyde groups at the α-end group by using functional initiators like potassium 3,3-diethoxy-1-propanoxide. The acetal-functionalized polymers PEG and PEG-*b*-poly(lactide) obtained via this method could be converted into aldehyde-functionalized ones via deprotection with diluted hydrochloric acid.[187–189] When working at the ω-end group, it is also possible to introduce an unprotected aldehyde group directly after anionic polymerization by the addition of *N*-formylmorpholine,[190] as well as via lactone termination after ROMP.[191] Further, catalytic chain transfer polymerization[192,193] and RAFT polymerization[194] can be used to produce polymers with aldehyde end groups. Recently, an aldehyde-containing trithiocarbonate CTA has been synthesized and employed successfully in RAFT polymerization of several vinyl monomers, which could afterward be conjugated to hydroxylamine-functionalized polymers, obtained from another functional CTA, via a reversible oxime linkage.[194] In this context, it should be mentioned that several methods exist to synthesize well-defined polymers with hydroxylamine end groups, for example, using functional initiators for ATRP or CTAs for RAFT,[195–197] and thus, the reaction between aldehydes and hydroxylamines, among the other carbonyl reactions discussed above, is a versatile tool for polymer conjugation and the construction of several other polymeric architectures.

5.12.3.5 Azides with Alkynes

The 1,3-dipolar cycloaddition between azides and alkynes yielding 1,4- and 1,5-substituted 1,2,3-triazoles (see **Scheme 6**) was introduced by Huisgen[198,199] already in 1963, but its high impact[11–14,200–202] on organic chemistry and polymer science was initiated in 2001, when Meldal and Sharpless both reported on the high efficiency and selectivity of CuAAC.[203–205] Using copper(I) as catalyst, the reaction between terminal alkynes, generally poor 1,3-dipole acceptors, and azides can be accelerated and preferentially results in the 1,4-adduct. Another advantage is that very high yields can be obtained under mild conditions and in almost all organic solvents as well as under aqueous conditions. In the same year, Kolb *et al.*[204] presented the concept of 'click chemistry', which envisioned – inspired by nature – "an expanding set of powerful, selective, and modular" processes for the conjugation of small units via heteroatom

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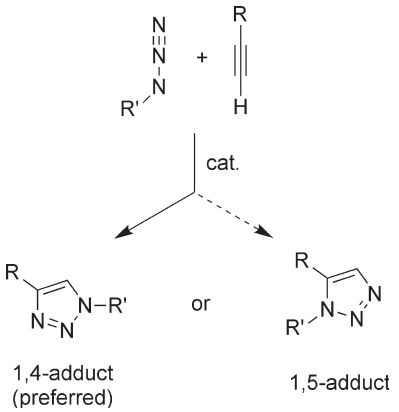

Scheme 6 1,3-Dipolar cycloaddition between azides and alkynes.

links. Among these, the 1,3-dipolar cycloaddition of azides and alkynes was suggested.

In 2004, Wu *et al.*[206] finally demonstrated the high efficiency of this reaction by using CuAAC for the convergent synthesis of dendrimers and thus opened the door for its application in polymer science.

In this section, the use of CuAAC as well as metal-free 1,3-dipolar cycloaddition for the functionalization of polymers via their side or end groups will be discussed after some general remarks. For more detailed discussion and further references concerning kinetic and mechanistic studies, a review by Binder and Sachsenhofer[12] is recommended.

As mentioned before, the 1,3-dipolar cycloaddition between terminal alkynes and azides can be conducted under conditions leading to high efficiency and selectivity. Especially valuable is its orthogonality to almost all other reactive groups allowing for the synthesis of polymers with multiple reactive handles as well as for diverse applications *in vitro* and *in vivo* due to its bioorthogonality.[184,203,205,207] Basically, this azide–alkyne cycloaddition is not affected by other typical reactive groups like amines, alcohols, aldehydes, ketones, esters, and others, as long as they cannot undergo cycloadditions themselves with one of the reactants (e.g., Demko and Sharpless[208,209] also reported on the cycloaddition of azides to sulfonyl and acyl cyanides) or deactivate the catalyst via complexation. As a slight exception, thiols should be mentioned, which were found to reduce azides after treatment at 100 °C for several hours or with a catalyst.[207,210,211] Also, Glaser coupling between two alkynes might occur as a side reaction.[212,213]

In general, there are two possible approaches to obtain polymers with the reactive handles required for this functionalization, that is, azide or alkyne groups: (1) The functionality can be introduced after polymerization, which is found very often in the case of a desired azide end group, which can be created by nucleophilic substitution of a bromide or chloride residue, for example. (2) The reactive group is already incorporated into one of the components utilized in the synthesis of the polymer, that is, in the monomers or the initiator or CTA, and thus available for functionalization directly after the synthesis of the polymer. Here, we will mainly focus on the latter approach because it allows for immediate polymer analogous reaction.

Furthermore, we have to distinguish between polymers with reactive side groups providing multiple reactive handles for functionalization and polymers with only one or two reactive end groups allowing for end group functionalization of polymer and bioconjugation.

In both cases, when the reactive groups are already embedded in the components for the synthesis of the polymer, their compatibility with the polymerization mechanism needs to be taken into consideration. In the following, some examples will be given of disadvantageous combinations that should be avoided. Obviously, alkyne groups might interact with the copper catalyst used in ATRP; hence, monomers like propargyl methacrylate cannot be polymerized in a controlled manner via ATRP.[214] The same holds true for the different ruthenium complexes used as catalysts in ROMP,[215] and explains why instead of the alkyne group the trimethylsilyl (TMS)-protected analog is used very often.[216–219] Moreover, the propagating polymer chain in an anionic polymerization can be terminated by the acidic terminal proton of the alkyne group.[220] Azide groups, on the other hand, can cause problems in cationic ring-opening polymerization (CROP),[11,221] and interfere with electron-deficient vinyl monomers in radical polymerization or simply decompose, especially at elevated temperatures.[222,223]

In the following subsections, several examples of successful synthesis of reactive polymer precursors and their functionalization via CuAAC will be given, mainly focusing on polymers with functional side groups, while also giving some examples of reactions of the end groups.

5.12.3.5.1 Polymer side chain modifications involving azides and alkynes

2-(Pent-4-ynyl)-2-oxazoline could be polymerized and copolymerized with 2-alkyl-2-oxazolines via CROP initiated by methyl triflate. The obtained polymers exhibited narrow molecular weight distributions, were water-soluble, and could be converted quantitatively with methylazidoacetate or (trimethylsilyl)methylazide in water using a slight excess of the respective azide (1.1–1.6 equivalents per alkyne) and copper (II) sulfate with sodium ascorbate to generate the copper(I) catalyst *in situ*.[221] These results are of particular interest because the same group had also presented the synthesis of other poly (2-oxazoline)s with further functional groups like aldehyde or amine groups previously,[224,225] so that the combination of the respective monomers is very likely to yield polymers with multiple orthogonally reactive groups.

Ring-opening polymerization (ROP) has also been used for the synthesis of well-defined polyesters with alkyne side groups, namely, poly(α-propargyl-δ-valerolactone) and its copolymers with ε-caprolactone (ε-CL).[226] Ethanol was used as initiator, and the polymerization was mediated by $Sn(OTf)_2$. These polymers could be functionalized with azide-terminated PEG-1100 monomethylether and an azide-functionalized pentapeptide (GRGDS) successfully and were found to be biocompatible. For these conjugation experiments, copper(II) sulfate and sodium ascorbate were used in a mixture of water and acetone at 80 °C; however, the use of milder, nonaqueous reaction conditions, for example, copper(I) iodine in catalytic amount with triethylamine in THF at 35 °C, might be recommended for polyesters, especially if the less stable poly(lactide) (PLA) is involved.[227]

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Elaborate studies on the preparation of different poly(oxynorbornene)s via ROMP were undertaken by Binder and Kluger,[215] investigating, among other things, the polymerization of a 7-oxynorbornene bearing an alkyne group, namely, exo-*N*-prop-2-ynyl-7-oxabicyclo[2.2.1]-hept-5-ene-2,3-dicarboximide. Due to undesired interaction of the alkyne moiety with the catalyst, this polymerization resulted in polymers with polydispersity indices (PDI) higher than 1.5. However, alternative methods for the synthesis of well-defined poly(oxynorbornene)s with either alkyne or azide side groups were demonstrated via postpolymerization modification. These reactive polymers could then be functionalized in various experiments using CuAAC with bromotris(triphenylphosphine)copper(I) as catalyst and *N*,*N*-diisopropylethylamine (DIPEA) in deoxygenated dimethylformamide (DMF) (50 °C, 48 h).

Different authors tried to polymerize methacrylate- or styrene-based monomers with an alkyne side group. For example, propargyl methacrylate could be polymerized via RAFT polymerization using *S*-1-dodecyl-*S*′-(α,α′-dimethyl-α″-acetic acid) trithiocarbonate and 2,2′-azobisisobutyronitrile (AIBN) in toluene (80 °C, 3 h) resulting in poly(propargyl methacrylate) with a molecular weight, M_n, of 25 000 g mol^{-1} and a PDI of 1.64.[228] This polymer could successfully be used in combination with poly(2-azidoethyl methacrylate) for the buildup of multiple layers on multiwalled nanotubes (MWNTs) via layer-by-layer click chemistry. However, several groups have shown that terminal alkyne groups interfere with radical polymerizations; for instance, crosslinking was observed during nitroxide-mediated polymerization (NMP) of *p*-ethynyl-styrene,[216] and the attempt to polymerize propargyl methacrylate via RAFT polymerization resulted in a product insoluble in organic solvents like THF and *N*,*N*-dimethyl acetamide.[219] The amount of crosslinking probably depends on the particular polymerization conditions, namely, temperature and time, and, depending on the desired application of the reactive polymer, the resulting product might be satisfactory. However, for well-controlled radical polymerizations, the use of a protective group is recommended. In both cases discussed above, the TMS-protected analog allowed for the synthesis of well-defined polymers with pendant alkyne groups after deprotection of the polymer with tetra-*n*-butylammonium fluoride (TBAF).[216–219] Subsequently, azide-terminated poly(vinyl acetate) could be grafted to the poly(propargyl methacrylate) in a CuAAC using copper(I) iodine and dibutylurea (DBU) in THF,[219] or an azide-functionalized fluorescent dye as well as carbohydrates could be conjugated using bromotris(triphenylphosphine)copper in combination with DIPEA,[218] to give only a few examples.

An early example of post-polymerization modifications on azide-containing macromolecules was the labeling of methionine analogs as azidoalanine and others on the *Escherichia coli* cell surface with acetylene-functionalized PEG via CuAAC using pure CuBr.[229] However, classical synthetic polymers with azide side groups have also been produced and functionalized successfully. For example, poly(3-azidopropyl methacrylate) was synthesized via ATRP with copper(I) bromide and 2,2′-bipyridine,[214] and afterward converted with propargyl alcohol and other model alkynes. Here, only 1.1-fold excess of the respective alkyne over the azide side groups was needed for almost full conversion (>95%) under mild conditions (2 h stirring in oxygen-free DMSO or DMF) with copper(I) bromide (0.5 equivalent) as catalyst.

Besides controlled radical polymerization (CRP), (C)ROP also allows for the synthesis of azide-carrying polymers like poly(2-(4-azidophenyl)oxazoline)[230] or poly(α-azido-ε-CL-*co*-ε-CL).[227] The latter is usually synthesized via nucleophilic substitution of the halide substitutent in poly(α-chloro-ε-CL-*co*-ε-CL) with sodium azide, but copolymerization of α-azido-ε-CL with ε-CL has also been suggested.[227] Independent of the synthesis of this copolymer, it could be functionalized via CuAAC by means of a catalytic amount of copper(I) iodine and triethylamine in THF with propargyl benzoate, 3-dimethylamino-1-propyne, *N*,*N*,*N*-triethylpropargyl ammonium bromide, and PEG with a *N*,*N*-diethylpropargyl ammonium bromide end group. Under the same conditions, the less stable copolymer poly(α-azido-ε-CL-*co*-*DL*-LA) was functionalized without indication for degradation.

Orthogonality of the CuAAC to polymer analogous reactions via carbonyl groups was demonstrated in a very effective one-pot functionalization reaction of a poly(norbornene) with azide- and ketone-containing side groups. This copolymer was reacted with phenylacetylene and benzhydrazide at the same time, using copper(II) sulfate and sodium ascorbate as catalyst (2 h at 25 °C).[184] The azide side groups were converted into triazoles and the ketone side groups into hydrazones, both quantitatively.

As a general remark, it should be mentioned that the very high efficiency of post-polymerization modifications via azide–alkyne cycloaddition at several sites along the polymer backbone is often attributed to the formation of the triazole moiety, which is said to have a catalytic effect on subsequent cycloaddition reactions in the vicinity and thus turns this polymer modification method into an autocatalytic process.[231]

5.12.3.5.2 Polymer end group modifications involving azides and alkynes

The development of CRP techniques also paved the way to a variety of synthetic possibilities to create functional polymer end groups. An azide or alkyne end group can either be obtained via postpolymerization modification or be already incorporated in the initiators used in ATRP, the unimer for NMP, or the CTA for RAFT polymerization, respectively. One of the most popular approaches is probably the introduction of an azide at the ω-end group of a polymer synthesized via ATRP.[232–234] For this purpose, the halide resulting from ATRP is simply exchanged in a nucleophilic substitution with sodium azide.[233,234] Using this reactive handle, numerous polymers with functionalized end groups were produced and block copolymers could be obtained via conversion with acetylene-terminated polymers.[235–238] Another group presented an azide-carrying initiator for ATRP, which could be used subsequently for the controlled polymerization of methyl methacrylate in combination with *N*-alkyl-2-pyridylmethanimine and copper(I) bromide, and then for the functionalization of the obtained polymer via CuAAC at the terminal azide in a one-pot synthesis using the same copper catalyst.[239] Also an azide xanthate for macromolecular design via the interchange of xanthates (MADIX) polymerization was developed and employed for the synthesis of poly(vinyl acetate) azide.[219] Furthermore, alkyne-functionalized initiators for ATRP[235,240] were synthesized, and different CTAs with either

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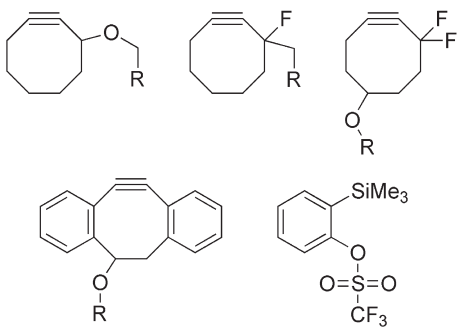
azide or alkyne groups were designed for RAFT polymerization,[241–245] one of them even yielding heterotelechelic polymers with an azide α-end group and a dithiopyridine ω-end group.[243] Such a heterotelechelic poly(*N*-isopropyl acrylamide) (PNIPAAm) could successfully be reacted with an alkyne-modified biotin using copper(II) sulfate with sodium ascorbate leaving the ω-end group unmodified under these particular conditions and thus ready for conjugation to different thiol-exhibiting biomolecules, for example, the protein bovine serum albumin (BSA). In general, the combination of controlled polymerization with this type of 'click chemistry' at the polymer end groups allows for the synthesis of a variety of linear polymer architectures like heterotelechelic polymers,[240,243,246–251] macromonomers,[252,253] and block copolymers,[235–238,240,242,244,254,255] as well as biohybrids.[256–262] Beyond linear architectures, also cyclic polymers, graft and star copolymers, polymeric networks, polymer-decorated surfaces and nanoparticles, dendritic architectures,[263,264] and so on, can be constructed utilizing the described reactive handles in side groups as well as in end groups.[12,13,265–269]

5.12.3.5.3 Metal-free 1,3-dipolar cycloaddition

Despite the broad applicability of CuAAC as a powerful tool for the design of diverse polymer architectures, the necessity of the metal catalyst for high efficiencies limits its usage for the synthesis of biomedical and pharmaceutical products as well as in *in vivo* applications due to the toxicity of copper.[270] Hence, great efforts have been undertaken to develop other copper-free 'click' methods,[270,271] among which are the approaches employing alkyne species with increased reactivity, which will be discussed briefly below. One alternative to CuAAC is the so-called strain-promoted azide–alkyne coupling (SPAAC). Therefore, cyclooctynes are used as alkyne component (see Scheme 7), which are activated by the ring strain ('first generation cyclooctynes').[272] Their reactivity is further increased if electron-withdrawing substituents are introduced in α-position to the triple bond. Second- and third-generation cyclooctynes exhibit one or two fluoro substituents in α-position, respectively,[273,274] which results in an acceleration of the reaction with azides. Another possibility to activate cyclooctynes is via increased ring strain as, for example, in 4-dibenzocyclooctynol,[275] and also benzynes like *o*-(trimethylsilyl)phenyl triflate are used as alkynes and result in benzotriazoles upon conversion with azides.[276] Since no metal catalyst is required and since it also represents a bioorthogonal reaction,[207,277,278] which can be performed under physiological conditions, SPAAC is already frequently applied in organic chemistry and biology, even in living cells and living animals.[272,273,277–285] Unfortunately, the yields are still relatively low in comparison with CuAAC, the reaction is not regioselective, and the synthesis of these alkynes is usually complex.



Scheme 7 Chemical structures of selected cyclooctynes and o-(trimethylsilyl)phenyl triflate used for a metal-free 1,3-dipolar cycloaddition.

In the broadest sense, cycloaddition-retro-Diels–Alder (cr-DA) reactions also can be listed here. They involve the formation of 1,2,3-triazoles from azides and trifluoromethyl-substituted oxanorbornadienes, which are activated by electron-withdrawing groups next to the alkyne, under release of furan.[286,287]

Recently, SPAAC also found its first applications in polymer chemistry. Using small crosslinkers with two cyclooctyne moieties, poly(*tert*-butyl acrylate) four-armed stars with azide end groups could be crosslinked via SPAAC-forming networks, which result in hydrogels after hydrolysis of the *tert*-butyl esters.[288] A comparable crosslinker with two dibenzocyclooctyne groups was used to stabilize a surface coating based on a copolymer of 2-azidoethyl methacrylate and methyl methacrylate on an alkyne-functionalized glass substrate. The obtained 'clickable coating' was functionalized with coumarin derivatives exhibiting reactive handles like dibenzocyclooctyne or trifluoromethyl oxanorbornadiene in a comparative study. The octyne showed the highest reactivity, whereas the oxanorbornadiene reached a similar level of functionalization only after a longer time.[289] The good reactivity of dibenzocyclooctynes could even be exceeded by a recently developed aza-dibenzocyclooctyne, which further allows for straightforward conjugation via the nitrogen atom.[290] Thus, it could be bonded to PEG, which was then used for effective PEGylation of the azide-functionalized enzyme CalB via SPAAC.

To summarize, the efficiency and biocompatibility of copper-free alternatives for the 1,3-dipolar cycloaddition of azides and alkynes have been demonstrated; first examples of use in polymer chemistry have already been successful, and further application for post-polymerization modifications can be expected. A small drawback, however, is the usually complex synthesis of the described alkyne analogs, and the applicability of these reactions in materials science would probably increase tremendously if the synthetic effort was reduced or if universally applicable cyclooctynes, for example, became commercially available.

5.12.3.6 Dienes and Dienophiles

Dienes and dienophiles undergo 2 + 4 cycloadditions, also termed 'Diels–Alder' reactions. Molecules containing 1,3 conjugated double bonds, including those with heteroatoms, can be considered as dienes. As dienophiles, alkenes and alkynes, as well as double bonds between one or two heteroatoms, can be considered. The reaction yields cyclohexene derivatives.

An important characteristic of the Diels–Alder reaction is that it is thermally reversible through a retro Diels–Alder reaction. The reaction temperature and processing temperature of products thus need to be considered to avoid decomposition. On the other hand, intentional retro Diels–Alder may be a convenient method for cleaving a linkage. For instance, furan can be used as a protecting group for maleimides that can be removed thermally (see Section 5.12.3.8).

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Not all dienes will readily react with all dienophiles. The reactivity depends on the amount of overlapping of the orbitals of the involved atoms and their energetic difference. The reaction takes place between the highest occupied molecular orbital (HOMO) of one molecule, and the lowest unoccupied molecular orbital (LUMO) of another molecule. The HOMO of electron-rich dienes may react with the LUMO of electron-deficient dienophiles in a normal Diels–Alder reaction. The LUMO of electron-poor dienes may react with the HOMO of dienophiles with a high electron density in an inverse Diels–Alder reaction. Electron density thus needs to be considered when choosing two reaction partners.

For many combinations of dienes with dienophiles, the reactions are regioselective, very robust, and require only very mild reaction conditions. Diels–Alder reactions have thus efficiently been used in post-polymerization modifications.

5.12.3.6.1 Polymer end group modifications involving Diels–Alder reactions

A molecule easy to integrate into an initiator, stable during a radical polymerization, and reactive toward electron-poor dienophiles is anthracene. ATRP of styrene and divinylbenzene from an anthracene-modified initiator resulted in cross-linked cores exhibiting the anthracene moieties. These were then clicked with maleimide-terminated polymers to yield multiarm stars.[291]

The 4 + 2 cycloaddition is orthogonal to the 3 + 2 dipolar cycloaddition of azides and alkynes, and both could be combined to form ABC triblock structures: An anthracene-modified ATRP initiator was used to polymerize styrene; substitution of the terminal bromide with azide afforded a heterotelechelic polymer with two different click groups. Two different polymers carrying maleimide and alkyne end groups, respectively, were added in a one-pot reaction to give the triblock.[294]

Maleimides are highly reactive dienophiles and find application in designing polymer architectures. Maleimides have been incorporated into initiators for ATRP or attached to PEG chains. In order to prevent side reactions during polymerization, maleimides are protected with furan in a Diels–Alder reaction. Retro Diels–Alder deprotection and reaction of the (protected) maleimide-functionalized polymers with dienes can be carried out in a single step, where furan is released and the maleimide adduct with, for example, anthracene is formed (**Scheme 8** (**a**)). By employing a trianthracene core, three-armed stars were accessible.[292,295]

A very convenient method for end group modification of RAFT polymers is to make use of the terminal thiocarbonyl group as a dienophile. With specially designed CTAs, carrying electron-withdrawing groups, the thiocarbonyl group reacts readily with dienes such as cyclopentadiene or open-chain alkadienes. Benzyl(diethoxyphosphoryl) dithioformate and benzylpyridin-2-yldithioformate have been used as CTAs to polymerize various polymers, which could be clicked to a variety of dienes and multidiene compounds yielding diblock copolymers[283] and stars (**Scheme 8**(**b**)).[296]

5.12.3.6.2 Polymer side chain modifications involving Diels–Alder reactions

Furan undergoes a variety of Diels–Alder additions as a diene[297] and has been used as a reactive site in polymer side groups. (*p*-Vinylphenyl)furfuryl ether was copolymerized with styrene, yielding a polymer with pendant furan groups. It could be crosslinked with a bismaleimide and decomposed again through a retro Diels–Alder reaction at elevated temperature.[298] A similar Diels–Alder chemistry was used on copolymers of *N*-dimethylacrylamide and furfuryl methacrylate to generate thermosensitive hydrogels through gelation with a bismaleimide.[299]

Trans, *trans*-hexa-2,4-dienylacrylate was successfully copolymerized with styrene via RAFT. The pendant diene groups were used to graft pyridin-2-yldithioformate-terminated polymers onto the copolymer, resulting in a comb polymer.[300]

A similar approach to develop comb polymers was accomplished by copolymerization of *p*-chloromethylstyrene with styrene. Postpolymerization, the chlorides were substituted with 9-anthracenemethyl alcohol, which then served as dienes in the reaction with maleimide-terminated polymers prepared as described above.[295]

5.12.3.7 Halides

5.12.3.7.1 Substitution

General substitution reactions have the focus of various studies, in particular the nucleophilic substitution on poly(*p*-vinyl benzyl chloride) (chloromethylated polystyrene), which can be obtained by either chloromethylation of polystyrene or direct polymerization of *p*-vinyl benzyl chloride.[301]

As such, substitution reactions have also been used for the preparation of polymer carrier or polymer supports, which often consist of cross-linked styrene-based copolymers featuring chemical groups that allow further functionalization, for example, benzyl chloride. In principle, one can differentiate three classes: polymer reagents, polymer catalysts, and polymer substrates. For example, Grubbs and Kroll[302] described the synthesis of a polymer rhodium catalyst. Another example represents quarterinization of cross-linked poly(*p*-vinyl benzyl chloride) with trimethylamine or *N*-chloromethylphthalimide followed by saponification, which results in cationic ion exchange resins.[303,304] More examples are summarized in the literature.[305]

5.12.3.7.2 Palladium-catalyzed coupling and cross-coupling reactions

Substitutions of alkyl or aryl halides can also be conducted utilizing the broad variety of Pd-mediated reactions, such as Heck, Sonogashira, Suzuki or Stille coupling. For these reactions, different functional groups can be used, such as alkene, alkyne, boronic acid or ester, or organotin, respectively. Coupling can usually be conducted under mild conditions.[306] Poly(*p*-bromosytrene) is one of the most commonly used polymers, which is readily available through radical or anionic polymerization.[307] To circumvent steric hindrance of catalyzed reactions on polymer chains, various optimizations have been described in the literature. For example, use of $[PdCl_2(PhCN)_2]$ as the catalyst and tri-*tert*-butylphosphine as ligands resulted in conversions up to 99% at room temperature; however, long reaction times of up to 96 h have to be taken into account.[308]

Pd-catalyzed coupling reactions have also been used for the preparation of Lewis acid organoboron polymers, which are exciting candidates in materials science due to their coordination behavior.[309]

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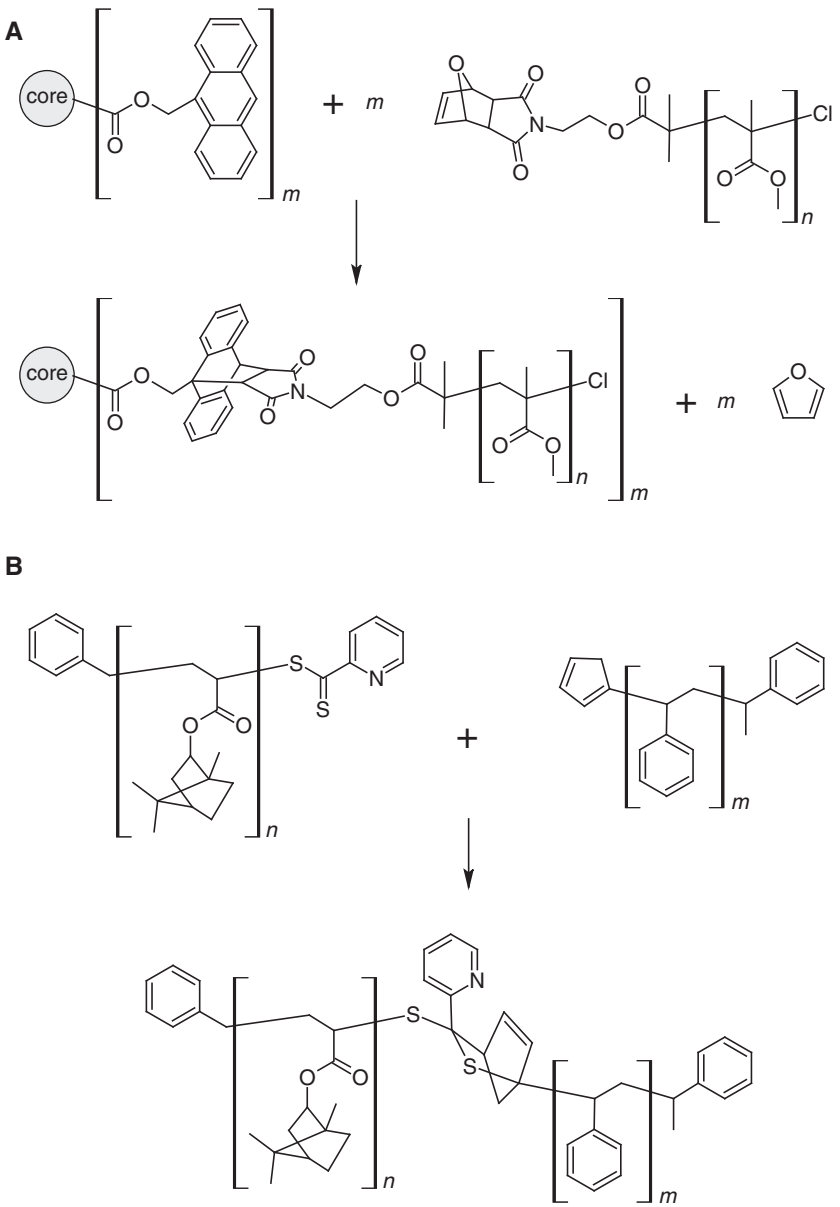

Scheme 8 (a) 2 + 4 Cycloaddition of PMMA with a protected maleimide end group with anthracene functional cores, for example, polystyrene derived from an anthracenyl initiator and crosslinked with divinylbenzene,[291] or a trifunctional core ($m = 3$).[292] (b) Example of end group conjugation of two different polymers with a dithioester as dienophile and cyclopentadiene as diene.[293]

5.12.3.7.3 Atom transfer radical addition

Alkyl halides as side chain functional groups have been employed in post-polymerization modifications utilizing atom transfer radical addition (ATRA).[310] This transition metal-catalyzed reaction has been investigated for the functionalization of polyesters containing α-chloro-ε-caprolatone repeating units. Jérôme and co-workers have demonstrated that it is possible to modify polyesters with very different functional groups, such as alcohols, esters, epoxides, and poly (ethylene glycol), if the respective vinyl component is available.[311–313] ATRA has further been used to graft polymers onto C60. As an example, defined C60 end-functionalized four-armed polymers have been synthesized.[314]

5.12.3.8 Thiols

Thiols, or mercaptans, sulfhydryls or hydrosulfides, are highly versatile functional groups as they undergo a variety of different reactions.[15,315–324] Many reactions proceed rapidly and with high selectivity, produce high yields under mild conditions, and require only simple purification. For this, the multifaceted thiol click chemistry finds many applications in polymer analogous modifications, which may also be elegantly combined with other, orthogonal clicking reactions.[15,16,325] As many biomolecules contain thiols (or reducible disulfides), thiol click chemistry is a very important tool in the preparation of polymer–bio hybrid materials.[326,327]

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Section 5.12.3.8.1 discusses various click reactions thiols may undergo, while the following sections provide a general overview of post-polymerization modifications involving thiols, divided into polymer end group (Section 5.12.3.8.2) and polymer main chain (Section 5.12.3.8.3) modifications. For more comprehensive information, the interested reader is directed to literature reviews cited in these sections.[11,15,16,325] In addition to organic reactions, thiols coordinate very efficiently to metals, enabling surface modifications through self-assembly. Not falling into the category of post-polymerization modifications, however, this chemistry will not be covered here.

5.12.3.8.1 Thiol reactions

5.12.3.8.1(i) Nucleophilic substitution

Being more acidic than the homologous alcohols, rather weak bases may be used to deprotonate thiols effectively in aqueous solutions. The resulting thiolates are very strong nucleophiles,[315] their nucleophilicity increasing in the order of alkyl, propionate, glycolate, and aromatic substituents.[15,315,318] As very soft nucleophiles, thiolates readily substitute soft-leaving groups on carbon or sulfur atoms. Halidoalkanes, such as the highly reactive α-bromocarbonyl or pentafluorophenyl compounds, require a base catalyst,[328] whereas the ring opening of epoxides with thiols may also be catalyzed with Lewis acids.[329] These reactions yield thioethers.

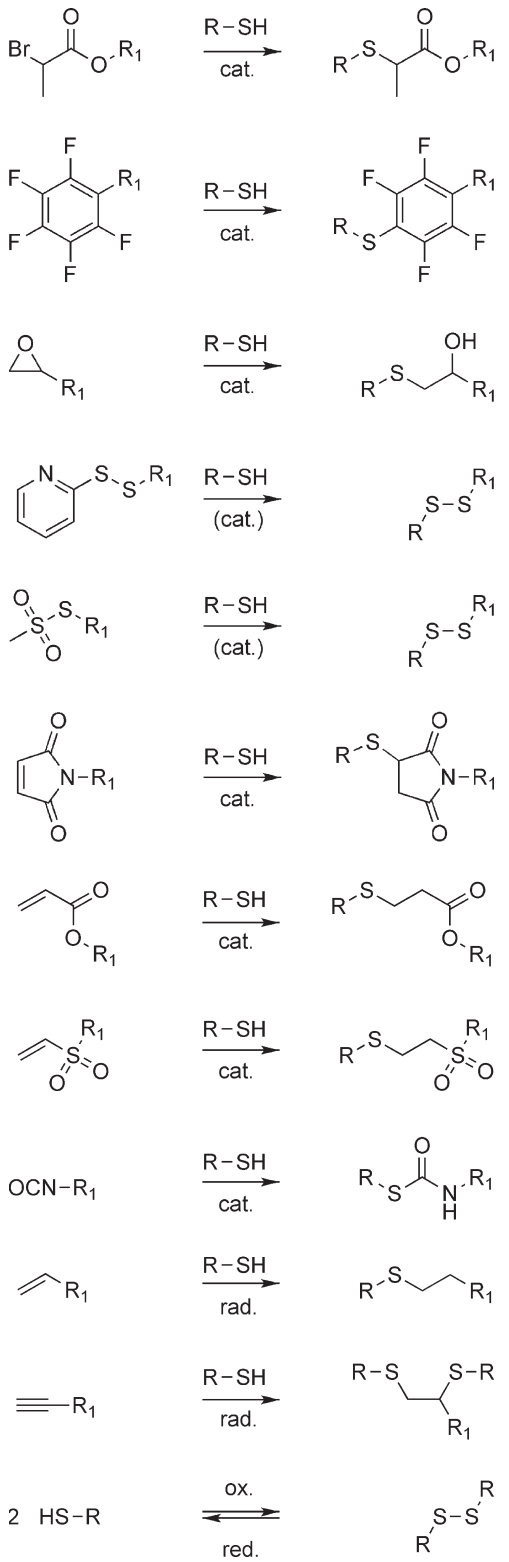
A special class of substrates that undergo nucleophilic attack by thiols or thiolates comprises those with electrophilic sulfur atoms, such as pyridyl disulfides, methane thiosulfonates, or thiosulfates (Bunte salts). These reactions produce unsymmetrical disulfides in very rapid and selective reactions, which may be cleaved on demand by reduction. Upon reaction with a thiol, Ellman's reagent (5,5′-dithiobis-(2-nitrobenzoic acid)) releases 2-nitro-5-thiobenzoate, the absorbance of which can be used for quantitative analysis.

5.12.3.8.1(ii) Nucleophilic addition

As strong nucleophiles, thiols add readily to activated (electron-poor) enes, such as maleimides, acrylates,[330,331] or vinylsulfones forming thioethers, and to isocyanates forming thioureas.[332–334] Nonaromatic isocyanates have been shown to react at a slower rate than phenyl isocyanate.[15] For the thiol-Michael addition to activated enes, reaction rates are greatly increased with increasing nucleophilicity of the catalyst, such as hexylamine or triisopropyl phospine. Increasing electron deficiency of the double bond increases the thiol addition rate.[15] Thiol–ene and thiol–isocyanate reactions may be performed in water and thus offer the possibility for bioconjugation (Scheme 9).

5.12.3.8.1(iii) Radical addition

Thiyl radicals are generally electrophilic, with electrophilicity increasing in the order of aromatic, glycolate, propionate, and alkyl substituents.[15,315,318] They thus react with electron-rich enes,[315,317,335–339] and with alkynes.[16,315,316,318,320,321] As compared to enes with electron-withdrawing groups (such as maleimides), which can be used for nucleophilic addition, nonactivated alkenes, for example, allyl ethers, can readily be employed in radical addition reactions. Allyl methacrylate can be selectively reacted at the methacrylate group in a nucleophilic thiol-ene reaction, followed by a radical thiol-ene reaction at the allyl group.[340] For cyclic enes, ring strain further increases the reaction rates.[341] While addition of thiols to enes produces



Scheme 9 Overview of reactions of thiols with various substrates as detailed in the text. cat., catalyst; rad., radical; ox., oxidation; red., reduction.

thioethers, alkynes add two equivalents of thiols to yield 1,2 dithioglycols, where the second addition (thiol + vinylthioether) is about 3 times faster than the initial thiol–yne reaction.[342] Both thiol–ene and thiol–yne reactions have a

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high tolerance for functional groups and are efficient and robust methods with single radicals being capable of mediating 10^2–10^4 addition reactions.[15,343] Radicals may be provided either by thermal decomposition of initiators or by photo-cleavable initiators. UV light initiation can eliminate the need for high temperatures, and more complete reactions with a higher degree of control can be obtained under photochemical conditions.[16,315–320,322–324]

5.12.3.8.1(iv) Oxidation and reduction

The half-reaction $RS–SR + 2e^- \rightarrow 2RS^-$ has a standard reduction potential of −0.25 V. A variety of mild, easy-to-handle, and cheap oxidizing agents, such as oxygen, iodine, hydrogen peroxide, or Fe(III) salts, may thus be applied to form symmetrical disulfides from thiols. On the other hand, the absence of oxidizing agents – especially oxygen – may be a necessary precaution to eliminate oxidation pathways where unintended. Disulfides, both symmetrical and unsymmetrical, can be very selectively converted into thiols by reducing agents such as dithiothreitol (DTT), *tris*(carboxyethyl)phosphine (TCEP), or sodium dithionite ($Na_2S_2O_4$).

5.12.3.8.2 Polymer end group modifications involving thiols

5.12.3.8.2(i) Thiol end groups

A major part of thiol-involved post-polymerization modifications falls into this category, because thiol end groups are easily accessible through the modification of the dithioester, trithiocarbonate, dithiocarbamate, or xanthogenate moieties retained as end groups in RAFT polymerization.[344,345] Thiols may be released from these groups by ester/carbonate cleavages employing, for example, amines or hydrides. When isolation of the terminal thiols is compromised by side reactions of the terminal thiol, such as oxidative interchain coupling (oxidation) or intrachain addition (backbiting), modification of the released thiol *in situ* in a one-step reaction is favorable.[346–349]

A very common technique for RAFT end group modification is the reaction of terminal thiols with modified maleimides or acrylates as thiol-Michael acceptors. Among others, hydroxyl[350] and pyrene[351,352] end groups have thus been introduced into polymers. Reacting thiol-terminated polymers with a triacrylate core produced three-armed stars.[353]

Aminolysis of terminal dithioesters on polystyrene, poly[(meth)acrylates], and poly[(meth)acrylamides] in the presence of functional methane thiosulfonate reagents affords terminal-functionalized disulfides in (near) quantitative yields. Using this approach, a butynyl end group as 'adaptor' to succeed with alkyne–azide clicking (CuAAC) was installed into various polymers. The disulfide bond enabled cleaving the polymers from a surface after being grafted to it by CuAAC.[346] Functional methane thiosulfonate (MTS) reagents could also be employed to introduce fluorinated block,[354] biotarget,[355] or fluorescent dye[356] end groups into stimulus-responsive polymers.

Thiol–bromo click chemistry, that is, nucleophilic substitution of activated bromides, can also be applied during the aminolysis of RAFT polymers to give thioether-bound functional end groups.[349]

The efficiency of thiol–isocyanate click chemistry was demonstrated on thiol-terminated poly(*N*,*N*-diethylacrylamide) with a variety of isocyanates, including the ones carrying further functional groups such as double bonds, halogens, or aromatics.[357]

ATRP from a difunctional disulfide initiator was used to prepare polystyrene with a disulfide bridge in the middle. This bond could be cleaved with DTT, and the resulting monothiol-terminated polymers could be oxidized to the original disulfide using $FeCl_3$ again. ATRP from a different difunctional initiator afforded polystyrene with α and ω bromo end groups which were converted into thiols with thiodimethylformamide. The resulting telechelic dithiol could be oxidized to a high-molecular-weight disulfide.[358] A similar approach to reducible polymers was achieved using a difunctional RAFT agent with subsequent conversion of the dithioester end groups to thiols, allowing reversible oxidation/reduction.[359]

5.12.3.8.2(ii) Thiol-reactive end groups

A large variety of thiol clicking partners have been introduced as polymer end groups, both before polymerization by functionalization of the initiator and by post-polymerization reactions.

Some 'adaptors' have been presented that can be used on thiol-terminated polymers (e.g., prepared by RAFT) to introduce a thiol-reactive site at the end group. Use of an excess of bis(maleinimido)diethylene glycol on thiol-terminated poly(*N*-isopropylacrylamide) (PNIPAM) produces maleinimide-terminated PNIPAM. This polymer was accessible with various thiols, including low-molecular-weight thiols as well as thiol-terminated polystyrene.[360]

Similarly, divinyl sulfone can be used to convert thiol end groups into Michael acceptor functionalities. BSA was coupled to poly[poly(ethylene glycol) methylether acrylate] via its free cysteine group.[348]

Aminolysis of trithiocarbonates of various RAFT-made polymers in the presence of dipyridyl disulfide produces pyridyl disulfide-terminated polymers. These groups with electrophilic sulfurs could be used for coupling thiol-modified biomolecules.[347]

Another example is the base-catalyzed thiol–ene addition of a thiol released *in situ* from RAFT-made PNIPAM to allyl methacrylate, generating a polymer with a terminal allyl group. This could then be reacted in a radical-mediated thiol–ene reaction to further modify the end groups. Using propargyl acrylate in a similar approach, PNIPAM with a terminal acetylene unit was prepared and used for the addition of two equivalents of thiols in a radical thiol–yne reaction.[340]

RAFT end groups can be replaced with the residues on diazo initiators. This approach has been employed to introduce furan-protected maleimides. After thermal deprotection, the maleimide end groups were used for protein conjugation.[361]

Both CTAs for RAFT polymerization and initiators for ATRP have been synthesized with pyridyl disulfide groups. Conjugating these compounds to BSA allowed grafting of polymers from this protein by ATRP[362] and RAFT without loss of its bioactivity.[363] Polymers derived from pyridyl disulfide-modified CTAs could also be conjugated to BSA in a polymer analogous thiol click reaction.[364]

ATRP is an advantageous method as it produces polymers terminated with halides. The terminal bromides of poly(methyl acrylate) have been modified with thioglycerol in a thiol–bromo click substitution reaction. The two terminal hydroxyl groups were then acylated with 2-bromopropionyl bromide to equip the end group with two initiators for ATRP,

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thus constituting an effective synthetic pathway for bromo-terminated macromolecular dendrimers.[365]

ATRP can also be used in combination with an olefin-modified initiator. After polymerization, the double bond was radically reacted with mercapto acetic acid. The authors additionally performed azid–acetylene clicking at the other end group of the polymer and showed that both types of reaction are compatible and may be performed in either sequence.[366]

A furan-protected maleimide with an alcohol group was used as initiator for the polymerization of lactic acid, which could be followed by deprotecting the maleimide via retro-Diels–Alder chemistry and conjugation with thiols to the end group.[367]

Further methods to create thiol-reactive end groups on polymers have involved reacting hydroxyl end groups originating from the CTA mercaptoethanol in a free radical polymerization with divinylsulfone.[368] The hydroxyl end group of PEG or pluronic can be modified to bear thiol-reactive groups, such as pyridyl disulfides or methoxycarbonyl disulfides. Examples are discussed in literature reviews.[361]

Limitations to the use of radical thiol–ene coupling to produce stars or diblock copolymers have been reported. In the attempts to click ene-terminated polymers to thiol-terminated polymers or to small cores containing multiple thiols, only very low yields of the desired diblocks and stars were found, which was attributed to bimolecular termination processes.[369]

5.12.3.8.2(iii) Heterotelechelic polymers involving thiol reactions

Due to the high selectivity of many thiol-click reactions, they are well compatible with other click chemistries. Several combinations of two orthogonal reactions have thus been applied to produce heterotelechelic polymers. Thiol-reactive end groups, such as methane thiosulfonates, pyridyl disulfides, and maleimides, have successfully been combined with activated ester and azide groups at the opposite chain end, to produce polymers carrying two different biological[355,370] or fluorescent dye[356,371] end groups.

5.12.3.8.3 Polymer main chain modifications involving thiols

5.12.3.8.3(i) Monomer units containing thiols

Polymers with a pendant thiol group, including partially esterified poly(acrylic acid), but also modified chitosan, cellulose, or alginate find applications as mucoadhesive polymers as they bind to cysteine-rich subdomains of mucus glycoproteins through disulfide exchange or oxidation.[372]

5.12.3.8.3(ii) Monomer units containing thiol-reacitve sites

A readily polymerizable monomer containing a thiol-reactive site is pentafluorostyrene, which undergoes substitution of the *para*-fluoride with base catalysis after polymerization. After polymerization via NMP, glycopolymers were prepared from poly(pentafluorostyrene) by employing a thiol-functionalized glucose with acetate-protected alcohol groups.[373]

Poly(butadiene) with its pendant vinyl groups is a suitable candidate for side group thiol–ene modification and was shown to react readily with thiolated biomolecules such as amino acids, sugars, or cholesterol with sunlight as initiator. Due to the closeness of the vinyl groups, cyclization of neighboring side groups occurs as a side reaction.[374]

Controlled radical polymerization techniques and tin-mediated ROP can be used to polymerize monomers containing alkenes, such as 1-[(3-butenyloxy)methyl]-4-vinylbenzene (copolymer with styrene using RAFT), but-3-enyl methacrylate (copolymer with methyl methacrylate using ATRP), or 6-allyl-ε-caprolactone (ROP), to yield polymers with alkene side groups. These were modified with a variety of thiols showing the robustness of this chemistry and its compatibility with azide–acetylene click chemistry.[366]

Copolymerization of styrenic derivatives carrying alkenes with maleic anhydride gave polymers with two orthogonally reactive groups which could be addressed with amines (maleic anhydride) and thiols (alkenes).[375]

Another specially designed monomer for thiol conjugation is pyridyl disulfide ethyl methacrylate, which was successfully polymerized by ATRP[376] and RAFT.[377] In a diblock copolymer with *N*-hydroxysuccinimidyl methacrylate, both blocks could independently be addressed with thiols and amines, respectively, in a one-pot reaction. A styrenic derivative carrying two pyridyl disulfide groups offered the possibility of easily attaching thiolated PEG side chains to a water-soluble copolymer, without endangering the integrity of the acetal bridges within the polymer. Upon pH-responsive cleavage of the acetal groups, the bioinspired polymeric carriers became membrane-disruptive and were studied for direct cellular uptake.[378]

5.12.4 Conclusions and Outlook

Post-polymerization modifications represent a synthetically very appealing approach for the synthesis of functional polymers. Different synthetic concepts of organic reactions are merging in polymer science leading toward the synthesis of architecturally well-defined multifunctional polymers. The different classes of reactions provide the synthetic polymer chemist with tools of unprecedented precision, thereby opening the doors for materials synthesis in an interdisciplinary world. Even though the idea of post-polymerization modifications, as well as the chemistries employed, is rather old, it appears that this research topic of polymer chemistry will gain a dramatic new momentum and we can look forward to future developments in high-precision polymer synthesis.

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5.13 Supramolecular Polymers

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5.13.1 Introduction

5.13.1.1 Definition of Supramolecular Polymers

Supramolecular chemistry is based on the formation of larger entities – beyond the classical molecular covalent chemistry – by intermolecular noncovalent interactions.[1–5] Several types of interactions (e.g., metal-to-ligand coordination, hydrogen bonding, ionic interactions, and π–π interactions) can keep the whole assembly together. In principle, two different types of these assemblies can be distinguished: (1) supermolecules, which are well-defined oligomeric structures, and (2) polymolecular assemblies, which consist of a large number of monomeric species.[6] The latter could be covalent molecules, even macromolecules. Therefore, it is apparently difficult to precisely define supramolecular polymers. If the only criterion is that a supramolecular polymer 'consists of noncovalently linked monomers', polymeric micelles, even a simple crystal formed by an organic compound would be a 'supramolecular polymer'.[7] In contrast, Meijer and co-workers coined a new definition: 'supramolecular polymers are defined as polymeric arrays of monomeric units that are brought together by reversible and highly directional secondary interactions, resulting in polymeric properties in dilute and concentrated solution as well as in the bulk. The directionality and strength of the supramolecular bonding are important features of systems that can be regarded as polymers and that behave according to well-established theories of polymer physics'.[8,9]

In simple terms, a long sequence of units (i.e., monomers, polymers) connected by secondary (noncovalent) interactions can be considered as a supramolecular polymer (**Figure 1**).[10] The covalent counterparts of the depicted supramolecular polymers are macromolecules, which are formed by polyaddition and polycondensation.

5.13.1.2 Noncovalent Interactions

Besides the structural classification of monomers (i.e., nature of the building blocks), supramolecular polymers can be distinguished according to the nature of the noncovalent interaction (for selected recent reviews, see References 9, 11–17). In contrast to the strong covalent bonds (150–1000 kJ mol^{-1}), noncovalent interactions are much weaker (typically in the range from 1 to 120 kJ mol^{-1}). Among these, van der Waals and p-donaor-acceptor interactions are considered as rather weak, whereas hydrogen bonding, hydrophobic-hydrophilic interactions and ion pairing represent noncovalent interactions of medium strength; metal-to-ligand coordination is general the strongest noncovalent type of bonding.

However, most of these interactions are reversible, due to their weaker strength and noncovalent nature. Therefore, the monomeric units of a supramolecular polymer can be assembled and easily disassembled resulting in new interesting properties and potential applications. The toolbox of these different interactions opens the door to synthesize different supramolecular polymers with 'tailor-made' properties, which reveal the key property: reversibility.[11]

In addition, the directionality of the noncovalent bond represents an important aspect when considering the synthesis of supramolecular polymers. In classical polymers, the covalent bonds are the direct linkage of two monomeric units. In contrast, supramolecular polymers often feature interactions with lower directionality (e.g., ion-pairing and π-donor–acceptor). Only hydrogen bonding and metal-to-ligand interactions allow a very high directionality, even comparable to a conventional covalent bond. The directionality and the strength of the noncovalent interactions are the important parameters for the formation of supramolecular polymer.

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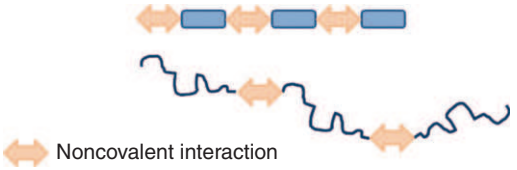

Figure 1 Schematic representation of supramolecular polymers consisting of monomers (top) and polymers (bottom), respectively, linked via noncovalent interactions.

5.13.1.3 Supramolecular Polymerization

Classical polycondensations and polyadditions, involving the formation of covalent bonds, require monomers with – at least – two functional groups. In case of linear polymers, either one monomer with two different functional groups (AB) or two monomers each bearing two functional groups (AA and BB) can be utilized for the polymerization. Supramolecular polymers can be assembled by the polymerization of monomers carrying at least two functional groups, which will form the required noncovalent interaction (Figure 2). Comparable to their covalent counterparts, AB-type monomers (e.g., Ic) and an AA-BB-type monomer pair (Ib) can also be applied. In principle, two different types of monomers can be distinguished: directly interacting monomers (Ia–c) and monomers which are connected by the help of a metal ion (IIa–c). Supramolecular polymerizations of type I include, mainly, hydrogen bonding, π-donor–acceptor, and ion-pairing. The latter can also be involved in type II polymers which are mainly formed by coordinative interactions. Self-complementary monomers (e.g., Ia and IIa) result in supramolecular polymers consisting of only one monomeric unit. In addition, complementary binding units

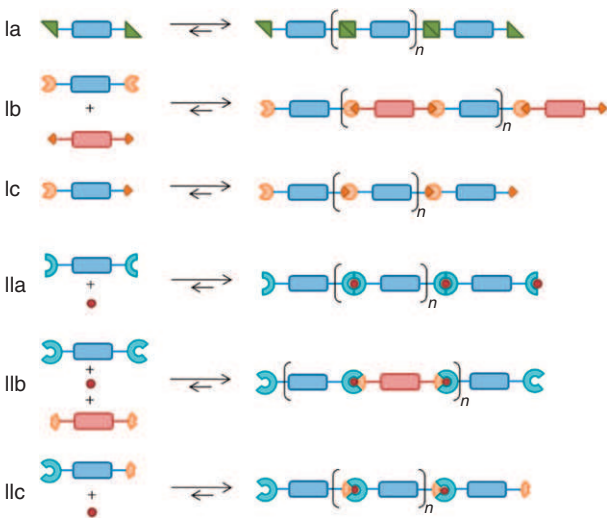

Figure 2 Schematic representation of different supramolecular polymerizations. Type I: supramolecular polymerization of directly interacting monomers (a: self-complementary, b: complementary AA and BB monomers, and c: complementary AB monomer); type II: supramolecular polymerization of monomers by metal ions (a: self-complementary, b: complementary AA and BB monomers, and c: complementary AB monomer).

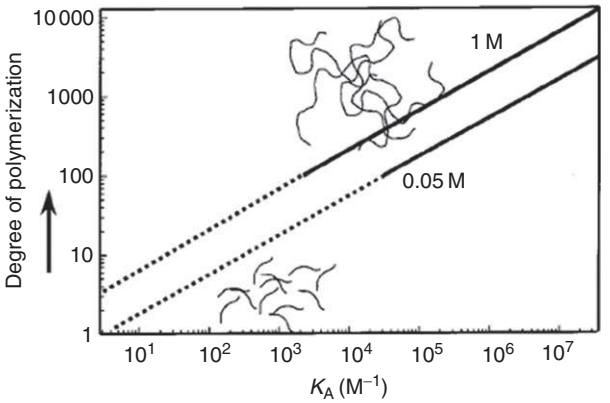

Figure 3 Theoretical plot of the DP versus the association constant (K_A in M^{-1}) for a supramolecular polymerization (two different concentrations, isodesmic self-assembly model). Reprinted from Reference 8, © 2001 American Chemical Society.

can be utilized for the synthesis of homopolymers (Ic, IIc) as well as alternating copolymers (IIb, IIc).

In contrast to their covalent counterparts (i.e., polyaddition and polycondensation), supramolecular polymerizations are usually reversible, that is, depolymerization cannot be neglected. Consequently, heating or dilution of a supramolecular polymer will have a tremendous effect (decrease of the molar mass), unlike for a common macromolecule. The molar mass of polymers synthesized by polyaddition or polycondensation processes is determined by the conversion of the monomer (p) (Carothers' equation: degree of polymerization (DP) = $1/(1-p)$). Due to the reversibility of noncovalent interactions, the molar mass of supramolecular polymers will be determined, as a first approximation, by the strength of the interaction, that is, the equilibrium constant. The correlation between the association constant and the DP (Figure 3) elucidates that high association constants and high monomer concentrations are a prerequisite to obtain supramolecular polymers with high molar masses. Furthermore, concentration, temperature, and other reaction conditions will strongly influence the entire synthesis.

This point of view simplifies the mechanism of the supramolecular polymerization. Looking into more detail, three main mechanisms can be distinguished: (1) isodesmic supramolecular polymerization (ISP), (2) ring-chain-mediated supramolecular polymerization, and (3) cooperative supramolecular polymerization (Figure 4).[9] This chapter will be limited, in particular, to linear supramolecular polymer systems; therefore, the formation of supramolecular gels[18–21] and liquid crystalline (LC) phases[22–24] will not be discussed in detail.

5.13.1.3.1 Isodesmic supramolecular polymerization

Looking into more detail, the ISP (also called 'multistage open association'[10,25,26]) is characterized by the formation of one reversible, noncovalent bond between monomers, oligomers, and later polymers (Figure 5(a)). The bond which is formed is identical throughout the whole polymerization, that is, the reactive groups of monomers, oligomers, and polymer chains will have the same reactivity. Each step is characterized by the intermolecular equilibrium constant K (Figure 5(b)) which is therefore independent of the chain length. In contrast to the

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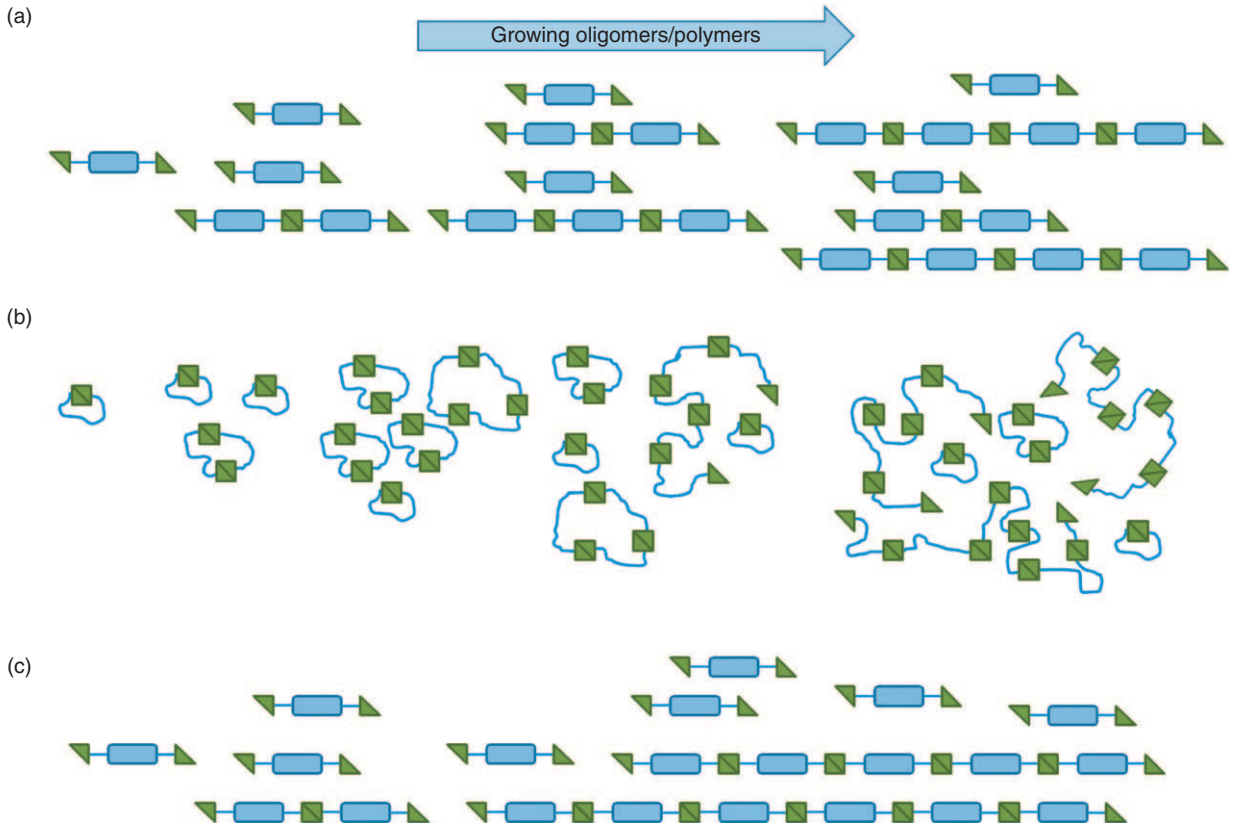
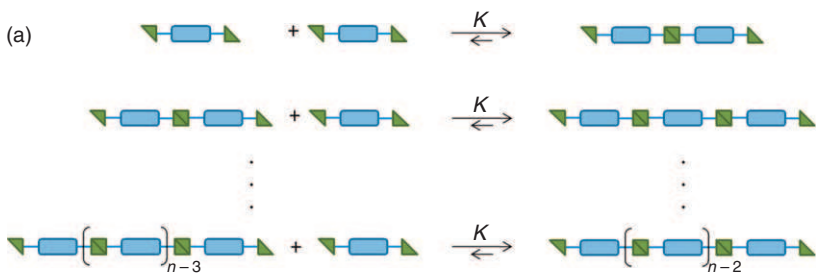


Figure 4 Schematic representation of the three main polymerization mechanisms: (a) ISP, (b) ring-chain-mediated supramolecular polymerization, and (c) cooperative supramolecular polymerization.



(b)

$$[\text{dimer}] = K \cdot [\text{monomer}]^2$$

$$[\text{trimer}] = K \cdot [\text{dimer}] \cdot [\text{monomer}] = K^2 \cdot [\text{monomer}]^3$$

$$[n\text{-mer}] = K^{n-1} \cdot [\text{monomer}]^n$$

Figure 5 (a) Schematic representation of the ISPs of a bifunctional monomer (Ia). (b) The intermolecular equilibrium constant K is independent of the chain length.

ring-chain-mediated polymerization, no cyclic structures are formed.

The number- and weight-averaged DPs ($\langle DP \rangle_n$, $\langle DP \rangle_w$) can be calculated from the monomer concentration and the equilibrium constant according to eqns [1] and [2] (for $K[\text{monomer}] < 1$).[27]

$$\langle DP \rangle_n = \frac{1}{1 - K[\text{monomer}]} \quad [1]$$

$$\langle DP \rangle_w = \frac{1 + K[\text{monomer}]}{1 - K[\text{monomer}]} \quad [2]$$

$$PDI = 1 + K[\text{monomer}] \quad [3]$$

The polydispersity index (PDI, eqn [3]) converges to the limiting value of 2.0 in the ideal case ([monomer] approaches $1/K$), comparable to a standard step-growth reaction (for a more detailed insight into the theory of polycondensation/polyaddition processes, see Chapter 5.01 in this volume).[8,15]

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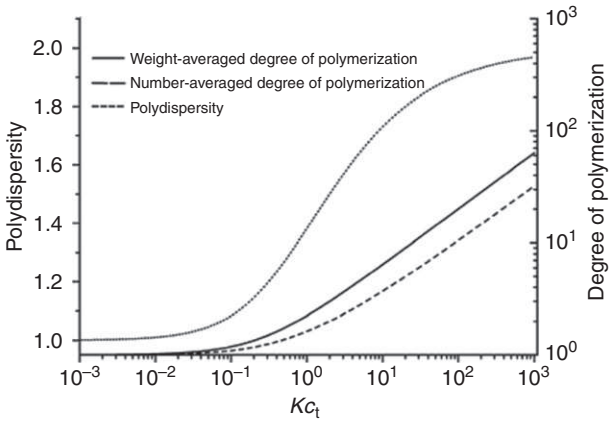

Figure 6 Number- and weight-averaged DPs (<DP>$_n$, <DP>$_w$) and PDI as a function of equilibrium constant and total concentration of monomer (Kc_t). Reprinted with permission from Reference 9, © 2009 American Chemical Society.

The correlation of these parameters with the dimensionless concentration Kc_t, where K is the equilibrium constant and c_t is the total concentration of the monomer, is depicted in Figure 6. A high DP can only be reached for high values of Kc_t, that is, high monomer concentrations and high equilibrium constants are required. High concentrations can often not be achieved due to the low solubility of the monomers and therefore the equilibrium constants must be very high ($K > 10^6$) in order to obtain supramolecular polymers with high molar masses. It is noteworthy that the monomer is still the most present molecule in the solution, independent of the values of the equilibrium constant and the total concentration. As for their covalent counterparts, the exact stoichiometry of the functional groups is required in order to obtain polymers with high molar masses. Self-complementary functional groups lead automatically to the ideal stoichiometry; complementary monomers require the exact 1:1 ratio. In addition, the molar masses can be adjusted in this case by addition of chain-stopping agents.[28–30]

The determination of the molar mass of these polymers is often difficult, because the analytical methods commonly used for 'classical' macromolecules (e.g., size exclusion chromatography (SEC) and mass spectrometry) cannot be applied due to the weak and/or kinetically labile supramolecular bonds. However, several spectroscopic techniques (e.g., nuclear magnetic resonance (NMR) or UV/vis absorption), calorimetry, and analytical ultracentrifugation (AUC) can be applied to determine the molar masses.[9] The ISP of bifunctional monomers can be compared to the ideal linear reversible polycondensation (see Chapter 5.01 in this volume), which complies to the 'principle of equal reactivity' according to Flory.[31,32]

5.13.1.3.2 Ring-chain-mediated supramolecular polymerization

The second main mechanism for the formation of supramolecular polymers is the ring-chain-mediated supramolecular polymerization (Figure 4(**b**)). A bifunctional monomer is polymerized; this monomer, all other oligomers, and polymer chains feature an equilibrium between a linear and a cyclic form (Figure 7). The ring is formed by an intramolecular reaction of the end-groups; an intermolecular reaction will lead to a longer chain. Obviously, a prerequisite for this mechanism is a flexible monomer, for instance, flexible polymer chains or aliphatic chains that can link both supramolecular binding units.

The ratio of both equilibrium constants (intra- and intermolecular) determines the effective molarity (EM, eqn [4]).[9] Cyclization is favored for EM > 1; linear chains are formed when EM < 1. Therefore, ring closure is favored at low concentrations due to the larger distances to the next potential reaction partners, which are longer than the end-to-end distance:

$$\mathrm{EM} = \frac{K_{\mathrm{intra}}}{K_{\mathrm{inter}}} \qquad [4]$$

5.13.1.3.3 Cooperative supramolecular polymerization

The third and last mechanism, which will be discussed in detail, is the cooperative polymerization, in particular the nucleation–elongation polymerization (NEP).[9,27,33,34] At first glance, the mechanism of this supramolecular polymerization (Figure 8) appears very similar to the ISP. The major difference between both is that in ISP all steps have the same equilibrium constant K, while the NEP features two equilibrium constants, one for the nucleation (K_N) and one for the chain elongation (K_E), which is higher. In Figure 8, the nucleus is the dimer; its formation is disfavored ($K_N < K_E$) and the subsequent elongation is favored ($K_N > K_E$). As a result, the weight fraction of the monomer will be significantly higher than for an isodesmic polymerization.[27] The monomer concentration plays a crucial role also for the NEP. Below the critical concentration, hardly any polymerization occurs.

The cooperative supramolecular polymerization can be caused by electronic effects, hydrophobic effects, and structural effects, for example, formation of helical structures. Chain-growth polycondensation can be considered as the covalent counterpart (see also Chapter 5.06 in this volume).

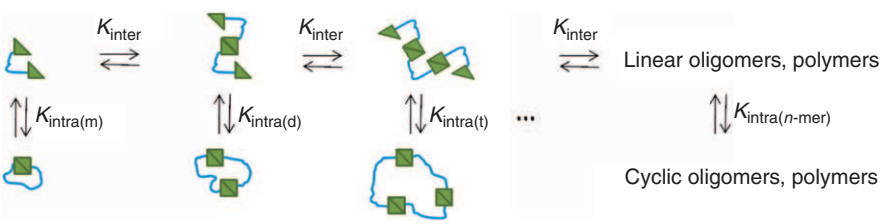

Figure 7 Schematic representation of a ring-chain-mediated supramolecular polymerization. The intermolecular binding constant (K_{inter}) is associated with the intermolecular binding of two molecules; the intramolecular binding constant ($K_{intra(n\text{–}mer)}$) is associated with intramolecular ring closure of monomers, oligomers, and polymers.

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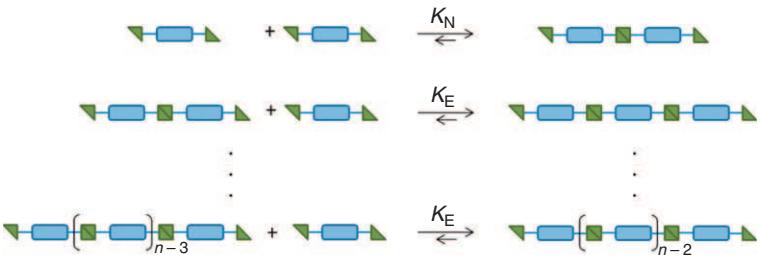

Figure 8 Schematic representation of cooperative supramolecular polymerization (elongation–nucleation). K_N is the equilibrium constant for the nucleation and K_E the constant for the elongation ($K_N < K_E$).

These three main mechanisms, which were discussed above (for a more detailed overview, see Reference 9), for the formation of supramolecular polymers are comparable to their covalent counterparts: polyaddition and polycondensation.

In the following, supramolecular polymers will be evaluated in more detail with respect to their supramolecular binding unit, in particular transition metal complexes, ionic interactions, as well as hydrogen bonds. Selected examples of these materials will be covered.

5.13.2 Metallo-supramolecular Polymers

5.13.2.1 General Aspects

In recent years, metal–ligand coordination has evolved into one of the most versatile tools for the preparation of supramolecular polymers by self-assembly, since (1) the coordination bond is highly directional, (2) the structure of the ligand can easily be varied by applying organic chemistry reactions, and (3) the thermodynamic as well as kinetic stability can be fine-tuned via the appropriate combination of ligand types and metal ions.[35] The combination of traditional organic polymers with inorganic coordination chemistry opened avenues to new classes of functional materials. The tailored mechanical properties of conventional polymers are accompanied by the additional features introduced by the metal ion, for example, molecular magnetism,[36–41] conductivity,[42–45] nonlinear optics,[46–49] or ferroelectrics.[50–53] The general structural motifs accessible by this type of self-assembly have been classified into lattice, cyclic, and filamentous motifs as well as interlaced systems, according to Swiegers and Malefetse.[54]

Before detailing the metallo-supramolecular coordination polymers with respect to structures, properties, and potential applications, the term 'coordination polymer' needs to be defined adequately. One has to be aware that the inorganic and supramolecular communities use the term 'coordination polymer' in quite different contexts. Inorganic chemists also consider one-, two-, and three-dimensional coordination networks as coordination polymers. However, these materials are mainly crystalline solid-state materials that typically disassemble into discrete molecular units upon dissolution. In literature, these types of compounds are also often referred to as 'metal–organic coordination networks' or 'metal–organic frameworks' (MOFs).[55] Application of highly porous MOFs in the fields of gas storage has recently been reviewed elsewhere.[56–58] Within this chapter, only species that retain their polymeric nature in solution also will be discussed; consequently, materials existing in a polymeric form only in the solid state and/or form due to lattice energy considerations are excluded.

In the field of supramolecular chemistry, the definition of 'coordination polymer' is more precise and is strongly related to macromolecular chemistry. Here, a coordination polymer is a material that has been constructed by a supramolecular approach: the polymer chain is built up by the formation of coordinative bonds, that is, metal ions and ligands form Lewis-type acid–base pairs with one partner acting as a donor and the other one as an acceptor to form a dative bond.[35,59,60] These interactions have to be strong enough to retain the polymeric structure in solution also. Furthermore, coordination polymers should exhibit properties that are characteristic for (conventional) polymers, such as enhanced viscosity, compared to their monomeric building blocks, and/or a glassy solid state.[35] A classification of the wide field of such coordination polymers has already been carried out by Rehahn[61] in 1998 – the majority of these compounds can be assigned to polymers with only main group elements in their backbone or those with transition metal ions as integral parts of their main chain. In the following, the focus will be on coordination polymers of the latter type, showing an alternating incorporation of metal ions and organic ligand molecules (**Figure 2**, **IIa–c**).

5.13.2.2 Metal-binding Motifs in Metallo-supramolecular Polymers

Since metallo-supramolecular polymers rely on metal–ligand bonds, both partners – the transition metal ion and the organic ligand – need to be taken into consideration. The ligand must simultaneously enable the complexed metal ion of the embedded transition metal to exhibit a desired property (e.g., low oxidation/reduction potentials) and facilitate polymer formation while maintaining control over physical attributes of the overall material (e.g., solubility).[62] Besides this interplay, the coordination numbers of the metal ion and the organic ligand are also of utmost relevance. In order to achieve linear polymers via bidirectional chain growth, two opposing points of contact are required at the metal center, and the ligand entity itself (e.g., monomer, oligomer, or polymer) must be capable of binding two metal ions. Furthermore, the ligands should possess high binding affinities toward the metal ions in order to allocate a sufficient thermodynamic driving force to facilitate polymerization and to yield polymers with high molar masses.

Commonly, bidirectional, ditopic ligands are used for the synthesis of metallo-supramolecular polymers. They show a

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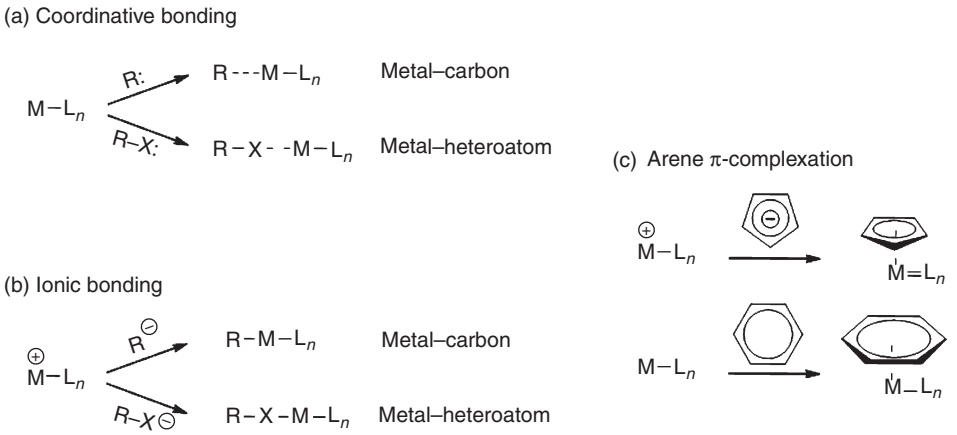

Figure 9 Schematic representation of the three main types of metal-to-ligand interactions. (Scheme redrawn according to Reference 62.)

broad diversity in the ability to bind metal ions. The three main motifs employed in this respect – (a) coordinative and (b) ionic boning as well as (c) metal–arene complexation – are depicted in Figure 9.[62]

5.13.2.3 Supramolecular Polymers via Coordinative Bonding

As mentioned above, metallo-supramolecular polymers based on dative-type interactions between metal ions and organic ligands are often referred to as coordination polymers. Coordination occurs between transition metal ions (mainly in their lower oxidation states) and, in particular, neutral donor moieties such as amines, imines, ethers, ketones, nitriles, phosphines, and thio compounds. As shown in the example of pyridine-based ligands, these interactions can be further utilized to form mono-, bi-, or tridentate systems (Figure 10).[35,63] The particular influence of the denticity of the ligand on the complex stability was investigated in detail by Dobrawa and Würthner using the example of Zn^{II}-oligopyridine complexes. Binding constants in the range of $K = 10^3\,M^{-1}$ (for the Zn^{II}/pyridine interaction) to $K > 10^8\,M^{-1}$ (for the Zn^{II}/terpyridine interaction) clearly revealed the chelation effect.[35,64]

Metallo-supramolecular polymers formed by metal-to-ligand coordination feature the broadest spectrum in terms of metal–ligand stability. Many examples for both subclasses, that is, kinetically labile and kinetically inert compounds, are known in literature.[35,61,65] In solution, the former ones – typically based on first-row transition metal ions in + II or + III oxidation states – readily depolymerize or form soluble equilibrium polymers under appropriate conditions. According to Rehahn, decomposition, that is, disassembly, exclusively occurs via ligand replacement reactions only. Thus, kinetically labile polymers should be investigated in noncoordinating solvents and in the absence of other molecules that could compete with the ligands coordinated to the metal ions.[66] Kinetically inert coordination polymers can be found with heavy transition metal ions, such as Pt^{II}, Pd^{II}, or Ru^{II}. The robustness of such materials is revealed by the fact that their polymeric structure is retained, even when strong external stimuli are applied (e.g., pH value, heat, light, ultra sound, and competing ligands).[63] In general, these factors influence the stability of coordination polymers and thus the aspect of tuning the metal–ligand affinity appears to be nontrivial. Two basic concepts are known to increase the strength of the metal–ligand interaction: (1) utilizing donor ligands with very high metal ion affinity or (2) increasing the number of donor atoms that bind to the metal ion (multidentate bonding and chelation). Combining these two strategies enables exceptional control over the physical properties of coordination polymers.

The synthesis, properties, and potential applications of metallo-supramolecular polymers of the 'coordination polymer' type have been the topic of many recent reviews, and reference for further reading is given to these excellent summaries and the work cited therein.[35,59,61,62,65,67–70] Within the scope of this chapter, only a few examples will be highlighted.

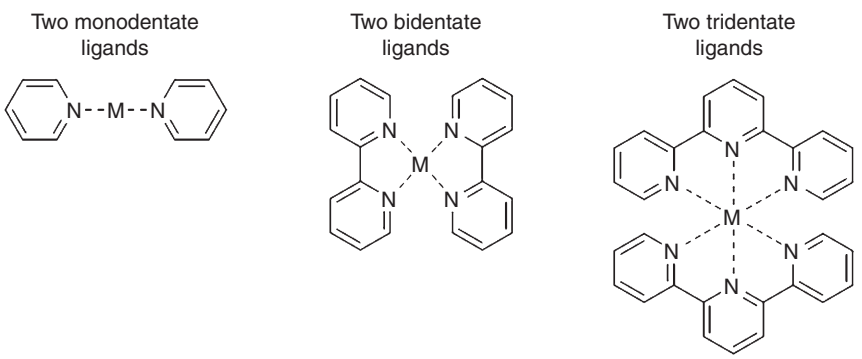

Figure 10 Schematic representation of representative examples of metal–ligand coordination involving pyridine-based ligands of different denticities.

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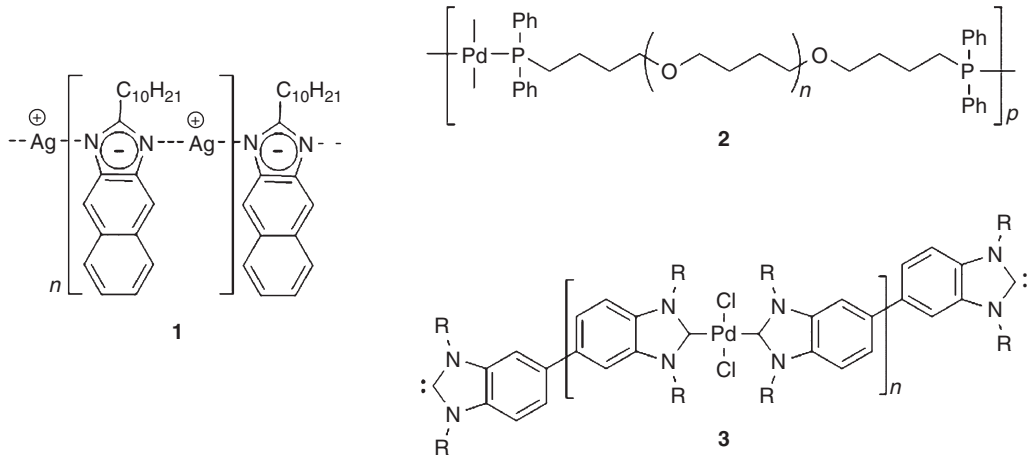

Figure 11 Schematic representation of coordination polymers based on ditopic monodentate ligands.

First, coordination polymers based on a single monodentate ligand will be shortly introduced. In comparison to metallo-supramolecular polymers containing bi- or even tridentate ligands, only very few examples have been reported up to now where a high stability of the compounds could be observed. The selected examples, as shown in Figure 11, cover the entire range of kinetic stability – from labile (1) to inert (3). Liu *et al.*[71] reported the formation of coordination polymers, such as 1, as monolayers at the water/air interface by interaction of imidazol-type ligands with Ag^{I} ions (Figure 11). As expected, fast equilibration of highly kinetically labile 1 and related Ag^{I} polymers (see References 72–74 for further examples) could be observed upon solution in polar organic solvents. The proposed polymeric structure of 1 was concluded from UV/vis absorption and X-ray photoelectron spectroscopy of transferred films on quartz or indium tin oxide (ITO) slides.

Metallo-supramolecular polymers based on ditopic monodentate bisphosphine ligands feature a medium kinetic stability. The group of Sijbesma investigated the properties of 2 (Figure 11), synthesized from a bisphosphine and $PdCl_2$, in solution;[75] due to the strong donor character of the phosphine units, the polymeric structure was retained even in highly coordinating solvents (e.g., acetonitrile). Molar masses (M_n) in the range of 70 000 g mol^{-1} could even be determined by SEC, a technique that is demanding to apply for coordination polymers due to conditions (e.g., high dilution and coordinating solvents) generally supporting disassembly and dissociation.[76] Applying external stimuli in terms of sonification resulted in reversible chain scission by dissociation. After sonification, the molar mass was restored by reassembly of the fragments. The authors could show that no covalent bonds were broken during this process, but that it is highly selective for the comparably weaker phosphine–Pd^{II} coordination bonds. Even after several cycles of sonification and re-equilibration, the original molar mass was restored (Figure 12).[77] This outstanding example for an almost fully reversible coordination polymer might enable the control

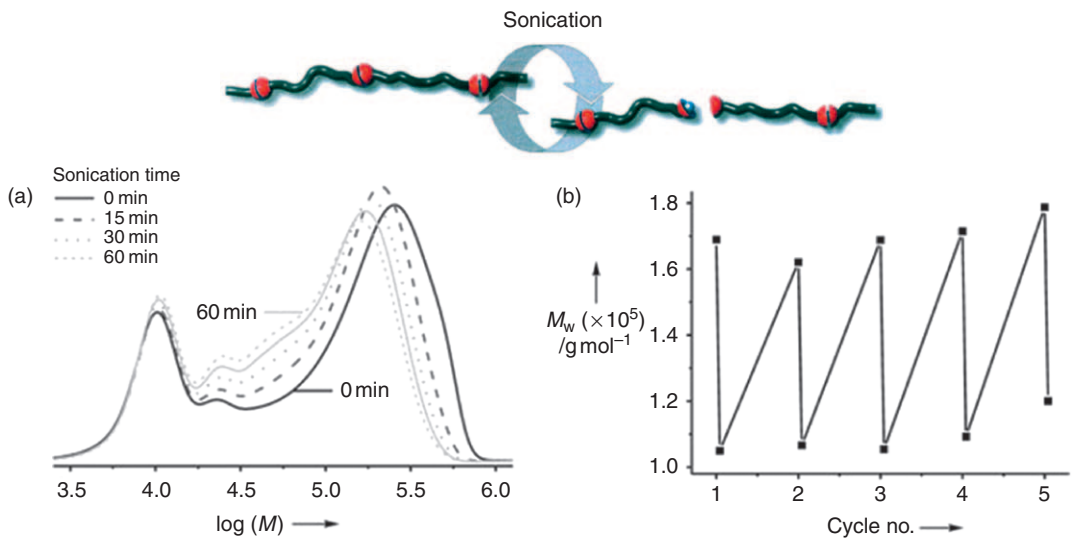

Figure 12 Ultrasound-induced decrease in the molar mass of **2** (1.5 mM in toluene): (a) molar mass distribution of samples taken during sonification; (b) weight-averaged molar mass during a reversibility experiment of five cycles of sonification (1 h) followed by equilibration (23 h). Reprinted with permission from Reference 77, © 2004 Wiley-VCH.

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of ligand exchange processes and the potential preparation of heterocomplexes that are difficult to achieve via other synthetic routes. However, increasing the scission rate remained the limiting factor, as addressed by Friese and Kurth.[59]

The other extreme – remarkably high kinetic inertness – can be highlighted by carbene-based polymers, such as 3 (Figure 11). Though the chemistry of carbene–metal complexes has developed over the last decades, their utilization as building block in macromolecular chemistry has only been introduced recently by the group of Bielawski[78,79] Chelating or pincer-type carbene ligands have been known for over two decades,[80] but a lack of accessibility to suited ditopic carbene-based systems prevented their application in supramolecular chemistry. Recently, rigid bis(carbene) derivatives ready for incorporation into advanced metallo-supramolecular polymers have been reported.[79,81,82] For instance, the Pd^{II}-containing polymer 3 was synthesized by Kamplain and revealed remarkably high chemical and thermal stability to air and moisture. Furthermore, molar masses in the range of $M_n = 10^4\,g\,mol^{-1}$ could be estimated applying SEC.

As pointed out above, for the coordination polymers based on ditopic monodentate ligands, examples for kinetically labile and inert compounds are known; the same stands for their counterparts containing ditopic bidentate ligands. With increasing denticity (i.e. chelating ability) of the ligands an increase in the stability of the derived coordination polymer, with respect to dissociation in solution, can be observed. Additionally, the nature of the metal ion involved has to be considered in more detail. One has to distinguish between transition metal ions preferring a tetrahedral (e.g., Cu^I and Ag^I) or an octahedral (e.g., Fe^{II} and Ru^{II}) coordination sphere.

Advanced supramolecular architectures – such as helicates, catenanes, rotaxanes, or grids – constructed from oligopyridines and Cu^I or Ag^I ions have been known from the early 1990s (e.g., see Reference 61 and literature cited therein). In general, these complexes are kinetically labile and, thus, their unsuitability to serve as templates for the preparation of well-defined coordination polymers remained a paradigm in supramolecular chemistry.[83]

The first examples of well-defined coordination polymers constructed from kinetically labile metal ions and ditopic 2,2′-bipyridine and phenanthroline-type ligands (4, Figure 13) were reported by the groups of Rehahn and Schubert, respectively.[66,84] Both Cu^I and Ag^I ions formed extended polymeric chains when noncoordinating solvents were applied; their solubility could be increased by *n*-alkyl chains on the organic ligands in order to enable characterization by viscosimetry. The expected instability of the coordination polymers in the presence of coordinating solvents was confirmed by detailed NMR spectroscopic studies: even small amounts of a competitive solvent (e.g., acetonitrile) led to a drastic decrease in the DP.

Contrary to the kinetically labile bipyridine or phenanthroline complexes with Cu^I or Ag^I ions, their counterparts with Ru^{II} ions are kinetically inert, and complexation of oligopyridines can be considered as almost irreversible. Furthermore, the coordination chemistry of the Ru^{III}/Ru^{II} couple allows the directed synthesis of mixed-ligand (i.e., heteroleptic) complexes and, therefore, the preparation of advanced linear as well as dendritic metallo-supramolecular architectures.[85] Coordination polymers of Ru^{II} ions and ditopic oligopyridine ligands were already reported in the early 1950s, but those materials were rather undefined and could hardly be characterized by that time.[86]

Rehahn and co-workers published the synthesis of the racemic coordination polymer 5 from a tetrapyridophenanzine ligand and a $Ru(bpy)Cl_3$ precursor complex (bpy: 2,2′-bipyridine, Figure 13).[87–89] A high molar mass of 5 ($M_w = 47\,000\,g\,mol^{-1}$,

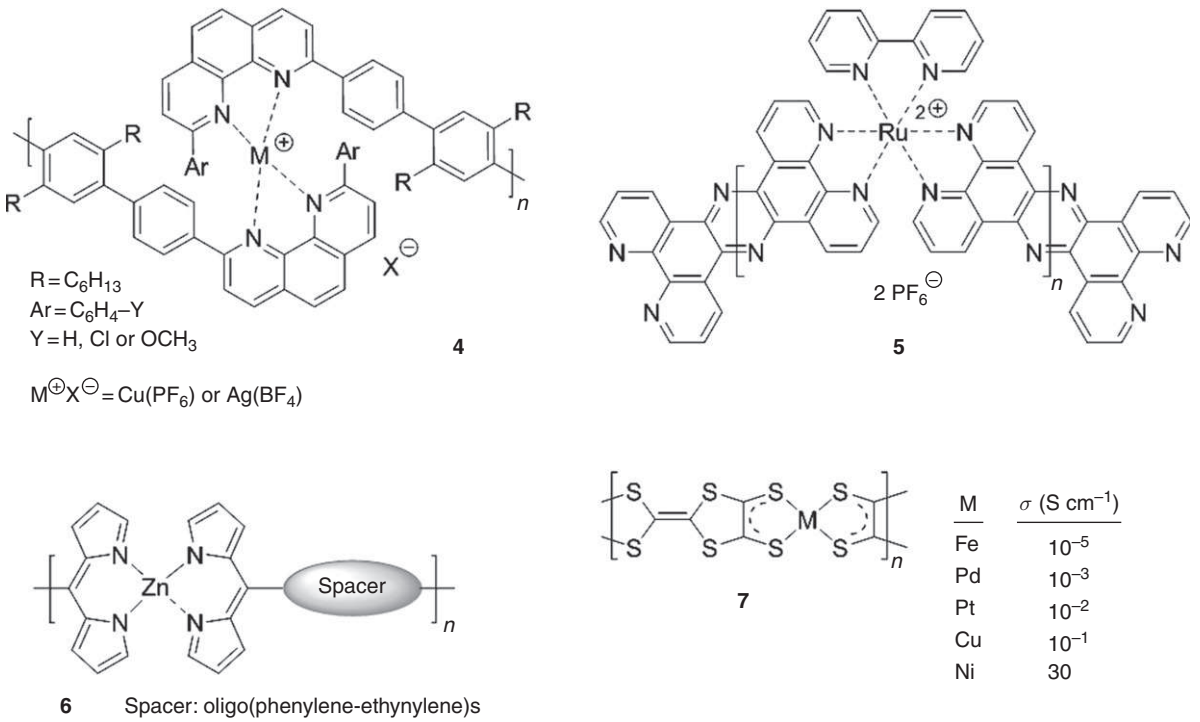

Figure 13 Schematic representation of coordination polymers based on ditopic bidentate ligands.

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DP = 47) was concluded from small-angle X-ray scattering (SAXS) experiments. Good solubility in polar organic solvents (e.g., dimethylacetamide and acetonitrile) or water (with Cl^- as counter ion) was observed without any sign of depolymerization due to competitive solvent effects. The same polymer was also prepared later by Chen and MacDonnell starting from an enantiomerically pure Ru^{II} complex leading to a defined chirality, as shown by circular dichroism (CD) spectroscopy.[90]

Due to their stability and the photophysical properties of the incorporated Ru^{II} complexes, the coordination polymers containing the Ru^{II}-tris(bipyridine) motif are considered as potential photoactive materials in dye-sensitized photovoltaic devices or organic light-emitting electrochemical cells (LECs).[91–93] A variety of Ir^{III}-containing polymers as emissive materials for polymer light-emitting diodes (PLEDs) have also been reported in recent years.[69] In those cases, two or three bidentate cyclometalating ligands (e.g., phenylpyridine) are coordinated to the Ir^{III} centers. Contrary to the Ru^{II} metallopolymers, their Ir^{III} counterparts are for synthetic reasons generally prepared not via self-assembly approaches, but by Pd^0-catalyzed cross-coupling procedures, involving functionalized small-molecule Ir^{III} complexes.

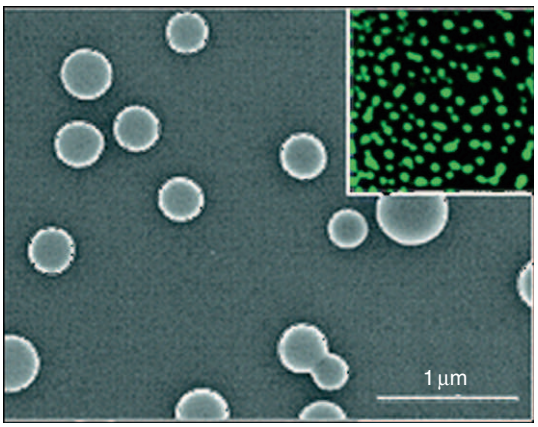

Figure 14 Representation of a scanning electron microscopy picture of nanosized particles obtained from coordination polymer **6** (angular spacer, 3×10^{-3} M in THF). Inset: Fluorescence micrograph with 25 μm sides of each square. Reprinted with permission from Reference 94, © 2006 American Chemical Society.

Recently, neutral coordination polymers **6** (**Figure 13**) prepared from anionic ditotic dipyrrin-type ligands and Zn^{II} ions were reported by Maeda *et al.*[94] Different linear and angular oligo(phenylene–ethynylene)s were introduced as spacer units to yield highly emissive polymers that, furthermore, formed nanoscale objects of different shapes depending on the ligand geometry (i.e., linear vs. branched) and solvent polarity (**Figure 14**). This aggregation is believed to follow a stepwise mechanism known from protein folding: initial formation of the coordination polymers is followed by aggregation of single chains by π–π stacking; formation of spheres occurs which assemble into larger aggregates. A similar concept for supramolecular aggregation was also proposed by Mirkin: colloidal particles for catalytic applications were obtained by precipitation of Schiff-base-type coordination polymers.[95]

The first linear coordination polymers, based on Schiff-base ligands and rare earth metals, were already reported in the 1990s by Chen *et al.*[96] Highly soluble materials of molar masses in the range of $M_n = 30\,000\ \mathrm{g\,mol^{-1}}$ could be characterized by NMR spectroscopy, viscosimetry, as well as SEC, and revealed good thermal stability and high glass-transition temperatures. The same group later expanded their concept to other Ln^{III} polyelectrolytes **8** (Ln = La, Gd, Eu, Y, Yb) with enhanced photoluminescence properties (**Figure 15**).[97–99] Furthermore, Zn^{II}-salen complexes were incorporated into the backbone of organic polymers utilizing a self-assembly strategy (e.g., **9**, **Figure 15**). The impact of the substituents on the imine nitrogen atom[100] as well as of the conjugated system[101] on the overall photophysical properties of the materials was investigated. Both approaches allowed the variation of the photoluminescence behavior; increasing the length of the conjugated spacer resulted in a red-shift of the emission maximum.

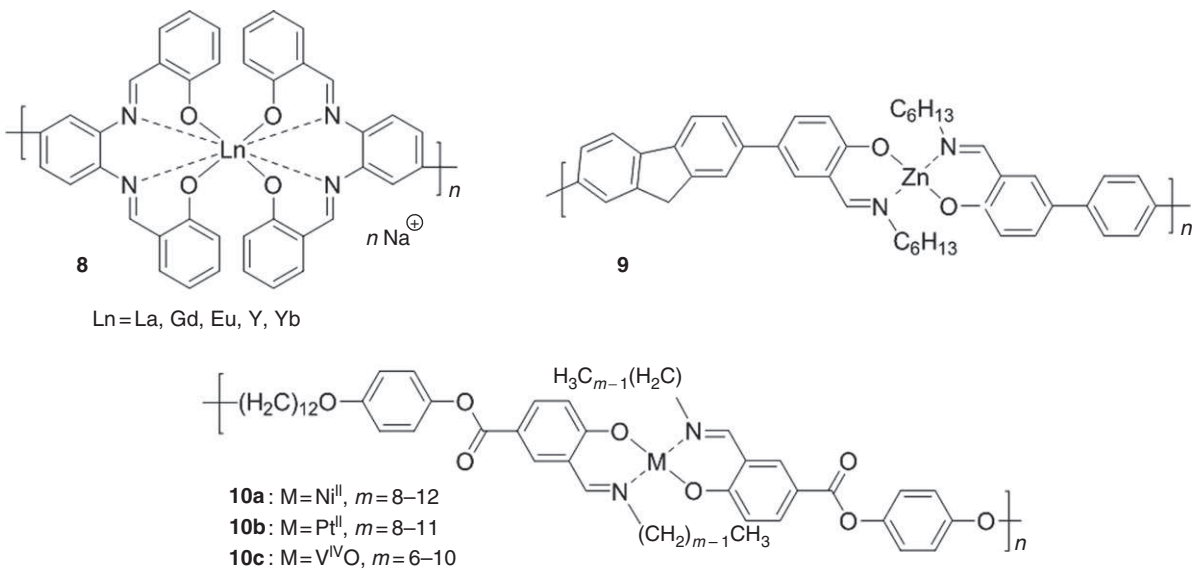

Figure 15 Schematic representation of coordination polymers based on Schiff-base-type ditopic ligands.

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When fabricated into PLED devices, green electroluminescence was observed for all examples.

The same supramolecular connectivity was applied for the preparation of LC materials (for other supramolecular materials with LC properties, see Reference 102 and literature cited therein). Mesogenic organic polymers will acquire molecular orientation in a magnetic field; this effect can be enhanced by incorporating highly susceptible, paramagnetic ions into the (coordination) polymer. Work in this particular field was pioneered by the group of Serrano who reported on coordination polymers with paramagnetic Cu^{II} centers within the polymer chains.[103–105] Electron paramagnetic resonance (EPR), magnetization, and susceptibility measurements showed paramagnetic behavior of the samples with little antiferromagnetic interaction between the Cu^{II} centers. In melt-drawn fibers, a large nematic-order parameter could be observed (for related work based on coordination polymers with Cu^{II}-(β-diketonato)-complexes as supramolecular motif, see Reference 106). In this respect, the self-assembly of salen-type ligands, by varying the imide substituent[103,107–110] or the length of the flexible spacer part,[103,107,109,111] with various metal ions[107,108,112] has been reported. Caruso *et al.*[108] investigated the role of the coordinated metal ion, keeping all further parameters constant. Polyesters **10** (**Figure 15**) showed a nematic mesophase, whose stability could be increased with increasing size of the metal ion (i.e. Ni^{II} vs Pd^{II}). However, the phase was found to become enantiotropic in the process. Furthermore, the $O=V^{IV}$ ion, preferring a square-pyramidal coordination sphere, was utilized, resulting in a material (**10c**) with an additional enantiotropic, smectic mesophase.[108]

Besides coordination to nitrogen-containing ligands, examples are also known where transition metal ions interact with ditopic bidentate ligands via oxygen or sulfur atoms. According to the general concept of 'hard and soft acids and bases' (HSAB), early transition metal ions (e.g., group IV) exhibit pronounced oxo- and azophilicities,[113] whereas late transition metal ions (e.g., group X) generally show high thiophilicities.[114] Proper adjustment of transition metal ion and heteroatom-containing ligand might lead to coordination polymers with fine-tuned properties. One example in this field is the electrically conductive tetrathiolate-based system of the general structure **7** (**Figure 13**) already reported by Rivera *et al.* in 1979.[115] Since sulfur can interact with a broad range of metal ions, conductivities of **7** could be varied from $10^{-5}\,S\,cm^{-1}$ for Fe^{II} to a remarkable $30\,S\,cm^{-1}$ for Ni^{II}. Also other structurally related thiolate-type ligand systems were reported (see Reference 61 and literature cited therein), but the intrinsic low solubility and fusibility of these materials prevented further applications.

With respect to tunable photophysical properties, two types of coordination polymers, both containing ditopic tridentate ligands, are in the focus of current research: systems containing a so-called palladium pincer (**11**)[116–119] or a metal bisterpyridine complex (**12**)[63,65,120] as the supramolecular linkage (**Figure 16**).

The utilization of pincer-type complexes as building block in metallo-supramolecular polymers was pioneered by Yount *et al.*[117] It was shown in a basic study on coordination polymer **11a** (**Figure 17**) that the dissociation dynamics can be tuned independently of the system's binding constant by variation of the substituents R of the amino groups. Though the binding constants (for R = Me or Et) in dimethylsulfoxide were not affected, the dissociation rates differed almost by a factor of 100. This effect was attributed to the different steric situation at the palladium(II) centers. Furthermore, the binding constant appeared to be independent of the nature of the solvent ($K = 10^3\,M^{-1}$ in $CDCl_3$, MeOD, and D_2O/DMSO).

Beyond the precedent example which is of relevance for the understanding of the general behavior of coordination polymers containing pincer-type building blocks, the related work of Weck and co-workers points to potential advanced optoelectronic applications, such as PLEDs, liquid crystal displays (LCDs), thin film transistors, or optical storage devices.[118,121] Supramolecular cruciforms (**11b**, **Figure 17**) were obtained by self-assembly of a pyridyl cruciform with a ditopic pincer precursor. These cross-conjugated materials possess a high degree of conjugation, are highly fluorescent, and exhibit a spatially orthogonal arrangement of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Introducing electron-donating or -accepting moieties at the 4′-position leads to discrete two-dimensional chromophores with the HOMO lying around the axis (carrying the electron-donating substituents) and the LUMO being localized around the axis (carrying the electron-accepting ones).[122] Variation of these substituents enabled tunability of the optical as well as redox properties of the coordination polymers. Reversibility of the self-assembly process could be confirmed

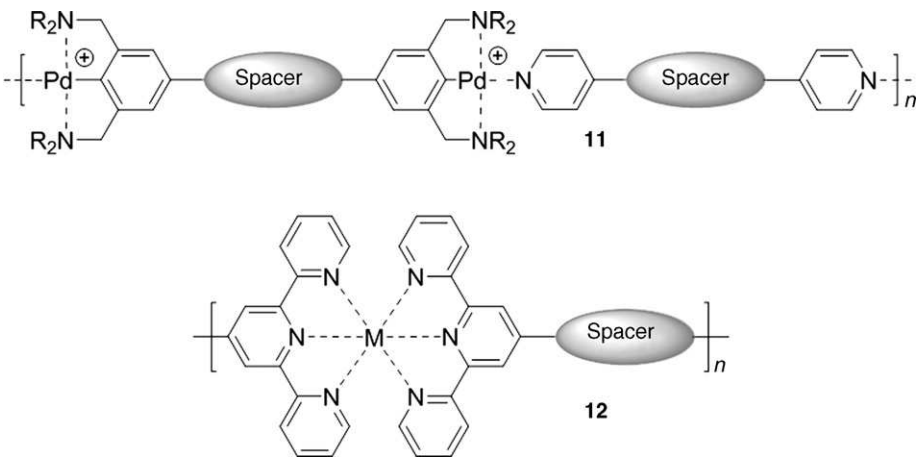

Figure 16 Schematic representation of coordination polymers containing pincer (**11**) and terpyridine complexes (**12**).

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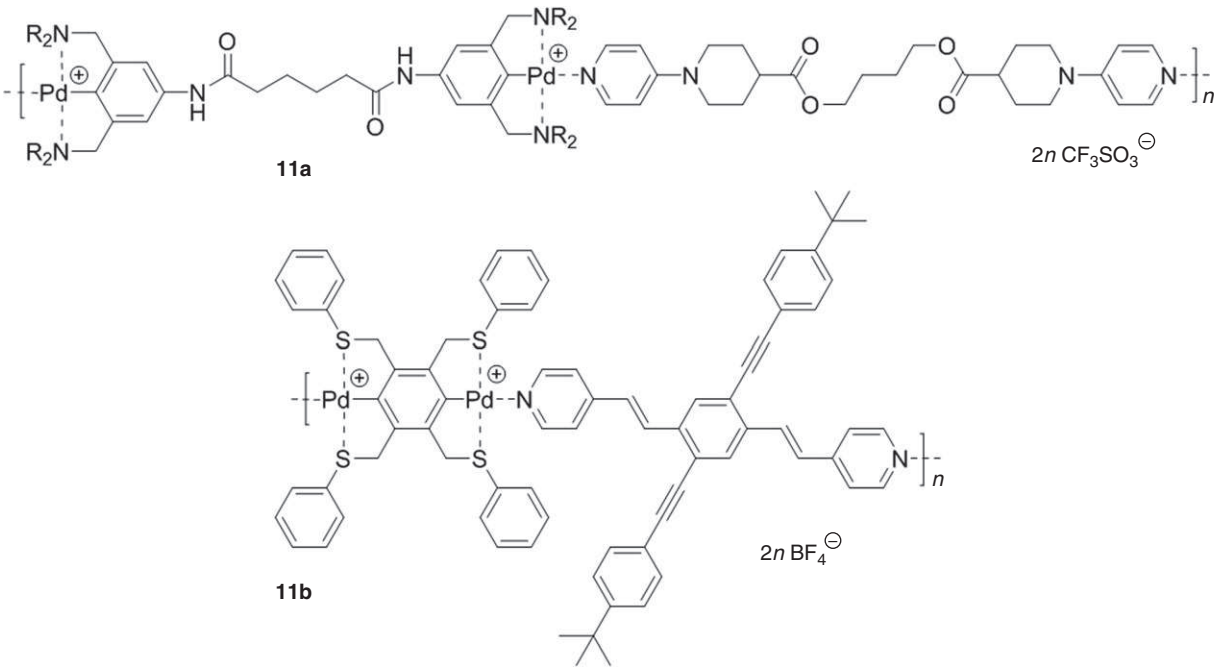

Figure 17 Schematic representation of two coordination polymers based on Pd^{II} pincer complexes according to the groups of Craig (**11a**) and Weck (**11b**).

by adding a stronger ligand (i.e. PPh_3)[123] capable of replacing the pyridyl cruciform; the ligand exchange was monitored by UV/vis absorption spectroscopy. Furthermore, the dependency of the DP on the stoichiometry was investigated by viscosimetric experiments, revealing a maximum in viscosity at a 1:1 ratio of ditopic pincer precursor and cruciform.[121]

By far, the most common type of metallo-supramolecular polymers known to literature is based on 2,2′:6′,2″-terpyridine (tpy) ligands. The chelating terpyridine unit offers a further increase in the binding constant (when compared to bpy) and the formation of octahedral 2:1 ligand–metal complexes circumvents the formation of enantiomers as discussed above for the octahedral coordination of three bpy ligands (**5**, **Figure 13**).[35] The wide scope of modern terpyridine chemistry has been summarized in a monograph by Schubert *et al.*[63] Within the scope of this chapter, only coordination polymers prepared from ditopic terpyridines (**12**) will be discussed (**Figure 16**). For other types of terpyridine-containing macromolecules, the reader is referred to various previous comprehensive review articles.[68,85,92,120,124]

The general concept for coordination polymers based on terpyridine ligands was introduced by Constable in 1995.[125] Since then, enormous experimental effort has been made in order to incorporate terpyridine complexes of heavy transition metal ions in their low oxidation state (e.g., Ru^{II}, Os^{II}, Ni^{II}, and Ir^{III}) into coordination polymers. In general, the resulting structures are kinetically inert and combine high thermal, chemical, and photochemical stability with interesting (electro)-optical and magnetic properties. Moreover, the high stability of the coordinative bonds provides the possibility to characterize this type of structures by means of various techniques, including SEC and mass spectrometry. About 10 years ago, Kelch and Rehahn[126] reported the most well-known investigation on metallo-chain-extended polymerization. The soluble metallo-supramolecular polymer **12a** (**Figure 18**) was prepared following two different synthetic routes: (1) the coordination of the ditopic terpyridine ligand with an activated Ru^{III} species and (2) Pd^0-catalyzed polycondensation of a preformed Ru^{II} bisterpyridine complex with the bridging unit ('complex first' method). Comparing the obtained products by means of viscosimetry and ^1H NMR spectroscopic end-group analysis revealed that the latter strategy only led to oligomeric structures whereas the former resulted in high molar mass species (DP > 30).

Other examples of coordination polymers based on bisterpyridines containing Fe^{II} or Ru^{II} ions that were synthesized via the 'complex first' method were published by Storrier *et al.*[127,128] as well as Ng *et al.*[129] Both groups utilized the Fe^{II} or the Ru^{II} bis-complex of 4′-(4-aminophenyl)-2,2′:6′,2″-terpyridine for polycondensation reactions with bifunctional carboxylic acid derivative monomers resulting in metallo-supramolecular polyamide-[127,128] or polyimide-type coordination polymers.[129] In addition to their inert character, complexes of the type $[Ru(tpy)_2]^{2+}$ are known to exhibit characteristic d-π* metal-to-ligand charge-transfer (MLCT) transitions;[130] thus, coordination polymers derived from π-conjugated bisterpyridines and Ru^{II} ions (the same stands for other second or third d-block elements, such as Os^{II} or Ir^{III}) might be useful as photoactive materials in light-emitting devices or organometallic solar cells.

In general, the formation of a metal bisterpyridine complex follows a two-step mechanism: (1) a metal monoterpyridine complex is formed by coordination of one terpyridine ligand to one metal ion; (2) the metal bisterpyridine complex is formed by adding another terpyridine ligand to the system. In solution, exchange processes between the ligand, metal ion, mono-complex, and bis-complex can occur – depending on the nature of the employed metal ion and the electronic/steric properties of the terpyridine ligand.[59,131]

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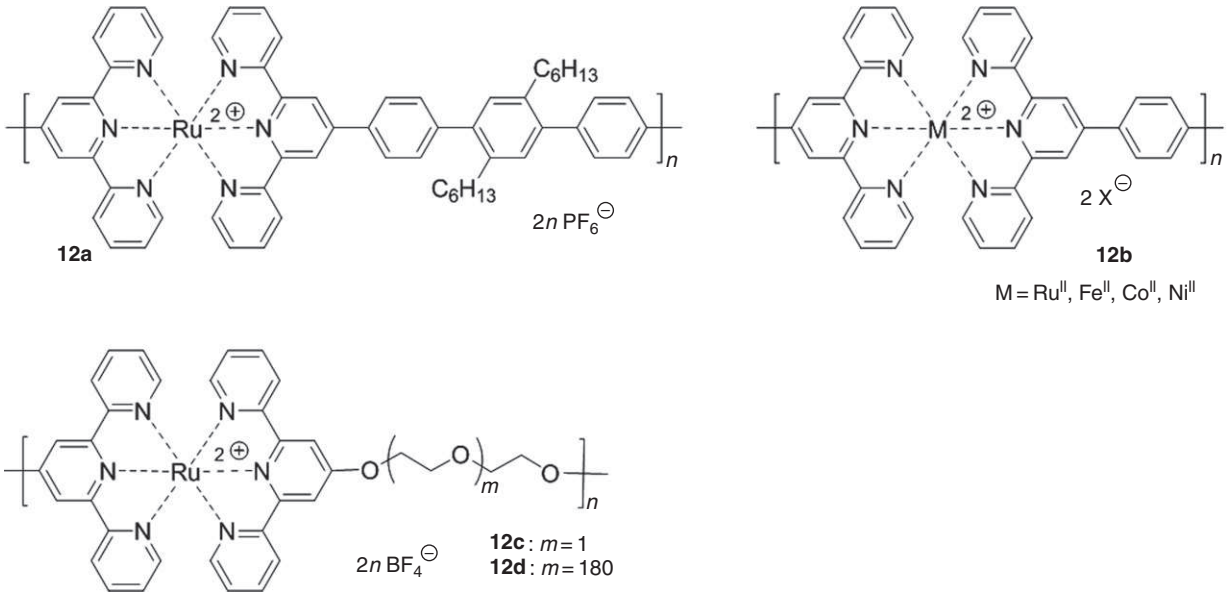

Figure 18 Schematic representation of various coordination polymers based on bisterpyridine ligands (see also Chapter **5.27** in this volume).

The group of Kurth prepared a library of metallo-supramolecular polyelectrolytes (MEPEs) by utilizing rigid, π-conjugated bisterpyridines and various transition metal ions (e.g., Fe^{II}, Ru^{II}, and Co^{II}, see Figure 19).[132,133] The optical, electrochemical, and electrochromic properties of the synthesized metallo-suprastructures could be easily investigated due to their good solubility in different solvents including water. Furthermore, conclusions on the structure–property relationship of the designed structures could be drawn and important insights concerning the design of electrochromic materials could be gained: switching rates and kinetic stability of MEPEs are influenced by the electronic nature of the substituents located on the external pyridine ring of the ligands (Figure 19). While electron-donating groups induced faster switching rates, electron-withdrawing groups reduced the rates and, thus, decreased the stability. The optical properties were affected mainly by steric factors close to the metal center. Consequently, bulky groups enhanced the optical memory by protecting the metal center from being reduced, and larger conjugated spacers linking the terpyridine moieties resulted in an increased molar absorbance of the MLCT.

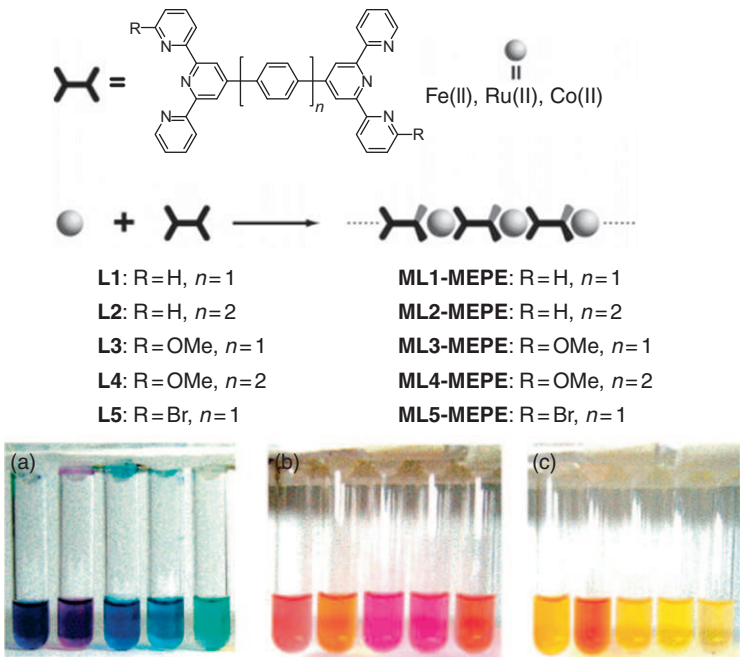

Figure 19 Top: schematic representation of terpyridine-based coordination polymers according to Kurth and co-workers. Bottom: representation of the colors of the coordination polymers in dilute solution (from left to right: ML1–ML5; (a): Fe^{II}, (b): Ru^{II}, and (c): Co^{II}). Reprinted with permission from Reference 133, © 2008 American Chemical Society.

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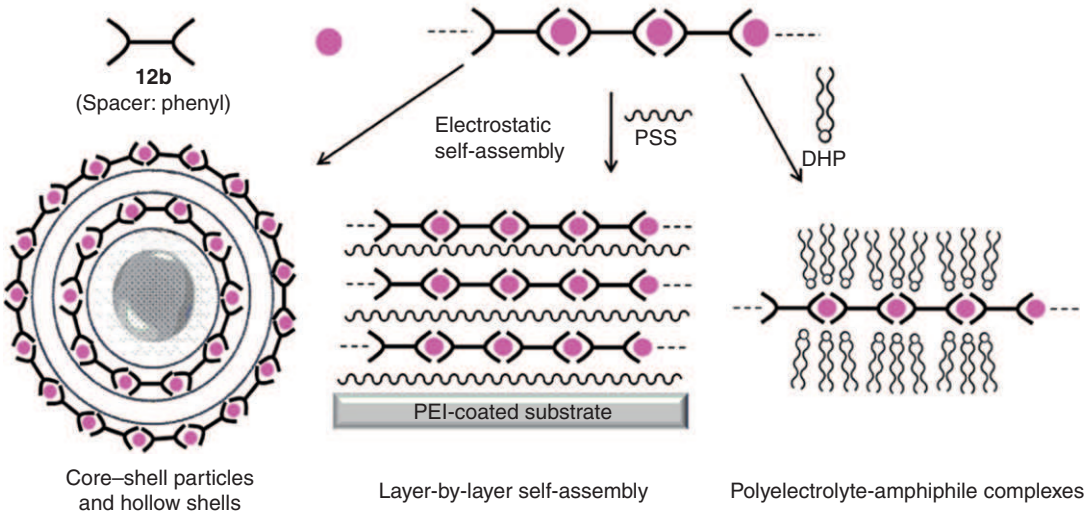

Figure 20 Representation of the hierarchical self-assembly of **12b** by electrostatic self-assembly process reported by Kurth and co-workers. PSS, poly(styrene sulfonate); PEI, poly(ethylene imine); DHP, dihexadecyl phosphonate.[134–136] Picture redrawn according to Reference 35.

In addition, the utilization of terpyridine-containing coordination polymers with Fe^{II}, Co^{II}, or Ni^{II} ions as building blocks for the hierarchical self-assembly into more advanced supramolecular structures was investigated by Kurth and co-workers (Figure 20).[134–136] Due to their polyelectrolyte character, **12b** could be assembled by a layer-to-layer technique to form alternating layers with polyanions (e.g., poly(styrene sulfonate), PSS) on substrates coated with poly(ethylene imine) (PEI) (Figure 20, middle).[134] Furthermore, polystyrene latex particles were used as template for the formation of core–shell architectures. Melamine–formaldehyde particles were also used; in this case stable hollow-shell particles were obtained after removal of the template by decomposition (Figure 20, left).[135] In a last example, the authors replaced the initial counter-ions by amphiphilic anions (e.g., dihexadecyl phosphonate, DHP); this yielded the so-called polyelectrolyte-amphiphile complexes (PACs, Figure 20, right).[136] The PACs were well soluble in organic solvents, spreading at the air–water interface, and the resulting Langmuir monolayer could be transferred onto solid supports utilizing the Langmuir–Blodgett (LB) technique.[137] Furthermore, the PACs could be aligned by co-absorption with long-chain alkanes onto graphite surfaces.[138]

One further interesting feature of these PACs is the possible spin-crossover phenomenon.[139–142] Complexes of Fe^{II} in an octahedral ligand field can adopt both the low-spin (LS) $^1A_{1g}$ and the high-spin $^5T_{2g}$ configuration (Figure 21). It is known that 2,2′:6′,2″-terpyridines induce a strong ligand field; therefore the metal ions are forced into a LS state. For Fe^{II} ions, the terpyridine coordination polymers are diamagnetic, since all electrons are paired. At low temperature, PAC-**12b** (M = Fe^{II}) assembled densely both in LB films and in the crystalline state and therefore did not affect the strong crystal field around the Fe^{II} ions. Upon heating of the multilayer, the alkyl chains melted, resulting in a distortion of the metal ion coordination geometry. Consequently, the crystal field splitting of the d-orbital subsets decreased, resulting in a reversible spin transition from a diamagnetic LS to a paramagnetic LS state.[140,141]

Schubert and co-workers focused on the synthesis and characterization of chain-extended polymers based on the

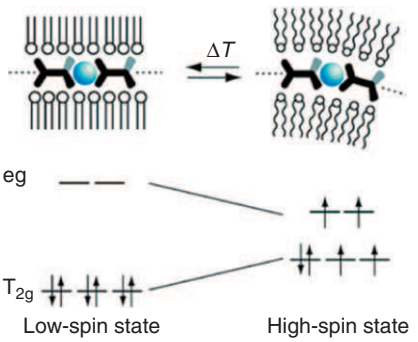

Figure 21 Upon heating of PAC-**12b** (M = Fe^{II}), the alkyl chains of the mesophase melt, resulting in a distortion of the metal ion coordination geometry. The unfavorable coordination of the terpyridines around the Fe^{II} cations induced a lowering of the energy gap between the d-orbital subset, giving rise to a reversible transition from a diamagnetic LS state (left) to a paramagnetic high-spin state (right). Reprinted with permission from Reference 140, © 2005 American Chemical Society.

$[Ru(tpy)_2]^{2+}$ connectivity by employing oligomeric (**12c**) or polymeric spacers (**12d**) (Figure 18).[143–147] The authors could show that the length of the spacer is crucial for controlling the formation of linear and/or cyclic species and, therewith, the DP. The polymeric nature of **12c/d** was confirmed by viscosity measurements; to suppress the polyelectrolyte effect of the multiple-charged Ru^{II} coordination polymers, the addition of different concentrations of salt was required for these experiments. Atomic force microscopy (AFM) investigations revealed a lamella organization of the polymer chains. Further studies to determine the molar mass of the coordination polymers were performed by AUC and SEC.[144,145]

In general, for metallo-supramolecular polymers, the application of conventional characterization techniques is demanding. For instance, in order to determine the molar mass of the coordination polymers, apart from ^1H NMR spectroscopy, SEC is one of the most common tools for characterization. In the case of metal–ligand interactions, the main difficulty to deal with in the

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application of SEC is the fragmentation of the complex during the measurement (i.e. disassembly of the polymer chains). However, after the optimization of the SEC conditions, the method proved to be suitable for the evaluation of metal-containing supramolecular homo- and block copolymers based on transition metal ions with very high binding strength (e.g., Ru^{II}).[144,148] Recently, Chiper *et al.* extended the scope of SEC characterization further to other metallo-bisterpyridine homopolymers: the results also revealed that the $[Ni(tpy)_2]^{2+}$ connectivity behaves as an inert system and, therefore, SEC could be applied in this case also as a characterization technique.[76] Moreover, chain-extended polymerizations were performed using low molar mass ditopic poly(ethylene glycol) (PEG)-terpyridine systems leading to the formation of high molar mass Ni^{II}-containing coordination polymers. Due to the paramagnetic nature of Ni^{II} ions, ^{1}H NMR spectroscopy could not be used as an alternative characterization method and, thus, for the moment such metallo-supramolecular polymers remain challenging with respect to their analysis.

Combining further first-row transition metal ions, known to exhibit weaker interactions with terpyridine ligands (e.g., Fe^{II}, Zn^{II}, and Co^{II}), results in an increased lability of the derived coordination polymers. Thus, the main challenge for these systems is their characterization which has to be adapted to the specific features of the created $[M(tpy)_2]^{2+}$ connectivity. It was concluded from detailed investigations on various types of terpyridine-containing coordination polymers[149–151] that for more dynamic systems, based on, for example, Fe^{II} and Co^{II} terpyridine complexes, their characterization cannot be performed by SEC.[76] The formation of high molar mass coordination polymers based on a α,ω-bis(2,2′:6′,2″-terpyridin-4′-yl)-functionalized PEG macroligand (**13**, $M_n = 8000\,g\,mol^{-1}$) was studied with various transition metal ions (**Figure 22**). The experimental results of the study proved the influence of different metal ions (e.g., Cd^{II}, Cu^{II}, Co^{II}, Ni^{II}, and Fe^{II}) on the DP. The molar masses were estimated on the basis of concentration-dependent viscosity measurements. The relative viscosity of the materials could be directly correlated qualitatively to the thermodynamic stability of the $[M(tpy)_2]^{2+}$ complexes.

The same group elaborated an approach for the synthesis of the so-called $\mathbf{AB}_n\mathbf{A}$ block copolymers via Ru^{II} ion complexation (**Figure 23**).[152] The applied combinatorial optimization approach allowed a systematic screening to identify the best reaction conditions for the one-pot polymerization of 1,16-bis(2,2′:6′,2″-terpyridin-4′-yloxy)-hexadecane (**B**) with $RuCl_3$ under reductive conditions. In addition, the gained knowledge was further applied to the designed synthesis of a Ru^{II} $\mathbf{AB}_n\mathbf{A}$ supramolecular triblock copolymer utilizing α-terpyridine-ω-methyl-functionalized PEG (**A**) as a chain-stopper in the self-assembly of **B** with Ru^{II} ions (**Figure 23**). The resulting metallo-supramolecular copolymer could be characterized by means of ^{1}H NMR and UV/vis spectroscopy as well as SEC. The amphiphilicity of the synthesized structures was proven by the formation of micelles in water which were investigated by dynamic light scattering (DLS), AFM, as well as transmission electron microscopy (TEM). The concept was later expanded to first-row transition metal ions (i.e. Ni^{II}, Fe^{II}, and Co^{II}, see **Figure 23**).[28] The formation of these $\mathbf{AB}_n\mathbf{A}$ supramolecular triblock copolymers was explored utilizing individual synthetic approaches and characterization methods, optimized for the respective transition metal ion.

Two chiral bisterpyridine ligands (**14** and **15**, **Figure 24**) were utilized by the groups of Kimura *et al.*[153] and Bernhard *et al.*[154] for the preparation of helical coordination polymers (for examples of other chiral bisterpyridines, see References 155, 156). As proven by CD spectroscopy, both enantiomers of **14** were self-assembled with Fe^{II} ions into polymers of different helicities depending on the chirality of **14**.[153] In a similar approach, the self-assembly of **15** with Fe^{II} ions was monitored by UV/vis and CD spectroscopy, enabling the assignment of the absolute structure of the helical coordination polymer.[154] Highly ordered domains of polymer chains were observed applying scanning tunneling microscopy (STM).

According to the detailed studies of Dobrawa *et al.* on the thermodynamics of the complexation between terpyridine ligands and Zn^{II} ions,[64] the $[Zn(tpy)_2]^{2+}$ connectivity offers an interesting interplay of the reversibility of complexation in solution due to rather low binding constants and the remarkable stability of the designed structures in the solid state. A variety of bisterpyridines bearing organic fluorophore spacer units were prepared and utilized for the synthesis of coordination polymers **16a** by self-assembly with Zn^{II} ions (**Figure 25**).[157] The polymers revealed very good fluorescent properties (i.e., very intense red-light emission), with the potential to be incorporated as emissive layers into supramolecular PLEDs.[158,159] In these materials, the role of the Zn^{II} ions

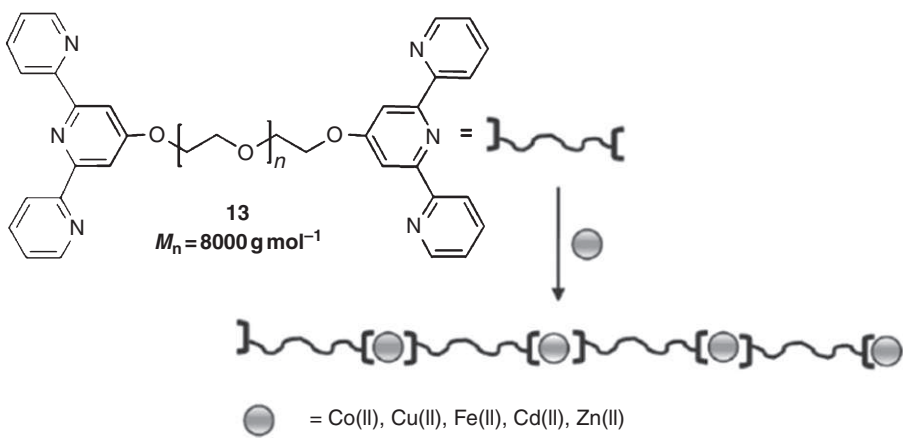

Figure 22 Schematic representation of the synthesis of chain-extended coordination polymers based on macroligand **13**. Reprinted with permission from Reference 65, © 2009 Wiley-VCH.

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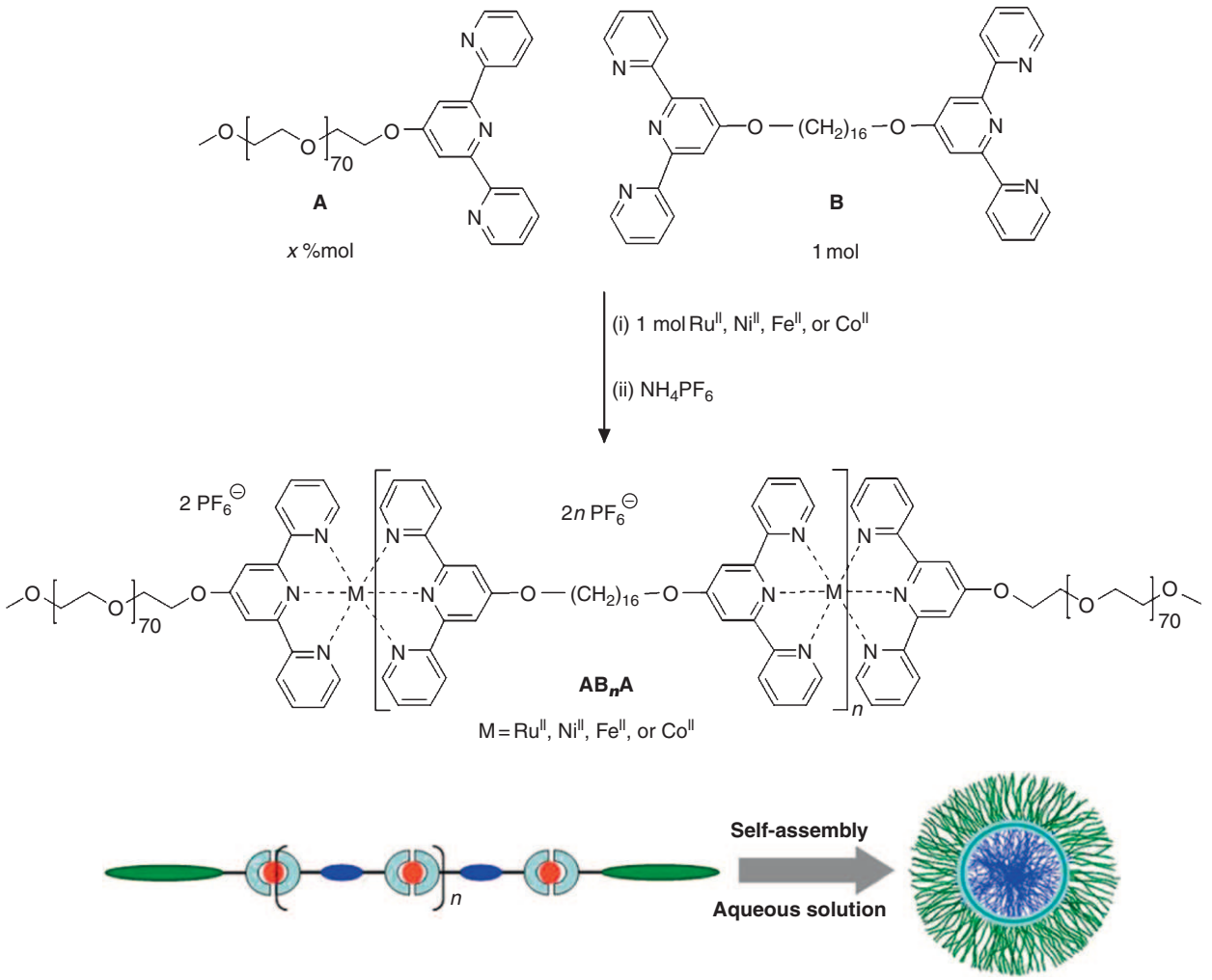

Figure 23 Schematic representation of the synthesis of the metallo-supramolecular **AB$_n$A** block copolymer.[28,152] Reprinted with permission from Reference 65, © 2009 Wiley-VCH.

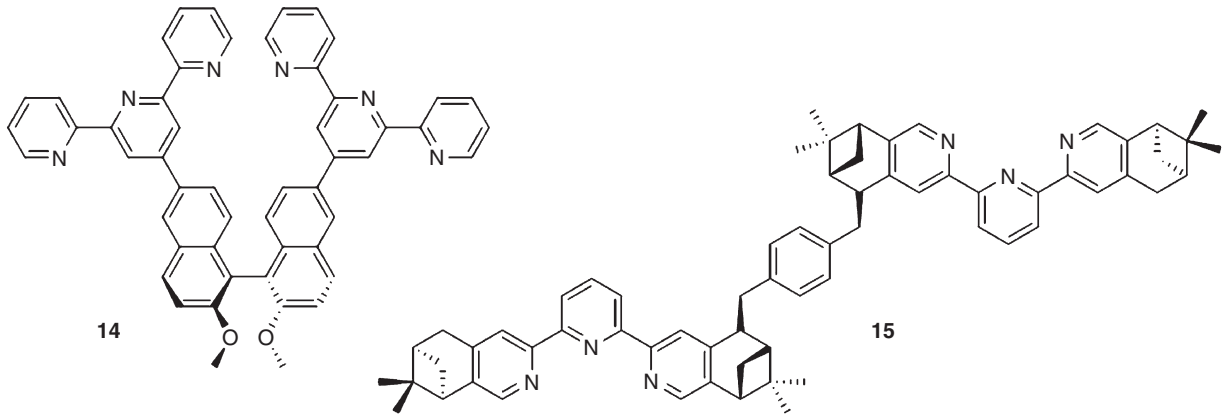

Figure 24 Schematic representation of chiral bisterpyridine ligands utilized for the synthesis of helical coordination polymers.

is purely a structural one, with the photophysical properties of the fluorophore spacer being hardly influenced by the metal ions. In contrast, utilization of Fe^{II} ions resulted in a significant reduction of the fluorescence quantum yield.

These findings inspired a range of research groups to further contribute to this field. In particular, advanced π-conjugated architectures, rigid as well as flexible ones, were introduced as spacer units in metallopolymers **16**, and in recent years highly

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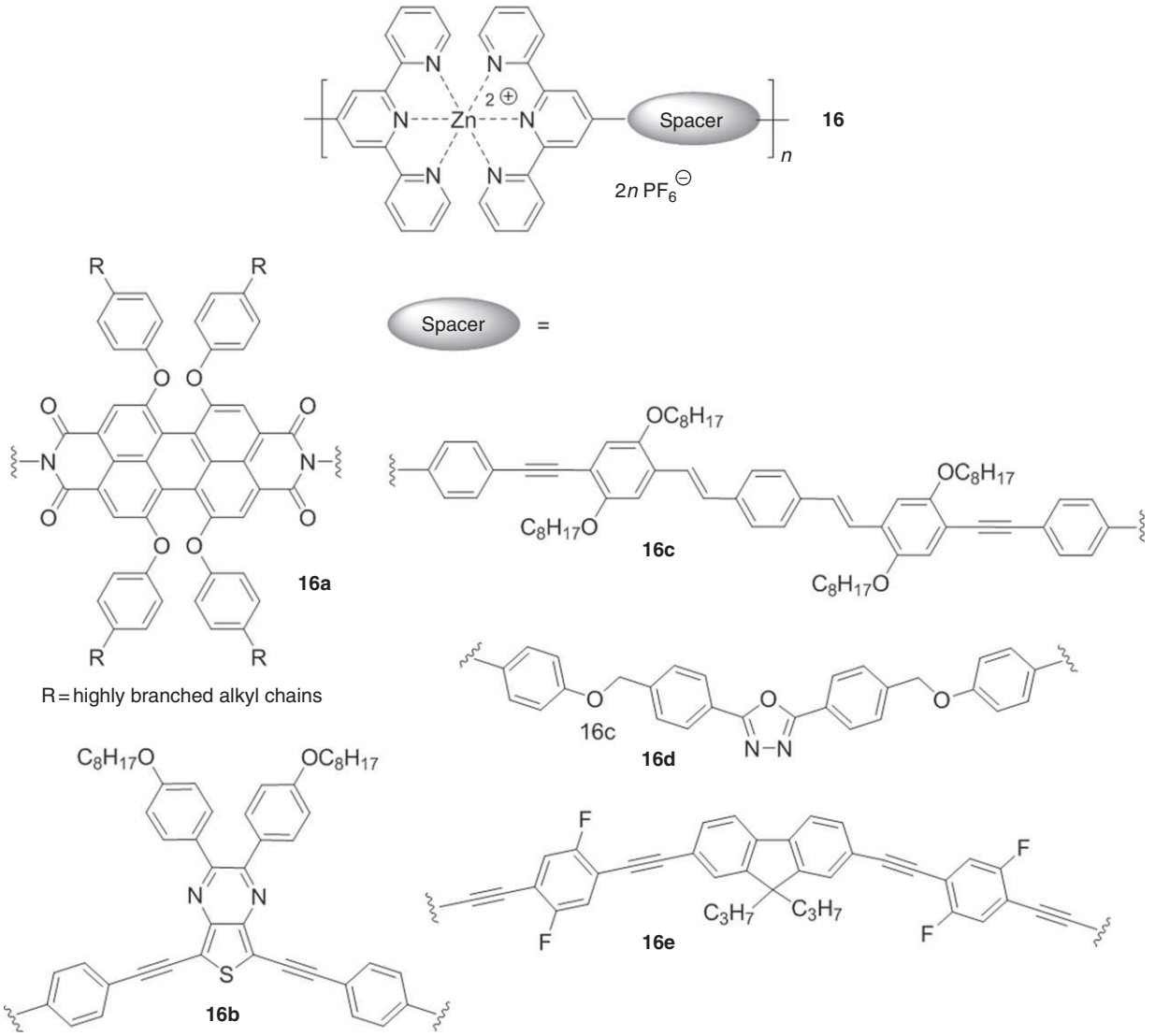

Figure 25 Schematic representation of various types of coordination polymers based on Zn^{II} ions and conjugated bisterpyridine ligands.

diverse libraries of Zn^{II}-containing coordination polymers have been reported by Schubert (e.g., **16b/c**),[160–162] Che (e.g., **16d**),[163] as well as Lin (e.g., **16e**)[164–166] and their co-workers (**Figure 25**). In general, all coordination polymers **16** were characterized by means of ^{1}H NMR spectroscopy, viscosimetry, and photophysical as well as electrochemical methods. Bright photoluminescence depending on the nature of the conjugated spacers was observed in all cases and some materials were subsequently incorporated into electroluminescent devices. Overall, metallo-supramolecular polymers based on Zn^{II} ions with tunable and predictable photophysical properties are easily synthesized and, furthermore, can be processed from solution (e.g., by spin-coating or inkjet printing), thus they can be considered as emissive materials in PLED devices.[160,163–166] In order to achieve a good processability, adequate solubility in organic solvents is a requirement. However, most of these known systems exhibit a considerably low solubility, even in the presence of long or branched alkyl chains. As a significant improvement, Schubert and co-workers introduced polymer chains on the backbone of the metallo-supramolecular polymer to enhance both processability and film-forming ability.[167]

Vermonden *et al.* investigated water-soluble coordination polymers obtained by self-assembly of oligoethylene-bridged bis(pyridine-2,6-dicarboxylic acid) (**17**) with Zn^{II} and Ln^{III} ions (e.g., Nd^{III} and La^{III}, see **Figure 26**).[168,169] Here, the intrinsic weak binding of monopyridine ligands was enhanced by introducing carboxylic acid groups in both ortho-positions;[35] due to additional metal–carboxylate interactions, significantly higher binding constants could be achieved. The coordination polymers were investigated by viscosity measurements, diffusion-ordered NMR spectroscopy (DOSY), and isothermal titration calorimetry (ITC) to elaborate the influence of parameters such as concentration, temperature, and stoichiometry on the formation of linear chains and macrocycles (in the case of Zn^{II} ions)[168] or three-dimensional networks (in the case of Ln^{III} ions, **Figure 26**).[169]

The previous example showed that, if rare earth metal ions are utilized for complexation of ditopic tridentate ligands, three-dimensional coordination polymer networks can be obtained. Due to their f-orbitals, these metal ions can establish

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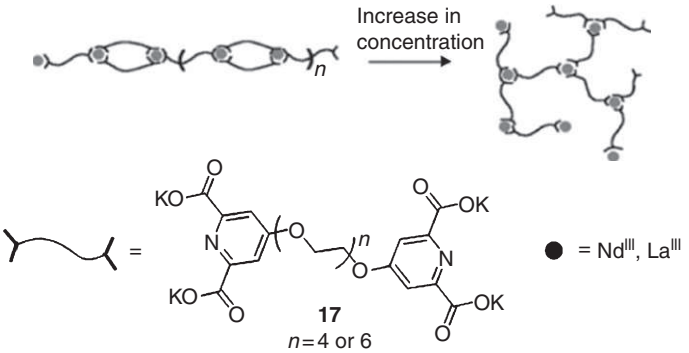

Figure 26 Structural characteristics of Ln^{III} coordination assemblies as a function of concentration. Reprinted with permission from Reference 169, © 2004 Wiley-VCH.

up to nine coordinative bonds and, therefore, bind up to three tridentate ligands. A remarkable example taking advantage of this special complexation behavior was published by Rowan and co-workers.[11,170–173] Ditopic BIP-type ligand **18** (BIP: 2,6-bis(1-methyl-1*H*-benzo[*d*]imidazol-2-yl)pyridine) was utilized for the synthesis of coordination polymers based on this ligand with 97% of Co^{II} or Zn^{II} and 3% of La^{III} or Eu^{III} yielding gel-like materials (Figure 27). All four possible combinations were realized, leading to reversible thermoresponsive polymers – upon heating the gel became fluid again. Furthermore, the polymers were found to be thixotropic, meaning the gels became fluid upon shaking; within 20 s of standing, the gel-like structure was restored. The intense luminescence of the gel with the couple Zn^{II}/Eu^{III} could be 'switched off' either by heating or adding a dilute solution of formic acid, which bound to the Eu^{III} centers and quenched the emission. The materials reported by Rowan *et al.* represent excellent examples for multi-responsive metallo-supramolecular coordination polymers.

Besides the previously detailed supramolecular polymers based on coordinative bonding, materials with covalent metal–carbon bonds are also known. Conjugated polymers with covalent metal–carbon bonds in the main chain advanced from a chemical oddity to today's one of the most important and best characterized class of metal-containing polymers.[70,114,174,175] Among others,

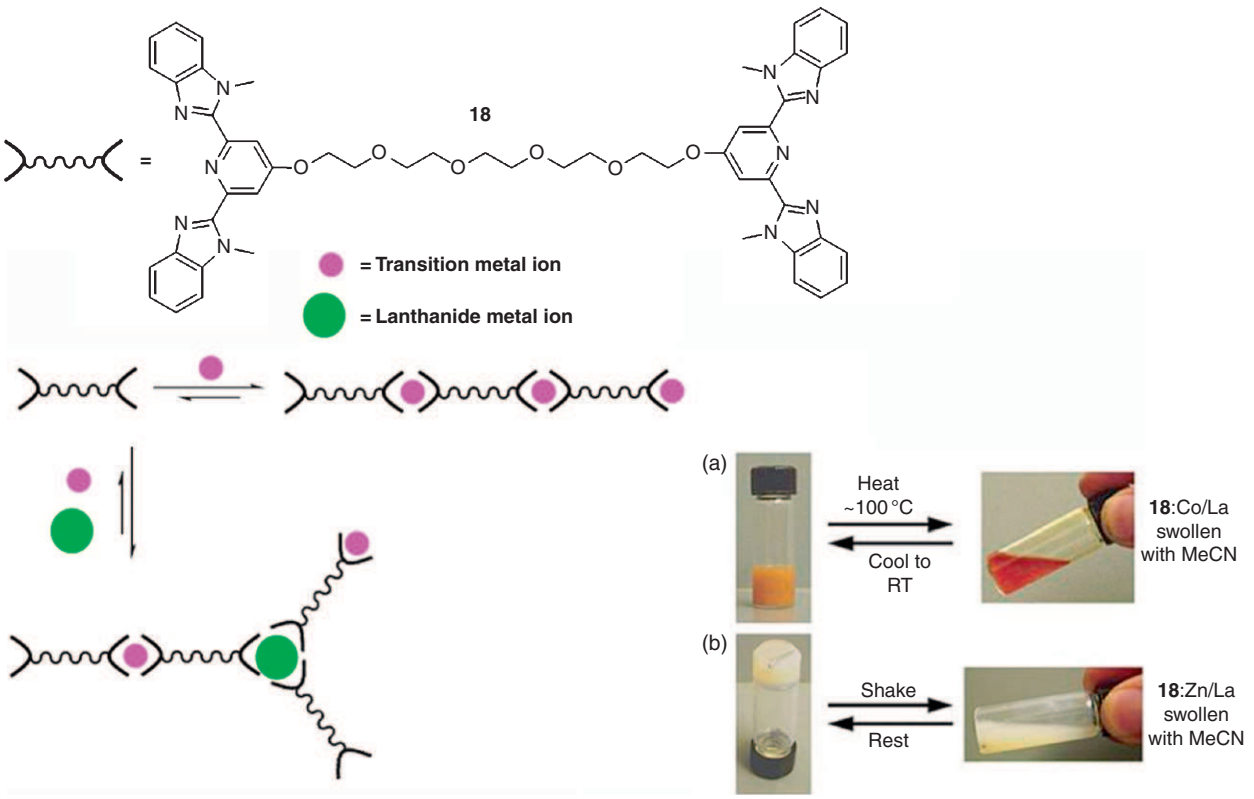

Figure 27 Left: schematic representation of the metallo-supramolecular polymerization of ligand **18** with transition and lanthanide metal ions. Right: thermoresponsive nature of a Co^{II}/La^{III} (a) and the mechanoresponsive nature of a thixotropic Zn^{II}/La^{III} system (b). Reprinted with permission from Reference 170, © 2003 American Chemical Society.

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rigid-rod acetylide polymers or polymetallaynes are, due to their unique structures and optoelectronic properties, in the focus of modern materials research. In general, transition metal ions of groups VIII–X can be utilized and, within the same group, heavier metals lead to more stable metallopolymers. Electronic communication between the transition metal d-orbitals and the π-conjugated system of the organic moieties leads to extended conjugated structures and, therefore, to functional materials that can be applied as photo- or electroluminescent,[176] LC,[177] as well as nonlinear optical (NLO) materials.[178] Within the scope of this chapter, this particular class of materials is not detailed any further and the reader is referred to the literature published elsewhere.[70,114,174,175]

5.13.2.4 Supramolecular Polymers Based on Metal–arene Complexation

The last group of metal-containing polymers that will be shortly elucidated within this chapter is the class of polymetallocenes – today one of the most widely studied types of organometallic polymers. Some generalized structures for polymetallocenes, all based on the combination of an arene sandwich complex and a linking moiety, are depicted in Figure 28. A broad range of transition metal ions have been incorporated into these types of structures and even hetero-bimetallic species have been reported. The field of polymetallocenes has been summarized by Manners and coworkers,[70,114] and only a few aspects of the broad topic will be discussed within the scope of this chapter.

Ferrocene was discovered in the early 1950s[179,180] and shortly afterwards the incorporation into a polymeric structure by radical polymerization of vinylferrocene was reported by Arimoto and Haven,[181] marking the birth of organometallic polymers. Various ferrocene-containing polymers have been prepared and an early focus was on technological aspects such as thermal stability, reaction protection, combustion catalysis, rubber vulcanization, and redox behavior.[182–186] Polycondensation reactions at elevated temperatures were the main synthetic tool to obtain polymers of polyketone, polyester, polyamide, polyamine, polyurethane, polyurea or polysiloxane type with ferrocene units in the main chain.[186–191] Furthermore, sulfur-containing polyferrocenylenes were prepared by Nuyken *et al.*[192] by polyaddition reaction of dimercapto-functionalized ferrocenes and diolefinic monomers (i.e. the so-called thiol–ene reaction).

Ferrocene-containing polymers with long, flexible spacer units have been investigated as NLO materials for second harmonic generation (SHG) applications (e.g., frequency doubling). The ferrocene moieties were shown to act as effective donors in crystalline NLO materials; due to their large hyper-polarizability values in combination with good thermal and photochemical stabilities,[193] the ferrocene was subsequently functionalized with a cyanoacrylate group. This NLO-phore was incorporated into a polyurethane copolymer (**20**) in a polycondensation reaction of building block **19** and 1,6-diisocyanatohexane ($M_n = 7600\,g\,mol^{-1}$ according to SEC, Figure 29).[194] Two possible orientations of the NLO-phore, corresponding to opposite dipole orientations, were both present in the main chain. Upon corona-poling of thin films of **20**, SHG activity with good signal stability was detected.

Besides flexible spacer units, π-conjugated spacer groups have also been utilized to obtain conjugated polymers with the ferrocene unit as part of the main chain (for early examples, see Reference 70). Utilizing effective Pd^0-catalyzed cross-coupling reactions (e.g., Suzuki (**21**),[195] Sonogashira (**22**),[196] or Nigishi (**23**)[197]) enabled the synthesis of soluble, high molar mass

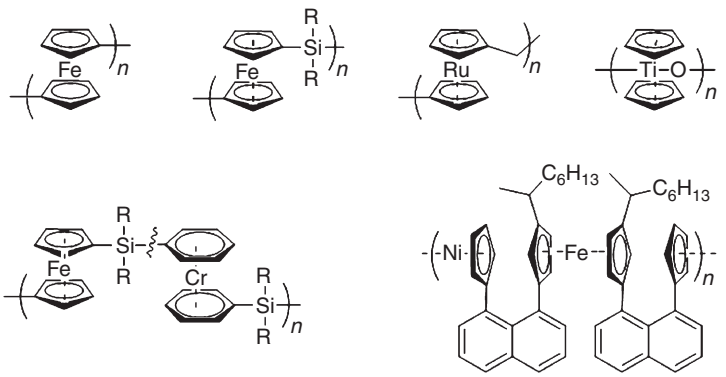

Figure 28 Schematic representation of typical polymetallocene structures.

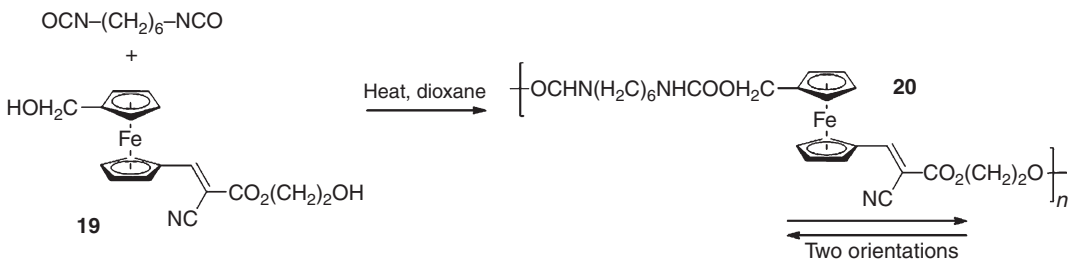

Figure 29 Schematic representation of the synthesis of a ferrocene-containing polyurethane for NLO applications.

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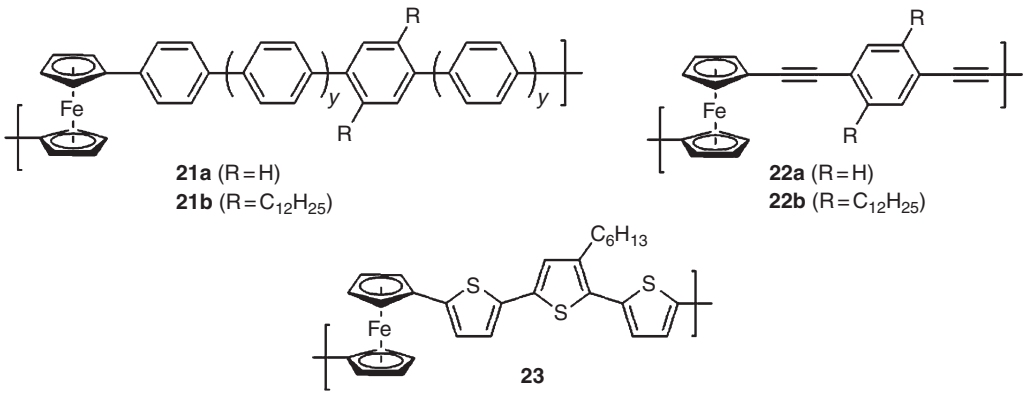

Figure 30 Schematic representation of ferrocene-containing conjugated polymers.

polymers for potential applications in the fields of photovoltaics[102,198] or memory devices.[199] Some representative structures obtained via metal-mediated polycondensation reactions are depicted in Figure 30. For a more in-depth overview on ferrocene-containing conjugated polymers, the reader is referred to recently published reviews.[114,200,201]

In the previous cases, the synthesis of the metal-containing polymers has been achieved by reaction of functionalized ferrocene derivatives with organic building blocks. Strictly speaking, these polyaddition/polycondensation approaches are beyond the aim of this chapter, since the central metal–arene complexes have not been formed in the actual polymerization step. However, only few examples for ferrocene-based materials are known to literature where the formation of the polymer has been realized by self-assembly of ditopic organic ligands with transition ions; in the context of metal–arene complexation, the ligands have to be end-functionalized with cyclopentadiene moieties.[202,203] In this respect, the fulvalene dianion (fulvalene = 5-(cyclopenta-2,4-dien-1-ylidine)cyclopenta-1,3-diene) represents the most straightforward building block and could be successfully utilized for the synthesis of polyferrocenylenes; due to the hexyl substituents, a sufficient solubility of the polymer 44 ($M_n = 4000\,g\,mol^{-1}$, PDI = 1.2) in comparison to analog unsubstituted derivatives[182] could be assured (Figure 31).[202] Utilizing high-performance liquid chromatography (HPLC), separation of single oligomers of 24a ($n = 1–5$) and 24b ($n = 1–6$) from polymer 24a ($n > 10$) could be achieved allowing the characterization of the individual species by photophysical and electrochemical means. The concept was developed further by Southard and Curtis who obtained the polymers 25 and 26 by a two-step condensation route; good solubility, high molar masses ($M_n = 42\,000–50\,000\,g\,mol^{-1}$), and very broad PDI values of 10–15 were observed.[203,204] The authors could show by cyclic voltammetry (CV) studies on 25 and 26 the occurrence of a moderate Fe···Fe interaction (two reversible oxidation waves with redox couplings ΔE of 0.17 and 0.19 V, respectively, were detected). This assumption could be supported by theoretical investigations: the bridging groups affect the molecular scale dielectric constant between the two metal sites, which – in turn – mediates the essentially through-space interaction.[203] Consequently, more polarizable groups will lead to stronger metal–metal coupling and less polarizable groups to reduced interactions; thus, for derivatives of 25 with perfluorinated phenyl rings, no detectable Fe···Fe interactions were observed.[205,206]

The so-called multidecker sandwich complexes represent another example of metallocene-containing polymers that can be obtained by applying a self-assembly strategy (Figure 32). Their general structures are deviant from the more common linear assemblies, such as 21–26. In particular, polymeric metallocenes of type (b), where the repeating metallocene units were held face-to-face by naphthalene or biphenyl spacers, were investigated by Rosenblum and co-workers.[207–211] Initially, only oligomeric species ($M_n \leq 4000\,g\,mol^{-1}$ as determined by viscosimetry experiments) were obtained by direct Pd^0-catalyzed coupling of chlorozinc-ferrocenes and ruthenocenes with 1,8-diiodonaphthalene.[207,208] Introducing solubilizing groups as well as changing the synthetic strategy subsequently allowed the preparation of polymers 28a with M_n values up to $18\,000\,g\,mol^{-1}$; for this purpose, a ferrocene monomer (27) was polymerized in the presence of a strong base by self-assembly with Fe^{II} ions at room temperature (Figure 33).[210] This general route allows the formation not only of Fe^{II} and Ni^{II} homometallic polymers, but also of heterometallic Fe^{II}/Ni^{II} (28b) or Fe^{II}/Co^{II} species (28c) with alternating order of the metal ions.[211] Studies of the electrical and magnetic properties of these structural unusual metallo(co)polymers revealed electrical conductivity of up to $6.7 \times 10^{-3}\,S\,cm^{-1}$ for I_2-doped samples.[211] Structural investigations of isolated oligomeric species led to the conclusion that the self-assembled polymers were of helical structure.[208]

However, the majority of metallocene-containing polymers and materials are today synthesized by more contemporary methods, in particular applying ring-opening polymerization (ROP) reactions as discovered by Brandt and Rauchfuss[212] and, subsequently, developed further by Manners and co-workers.[70,102,114,185,213] In general, bridged and often strained metallocenes are transformed into main-chain polymetallocenes utilizing thermal, anionic, photo, and metal-mediated methods, in solution or in the solid state. Applying these strategies, polymers with additional heteroatoms (e.g., X = Si, S, P, Ge, and B) in the polymer chain were obtained (Figure 34(**a**)). In related work by Buretea and Tilley[214] as well as Stanton *et al.*,[215] polyferrocenes with conjugated linkers were prepared by ring-opening metathesis polymerization (ROMP) of ferrocenophanes (Figure 34(**b**)). The solubility of these rigid

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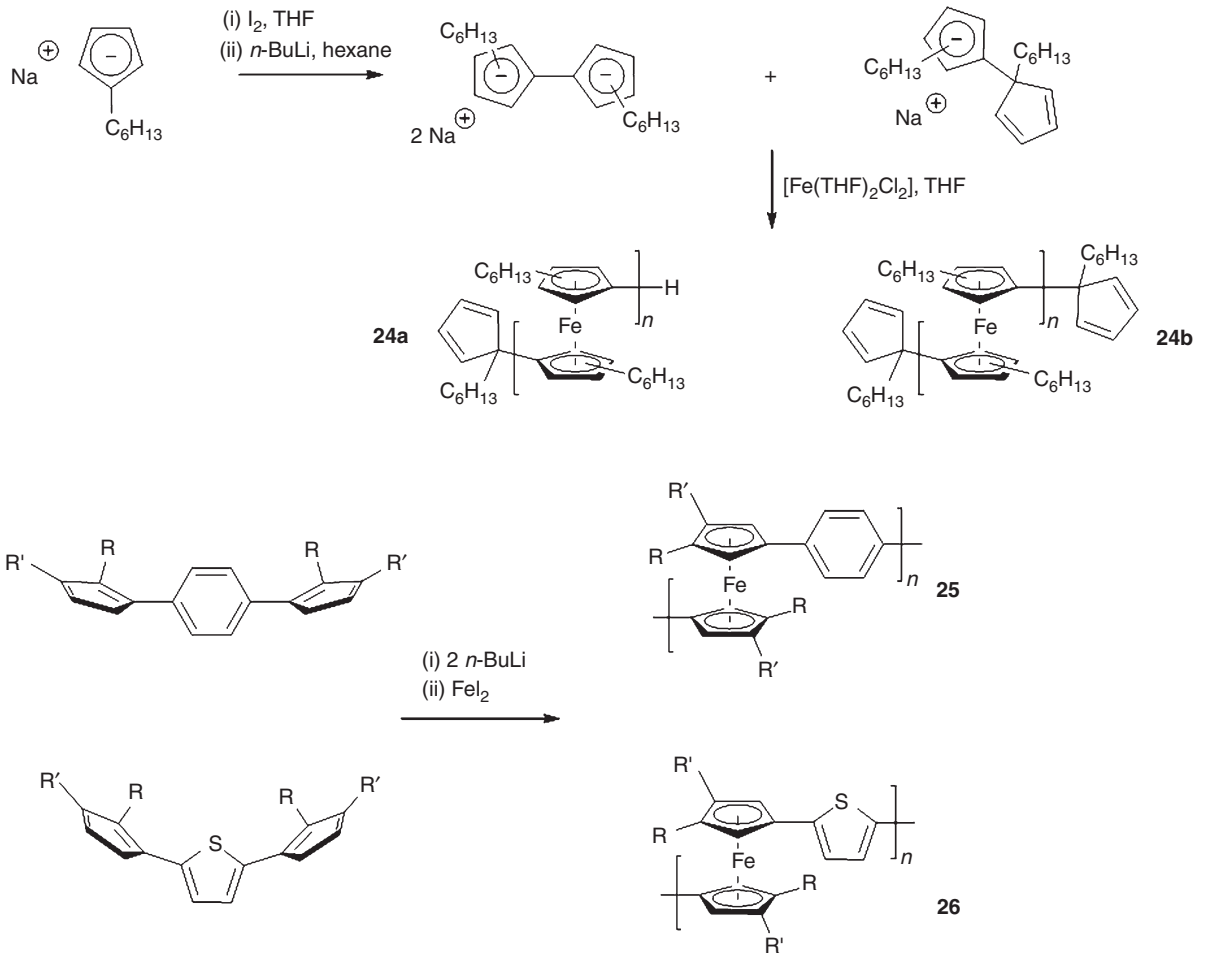

Figure 31 Schematic representation of the synthesis of ferrocene-containing polymers by self-assembly.

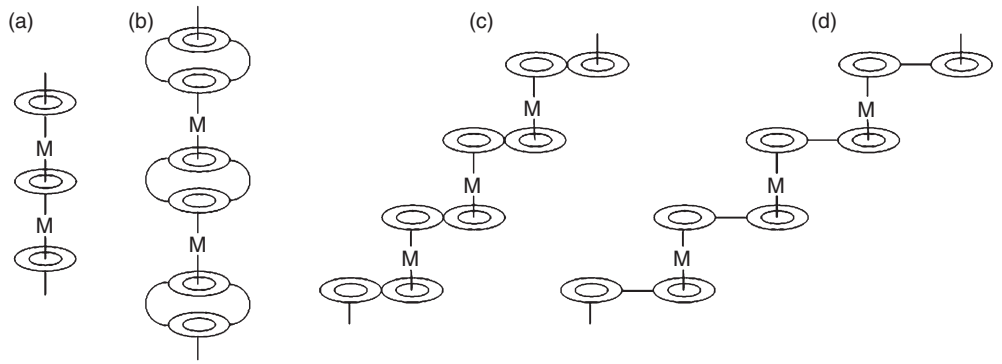

Figure 32 Schematic representation of the generalized structures of polymeric multidecker sandwich complexes (a and b) as well as linear polymetallocenes (c and d) (scheme redrawn according to Reference 70).

polymers and the DP ($M_n > 3 \times 10^5\,g\,mol^{-1}$) could be enhanced by introducing solubilizing alkyl groups. The key characteristic of these two approaches is that the polymerization proceeds via a (controlled) chain-growth mechanism. Therefore, polymetallocenes prepared by ROP or ROMP are not polymers in terms of polycondensation or polyaddition products and will not be detailed further.

5.13.3 Supramolecular Polymers Based on Ionic Interactions

Ionic supramolecular interactions leading to polymers via self-assembly are always asymmetrical processes – they are based on the attraction between positively and negatively charged species. In general, ionic interactions are – in contrast to metal–ligand

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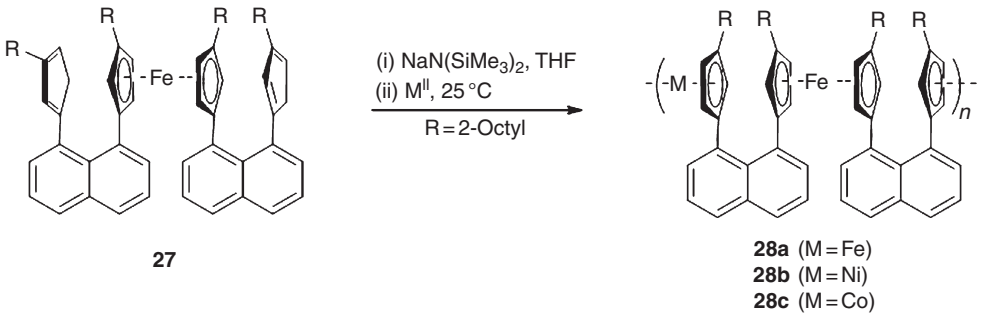

Figure 33 Schematic representation of the synthesis of homo- and heterometallic multidecker sandwich polymers.

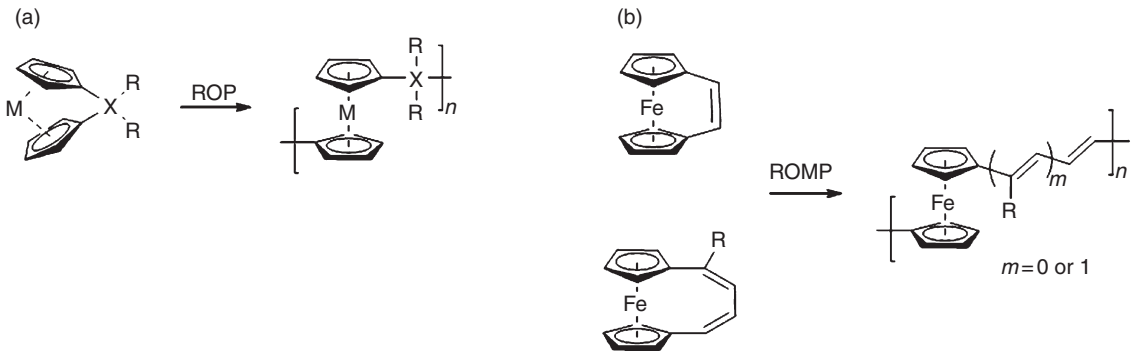

Figure 34 Schematic representation of the synthesis of main-chain polymetallocenes by (a) ROP and (b) ring-opening metathesis polymerization (ROMP).

coordination or hydrogen bonding – nondirectional and the scope of ionic self-assembly is limited due to the relatively weak binding strength in solution (ionic interaction: 12–20 kJ mol^{-1}; coordinative bond: 40–120 kJ mol^{-1}).[67] Self-assembly based on ionic interactions exhibits reversible binding that can be addressed by the solvent, since the ionic groups are well solvated in polar media leading to lower binding strength and/or dissociation.[17] The theory of ionic interactions in macromolecules has been summarized recently in an excellent review by Ciferri[216] and a few examples for supramolecular polymers based on ionic interactions will be highlighted shortly.

The self-assembly of ionic side chains with a (charged) polymer backbones into so-called polyelectrolyte-surfactant complexes is the most common type of ionic interaction that can be found in the field of supramolecular polymer science.[217,218] Poly(4-vinylpyridine) (**29**)[219] and other pyridine-containing polymers[220] are often utilized as cationic template and molecules containing sulfonic acid moieties can be coordinated to the polymer backbone as side chains via ionic interactions (e.g., **30**, **Figure 35**). Similar architectures were obtained by combining PEI with sulfonic acids[221] and poly(styrenesulfonate) or poly(acrylic acid) with quaternary ammonium salts.[222,223] For

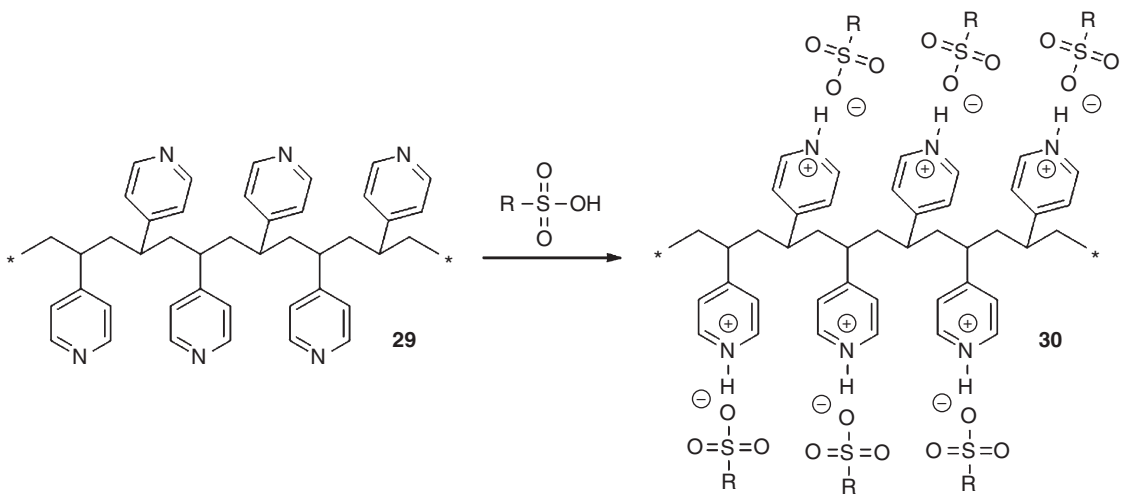

Figure 35 Schematic representation of the self-assembly of poly(4-vinylpyridine) and sulfonic acids based on ionic interactions.

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instance, ionic interactions between poly(4-vinylpyridine) and oligo(ethylene oxide) sulfonic acid led to the formation of coil-comb supramolecular block copolymers starting from poly (styrene)-*block*-poly(4-vinylpyridine). Phase separation into lamellar structures and, after addition of $LiClO_4$, conductivity could be observed.[224]

The decoration of poly(4-vinylpyridine) with sulfonic acid-functionalized dendritic wedges was investigated by Zhu *et al.*[225] The bulk organization of the material was found to be dependent on the ratio of dendritic wedges to the pyridine units of the polymer: transition from a lamellar to a hexagonal columnar phase with increasing wedge density was observed. The authors also showed that the wedges could move along the chain and from one chain to another. Besides the formation of graft and comb-like copolymers, disulfonic acids were applied for the formation of supramolecular networks. This cross-linking of the material allowed tuning of glass-transition and melting temperature while maintaining a high thermal stability.[226]

The generally low directionality and binding strength of single ionic interactions was overcome by Shelnutt and co-workers who combined multiple ionic interactions with highly directional π–π stacking interaction in order to self-assemble oppositely charged porphyrins (**31** and **32**) into nanotubes in acidic aqueous solution (**Figure 36**).[227] The nanotubes were stable in the dark and could be addressed by light illumination to organize into smaller rod-like structures that reassembled into nanotubes in the dark. The reversible switching behavior was attributed to a softening of the tube walls by disruption of the charge balance that is caused by photo-initiated intermolecular electron transfer processes.

The self-assembly of a perylene dye (**33**) with two positive charges and a Cu^{II} phthalocyanine derivative with four negative charges (**34**) was reported by Guan *et al.*[228] The aqueous self-assembly of these dyes resulted in the formation of one-dimensional chains that were proposed to be a helical twisted triple-stack structure stabilized by a combination of ionic interactions and π–π stacking (**Figure 37**). Though the ionic interaction alone is not directional, the combination of multiple ionic interactions and π–π stacking can result in a highly directional asymmetric self-assembly.

Stoddard and co-workers showed that the ion–dipole interaction (e.g., dialkylammonium ions and crown ethers) is both strong and highly directional.[229] Supramolecular main-chain polymers based on this type of interaction were investigated by Gibson and co-workers.[230–234] A heteroditopic molecule comprising a crown ether and a quaternary ammonium salt (**35**) was prepared and self-assembled into a supramolecular polymer with a maximum DP of 50 (determined by ^{1}H NMR spectroscopy and viscosimetry), which was strongly dependent on the concentration (**Figure 38**).[230] Furthermore, the analog homoditopic building blocks, that is, a bis(crown ether) and a bis(ammonium salt), with flexible spacer units were synthesized and their self-assembly behavior was studied.[231] At low concentration, the stoichiometric mixture yielded cyclic dimers, whereas with increasing concentration the formation of polymeric species was amplified. High selectivity with respect to the

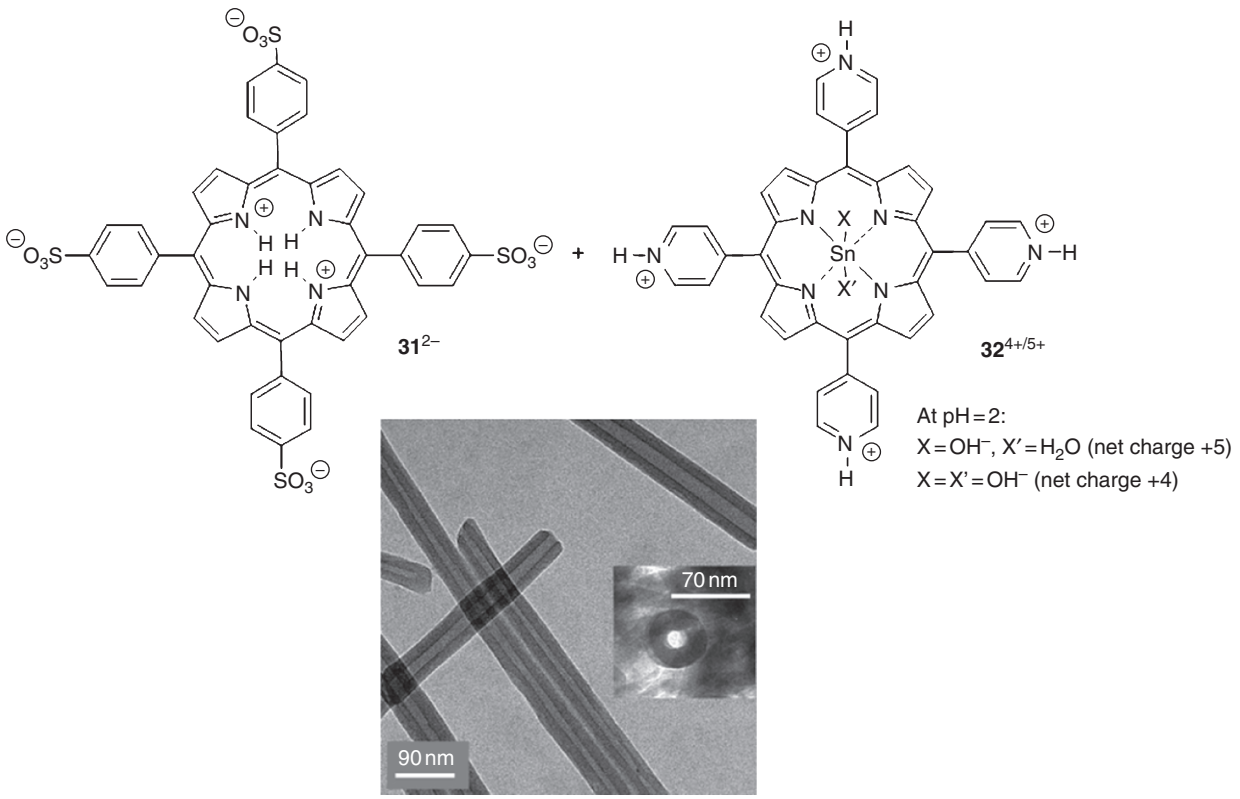

Figure 36 Top: Schematic representation of the oppositely charged porphyrins **31**$^{2-}$ and **32**$^{4+/5+}$ that self-assemble into nanotubes in acidic aqueous solution. Bottom: TEM image of the nanotubes; a tube trapped in a vertical orientation by a thick mat of tubes is shown as inset. Reprinted with permission from Reference 227, © 2004 American Chemical Society.

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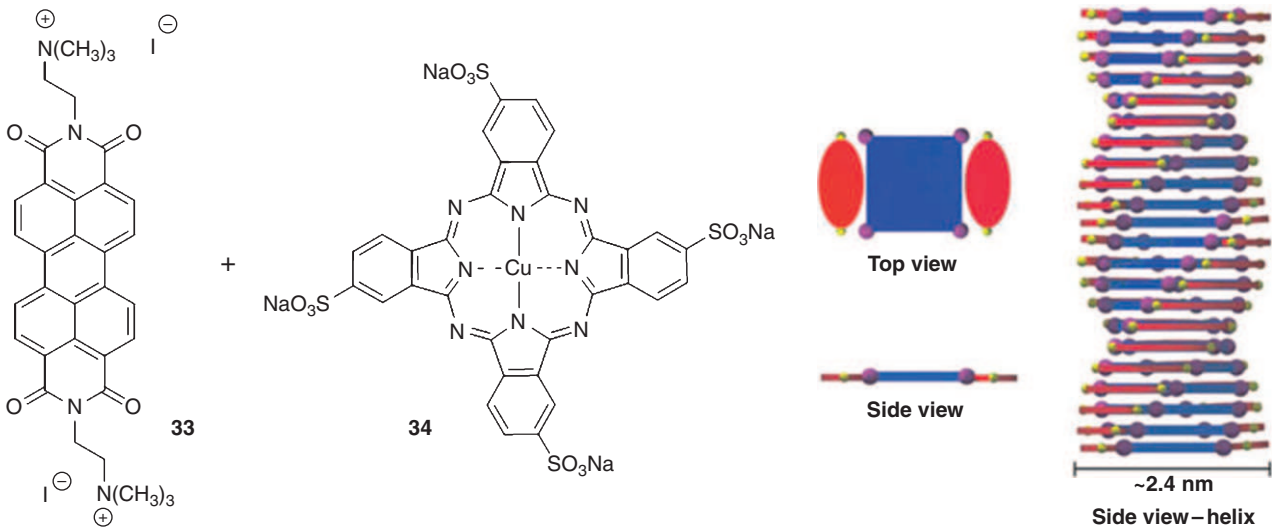

Figure 37 Schematic representation of oppositely charged perylene (**33**) and phthalocyanine dyes (**34**, left) that self-assemble into a helical stacked architecture (right). Reprinted with permission from Reference 228, © 2005 Wiley-VCH.

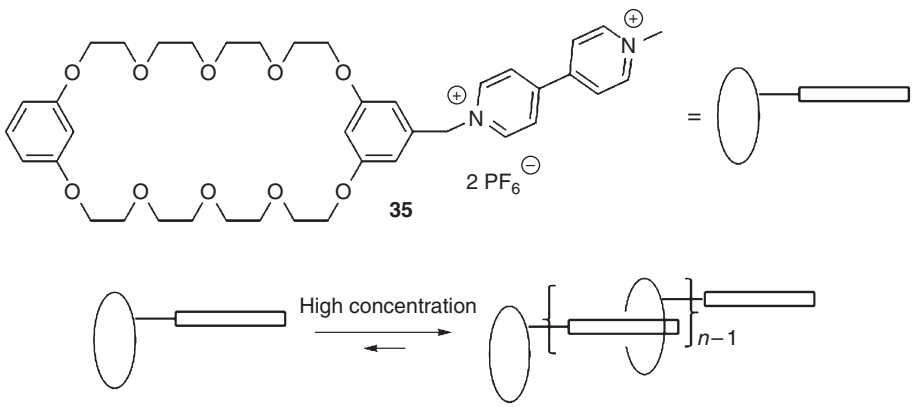

Figure 38 Schematic representation of the formation of supramolecular polymers via ion–dipole interactions.

formation of linear chain-extended polymers was observed for the self-assembly of a rigid cylindrical homoditopic bis(crown ether) with a rigid bis(ammonium salt).[232] Due to the higher binding strength of this system, a higher DP was obtained at lower concentration, however, at the cost of increased complexity. The wide scope of these strong directional ion–dipole interactions was recently utilized for the preparation of star-shaped[233] as well as hyperbranched polymers.[234]

5.13.4 Supramolecular Polymers Based on Hydrogen Bonding

5.13.4.1 General Aspects

In comparison, hydrogen bonding between neutral organic molecules is weaker than the previously discussed ionic interactions. However, this type of interaction holds a key role in supramolecular chemistry, due to its high directionality and versatility.[8,235–241] According to Jeffrey and Sanger,[242] three different types of hydrogen bonding can be distinguished: (1) strong hydrogen bonds, (2) medium or weak hydrogen bonds, and (3) nonclassical hydrogen bonds (Figure 39). Strong hydrogen bonds between two centers are characterized by short distances and high directional nature that is revealed by association energies higher than approximately 40 kJ mol^{-1}. The more weaker hydrogen bonds of the type 'D–H · · · A' feature a reduced directionality and lower bond energies between 20 and 40 kJ mol^{-1}. In such systems, the acceptor group A is strongly electronegative and the donor partner D may be electronegative or even a carbon atom. Finally, nonclassical hydrogen bonds are based on the interaction of D–H with π-conjugated systems as well as transition metal ions or boron hydrides.

The strength of each single-hydrogen bond is strongly dependent on solvent effects, in particular for polar and protic solvents. It has been shown that the addition of a polar solvent significantly weakens the hydrogen bond, often over orders of magnitude. Thus, the preparation of supramolecular polymers and materials is usually performed in aprotic and nonpolar solvents (e.g., alkanes, toluene, dichloromethane, and chloroform).[12]

The bonding strength is a crucial parameter for the synthesis of complex supramolecular architectures and can be influenced via the number of individual bonds involved. As a general rule,

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Strong hydrogen bonds	Medium/weak hydrogen bonds	Nonclassical hydrogen bonds
O−H----O⁻	D−H---A⁻	D−H---π
⁺O−H----O		D−H---M
		D−H---H−M
F−H----F⁻		D−H---H−B

Figure 39 Schematic overview on various types of hydrogen bonding (D: hydrogen bonding donor; A: hydrogen bonding acceptor; M: transition metal ion; B: boron) (scheme redrawn according to Reference 12).

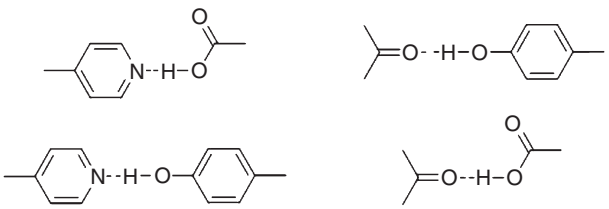

Figure 40 Schematic representation of interactions via one hydrogen bond.

more hydrogen bonds result in an enhanced binding interaction with an ideal value of about 7.4 kJ mol^{-1} per hydrogen bond. The most important types of interactions with increasing number of involved hydrogen bonds are depicted in Figures 40, 41, and 43.[12] In particular, multiple-hydrogen bonding in complex biomolecules, for example, nucleobase pairing in DNA,[243] inspired chemists to apply this binding motif for the preparation of supramolecular polymers also. The utilization of nucleobases as supramolecular binding motifs has been summarized by Sivakova and Rowan in a recent review.[319]

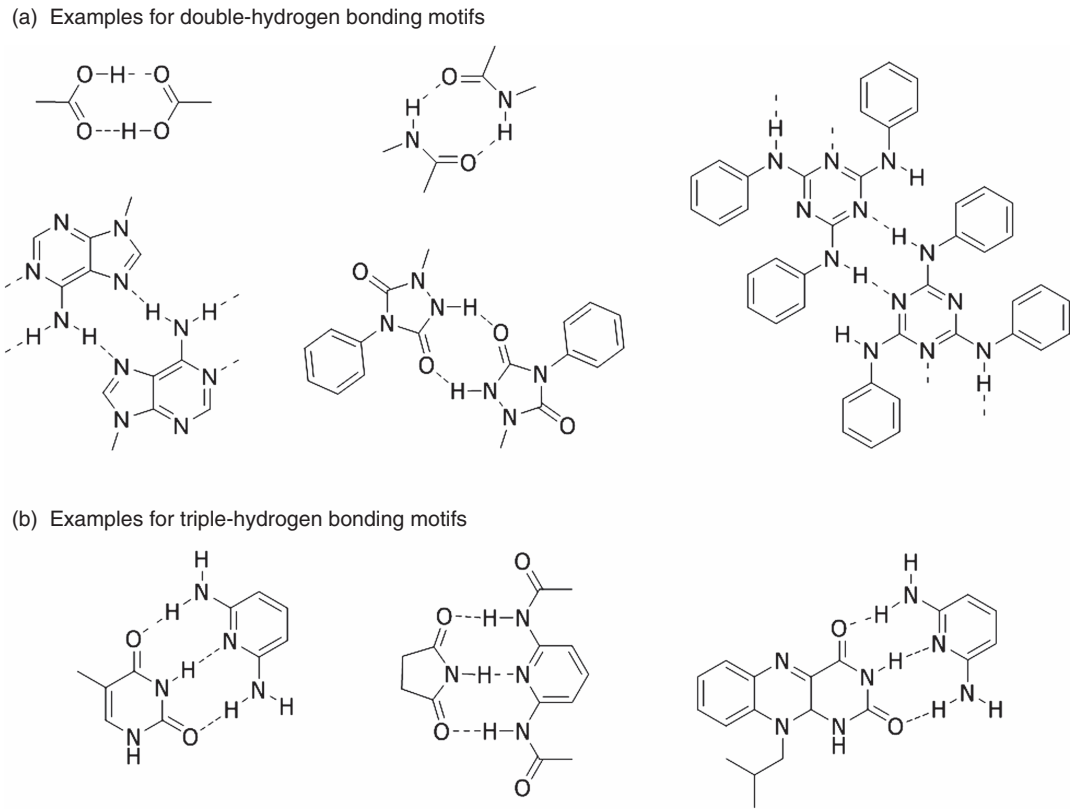

Figure 41 Schematic representation of interactions via two (a) or three hydrogen bonds (b).

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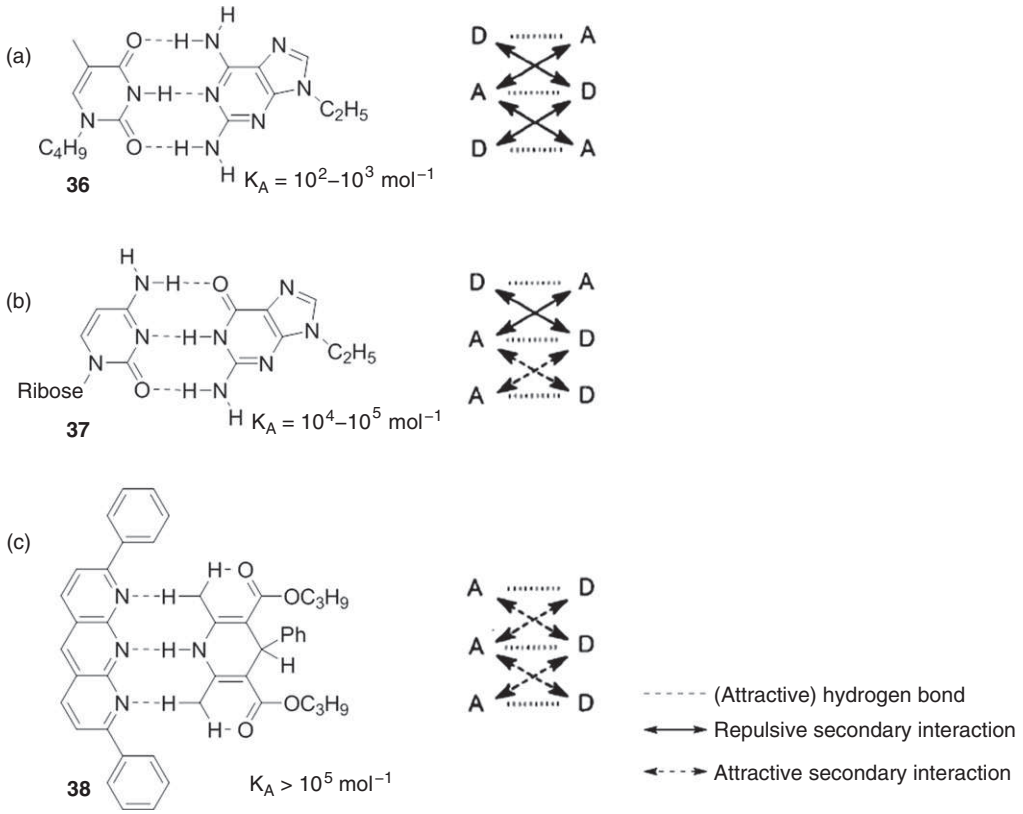

Figure 42 Schematic representation of triple-hydrogen bond containing motifs **36–38** of different stabilities (D: hydrogen bonding donor; A: hydrogen bonding acceptor, K_A: association constant in $CHCl_3$) (scheme redrawn according to Reference 8).

Besides simply increasing the number of hydrogen bonds, the particular arrangement of neighboring donor (D) and acceptor (A) sites is also of significant relevance for the strength of the overall interaction. Jorgensen and co-workers showed this by investigating different linear supramolecular arrays containing triple-hydrogen bonding (Figure 42).[244,245] The array of the composition DAD–ADA (36) showed an association constant (K_A) of about 10^2 mol^{-1} in chloroform. In the former case, only repulsive interactions have to be considered; on the other hand, additional attractive interactions in DAA–ADD systems (37) lead to an increase of K_A. Diagonally opposed sites of the same electronic nature repel each other electrostatically, whereas disperate sites attract each other. Consequently, the number of attractive interactions is maximized in assemblies of the type AAA–DDD (38) and, thus, K_A will be increased further (for other examples of AAA–DDD assemblies with high K_A values, see References 246, 247).

Very stable supramolecular assemblies can be obtained when synthetic quadruple[248–254] or even larger bonding units[255,256] were introduced. In particular, quadruple-hydrogen bonding systems combine directionality with a very high association constant in apolar solvents ($K_A > 10^6$ mol^{-1}). The self-complimentary of DADA (e.g., aminotriazines (39)[251] or ureidotriazines[257]) and DDAA arrays (e.g., 2-ureido-4-1*H*-pyrimidinone, 'UPy' 40) have gained significant importance for application in supramolecular polymers (Figure 43). However, tautomerism of the building blocks might be an issue leading to a loss of complementary and, consequently, complexation ability; for instance, a self-complementary DDAA array might tautomerize into a DADA system with a higher number of repulsive secondary interactions.[8] Zimmermann and co-workers developed a very stable self-complementary system; all possible tautomers were found to dimerize via quadruple-hydrogen bonding (one example (41) is depicted in Figure 43).[250] Prabhakaran *et al.* could show recently that tautomerism can be suppressed when rotational freedom was prevented by internal fixation.[251]

Due to the intrinsic self-complementarity of quadruple-hydrogen bonding systems, these arrays can, in general, not be applied for the combination of two different materials, for example, in alternating manner, in order to achieve sequence control. Though this limitation was recently overcome by Corbin and Zimmermann, who discovered that conformational changes of the AADD self-complementary system 41 into a non-self-complementary DAAD motif could be induced by diamidonaphthyridine (42), itself a strong ADDA hydrogen bonding system, leading to stable heterodimers (43, Figure 44).[250] Similarly, Chen and co-workers demonstrated that also the UPy moiety forms such heterodimers in the presence of diamidonaphthyridine (44).[258]

Multiple-hydrogen bonds represent a further extension of the general concept to introduce more connecting sites into a hydrogen bonding array. In particular, the DADDAD system introduced by Hamilton and co-workers[259–261] is the most important example for a sextuple-hydrogen bonding system

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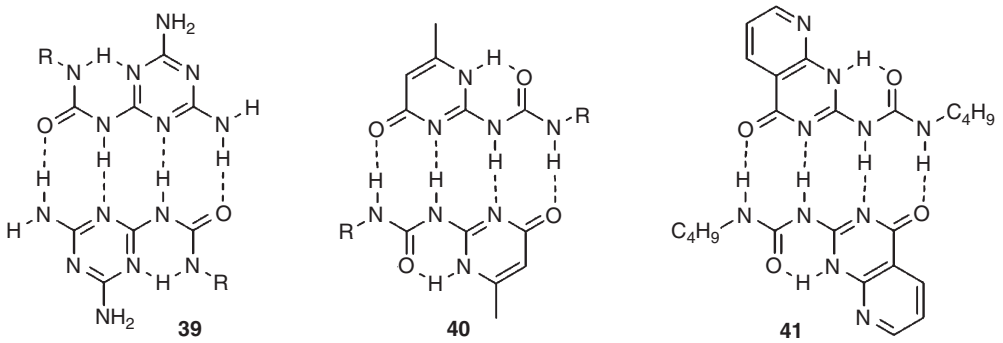

Figure 43 Schematic representation of quadruple-hydrogen bonding arrays.

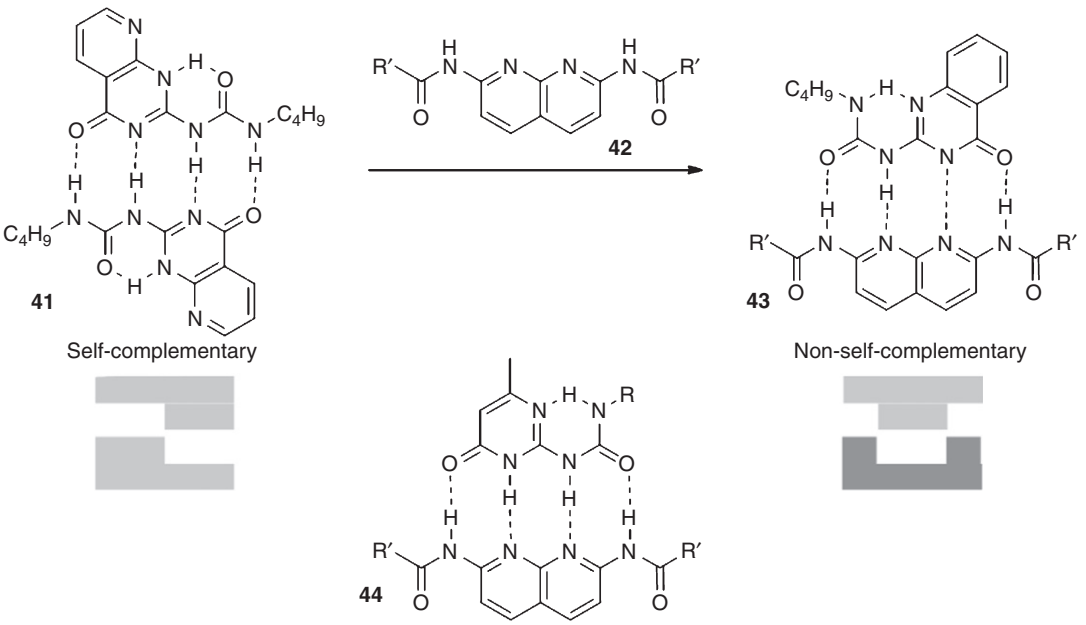

Figure 44 Schematic representation of the formation of heterodimers via quadruple-hydrogen bonding.

for the heteroassembly with, for example, derivatives of barbituric acid (45) or *N*-alkyl-cyanurate (Figure 45). The binding constant for this multivariant receptor, directing molecules in defined heterocomplementarity fashion, is about $10^5\,mol^{-1}$, close to the value reported for the dimerization of UPy-type derivatives. In another approach, non-self-complementary oligoamidic templates (46) were utilized for the assembly of structures via sextuple-hydrogen bonding (Figure 45); association constants of about $10^9\,mol^{-1}$ were found for this type of supramolecular array.[262]

Characterization of supramolecular systems based on hydrogen bonding involves the determination of the binding energies, the association constants, as well as the dynamics of the bonds. The often underlying complex equilibria are investigated by NMR spectroscopic techniques and,[263,264] in addition, complex mathematical fitting procedures. ITC is a highly efficient tool to determine thermodynamic parameters, such as the association energy as well as free enthalpy, entropy, and enthalpy of the binding process.[265,266] Infrared (in solution and in the solid state) and solid-state NMR spectroscopy are often applied to gain insight into the nature and the dynamic behavior of the hydrogen bonds.[267,268] Furthermore, the kinetics for breaking/reforming hydrogen bonds have been investigated extensively.[269]

5.13.4.2 From Hydrogen Bonding to Supramolecular Polymers

Supramolecular polymers based on single-hydrogen bonding have been reported; however, this approach has mainly been applied to assemble side chains to a polymer backbone, for example, via interaction between carboxylic acids and pyridine moieties[270–274] or for the interpolymer assembly via multiple, but isolated hydrogen bonds.[275] Chain-extension of small molecules based on single-hydrogen bonding were also reported, but

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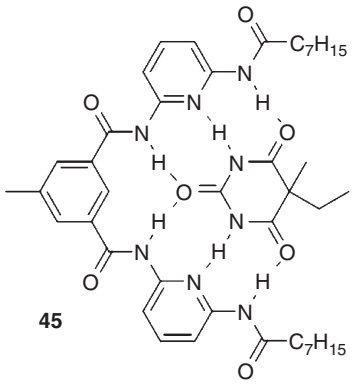

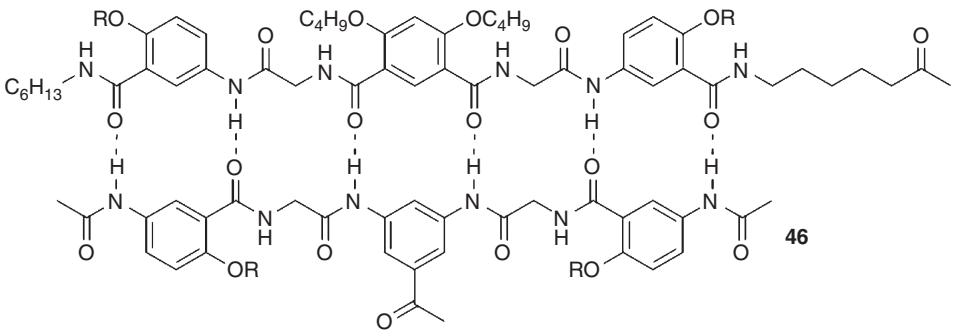

Figure 45 Schematic representation of sextuple-hydrogen bonding arrays.

only oligomeric species rather than supramolecular polymers were found.[13] From the few examples where materials with polymer-like behavior were discovered, the contribution by Pourcain and Griffin should be mentioned.[276] Supramolecular assemblies built up from a four-armed pyridine-functionalized compound and linear chain substituted at both ends with benzoic acids were investigated; LC, thermoreversible ladder-type polymers, as well as networks were observed.

Though interaction of molecules by double-hydrogen bonding is usually stronger compared to systems with only single-hydrogen bonds, their utilization in the field of supramolecular polymers is rare. For instance, uradiazole moieties (AD type) were introduced by Stadler in order to generate reversible cross-links within polymeric materials (**Figure 46**);[277] polybutadiene was functionalized with the hydrogen binding unit (degree of functionalization: 2%) leading to drastic changes in the thermal and the mechanical properties of the material. Further applications for supramolecular polymers with double-hydrogen bonding arrays in the side chain have been summarized comprehensively by Binder and Zirbs;[12] up to now, no examples have been published where such systems have been used to connect the main chain of a polymer.

Contrary to the previous examples, triple-hydrogen bonding arrays have been widely applied in the field of supramolecular polymers. The most common binding motifs are combinations of 2,6-diamino-pyridines, 2,6-diamino-1,3,5-triazines with flavine-, thymine-/uracil-, as well as succinimide derivatives (**Figure 41(b)**); furthermore, the Watson–Crick and Hogsteen base-pairing of nucleobases has been employed.[278]

Credit has to be given to Lehn and co-workers for recognizing the importance of the 2,6-diamino-pyridine/uracil interaction and utilizing it to develop the first supramolecular main-chain polymer

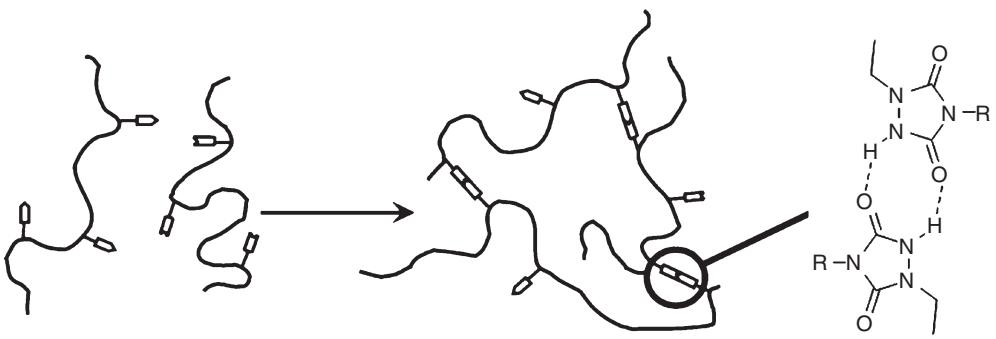

Figure 46 Schematic representation of the self-assembly of flexible polymers into networks by inter-/intramolecular uradiazole–hydrogen bonds. Reprinted with permission from Reference 12, © 2007 Springer.

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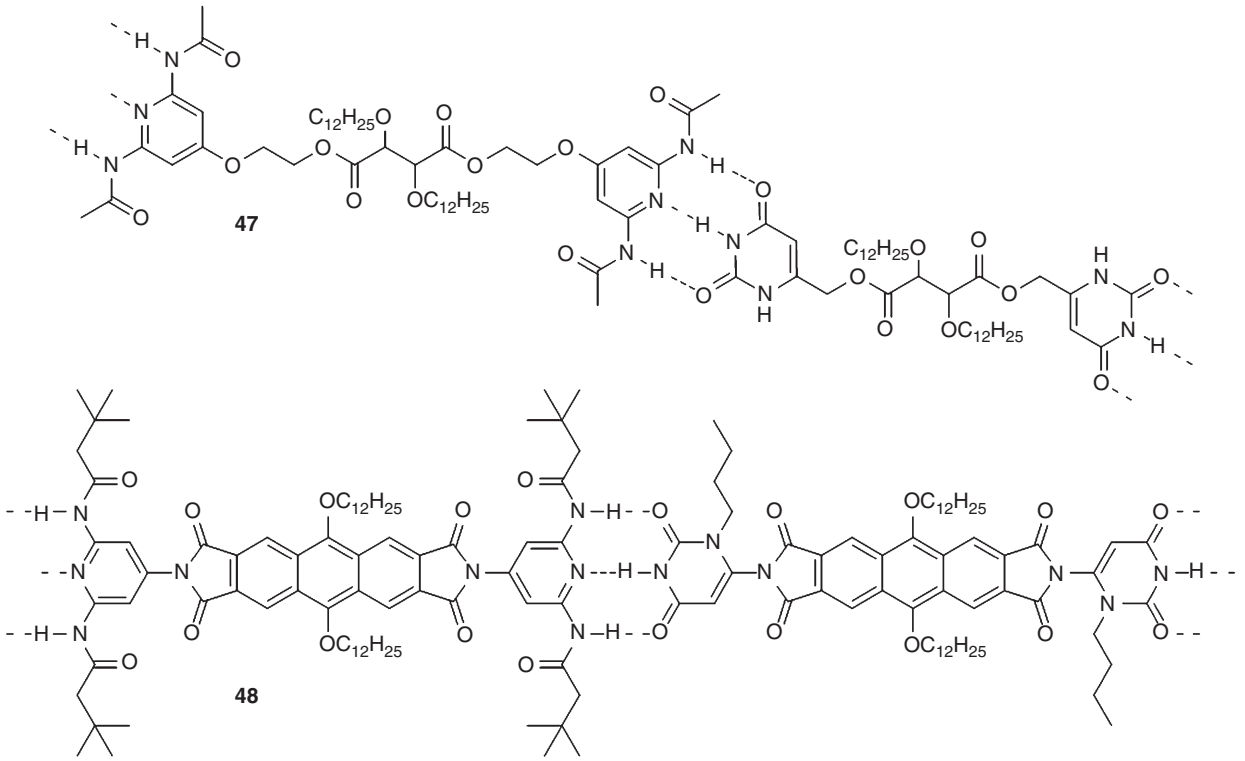

Figure 47 Schematic representation of supramolecular polymers based on triple-hydrogen bonding arrays.

(47) by triple-hydrogen bonding between difunctional orthogonal derivatives (Figure 47).[279,280] At a 1:1 ratio of both monomers, columnar superstructures were formed and liquid crystallinity over a broad range of temperature (from room temperature to about 200 °C) was observed, whereas the pure monomers were solids that melted into isotropic liquids without displaying a LC phase. The chirality of the tartaric acid spacer moieties was translated into supramolecular helicity and subsequent aggregation into fiber-like superstructures, a process that could be investigated by means of electron microscopy on nano- as well as on micrometer scales.[281] Furthermore, rigid-rod polymers 48, containing 9,10-dialkoxy-anthracene cores to connect the hydrogen-bonded groups via imide groups, were investigated. An increased molecular rigidity resulted in changes of the LC behavior: the system was not thermotropic, but a lyotropic LC phase was observed in apolar solvents that was birefringent and highly viscous.[282,283]

The group of Würthner utilized the same perylene derivative as for their metallo-supramolecular polymers (see, e.g., 16a, Figure 25) also for the preparation of polymer 49 via hydrogen bonding (Figure 48).[284] The two monomers self-assembled into well-defined mesoscopic structures exhibiting high photostability and high-fluorescence quantum yields. Investigation of the aggregation behavior revealed a complex behavior: besides triple-hydrogen bonding, π–π stacking and interaction with the hydrophobic alkyl chains were also observed – leading to superstructures at very low concentrations (10^{-5}–10^{-6} mol l^{-1}). Cylindrical strands with diameters of roughly 200–300 nm that formed in apolar solvents (e.g., methylcyclohexane) could be visualized by various microscopy techniques (Figure 48).

Supramolecular block copolymers containing end-group-modified telechelic poly(etherketone) (PEK) and poly(isobutylene) (PIB) in alternating manner were reported by Binder *et al.* and Kunz *et al.*[285–287] The involved supramolecular association was based on either a strong (i.e. 2,6-diamino-1,3,5-triazine and thymine) or a weak pair (i.e. 2,6-diamino-1,3,5--triazine and cytosine) of non-self-complementary partners for triple-hydrogen bonding (Figure 49). Combining the two strongly phase-separating polymers lead to a significant increase in miscibility. The structure formation in the liquid state was investigated by NMR spectroscopy revealing K_A values similar to those obtained for small-molecule analogs. In the solid state, sheet-like structures were concluded from solid-state NMR spectroscopy, TEM, and thermal measurements. Differential scanning calorimetry (DSC) gave further evidence for the presence of two separate phases.[285]

A similar approach to the work of Binder was followed by Rowan and co-workers who obtained main-chain liquid crystal materials held together by complementing nucleobases (i.e. adenine (A) and thymine (T) derivatives) and a rigid conjugated spacer (Figure 50).[288,289] Melt-mixing of the matching building blocks 50 generated materials with a much broader range of LC behavior in comparison to the individual components. The authors proposed that the utilized A- and T-derivatives favor a Hogsteen-type pairing of the bases (in contrast to the more common Watson–Crick base-pairing), thus leading to network formation and, therewith, increasing the overall aspect ratio in comparison to solely linear assemblies. As a consequence, stable phases with LC behavior were formed. The concept of inter-nucleobase linking was further applied, for example, for the self-assembly of homo- and heteroditopic bolaamphiphiles[290] as well as poly(tetrahydrofurane)s[291] bearing adenine- and thymine moieties. More examples and a detailed discussion

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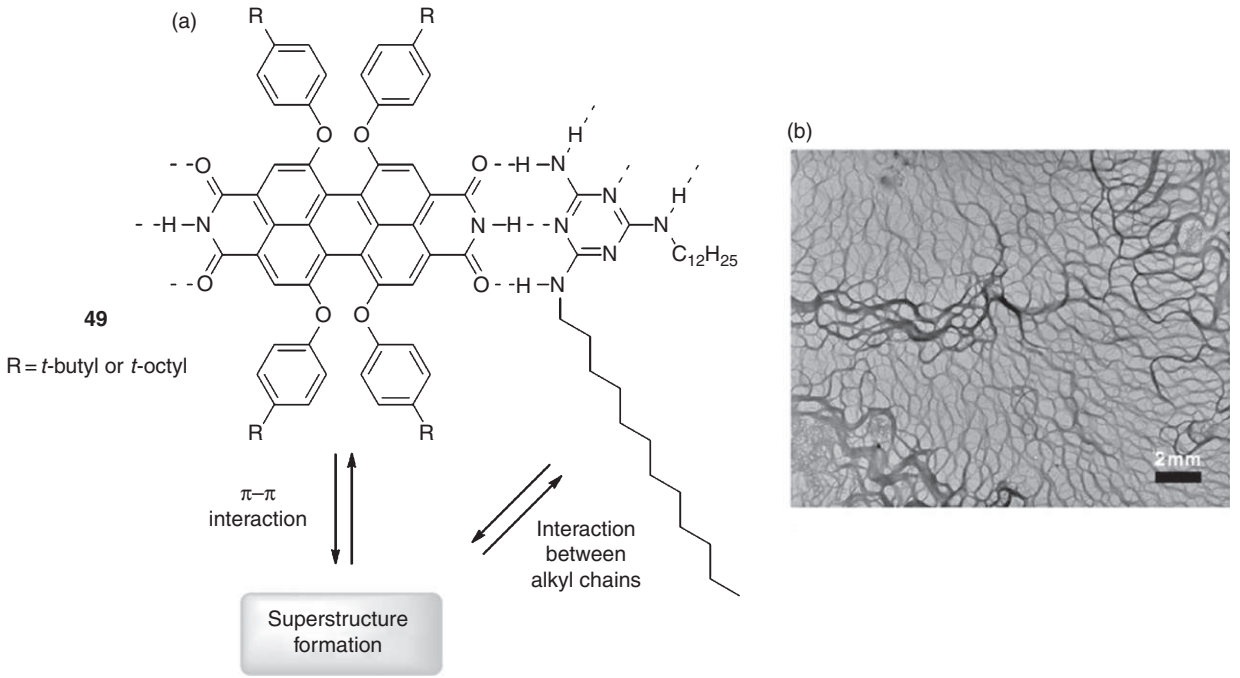

Figure 48 (a) Schematic representation of a supramolecular polymer based on triple-hydrogen bonding and a perylene core. (b) Transmission electron micrograph of mesoscopic superstructures that were obtained by evaporation of 5×10^{-5} mol l^{-1} of methylcyclohexane solutions of **49** on carbon–Formvar-coated nickel grids (200 mesh) and subsequent staining with uranyl acetate. Reprinted with permission from Reference 284, © 1999 Wiley-VCH.

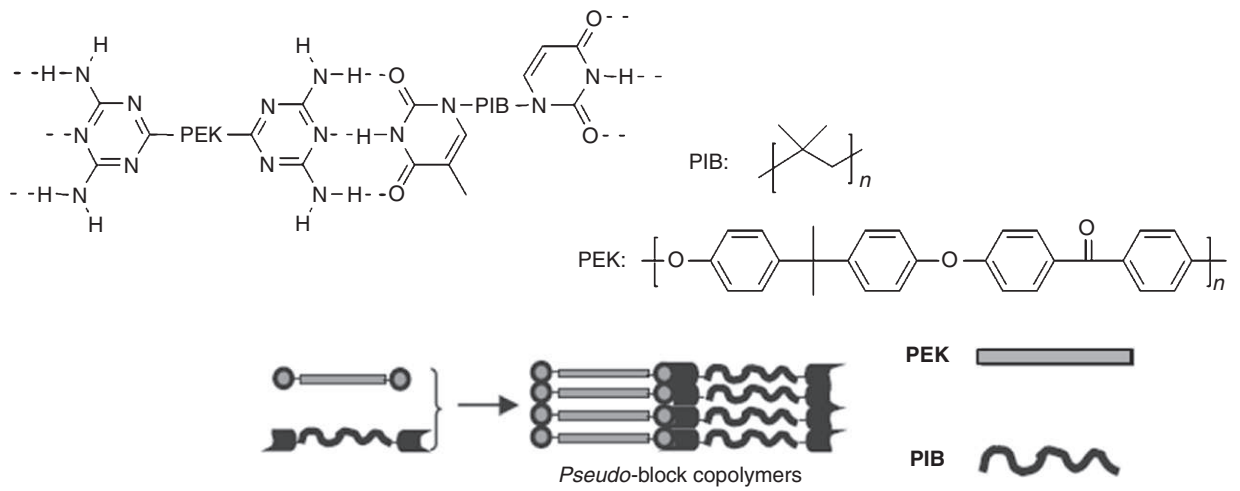

Figure 49 Schematic representation of a supramolecular block copolymer based on triple-hydrogen bonding. Reprinted with permission from Reference 287, © 2005 Wiley-VCH.

of the behavior of such supramolecular polymers can be found in excellent recent reviews published elsewhere.[12,244]

Quadruple-hydrogen bonding arrays have been widely employed as supramolecular building blocks in recent years and many examples of supramolecular polymers based on this motif have been reported.[12] According to Meijer, the association of small building blocks leading to materials with polymer-like properties in solution is restricted by the strength of the binding constant.[9,239] At a concentration of the monomers of about 1 M, a binding constant of $K = 10^5$ mol^{-1} will lead to a DP of about 100 (**Figure 3**). Thus, aiming for high molar mass polymers, a significantly higher value for K is a requirement. Quadruple-hydrogen bonding systems, such as the UPy (**40**) or the ureidotriazine unit, were developed featuring binding constants of about 10^7 mol^{-1} (see References 8, 9, 237, 292, 293 for reviews on quadruple-hydrogen bonding).

The first application of the enhanced association tendency of such systems was reported in 1999 by Lange *et al.*:[294] the dimerization ability of UPy was utilized for the assembly of PEG and poly(propylene glycol) (PPG) telechelics into polymer networks, not requiring additional stabilization such as crystallization or phase separation. Reversibility of the supramolecular polymerization was proven by the addition of about 30 equiv. of water per UPy unit (significantly reducing the viscosity of the solution)

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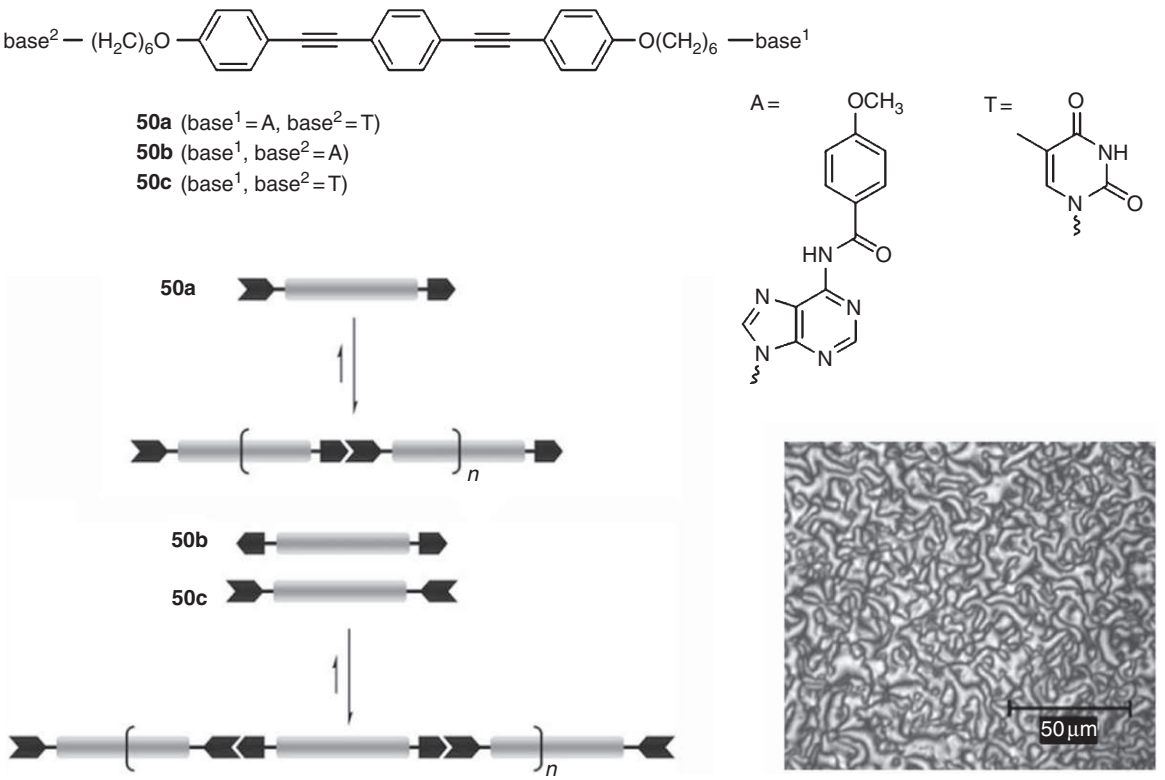

Figure 50 Schematic representation of homo- (**50a**) and hetero-difunctional building blocks (**50b** and **c**), their self-assembly into supramolecular polymers by triple-hydrogen bonding and polarized optical micrograph of **[50b···50c]**$_n$ at 135 °C. Reprinted with permission from Reference 288, © 2005 Wiley-VCH.

and excess of UPy monomers (leading to an almost quantitative depolymerization). In the following, the self-complementary UPy building block has been investigated intensively, experimentally as well as theoretically and reference is given to the extensive work by this group.[8,9,253,295–299]

The photoreversible formation of supramolecular polymers was studied by Takeshita *et al.*[300] For this purpose, dithienylethylene was employed as photochromic moiety, being able to change between open (**51**) and closed structures (**52**) via reversible [3,3]-Cope cyclization, and functionalized with UPy units on both sides (**Figure 51**). Irradiation at 366 nm led to the closed form, whereas the open form could be obtained upon irradiation at wavelength > 540 nm. For the open structure, the equilibrium between a *trans*- (**51a**) and a *cis*-arrangement (**51b**) strongly reduced the aggregation via hydrogen bonding, the closed form readily aggregated into polymeric structures. The tendency to

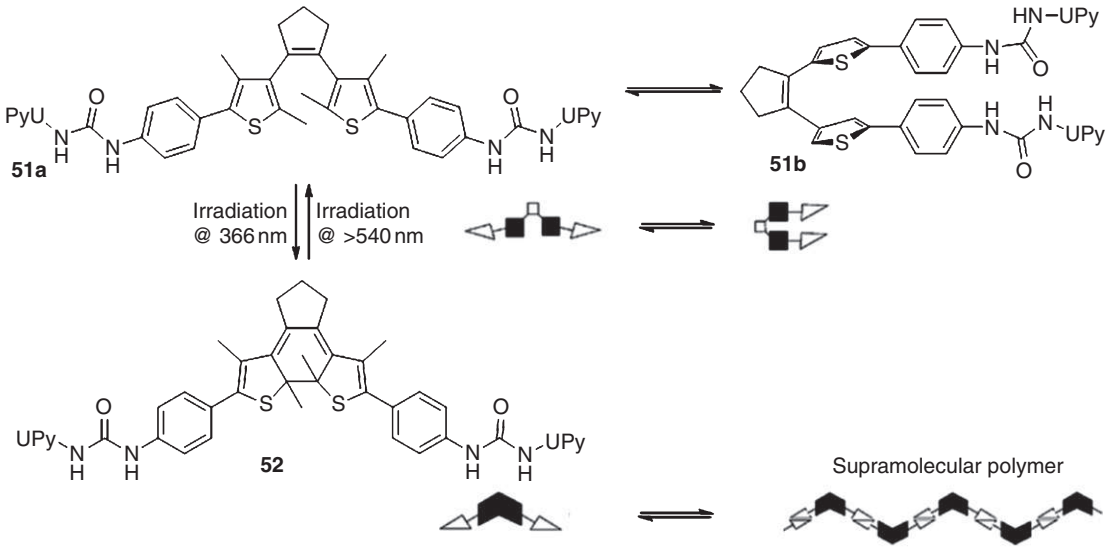

Figure 51 Schematic representation of the photoreversible formation of supramolecular polymers (figure redrawn according to Reference 300).

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form supramolecular polymers depending on the irradiation wavelength could be monitored by viscosimetry measurements.

Meijer and co-workers investigated the aggregation of combinations of UPy-functionalized π-conjugated oligofluorene, oligoperylene, and oligo(phenylene–vinylene) (OPV) segments. Association via hydrogen bonds in solution resulted in energy transfer from the (blue-absorbing) oligofluorene to the (green-emissive) OPVs. The enhancement of the energy transfer was attributed to the ordering of the functional groups by supramolecular aggregation.[301] Furthermore, dimeric OPVs could be assembled into disk-[302] as well as ladder-shaped structures,[303] exhibiting strong exciton coupling in solution. These solutions were combined with fullerenes leading to materials that could be processed via spin-coating into thin films (thickness around 100 nm) with good control over the morphology. Neutron-scattering experiments on the films revealed rod-like structures, similar to those observed in solution, with the fullerene derivatives blended close to the π-conjugated segments. Application as photovoltaic devices showed a photo-to-current transformation of about 12% that was attributed to the phase-separated morphology of the film.

The mixing of three different π-conjugated oligomers (i.e. a blue-emitting oligofluorene (**53**), a green-emitting OPV (**54**), and a red-emitting perylene bisimide (**55**)), all functionalized with self-complementary UPy units at both ends, yielded a supramolecular random copolymer (**Figure 52**).[304] The self-assembly into supramolecular polymers occurred both in solution and in bulk. Upon mixing of **53–55** in solution (at different stoichiometries), random noncovalent copolymers were formed that contained all three types of chromophores and exhibited energy transfer upon excitation of the oligofluorene donor unit (**Figure 52(b)**). Moreover, a white emissive

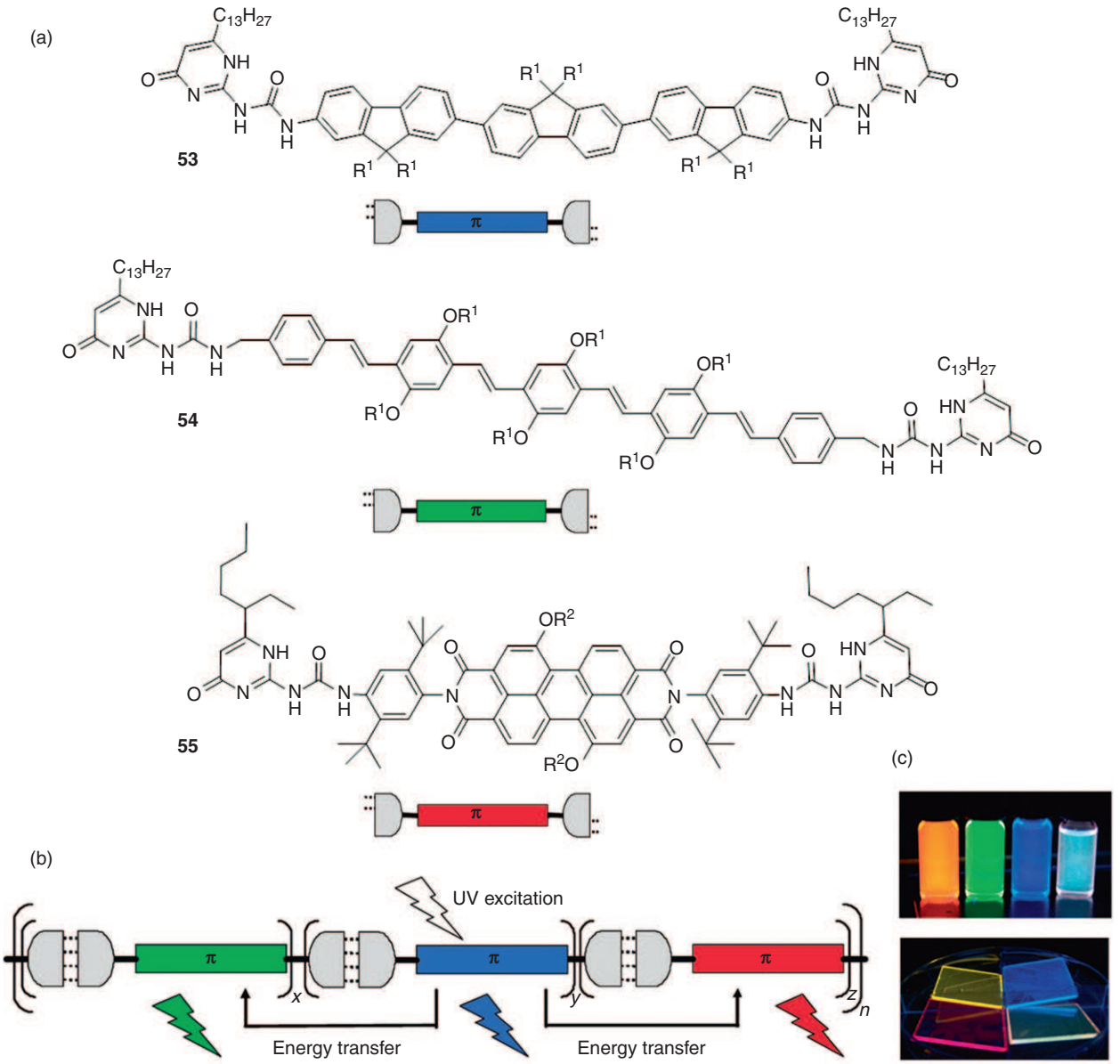

Figure 52 (a) Schematic representation of UPy-functionalized π-conjugated oligomers **53–55** (R^1 = (*S*)-3,7-dimethyloctyl, R^2 = 3,5-di-*tert*-butylphenyl); (b) schematic representation of the energy transfer within the supramolecular polymer; and (c) representation of the emission colors of the homopolymers in solution as well as in solid state. Reprinted with permission from Reference 304, © 2009 American Chemical Society.

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supramolecular polymer could be obtained in solution at a certain ratio of building blocks. In contrast to their unfunctionalized counterparts, the bis-UPy-functionalized chromophores could be processed by spin-coating to give smooth thin films on solid substrates. No phase separation was observed in the solid state and, furthermore, the energy transfer process was even more efficient compared to the solution; as a result, white fluorescence was achieved at significantly lower acceptor to donor ratios. The authors reported on light-emitting diodes based on these supramolecular materials: the homopolymers gave blue-, green-, and red-emitting devices, respectively (Figure 52(c)); at an optimized ratio of 53–55, white electroluminescence was observed.

Though ureidopyrimidone derivatives are one of the most powerful template for quadruple-hydrogen bonding, their self-complementary nature represents a drawback when targeting hetero-assemblies, for example, with alternating order of two building blocks. Thus, various types of non-self-complementary sextuple-hydrogen bonding systems, further increasing stability when compared to quadruple-hydrogen bonding, were developed. In particular, the so-called Hamilton-receptor (45)[259–261] has been frequently employed.

Lehn and co-workers utilized ditopic building blocks in order to assemble them into linear structures via Hamilton-receptor/cyanurate interactions (56), subsequently leading to fibers upon higher association (Figure 53).[305] Viscosimetry and NMR spectroscopy were applied to study the fiber formation. The concentration dependence of the aggregation in the presence and absence of a monotopic 'chain-stopper' as well as at imbalanced stoichiometric ratios of the two components was monitored. In both cases, a strong drop of the (virtual) molar masses of the supramolecular structures was observed, in accordance with the general mechanism for polycondensation reactions (see Figure 4). It could also been shown by electron microscopy and neutron-scattering experiments that in nonpolar solvents (e.g., decane or toluene) bundles of fibers were formed.[306] In a similar approach, the combination of two strongly different polymeric blocks (i.e. microphase-separating PEK and PIB, see also Figure 49) was reported by Binder and co-workers. In continuation of previous work (see also Figure 49), based on the sextuple Hamilton-receptor/barbituric acid interaction, a supramolecular block copolymer was obtained.[287]

The concept of multiple-hydrogen bonding was combined with (partially) reversible covalent bonds (e.g., imines), resulting in dynamic combinatorial libraries,[307] the so-called 'double dynamers'.[308] Exchange of the components due to their dynamic bonds generated a constitutional diversity on both the molecular and the supramolecular levels (Figure 54). Selection processes could occur, driven either by hydrogen bonding interactions or by the partially reversible covalent bonding system. The authors envisioned new materials with strongly modulative properties from their concept.

Finally, the high potential of supramolecular materials based on multiple-hydrogen bonding is mirrored by the application as self-healing and thermoreversible rubbers. Cordier *et al.* utilized fatty acid dimers made from natural renewable resources (i.e., vegetable oil) and introduced three types of functional groups that were able to self-assemble via multiple-hydrogen bonding – namely amidoethyl imidazolidone, di(amidoethyl) urea, and diaminotetraethyl triurea (Figure 55(a)).[309] The synthesis involved the condensation of the acids with diethylene triamine; subsequently, the obtained product was treated with urea. Initially, the product (SEC and viscosimetry measurements indicated the presence of oligomeric species rather than a polymer) resembled a translucent plastic that behaved like a soft rubber at 90 °C well above its glass-transition temperature (T_g = 28 °C). At elevated temperatures (above 160 °C), viscoelastic properties were observed and the material could be molded, extruded, and (re)shaped. After plasticization with dodecane in order to lower the T_g, the supramolecular material turned into a nontacky rubber-like polymer network (Figure 55(b)). The rheological and mechanical measurements revealed the rubber-like properties; for example, the stress–strain curves correspond to those of soft rubbers (Figure 55(c)): the strain at breaks exceeded 500% and, after elongation to 300% (speed of 2.5 mm min^{-1}) and release of stress, the residual strain was below 5%. The entire process of breaking and self-healing could be repeated many times.

5.13.5 Supramolecular Polymers Based on Multiple Supramolecular Motifs

Biomolecules are characterized by a combination of different supramolecular interactions and their noncovalent binding sites are highly selective. For instance, in enzymes and proteins (e.g., ATP synthase or hemoglobin), the ensemble of various supramolecular bonds is responsible for their specific structures and provides centers for highly selective catalytic biochemical transformations. The concept of 'asymmetric (or orthogonal) supramolecular interactions' describes noncovalent interactions that do not interfere with each other. Multifunctionality is a basic characteristic of biological systems. Contrary to these, synthetic supramolecular chemistry usually utilizes only one type of interaction at a time, for example, metal-to-ligand coordination, ionic interaction, or hydrogen bonding. Utilizing combinations thereof allows the synthesis of self-assembled supramolecular structures that might be addressed by different external stimuli. Applications of this approach in the field of polymer science have been covered by various recent review articles[16,17,310] and a few selected highlights, in particular based on the combination of metal-to-ligand coordination and hydrogen bonding within the polymer main-chain, will be introduced in the following.

Schubert and co-workers synthesized various types of heterotelechelic supramolecular building blocks containing a terpyridine ligand suited for transition metal ion complexation on the one and the self-complementary UPy moiety for quadruple-hydrogen bonding on the other side (Figure 56, top).[311–313] Besides a small-molecule building block (57),[311] a polymeric heterotelechelic substrate (58)[312] was synthesized by Sn^{II}-catalyzed ring-opening polymerization of ε-caprolactone and subsequent end-group functionalization with UPy. Self-assembly with Fe^{II} as well as Zn^{II} ions yielded supramolecular polymers with alternating supramolecular interactions (Figure 56, bottom). Viscosimetry measurements revealed high molar masses of the materials. External stimuli could be used to reversibly break the supramolecular bonds: the hydrogen bonding subunit showed a pronounced temperature dependency; the $[M(tpy)]^{2+}$ unit (M = Fe^{II} and Zn^{II}) could be opened by addition of strongly competing ligands.[19]

Moreover, a supramolecular initiator (59) – based on the 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide (TIPNO)-motif developed by the group of Benoit *et al.*[314] – for

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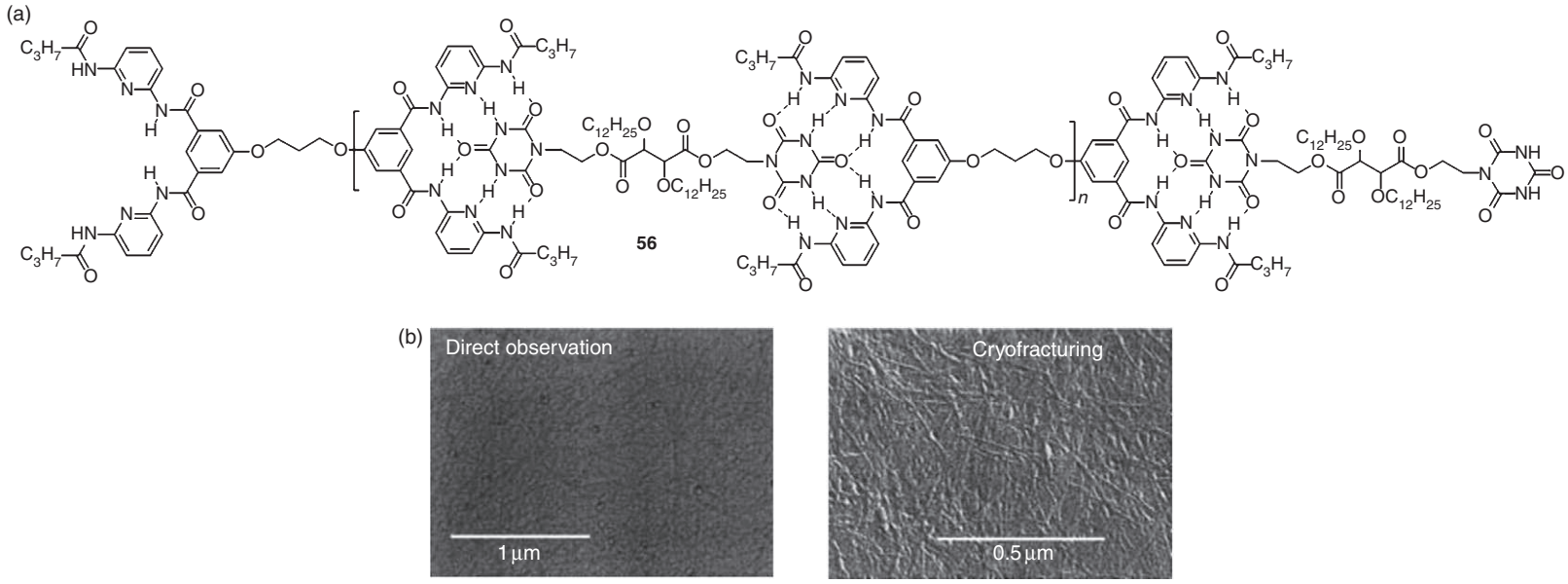

Figure 53 (a) Schematic representation of supramolecular polymer **56** based on Hamilton-receptor/cyanurate interactions. (b) Extended, dense fiber networks obtained from a solution of **56** (2.5 mmol l^{-1} in $CHCl_3$/heptane, 1:4 ratio) as evidenced by electron microscopy (left: direct observation; right: cryofracturing technique).[305] Reprinted with permission from Reference 305, © 2002 Wiley-VCH.

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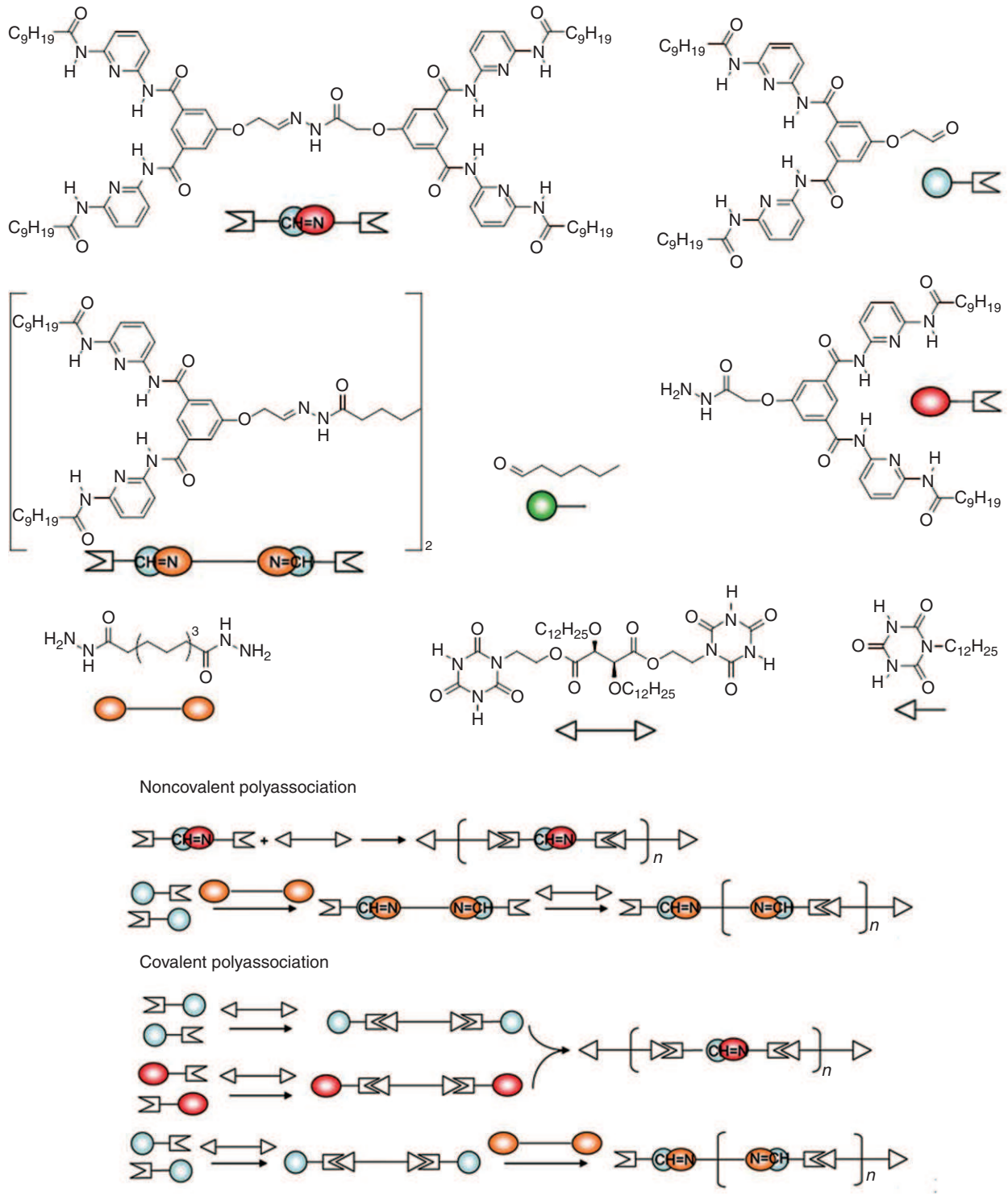

Figure 54 Schematic representation of the 'double dynamers' according to Lehn and co-workers. Figure redrawn according to Reference 308.

nitroxide-mediated polymerization (NMP) was reported recently (Figure 57).[313] This building block could be utilized for the controlled radical polymerization of styrene under NMP conditions to yield macroligand 60 ($M_n = 4800\,g\,mol^{-1}$ as determined by ^{1}H NMR spectroscopy). The integrity of both supramolecular functionalities could be confirmed by ^{1}H NMR spectroscopy, UV/vis absorption titration experiments with Fe^{II} salts, as well as comparing the SEC traces of 60 and the homoleptic Ni^{II} bis-complex of 60.

Pincer-type complexes were also utilized as linkage in supramolecular systems containing multiple types of interactions. Weck and co-workers synthesized polynorbornene via ROMP

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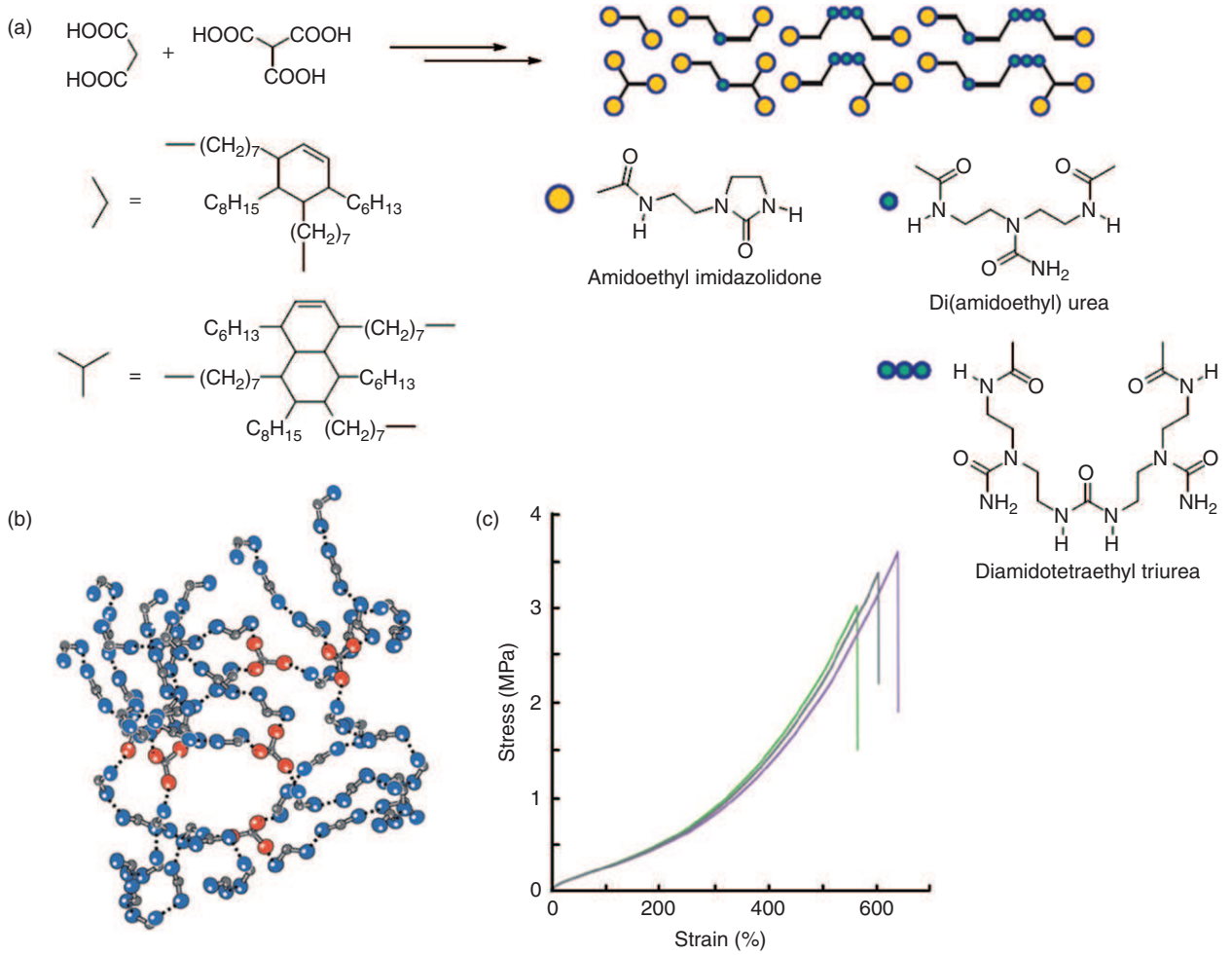

Figure 55 (a) Schematic representation of the preparation of a 'supramolecular rubber' based on multiple-hydrogen bonding. (b) Schematic representation of a network formed by mixtures of ditopic (blue) and tritopic (red) building blocks, self-assembled by directional interactions (dotted lines). (c) Stress–strain curve of the supramolecular rubber.[309] Reprinted with permission from Reference 309, © 2008 Nature Publishing Group.

where both the Pd^{II} pincer complexes and 2,6-diaminopyridine units for hydrogen bonding were statistically incorporated in the side chains allowing a modular self-assembly.[315] In a later contribution, crown ether moieties, suited as templates for ion–dipole interactions, were also utilized.[316] It was shown in all cases that selective recognition of the binding sites occurred with no disturbance due to the presence of the other supramolecular units. Recently, the same group applied this concept for the preparation of a well-defined ABC triblock copolymer based on both a Pd^{II} pincer complex and a Hamilton-receptor/barbituric acid array.[317] However, an extension of this approach toward supramolecular polymers in terms of polycondensation/polyaddition processes has not yet been realized.

As a last example, an orthogonal supramolecular array based on phosphine–metal coordination and hydrogen bonding was applied by Shi *et al.* for the immobilization of Rh^{I} catalyst for asymmetric hydrogenation reactions (Figure 58).[318] The supramolecular heterogeneous catalyst 61 was found to be superior to analog homogeneous species in terms of recovery and reusability. The polymer was characterized by extensive NMR spectroscopy experiments, in solution as well as in the solid state. Scanning electron microscopy (SEM) images indicated that 61 was composed of micrometer-sized particles (Figure 58(c)), while X-ray diffraction showed no indication for crystallinity of the solid.

5.13.6 Conclusion and Outlook

A large variety of supramolecular polymers utilizing reversible binding units, in particular transition metal complexes, ionic interactions, and hydrogen bonds, have been investigated in the past couple of years. The 'supramolecular polyaddition/polycondensation' approach features mechanisms which are comparable to their covalent counterparts. All three main mechanisms – isodesmic, ring-chain-mediated, and cooperative polymerization – include characteristics of the classical polyaddition/polycondensation behavior, that is, broad molar mass distribution (compared to chain-growth reactions), necessary for exact stoichiometry and stepwise growth of the polymer chains.

The selected examples provide an overview about the various possibilities, which this special polymer class offers. The main property, which has to be highlighted, is the reversibility of the supramolecular binding units which are located in the

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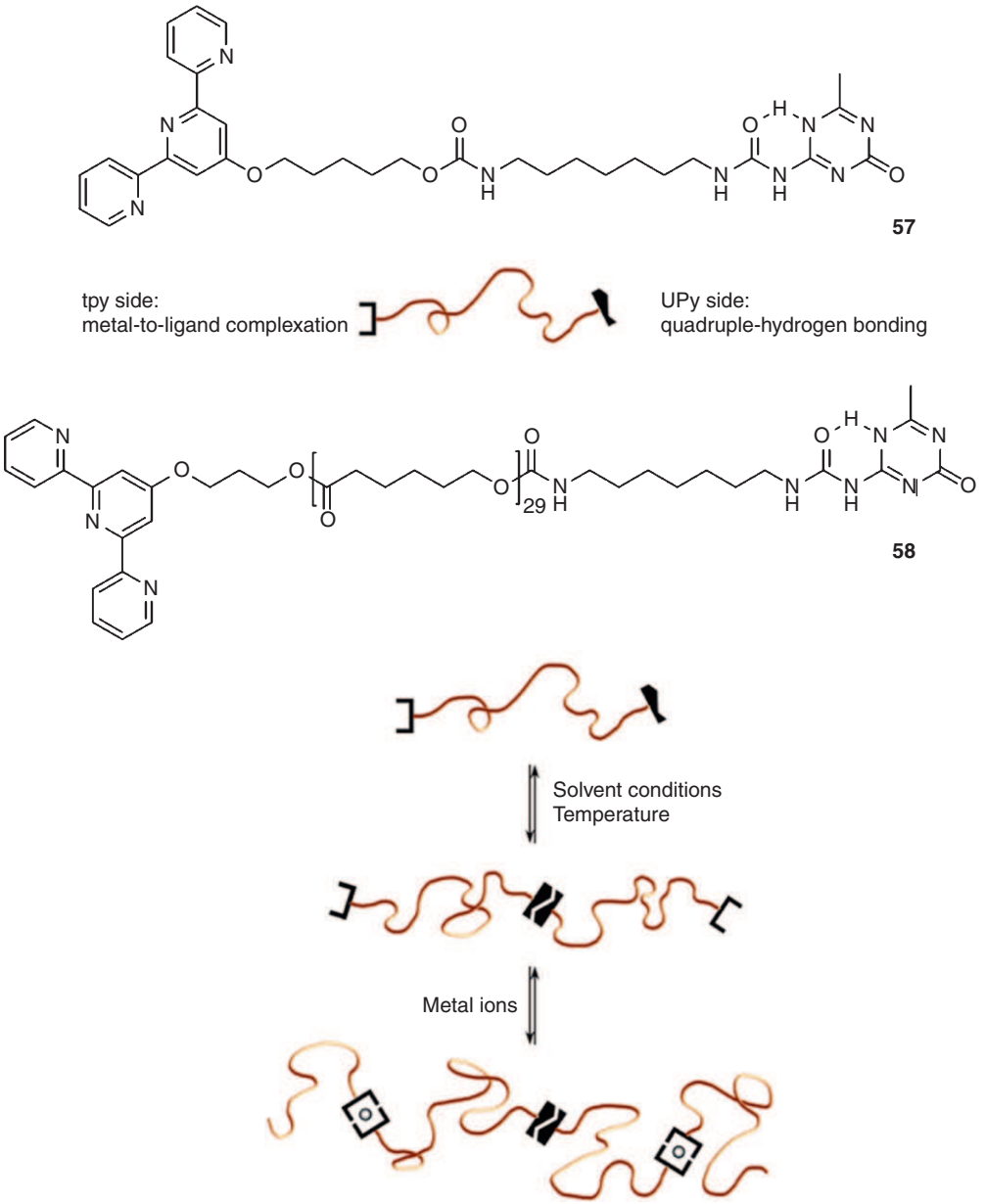

Figure 56 Schematic representation of heterotelechelic building blocks (**57** and **58**, top) for the self-assembly into polymers via orthogonal supramolecular interactions (bottom). Reprinted with permission from Reference 312, © 2005 American Chemical Society.

main chain. As a result, special considerations (e.g., high concentrations, solubility issues) have to be taken into account for the synthesis of these materials. In comparison to conventional polymers, characterization of supramolecular polymers is demanding. For instance, SEC – a versatile tool for investigating covalent polymers – is difficult to apply due to conditions (e.g., coordinating solvents and high dilution) generally supporting dissociation of the supramolecular polymers into discrete (small-molecule) fragments. On the other hand, outstanding properties can be achieved. The reversibility immediately leads to stimuli-responsive materials.[11,14,20,172] External stimuli can be used to influence the formation of supramolecular polymers and supramolecular gels. Amazingly, the reversible bonds in the polymeric chain still result in good mechanical properties.[319] In addition, the reversibility opens new possibilities and mechanical damages can be healed. Self-healing materials[320] can be principally achieved by different supramolecular interactions, in particular hydrogen bonds.[309,321,322]

Further applications taking advantage of the reversibility are thinkable, for instance, reversible adhesives or stimuli-responsive thickeners. In addition, the synthesis of these materials becomes modular, that is, the building blocks can be easily exchanged accompanied by a tuning of the properties of these materials, for instance, tuning of optoelectronic properties.[304]

The reversibility, well-known from Nature, makes supramolecular polymers interesting candidates for biological materials.[323,324]

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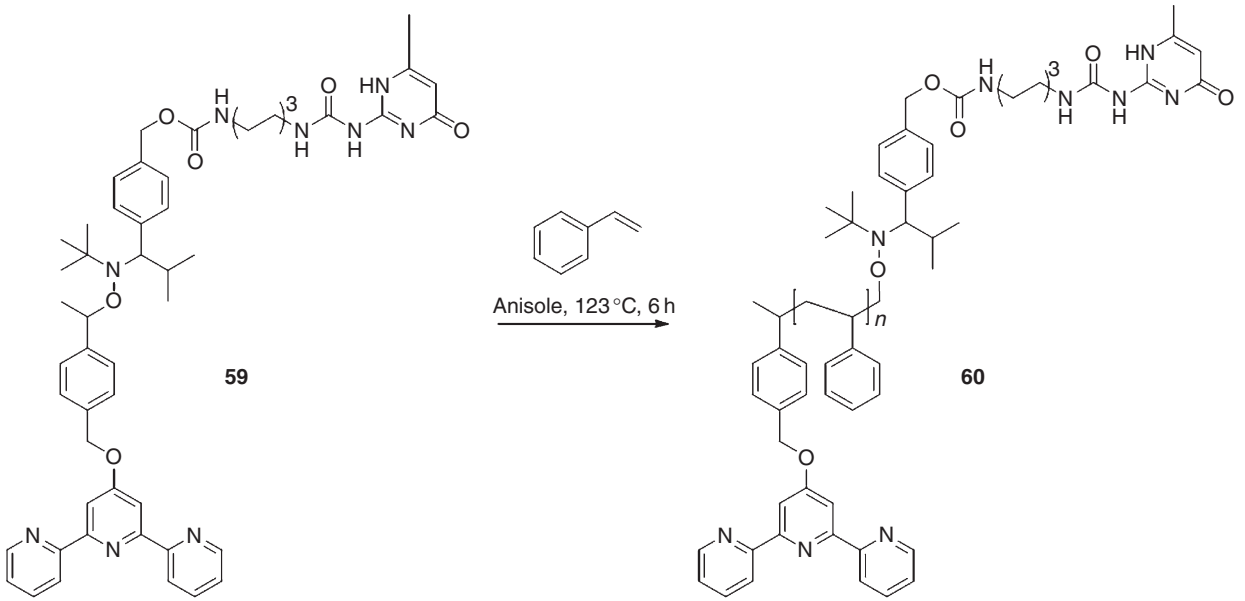

Figure 57 Schematic representation of a heterotelechelic macroinitiator (**59**) for NMP reactions.

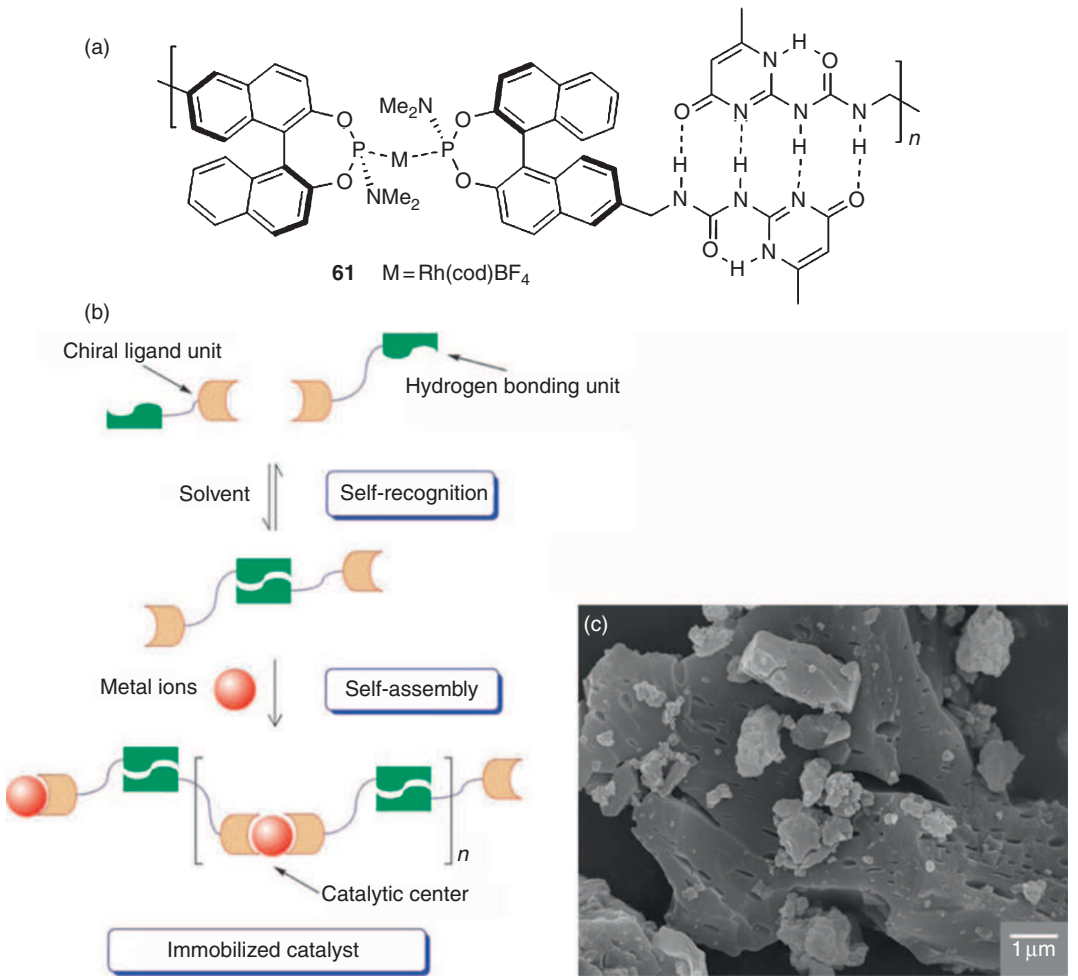

Figure 58 Schematic representation of the immobilized Rh^{I} catalyst (a; cod = cyclooctadienyl); the formation of **61** via orthogonal supramolecular self-assembly (b); and SEM image of micrometer-sized particles of **61** (c). Reprinted with permission from Reference 318, © 2006 Wiley-VCH.

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A wide field of (potential) applications is opened up for supramolecular polymers due to their interesting and often unique properties.[325,326] However, some more details of the synthesis have to be understood. In addition, the possibilities to control a supramolecular polymerization are rather limited, for instance, adjustment of the molar mass. These drawbacks led to the invention of living and controlled polymerization techniques in the classical polymer chemistry world, which allow the control over the molar mass as well as molar mass distribution, composition, sequence (e.g., random or block), and end-group functionalization of the formed polymers.

However, 'controlled/living' supramolecular polymerizations are still unknown. In particular, their main advantage – the reversibility – seems to be the key obstacle in achieving these goals. The next decades of research in supramolecular polymerization will face this challenge.

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5.14 Chemistry and Technology of Step-Growth Polyesters

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5.14.1 Introduction

5.14.1.1 Historical

The discoveries and theories of Staudinger led Carothers to initiate his work on step-growth (polycondensation) polymerization.[1] The initial studies by Carothers on the preparation of aliphatic polyesters from the condensation reaction of diacids and diols are often cited as the first intentional synthesis of linear polymers by step-growth reactions.[2,3] Carothers and his research group studied many aliphatic polyesters synthesized by the melt condensation of aliphatic alcohols and aliphatic carboxylic acids. Early observations of the ability to draw ductile fibers from the melt apparently resulted in a practical goal of the research to develop synthetic fibers; however, these aliphatic polyesters were abandoned as fiber candidates because of their low glass transition temperatures (T_g), low melting points (T_m), ease of solubility, and sensitivity to hydrolysis. The inclusion of aromatic terephthaloyl groups from dimethyl terephthalate (DMT) by Whinfield and Dickson[2] in the early 1940s led to a semicrystalline polyester with acceptable T_g and T_m range for fiber applications and resulted in the huge commercial success of poly(ethylene terephthalate) (PET). PET is now one of the world's most important commercial polymers and finds many uses with principal applications in fibers and food/beverage packaging. It is the leading polyester in terms of sales and production volumes.[3,4] Other commercially important semicrystalline polyesters include poly(butylene terephthalate) (PBT), poly(1,4-cyclohexanedimethylene terephthalate) (PCT), and poly(ethylene naphthalane-2,6-dicarboxylate) (PEN). Amorphous copolyesters, commonly containing 1,4-cyclohexane dimethanol (CHDM) and ethylene glycol (EG) as co-diols, have also assumed a high level of commercial importance based on their combination of mechanical and optical properties. Many excellent books and reviews have been written on aliphatic and aromatic polyesters.[5–8]

5.14.1.2 General Polyester Characteristics

Polyesters have the ester group –CO–O– in their backbones and even though this polar group affects some molecular properties, the intermolecular and intramolecular interactions are not as strong as the hydrogen bonding that enhances properties of polyamides and polyurethanes. Generally, the characteristics of polyesters are dependent on the geometry, polarity, and segmental mobility of their repeating units which have their

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origins in the size, shape, and chemical composition of the diacids and diols used to synthesize the polymers. Polyesters have a wide range of applications ranging from biodegradable biomedical materials in devices for all-aliphatic structures, to food packaging plastics, composite matrix resins, flexible substrates for electronic devices, and thermoformed plastic sheeting for signs for aryl-aliphatic structures, all the way to high-flow polymers for all-aromatic rigid liquid crystalline polyesters that are used to inject mold very small and demanding parts for many electronic devices.

This chapter will first discuss the synthetic processes most commonly used to prepare polyesters and then include sections on the three main classes of polyesters based on their structures: (1) all-aliphatic, (2) alkyl–aryl, and (3) all-aromatic backbones. Each section will summarize important members of the class, describe some specifics about synthetic processes for each, and briefly highlight useful properties, with some applications, of selected polyesters in each class.

5.14.2 Synthetic Processes for Polyesters

In essence any synthetic reaction to form an ester should be applicable to preparing polyesters. However, practical synthesis of polyesters is limited to a few reactions due to the need for the high conversions necessary to achieve high molecular weight, as shown by the well-known Carothers' equation (eqn [1]):[9,10]

$$X_n = 1/(1-p) \qquad [1]$$

where X_n is the number-average degree of polymerization and p is the degree of conversion of functional groups.

Direct esterification of diacids and diols or transesterification of dimethyl esters and diols are the most common reactions used to prepare polyesters on large commercial scale. These polymerizations are performed in high-temperature melt-phase reactions most often in continuous processes.

Many reactions with appropriate reaction conditions could be used to prepare polyesters with high molecular weight, regular chemical structures, and even well-defined end groups. End groups are currently an issue of high research interest in polyesters. The recent publications of Kricheldorf *et al.*[11] suggest that all step-growth polymers that are prepared via a kinetically controlled reaction contain predominately cyclic structures, even at high molecular weight. High molecular weight, above the entanglement molecular weight, is necessary to achieve optimum mechanical properties of polyesters and is obtained by carefully controlling the stoichiometry of the high-purity monomers with precise functionality and by removing the condensation product to achieve very high conversions with the absence of side reactions. These requisites, plus economic factors, limit synthesis of polyesters to several classic methods and the selection of synthetic methods is also dependent on types of polyesters. Therefore, this chapter starts out with a discussion on the most commonly used synthetic processes for preparing polyesters.

Several synthetic methods are practiced for the preparation of polyesters, including direct esterification and transesterification reactions. These polymerizations can be carried out in solution, in an interfacial reaction, in the melt, or in the solid state. A few other coupling reactions, such as the Heck ester forming reaction,[12] have been employed to prepare polyesters.[6,13–16] A recent review covers traditional and novel approaches for processes for the preparation of polyesters.[17] The choice of polymerization technique depends on several factors, including the availability of the needed monomers; monomer, polymer thermal stability, or solubility; steric constraints in the diols, and so on. A brief discussion of several of the principal synthetic routes to polyesters is given below. The synthetic discussion is preceded by a brief discussion on polyester catalysts.

5.14.2.1 Polyester Catalysts

Transesterification and direct esterification polycondensations require catalysts to enhance polymerization rates and to obtain high molecular weight polyesters. A great deal, if not most, of the fundamental information on catalyst performance in melt-phase polycondensations is either buried in patents or is held as trade secrets by various companies that produce commercial polyesters. Since melt-phase polycondensation polymerizations are run under such harsh conditions, for example, often 250 °C and above, it is difficult to obtain mechanistic understanding of the exact role that catalysts assume during these high-temperature reactions. For example, the catalyst compound that is added to the polymerization is likely converted in most cases to the intermediate form that enhances the various steps in the polymerization. In general, it has been stated that basic catalysts are usually used in transesterification reactions to increase the nucleophilicity of the alcohol due to the formation of secondary bonding to the alcohol-proton.[18] The role of the acid catalysts is to coordinate the carbonyl oxygen enhancing the positive charge (electrophilic nature) on the carbonyl carbon atom, but the true catalytic mechanism of the most widely used metal catalysts is still unclear. One reason is that the initial catalyst often suffers undesirable exchange reactions with reactants and thus the catalytic activity and concentration of products are unknown. In fact the overall catalytic activity is involved in many complex reactions and coordination equilibrium between catalyst and functional groups.

Catalysts may also influence side reactions in addition to their effect on polymerization reactions. Catalysts with good catalytic activity for accelerating polymerizations often may not be suitable for use in preparing polyesters due to their similar influence on side reactions. For example, titanium alkoxides, such as titanium tetraisopropoxide and titanium *n*-butoxide, are excellent catalysts with high reactivity for many polyester preparations including PET, poly(propylene terephthalate) (PPT), and poly(ethylene succinate) (PES) synthesis.[19,20] They also have been widely employed as catalysts for the synthesis of cycloaliphatic polyesters, especially for those containing bicyclic systems.[21,22] However, due to side reactions (hydrolysis, etc.) and color-forming reactions (yellow polymers) these catalysts often are not acceptable or they must be used at low levels with a combination of other catalysts and additives to moderate their activity.

Antimony catalysts, such as antimony trioxide, antimony acetate, and EG antimony, have been reported as catalysts for the synthesis of PET.[23–25] Antimony catalysts have high reactivity with minimal side reactions. In particular, antimony trioxide is an effective catalyst for both transesterification and polycondensation stages of the polymerizations. However, the

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use of antimony catalysts often leads to the gray discoloration of PET due to the reduction of antimony catalysts to antimony metal during polymerization.[24,25] Another important drawback of antimony catalysts is their toxicity properties.[26,27]

Important tin catalysts for polyester synthesis include distannoxane,[28] stannous oxalate,[29] stannous octoate,[30] dibutyltin oxide,[31] tin(II) acetylacetonate, tin dioxide, and stannous acetate.[32] Stannous oxalate was found to be especially effective catalyst for the synthesis of PPT.[29] Sometimes tin catalysts are used in combination with titanium alkoxides to prepare copolyesters.[33] Dibutyltin oxide was also used to be a co-catalyst of antimony acetate to catalyze the synthesis of PET.[31] Tin catalysts are often not favored for industrial applications because of concerns about their toxicity.[34,35] Aluminum catalysts, such as triethylaluminum, aluminum acetate, and aluminum trialkoxide, are usually used as co-catalysts of alkaline earth metals for PET synthesis. A mixture of zinc acetate dihydrate and antimony(III) oxide or dibutyltin oxide was used as catalysts in the preparation of polyesters containing the norbornane structure.[36]

Recently, the use of catalysts involving some heavy metals like antimony in commercial polyesters has raised considerable environmental concerns in food contact and other applications, including their presence in polyester waste streams. Obviously, less toxic metals are of interest and would be favored for environmental reasons. Bismuth triflate has received considerable attention as a catalyst more recently because the Bi^{3+} ion is the least toxic heavy metal ion.[37–39] The triflates of bismuth, sodium, magnesium, aluminum, zinc, tin(II), scandium, and hafnium were used to catalyze the direct polycondensations of aliphatic dicarboxylic acids and aliphatic diols.[40] The employment of bismuth triflate was found to produce higher molecular weight polyesters when compared to other triflate catalysts.[40] Currently, Bi triflate has been widely applied in organic synthesis, including the acetylation of various alcohols by acetic anhydride.[41] For the polycondensation with 1,4-butanediol (BD), triflates are problematic since most triflates can catalyze the formation of tetrahydrofuran (THF) above 100 °C; therefore, a low temperature (≤ 100 °C) is required for the polycondensation of BD in the presence of triflate.

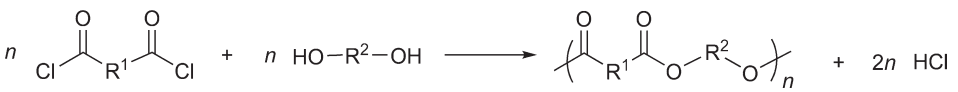
Various enzymes, such as lipases, novozyme435, and glycosidases, are used as catalysts for the synthesis of aliphatic polyesters based on aliphatic diols and diacids.[42–48] Enzymes work under mild conditions (≤ 100 °C) and can keep structure integrity when unstable monomers are polymerized. Furthermore enzymes have selectivity to reactions and avoid the occurrence of undesirable reactions. More importantly the enzymes are safe and avoid the introduction of metals.[49] Of course enzyme catalysts also have some serious disadvantages. For example, they are expensive and large amounts of these enzymes are required to obtain polyesters. Furthermore it is necessary to separate these enzymes from the reaction product at the end of the polycondensation.[46] Reviews are available on recent advances in enzymatic polymerization for polyesters.[49–51]

The development of various types of polyester catalysts was summarized recently.[52] In conclusion, high efficiency and environmentally friendly catalysts are the development trend for polyester catalysts. Some comments on specific catalyst compositions for the various polyester types are included in the following synthetic overview discussions.

5.14.2.2 Solution Polymerization

Several techniques are used to prepare polyesters in solution. The most used chemistry is the reaction of diacid chlorides and diols. This is the well-known Schotten–Baumann reaction, which is a reaction of acid chlorides with compounds containing active hydrogen atoms (–OH, –NH and –SH).[53]

The reaction of diols and diacid chlorides (eqn [2]) can be performed under mild conditions, at ambient temperatures or lower in the presence of a base, such as pyridine, which can act as a catalyst and an acid acceptor of the by-product HCl.[54,55]



[2]

Due to the high reactivity of acyl chlorides, the reaction of acyl chlorides with alcohol or phenol groups does not usually require a high temperature and it is essentially irreversible. Reactions of acyl chlorides with alcohols can also be carried out in bulk when the reactants and the polymer have low melting temperatures and are miscible. Acid chlorides are generally not suitable for synthesis of polyesters in the melt phase because of side reactions of the reactive acid chlorides. This solution-based chemistry is often employed when the final polyesters are not stable in the melt.[56] This reaction is typically performed in a dry inert solvent since water can react with the acid chloride in competition with the diol. Sometimes a higher boiling solvent can be used with a flow of an inert gas employed to remove the by-product HCl rather than using a base as an acid acceptor. The degree of reaction can be measured by titrating the hydrogen chloride removed. This type of solution polymerization is generally reserved for smaller scale polymerizations due to the high cost of acid chlorides, the need for dry solvents, and the cost of recycle of solvents, and the corrosive nature of the liberated hydrogen chloride.

The reaction rate, as well as the molecular weight of the polymer, is determined by many factors, such as the types of solvents, the base used as acid acceptor, the temperature, and even the order of addition of monomers.[57,58] For example, it has been reported that the reaction rate increased by more than 100 times when the solvent was changed from benzene to dichloroethane. It has also been found that the type of base can play an important role on the reaction rate. For instance, in the presence of triethylamine, the reaction of bisphenols with terephthaloyl chloride in dichloroethane is faster than 1,6-hexanediol. However, the order of the reaction rate is reversed when the weaker base pyridine was used.[59]

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The preparation of high molecular weight polyarylates from the direct reaction of aromatic diacids and bisphenols was accomplished using a condensation agent consisting of tosyl chloride, dimethylformamide (DMF), and pyridine. For example, the condensation of a 50/50 mixture of terephthalic acid (TPA) and isophthalic acid (IPA) and bisphenol A yielded a polyester with a weight average molecular weight (M_w) of 76 000.[60] A two-step solution copolycondensation was used to prepare high molecular weight polyarylates containing an aliphatic diol *p*-xylyleneglycol (PXG) at low temperatures (60 or 80 °C). The order of addition of monomers was studied and better results were obtained when PXG was initially reacted and then was followed by the reaction of bisphenols with the initially formed oligomers.[58]

Polyesterification reactions at room temperature were reported using carbodiimide condensation. This chemistry is reported to give high molecular weight polyesters from various aromatic dicarboxylic acids and dialkyl dicarboxylic acids and phenols. The mild conditions were found to be useful for the preparation of polyesters with chemically and thermally sensitive comonomers.[61] Low-temperature solution polymerization is also suitable for the synthesis of block copolymers because structural randomization resulting from the exchange reactions is limited at low temperatures. In addition to temperature, different microstructures ranging from random to alternating or block can be obtained by proper choice of other reaction conditions, such as solvents, base, and addition order of reactants.[58]

5.14.2.3 Interfacial Polymerization

Interfacial polycondensation reaction is an alternative process route to acylation based on the Schotten–Baumann solution reaction. This type of polymerization can be carried out interfacially by using a bisphenol dissolved in aqueous base (e.g., NaOH) solution and then adding the diacyl chlorides in an organic solvent, which is immiscible with water.[16] But this chemistry can also be successfully done in two immiscible organic solvents.[62] The two solutions are rapidly stirred and the polymer forms immediately at the interface. The polymer that is formed precipitates or remains soluble in the organic phase. In many cases a phase transfer catalyst, such as a tetraalkylammonium halide, is used to accelerate the reaction.[14] The reaction rate is relatively slow when aliphatic diols are used. Thus, this method is particularly useful for the preparation of aromatic polyesters where bisphenols are used, but is not appropriate for glycols with high pK_a values since it is not easy to form glycolate anions. This method is widely suitable for a vast number of bisphenols and diacyl chlorides.[6] However, it is difficult to obtain high molecular weight polymers when certain substituents reduce the basicity of the phenoxide ions or sterically hinder the reaction of the phenol groups.[6]

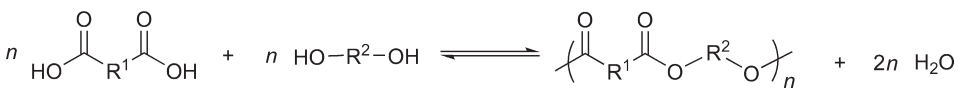
Acyl chlorides can react completely even with less-reactive bisphenols in this process. The reaction is proposed to be based on the S_N2 substitution mechanism, which involves the nucleophilic attack of a phenoxide ion on the acyl chloride.[16] However, it is believed that diffusion of reactants in the solution plays an important role in the overall mechanism and the processes are diffusion controlled.[54] The overall rate may be affected by many factors, including type of solvents, rates of stirring, temperature, phase transfer catalysts (quaternary ammonium salts), and even accelerators.[16,63] The transfer of phenoxide ions into the organic phase becomes easier in the presence of a phase transfer catalyst, which increases the polymerization rate. It is possible that side reactions, including the hydrolysis of the acyl chloride and β-elimination of HCl, may limit the molecular weights in some cases.[40] Therefore, nonaqueous systems can be used for interfacial polycondensation of bisphenols which have low reactivity toward acyl chlorides and whose phenylates have low solubility in water.[62]

Interfacial polymerization has an advantage in that it does not precisely require 1:1 stoichiometry in the comonomer charge since exact 1:1 stoichiometry is favored at the interface. The interfacial polycondensation procedure has been used to produce a wide variety of aromatic polyesters.[64,65] The interfacial polycondensation procedure can produce higher molecular weight polyesters than the melt polycondensation process. The main disadvantage is that large amounts of solvents are necessary.

5.14.2.4 Melt Polymerization

The melt-phase synthesis of polyesters by either direct esterification, starting with diacids and diols, or ester exchange, starting with diesters (usually the dimethyl esters) and diols is the most commonly used process to prepare polyesters on a large commercial scale. Melt-phase processes have a large advantage environmentally and economically since solvent recycle and/or disposal are not issues. Isolation of the polymer is also simplified since there are no solvents, nor additives to remove. In a continuous process this is most often accomplished by a tool that continuously chops the extruded rods of polyester from the finishing melt reactor into pellets. Two important prerequisites for successful preparation of polyesters in the melt include melt stability of the produced polymer and the melt viscosity of the polymerizing melt. An excellent discussion of melt-phase processes pertaining to the preparation of PET was recently published.[66] Because the two main reactions in melt polymerization, direct esterification and transesterification, are slow equilibrium processes, an acid or base catalyst is generally required to improve the reaction rate. Protonic acids, Lewis acids, and titanium alkoxides are typical acidic catalysts, which coordinate with the carbonyl oxygen and make the carbonyl carbon more susceptible to nucleophilic attack. As far as the basic catalysts are concerned, they convert the reacting hydroxyl group to the corresponding nucleophilic alkoxide anion, which is more effective intermediate for the interchange process.[5] Some specific catalyst systems are discussed in Section 5.14.2.1.

Direct esterification is the reaction of a diacid and diol or the self-condensation of a hydroxycarboxylic acid (eqns [3] and [4]):



[3]

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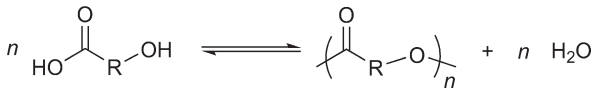


[4]

The dicarboxylic acid can provide protons to catalyze the reaction, but an additional acid catalyst is usually added to increase the reaction rate significantly since the concentration of carboxylic acid groups decreases as the conversion increases. A large number of compounds in the literature have been claimed as effective catalysts. These catalysts include strong protonic acids (such as H_2SO_4, benzene-, naphthalene-, and *p*-toluene-sulfonic acids); Lewis acids: oxides or salts of heavy metal ions (acetates are popular due to their higher solubility); and organometallic compounds of titanium, tin, zirconium, and lead. Titanium alkoxides and tin compounds, such as dialkyl-tin(IV) oxides, are frequently reported and have been found to be the most efficient catalysts.[67] A series of catalysts used in direct esterification have been reviewed.[68] However, certain catalysts can promote thermal degradation at high temperatures during the second stage of polymerization.[69] Thermal degradation can be minimized by adding phosphorus compounds, such as triphenyl phosphate or polyphosphoric acid, in calculated amounts at the end of ester exchange.[70] Although the role of the phosphorous-containing additives has not been totally defined, these additives are reported to complex with the organometallic catalysts, especially the titanium-based systems, and mitigate their activity.

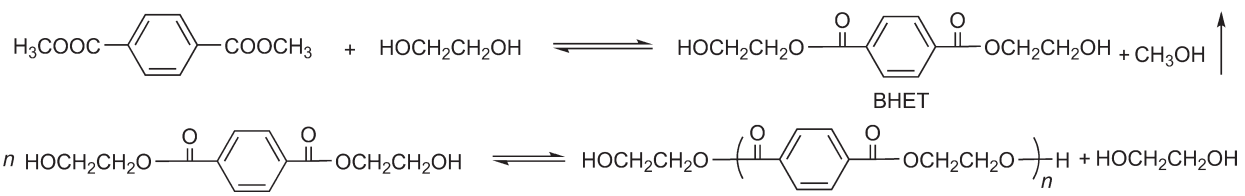
The by-product water in direct esterification must be effectively removed in order to push the equilibrium toward high molecular weight polyester since this is an equilibrium reaction. Thus high temperatures are required to achieve this. However, this reaction temperature must be chosen carefully to achieve a balance between the requirements for the reaction to proceed in a homogeneous melt and minimize the risk of thermal degradation over the required reaction time. The possible side reactions include ready decarboxylation or isomerization of *cis*-substituted reactants to *trans* structures. In melt-phase polymerizations it is difficult to achieve and maintain stoichiometric equivalence for the difunctional systems because the diol is usually quite volatile. Therefore, the diol is used in large excess with respect to the diacid in the initial stage. The direct esterification of a dianhydride and a triol is often used to produce cross-linked polyesters, such as glyptal polyesters based on phthalic anhydride and glycerol.[14,18] Recently, high molecular weight polyesters from direct polycondensations of dicarboxylic acids and aliphatic diols in bulk at mild temperature (35–100 °C) have been achieved by using special catalysts, such as scandium triflate and bismuth triflate.[40,71,72]

Transesterifications reactions (eqn [5]) are usually faster than direct esterifications and are very useful when the diacids have low solubility and/or are difficult to purify:[14]

[5]

Melt transesterification is often a practical route and suitable for large-scale industrial processes. It involves two different stages, namely the ester interchange stage and the polycondensation stage. The ester interchange process is generally carried out in the presence of an efficient transesterification catalyst, which is required to accelerate the reaction. Such catalysts include antimony oxide, carbonates, alkanoates, hydrides, or alkoxides of titanium, sodium, lithium, zinc, calcium, magnesium, and bimetallic alkoxides such as $NaHTi(OC_4H_9)_6$, $MgTi(OC_4H_9)_6$, and $CaTi(OC_4H_9)_6$.[5,15] The by-product from the initial ester exchange is an alcohol (i.e., methanol). This procedure is widely applied for the formation of homo- and copolyesters of aliphatic or alicyclic diols with aliphatic, alicyclic, aromatic, or heterocyclic diesters. The first stage is usually carried out at 150–200 °C until the alcohol is reacted completely. At the end of the ester exchange reaction, a bis (hydroxyalkyl)-terminated ester and/or an oligomer are obtained. The formation of bis(hydroxyethyl) terephthalate (BHET) and its oligomers during the preparation of PET is shown in **Scheme 1**.

In the second stage, the ester undergoes polycondensation by alcoholysis and forms the high molecular weight polyester.[5] The polycondensation step in the polymerization often requires a catalyst different from the ester exchange catalyst employed in the first step of the polymerization. For example, low levels of Ti alkoxides are often used for this stage, often in the presence of a phosphorous compound to moderate the activity of the titanium catalyst as discussed earlier. The by-product for each step of chain growth is the diol, which can be efficiently removed completely under reduced pressure at high temperatures from 220 to 290 °C to drive the equilibrium and obtain high conversion and high molecular weights. In order to achieve a homogeneous melt state of the polymer, the temperature generally is at least 20 °C above the highest melting temperature of the final product. Since each



Scheme 1 The formation of BHET and its oligomers.

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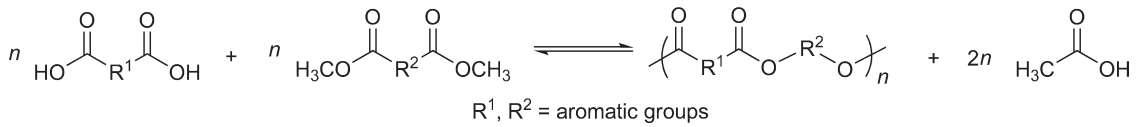
stage is an equilibrium and reversible process, continuous removal of the by-products is necessary to force the equilibrium to favor polymerization. It is extremely difficult to insure 1:1 stoichiometry due to the volatility of the diol as well as the possible sublimation of many diesters. Typically, the diol is added in at least 50 mol.% excess with respect to the diester. Thus this is helpful to insure 1:1 stoichiometry in the end and drive the ester exchange reaction to completion at a faster rate.

As stated earlier one main advantage of polymerizations in the melt is the elimination of solvents which simplifies product isolation, generally lowers production costs, and results in fewer environmental issues. Another attractive feature is that it is not necessary to worry about the solubilities of reactants and products in a solvent. Finally it is not necessary to control the stoichiometric balance of the two functional groups at the start of the polymerization if the diol is readily volatile. Stoichiometric balance is inherently achieved at the end of the second stage of the process. But melt polymerization requires relatively high temperatures to overcome the activation energy of transesterification between diester and diol. A partial or high vacuum is necessary to remove low molecular weight by-products (such as methanol and oligomers) and to push the equilibrium toward the formation of high molecular weight polyesters. However, the possible high viscosity of the reaction medium may prevent the removal of volatile by-products and lead to lower conversions. In the laboratory it can be somewhat difficult to transfer the product completely from the reactor; however, this is not a problem in large-scale continuous processes or even in large batch reactors where the molten product is extruded in rods and chopped into pellets.[11]

Acidolysis is a reaction of aromatic acetoxy group (or other ester-leaving group) with a carboxylic acid driven by the elimination of acetic acid (or other acid). The polymerization chemistry of preparing aromatic polyesters via the acidolysis is shown in eqn [6]:



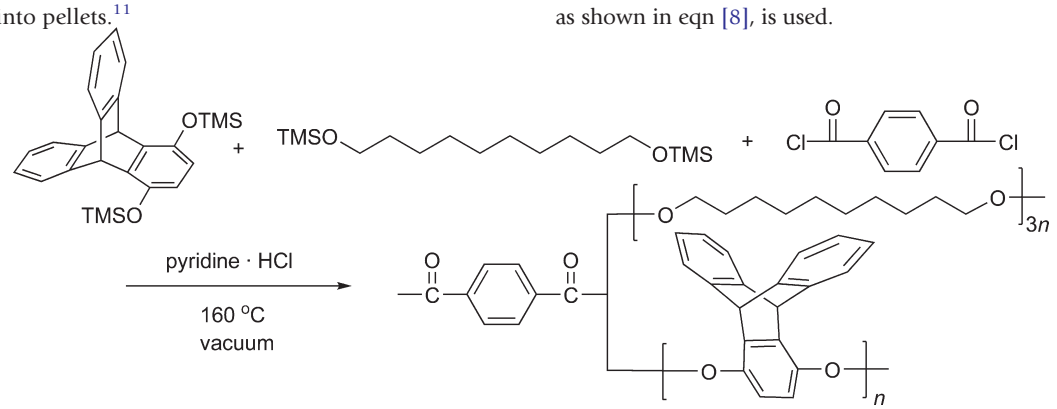
[6]

Acidolysis is suitable for the synthesis of all-aromatic polyesters. Typically, it is carried out at high temperature in the melt state and high vacuum to remove the by-product acetic acid and to push the equilibrium toward the direction of product formation.[14] The complex polymerization process has been studied extensively and clarified by Hall and co-workers.[73] The polymerization chemistry of preparing all-aromatic polyesters by the acidolysis route has been summarized.[56] The corrosive reaction environment and the high polymerization temperatures are routinely handled in special corrosion-resistant reaction systems in industry. However, the acidolysis polymerization often encounters some undesirable side reactions, including the cleavage of the acetate end groups to ketene and the free phenolic group and the decarboxylation at the oxybenzoic acid ends.

Polyesters can also be synthesized with di(trimethylsilyloxy) compounds and diacid chlorides by melt polymerization, shown in eqn [7]:[11]

[7]

For example, 1,4-di(trimethylsilyloxy) triptycene, 1,10-bis(trimethylsilyloxy)decane, and terephthaloyl chloride were copolymerized in the presence of pyridine hydrochloride at 160 °C to obtain the triptycene copolyesters in Swager's group.[74–76] The polymerization chemistry of triptycene copolyesters is shown in eqn [8]. In this chapter, due to the awkward structures required for representing copolyesters in the standard form, an abbreviated structural formula representation, as shown in eqn [8], is used.



[8]

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Kricheldorf *et al.*[11,77] also reported the polycondensation process of aliphatic dicarboxylic acid dichlorides with bis-trimethylsilyl catechol at 180 °C to yield cyclic polyesters.

5.14.2.5 Solid-State Polymerization

At times in melt-phase polymerization, when high melt viscosities make removal of the condensation products problematic, it is difficult to achieve the required conversions and molecular weights to have optimal properties for applications. A good example of this has been the commercial production of PET for stretch blow molded bottles. The first step in manufacture of a polyester bottle is to prepare injection molded preforms from PET pellets. Due to the melt strength needed in the preforms, as they are being blown into a bottle, a much higher molecular weight is required than is needed for other applications such as in polyester fibers. Attaining this high molecular weight in the melt phase was found to be difficult since the ability to achieve reasonable polymerization rates in melt-phase reactions involves raising the polymerization temperature to lower the melt viscosity so that the condensate can be removed to drive the reaction to the necessary high conversions. Long times in the melt at lower temperatures and short times at high temperatures often result in the formation of significant color from side reactions and other degradation products from chain end reactions. An example of a well-known thermal degradation reaction is shown in Scheme 2 and involves a chain cleavage and then elimination of acetaldehyde.[78]

Solid-state polymerization (SSP) was developed as a way to avoid the problems associated with conducting these melt-phase polymerizations under temperature and time conditions that led to unacceptable degradation reactions. A complete survey of SSP has recently been published.[79] In the SSP process used for polyesters, the polyester obtained from a melt-phase polymerization, which is usually mostly noncrystalline due to the fast cooling from the melt during the isolation step, is crystallized by heating above the T_g where the crystallization rate is fast. Since useful rates of polymerization in the solid state require temperatures significantly above the glass transition temperature, it is necessary to crystallize the prepolymer before subjecting the polymer pellets to SSP conditions. If this is not done properly, the amorphous pellets will fuse together and become unmanageable. The crystallized pellets or powder are then heated under vacuum or in a flow of inert gas at a temperature above the T_g but about 10–20 °C below the T_m. At such temperature, the polymer is thermally stable and the degradation reactions are eliminated or minimized. The chains have considerable mobility in the amorphous regions in the semicrystalline pellets and the catalyst is still active. The molecular weight increases in the amorphous regions since the end groups of the chain can migrate to react and the condensate can diffuse out of the amorphous regions. The polyesters thus obtained are of higher molecular weights and generally have less color and fewer side products that those obtained by trying to build high molecular weight in the melt phase.[5]

For the production of PET, it is reported that 16 000–19 000 M_n is readily achieved in the melt phase, but that SSP is required to achieve M_n in the 25 000 range. The conditions to achieve this increase in molecular weight involve heating semicrystalline pellets at around 200–220 °C for several hours under a nitrogen sweep. This is 40–60 °C below the melting point of PET which is approximately 260 °C. In addition to the increased molecular weight, the level of side products from the PET melt-phase process, such as acetaldehyde produced from chain cleavage and end group elimination as shown in Scheme 2, is greatly reduced since the temperature is below the activation energy for these side reactions and a gas flow helps to sweep acetaldehyde out of the pellets. Antimony oxides are cited often as excellent SSP catalysts for PET.

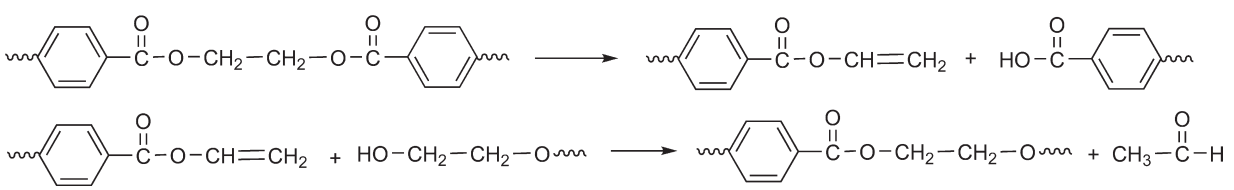
Other polyesters that readily undergo SSP are PBT, PPT, and poly(ethylene naphthalate) (PEN). Details on the SSP of various polyesters can be found in several chapters and references.[78,80,81]

5.14.3 Aliphatic Polyesters

5.14.3.1 Aliphatic Polyesters from Noncyclic Monomers

There has been a large renewal in recent years on the synthesis and properties of all-aliphatic polyesters.[82] All-aliphatic polyesters and copolyesters are of interest for biomedical applications because of the nontoxic properties of the polymers and their degradation products. Linear aliphatic polyesters possess excellent UV stability,[83–85] but they often have low T_gs and are hydrolytically and/or enzymatically degradable. Introduction of alicyclic units to the main chain of the polymer can impart enhanced T_gs and other mechanical properties due to the rigidity of the cyclic structures.[13] Therefore, this section discusses the information available on the synthesis and properties of aliphatic polyesters and catalysts used in polymerization.

Aliphatic polyesters can be synthesized from a large variety of linear and branched diacids and diols via many of the various synthetic methods discussed earlier. Their chemical and physical properties, such as crystallinity, T_gs, toughness, and degradability, can be modulated by carefully choosing the structures of the monomers. Due to the low T_ms of linear aliphatic polyesters, direct esterification of aliphatic diols and dicarboxylic acids in the molten state at high temperature (up to 240 °C) is the most synthetic convenient route. For example, PES, poly(trimethylene succinate) (PTS), and their copolyesters



Scheme 2 Thermal degradation reactions for SSP.

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with different compositions were synthesized via direct polycondensation in the presence of titanium catalysts.[19] Linear aliphatic polyesters are currently also synthesized by step-growth polymerization of a diol and a diacid derivative.[86] However, some aliphatic monomers, such as EG and dimethyl esters of succinic and adipic acids, may readily volatize at high temperature.[30] Polyoxalates and polymalonates are typically prepared from the corresponding diesters or diacyl chlorides instead of the diacids in order to avoid decarboxylation.[87] In fact, polyesters from oxalic and malonic acids are very susceptible to hydrolytic and thermal degradation and thus have few practical applications.

Anhydrides can replace diacids and react with glycol to produce polyesters. For example, succinic and maleic anhydrides are commercially available and can be used to prepare polyesters. Aliphatic polyesters can also be synthesized from diols and diacyl chlorides in solution at high temperature. However, the interfacial procedure is not suitable for the synthesis of aliphatic polyesters because aliphatic glycols do not usually provide an effective concentration of alkoxide ions in the presence of water.[16] A relatively new method to synthesize aliphatic polyesters is the enzymatic polycondensation of aliphatic diacids and diols under mild conditions in the presence of nonspecific lipases.[42,43,46,50] Takasu and Buzin *et al.* reported other new approaches, which allow for the direct polycondensation of aliphatic diacids and diols to produce high molecular weight polyesters in bulk under mild conditions by means of special catalysts, such as scandium triflate ($Sc(OTf)_3$) and bismuth triflate ($Bi(OTf)_3$).[40,71,72]

Even an available hydroxyl acid can be polymerized to produce aliphatic polyester.[86] An alternate and important method to synthesize aliphatic polyesters is ring-opening polymerization (ROP) of cyclic esters and their derivatives, such as ε-caprolactone, glycolide, and lactide.[86,88] However, ROP is outside the scope of this chapter and is included in another chapter in this work. In fact, lactic acid and other hydroxyacids, such as glycolic acid and 6-hydroxyhexaoic acid, can be polymerized by the direct condensation in an organic solvent and high molecular weights (up to 300 000 g mol^{-1}) were reported.[89] These copolymers, prepared by the A–B monomer condensation route, exhibit some properties that are different from the same composition prepared by the ROP process. For example, a ROP copolymer of L-lactide and glycolide has a T_m of 145 °C, while the copolymer prepared by condensation of the two hydroxyacids, at the same molecular weight, has a T_m of 135 °C. The differences are attributed to small variations in the sequence distributions of the comonomer units.[89]

In general, linear aliphatic polyesters are crystalline with low melting points and biodegradable with low hydrolytic stability. This type of property profile limits many commercial applications of linear aliphatic polyesters and copolyesters.[6] Many aliphatic polyesters from aliphatic diacids with different number of carbon atoms (2–19) and various diols have been synthesized and characterized.[30,86,90–92] Recently, the bio-based functional aliphatic polyesters were prepared from ω-carboxy fatty acids and diols in bulk or in diphenyl ether in the presence of Novozym 435 by two-step biocatalytic route.[92] The properties of the linear aliphatic polyesters are apparently affected by the chemical structures of their monomers. Odd–even effects of the number of carbon atoms of diol and diacid yield significant crystalline structure differences which result in a 'zig-zag' variation of melting points of the polyesters.[6]

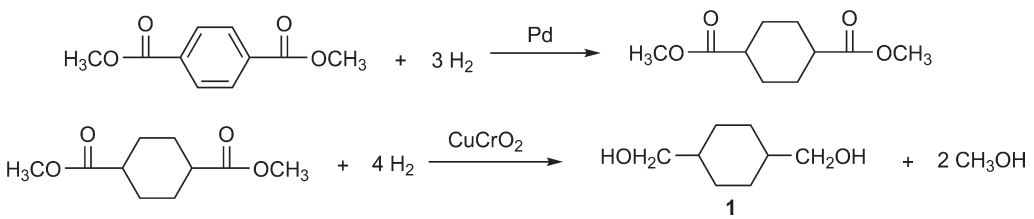
EG, 1,3-propane diol (PDO), BD, 1,6-butanediol, and so on are typically linear aliphatic diols used for the synthesis of polyesters.[40,86] Neopentyl glycol (NPG) is a particularly popular aliphatic 1,3-diol due to the absence of β-hydrogen atoms with respect to the ester groups. Furthermore, the introduction of methyl side groups to polyester chains is effective to improve hydrolytic stability and weatherability of polymers.[93,94] NPG has been incorporated into polyester backbones by replacing part or all of the other glycols.[95–99] Aliphatic copolyesters with diol end groups are widely synthesized and used as coatings or intermediates for polyurethanes. For example, aliphatic polyester diols, such as ethylene glycol/butanediol adipate (EBA), neopentyl glycol/butanediol adipate (NBA), and hexanediol adipate (HA), were used to prepare polyurethanes with increasing adhesive strength.[100] More detailed discussion of the applications of linear aliphatic polyesters has been reviewed in various books.[5,16,13,86,101,102]

5.14.3.2 Alkyl Polyesters with Cycloaliphatic Units

Generally, when alicyclic structures are incorporated into polyester backbones, the polyesters have higher glass transition temperatures and melting temperatures than the corresponding acyclic polyesters due to the limited chain motion. The properties of cycloaliphatic polyesters mainly depend on the specific structures, symmetry, and conformational features of the cyclic units and their compositions.

Many compounds containing cyclic structures are commercially available. CHDM **1** is a thermally stable commercial cycloaliphatic diol with an approximately 70/30 *trans*/*cis* ratio. It is readily incorporated into polyesters via high-temperature melt polymerization and has been used to prepare a variety of important commercial polyesters.[103–107] CHDM is produced by the hydrogenation of DMT as shown in **Scheme 3**.

PCT from CHDM was first manufactured by Eastman Kodak as a polyester fiber[104] and will be discussed in Section 5.14.4. 1,4-Cyclohexane dicarboxylic acid (CHDA) and its diester dimethyl-1,4-cyclohexane dicarboxylate (DMCD) are



Scheme 3 Preparation of CHDM.

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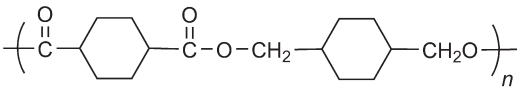
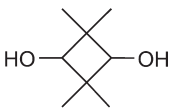
also important cyclic monomers for raising the T_g in aliphatic polyesters. The all cyclic polyester poly(1,4-cyclohexanedimethylene-1,4-cyclohexanedicarboxylate) (PCCD) 2 based on CHDA and CHDM has a repeating unit as follows:



2

PCCD has a T_g in the range of 40–70 °C and it does not have aromatic groups to absorb UV light; thus it possesses improved photo stability.[108–111] The T_m of PCCD is in the range of 220–235 °C and the polymer has a T_c located between 152 and 171 °C. The crystallinity of PCCD is affected by many factors, such as the isomeric state of CHDM and DMCD and the presence of branching reactions. During the polymerization, isomerization of *trans*-DMCD can occur and leads to an increase of the *cis* isomer content and a decrease of crystallinity. However, CHDM does not undergo isomerization during polymerization. Higher *trans* content often leads to a higher T_m, higher degree of crystallinity, and faster crystallization rates. PCCD has potential applications in many fields, especially in situations where weatherability or UV stability is required due to its resistance to weather and light.[108–111]

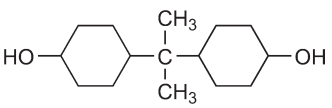
cis/*trans*-2,2,4,4-Tetramethyl-1,3-cyclobutane diol (TMCBD) 3 is a rigid, thermally stable, symmetrical, and commercial alicyclic diol which enhances many properties of polyesters. TMCBD can be prepared in high yield by pyrolysis of isobutyric acid to form dimethylketene, which spontaneously dimerizes to cyclic diketone. Hydrogenation of diketone in the presence of catalysts such as ruthenium[112] produces about 98% yield of *cis*/*trans*-TMCBD. TMCBD has the following structure:



3

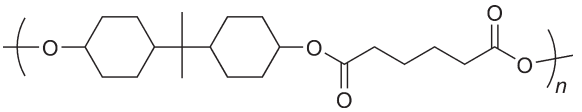
The monomer has often been used as a *cis*/*trans* (48/52) mixture in polymerization since it is tedious and expensive to isolate the pure isomers.[113] Recently, TMCBD-containing copolyesters were produced commercially by Eastman Chemical Company and they will be discussed in a later section. Although there has been considerable work on different aromatic polyesters derived from TMCBD by melt polymerization,[33,114] there appears to be little mention of incorporation of TMCBD into all-aliphatic polyesters. It is probably because the low reactivity of the secondary alcohols in TMCBD and the steric hindrance to these OH groups lead to problems in obtaining reasonable molecular weights with aliphatic and cycloaliphatic diesters and diacids.

2,2-bis(4-Hydroxycyclohexyl)propane (HBPA) 4 can be synthesized by hydrogenation of bisphenol A and has the following structure:



4

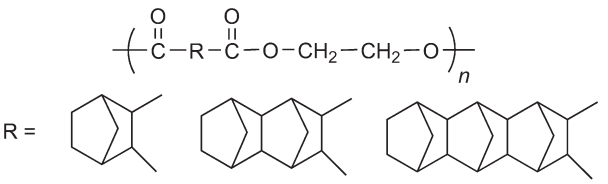
High molecular weight polyesters from HBPA with various diacids have been reported but an elimination reaction was also reported to be a problem.[115–117] Among these copolyesters, poly[2,2-bis(4-hydroxycyclohexyl)propane adipate] 5 exhibits enhanced physical properties, such as impact strength and elongation when compared to some other engineering plastics like PBT, polycarbonate (PC), and Nylon 66.[115]



5

This polyester, 5, exhibited superior notched impact strength and enhanced elongation due to the cyclohexyl rings, which can dissipate energy through molecular motions by the conformational transition of chair-boat-chair. The weak transitions of cyclohexyl rings in PCT were observed by Yee *et al.*[118] and proposed to contribute to the mechanical properties of these polyesters.

Bicyclic compounds, such as norbornane diesters and dimethanols, have been synthesized by Wilson and Hamb for the synthesis of polyesters.[36,119] Increasing the number of norbornane residues in polymer side chains results in increase in T_g (from 40 to 156 °C for structure 6 from left to right). This is because the bulky three-dimensional norbornane ring leads to reduced segmental mobility.



6

Bicyclo[2.2.2]octane and bicyclo[3.2.2]nonane rings containing polyesters were studied by Taimr and Smith.[21] The terephthalate polyester of 1,4-bis(hydroxymethyl) bicyclo[2.2.2]octane exhibits a high T_m (more than 300 °C), while the analogous polyesters based on 1,5-bis(hydroxymethyl) bicyclo[3.2.2]nonane possessed much lower T_ms (≤ 170 °C) due to the less symmetry of bicyclo[3.2.2]nonane ring. The cycloaliphatic polyesters from 2,6-decahydronaphthalene dimethanol and 1,2-CHDA/1,3-CHDA/CHDA were synthesized as coating components, which exhibited good weatherability.[120] More recently, a series of amorphous copolyesters 7 based on aliphatic diols (EG and CHDM) and different cycloaliphatic diesters, including DMCD, dimethyl bicyclo[2.2.1]heptane-1,4-dicarboxylate (DMCD-1), dimethyl bicyclo[2.2.2]octane-1,4-dicarboxylate (DMCD-2), dimethyl bicyclo[3.2.2]nonane-1,5-dicarboxylate (DMCD-3), and 1,4-dimethoxycarbonyl-1,4-dimethylcyclohexane (DMCD-M), were prepared. Their structures are shown as follows and the copolyester based on DMCD-2 was found to have a highest T_g (up to 115 °C) among these copolyesters.[22] All the cycloaliphatic copolyesters were observed to have secondary relaxations due to the conformational transitions of the cyclohexylene rings.

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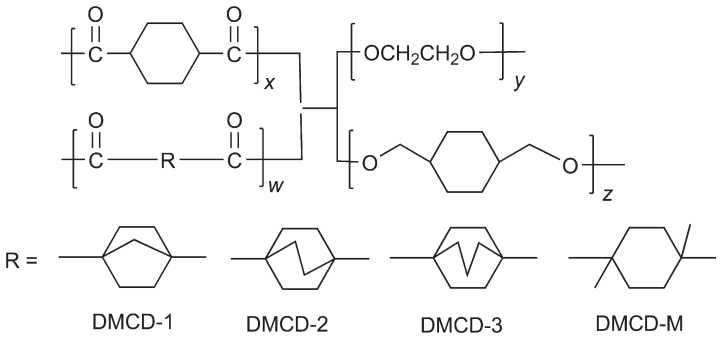
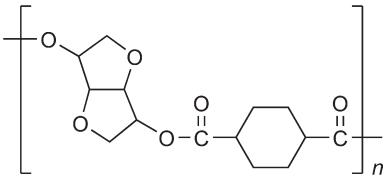


7

Isosorbide is a commercially available diol from renewable resources. A variety of aliphatic and aromatic polyesters were synthesized from isosorbide.[121–125] The bulky structure of isosorbide hinders crystallization, but it limits molecular mobility, and thus, isosorbide is useful to raise the T_g of a polyester by incorporating into the polyester backbone. For example, poly(isosorbide terephthalate) has a T_g up to 190 °C and exhibits superior thermal stability.[126] The T_gs of polyesters prepared from isosorbide also depend on its comonomers and can vary in a wide range. A recent paper reported the synthesis of the homopolyester 8 based on *cis*/*trans*-CHDA and isosorbide.[127] This cycloaliphatic polyester has the following structure:



8

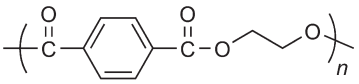
The homopolyester has a T_g more than 100 °C and even above 140 °C in some cases when the relative average molecular weights are higher than 10 000 g mol^{-1}.[127] In fact heat distortion temperatures above 100 °C are desirable for many potential applications. Succinic acid was also used to prepare polyesters of isosorbide to adjust T_g and increase the hydrolytic degradation rate. The T_gs of copolyesters may still remain above 100 °C when the content of succinyl units is less than 40 mol.%. Therefore, the homopolyester and copolyesters of isosorbide can be potentially used as transparent engineering plastics.[127] However, control and elimination of color in isosorbide-containing polyesters were reported to be a problem.[128]

5.14.4 Aryl–Alkyl Polyesters

5.14.4.1 Semicrystalline Polyesters

5.14.4.1.1 Poly(ethylene terephthalate)

PET 9 is a condensation homopolyester prepared from TPA or DMT and EG and has a repeating unit



9

PET was first commercialized by Imperial Chemical Industries, Ltd. (ICI) as 'Terylene'. Although unmodified PET plastics have been known for many years, PET use in injection-molding parts is disadvantageous because of the low rate of crystallization.[129] The melting point of commercial PET is located in the range of 255–265 °C. The glass transition temperature of PET is about 80 °C and can increase with increasing degree of crystallinity and orientation.[129] The slow crystallization rate of PET renders it useful in applications where mechanical orientation can induce crystallization during stretching processes such as in biaxially oriented films, in stretch blow molded beverage bottles, and in fibers. The application of PET in food and beverage containers accounts for more than 20% of PET consumption and is fast growing due to ease of processing, barrier properties, esthetic properties of the containers, recycle ease,[130] and cost. PET is suitable for oriented films and textile fibers when it has a number-average molecular weight M_n of 16 000–20 000 g mol^{-1}. More than 70% of the PET produced is used as fibers. The remaining 10% PET is consumed as extruded film and in engineering plastics, including electrical and electronic, automotive, lighting, power tools, sporting goods, and materials handling. However, higher M_n values of about 25 000 g mol^{-1} and greater are required for stretch blow molding preforms into containers. PET for fiber applications is produced directly in the melt phase and fiber spinning lines are often directly integrated at the end of the melt-phase PET production so that the fiber can be directly spun from the melt. PET used for stretch blow molding containers such as bottles is generally produced in a two-stage process. The melt-phase-polymerized PET is extruded, cooled, and the amorphous pellet extrudate is chopped into pellets and then crystallized. As discussed earlier, these semicrystalline pellets undergo SSP to produce high molecular weight PET.[131,132]

Synthesis of PET via melt polymerization generally requires a two-component catalyst system, such as zinc acetate and antimony trioxide, in order to produce high molecular weight material. New, highly active PET catalysts have been developed and some of them are commercially available.[133] The current development state of PET catalysts, such as antimony catalysts and titanium catalysts, were recently reviewed.[134] However, at

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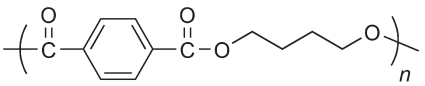
high temperatures and long time periods during the melt polycondensation of PET, some side reactions, such as thermal degradation and an intermolecular ether-forming reaction, can take place between the β-hydroxyethyl ester end groups and produce diethylene glycol (DEG), which is incorporated into the polymer chain. Thus the resulting resins possess a lowered melting point and crystallinity, decreased mechanical strength, lower thermo-oxidative resistance, and poorer UV stability.[135,136] It is generally accepted that PET degrades by random chain scission at the ester linkages. The thermal degradation mechanism can be found in several related studies.[5,69,137]

The PET industry is very large in terms of the amount of polymer that is produced although the volumes are considerably lower than the commodity polymers such as polyethylene, polypropylene, and polyvinyl chloride. In 2008, approximately 5.4 billion lbs of PET were used in bottle manufacturing in the United States. The global PET market size is estimated to reach approximately 105 billion lbs by 2011 and only about 20–30% of PET goes into bottle production. Because of the reversible nature of the ester bond of PET and the ease of collection of PET bottles, PET has had considerable success as a recycled polymer. For example, in 2008, approximately 1.5 billion lbs of PET was recycled in the United States from containers which is about a 27% recycle rate. Any melt reprocessing of PET lowers the molecular weight and yields PET with molecular weight too low for reuse in stretch blow molding bottles without a process to rebuild the backbone molecular weight. However, recycled PET can find direct use in many fiber and composite applications. Recycled PET can also be chemically degraded to monomers for repolymerization or to difunctional oligomers that can be used in coating and polyurethane adhesives.[138]

5.14.4.1.2 Poly(butylene terephthalate)

PBT **10** is a step-growth or condensation homopolyester prepared from BD with DMT and has the repeat unit:



10

PBT was originally brought into the market as a replacement for phenolic resins in automotive applications in the mid-1970s by Hoechst-Celanese. It is a semicrystalline thermoplastic polyester and has a melting point of 230 °C, which depends on sample preparation and annealing time. PBT has a much faster crystallization rate than PET, and this is important in differentiating it and leads to applications which are not amenable for PET use. PBT has a T_g range from 30 to 50 °C, even as low as 20 °C.[139] Its T_g can vary greatly with crystallinity and the choice of measurement method. Due to the high crystallization rate and the ease of processing, PBT is often used in injection-molding applications and in fiber-containing semicrystalline composites and is more widely used than PET in many of these applications. The success of this engineering plastic is primarily attributed to high mechanical strength, toughness, high heat distortion temperature (up to 215 °C for glass fiber-reinforced PBT), fast crystallization rates, high continuous use temperature (140 °C), dimensional and chemical stability, and short processing cycle times in injection molding. The global demand for PBT continues to increase. Of course, the properties of PBT could be strongly affected by the crystalline portion and the resulting morphology after processing.

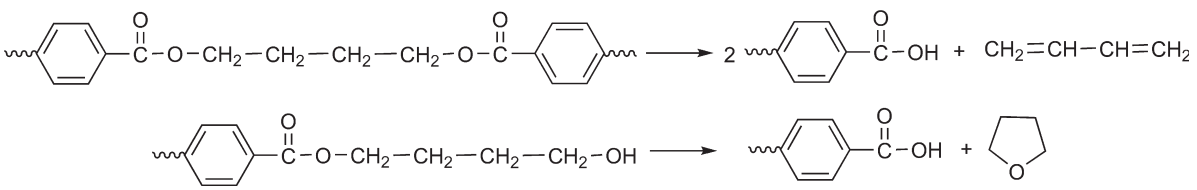
The properties of PBT can also be widely modified to meet the different needs in various fields of applications, such as electronics, automotive, and fiber cable industries. Typical methods include copolymerization, blending with other polymers, and addition of reinforcements, stabilizers, and so on. PBT has been widely used in electronics (computer housings), automotives (automobile bumpers), housewares, lighting, power tools, sporting goods, and plumbing. PBT exhibits good electrical insulation properties which are actually not affected by temperature and humidity.[129] However, these materials do not show good weather resistance without the presence of stabilizers. Polymer degradation can occur due to UV exposure, especially in the existence of heat, oxygen, moisture, or other pollutants. The degradation results in the loss of impact strength.

PBT, like PET, is usually synthesized via melt polymerization methods in a two-stage process.[8] Bishydroxybutyl terephthalate (BHBT) is formed during the first stage, that is, the transesterification of DMT with BD. Then PBT is formed from BHBT in the polycondensation stage with the elimination of BD. However, PBT undergoes faster chain β-scission reaction than PET after long reaction times at high-temperature melt conditions. In this case, 1,3-butadiene and carboxyl functionalities are the degradation products. THF can be formed when a 4-hydroxybutyl ester terminal group is transformed into a carboxyl group (**Scheme 4**).

PBT resins contain fewer impurities than PET because the side products of the polymerization, THF and butadiene, are volatile. Solid-state polycondensation can also be used to obtain high molecular weight PBT to meet specific applications.[78] Typically, the SSP of PBT occurs at a lower temperature (200–225 °C), but it exhibits a higher polymerization rate in the solid state than that of PET due to its low T_m.[78]

5.14.4.1.3 Poly(propylene terephthalate)

PPT **11** was first synthesized by Whinfield and Dickson in 1941 and this aromatic–aliphatic polyester has the following repeating unit:



Scheme 4 Formation of 1,3-butadiene and THF.

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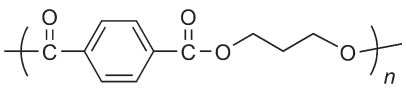


11

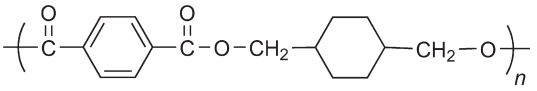
PPT was not commercialized until recently because PDO was not available on a commercial scale.[140,141] More recently PDO became available from Shell via a reported hydroformylation reaction of ethylene oxide using a cobalt catalyst.[142] DuPont has developed a commercial process for PDO from renewable resources by enzymatic fermentation of glycerol.[143] In 1998, PPT was commercially produced and has attracted much attention in fibers, films, and engineering thermoplastics applications. Other wide ranging applications have been developed in various fields, including carpet, textile and nonwoven fibers, papermaking machine fabrics, cheese packaging, and artificial leather. It was reported that PPT has a T_g between 42 and 72 °C dependent on thermal pretreatment process and T_m is about 237 °C.[144] PPT can be processed for use as magnetic recording disks, bottles, and electric connectors by molding, and it can also be melt processed to obtain fibers, films, and molded parts using various processing methods.[145]

Recently, much interest has been focused on PPT fibers because of its better elastic recovery than PET and PBT.[144,146–148] Furthermore, because of the excellent resilience, the properties of PPT are close to those of polyamides, such as nylon 66 in certain ways. Thus it combines certain advantages of polyamides and polyesters. PPT fibers also possess excellent dyeing in boiling water without carriers, stain resistance, high UV stability, low water absorption, and good electrostatic resistance.[20] PPT fibers have two trade names: One is 'Corterra' originally offered by Shell and the other is 'Sorona' by DuPont de Nemours. PPT has mechanical performances located in between those of PET and PBT, but its mechanical properties can be considerably enhanced for these glass-reinforced or other high-modulus short fiber-reinforced PPT materials.[145]

Although PPT was initially prepared from terephthalic acid (TPA) and 1,3-propanediol (PDO) in the 1950s, it has been mainly synthesized by transesterification of PDO with dimethyl terephthalate (DMT) similar to poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT). Recently, there exists a tendency to use the more economic TPA route. For example, Karayannidis and co-workers prepared PPT polyester directly from TPA and PDO in the presence of various catalysts, including antimony acetate, antimony oxide, titanium *n*-butoxide, and germanium oxide.[20] Titanium *n*-butoxide ($Ti(OBu)_4$) was found to be the effective catalyst for both esterification and polycondensation stages. These polyesters with $M_n < 70\,000\,g\,mol^{-1}$ are suitable for melt spinning.[141]

5.14.4.1.4 Poly(1,4-cyclohexanedimethylene terephthalate)

PCT 12 is prepared from DMT with *cis*/*trans* mixture of CHDM and has a repeating unit



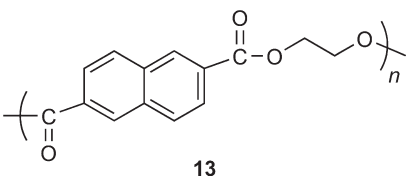
12

PCT fiber was successfully marketed in the industry for many years until it was discontinued in the 1980s.[104] PCT was also introduced as a molding resin with specific use such as connectors for the electronic and automotive markets. PCT has a high heat deflection temperature (~260 °C) and is much cheaper than liquid crystalline polymers. One specific advantage of PCT is that it has similar flow characteristics during molding with that of PET and PBT even at high temperatures; thus it can be used in conventional injection-molding equipments. PCT composites with glass-fiber reinforcement provide excellent high-temperature performance for injection-molded parts.

PCT has a high melting point which is determined by the *cis*/*trans* ratio of CHDM. The melting point of PCT is approximately 315 °C for *trans*-CHDM and 250 °C for *cis*-CHDM.[104] The T_g also increases from 60 °C to about 90 °C for *cis* and *trans*, respectively. Crystalline PCT exhibits a higher T_m than PET (300 vs. 260 °C) and an enhanced T_g (88 vs. 80 °C). PCT has a slower crystallization rate than PBT and its crystallization behavior is close to that of PET. PCT possesses low moisture uptake and the properties are less sensitive to moisture than PET and PBT because of the more hydrophobic CHDM units. Due to the high melting point and the high melt viscosity of PCT, high processing temperatures (up to 300 °C) during molding are required which can lead to thermal and thermo-oxidative degradation and dramatic drop in viscosity and can yield injection-molded parts with inferior properties.[149] The structural weakness of PCT comes from the two tertiary hydrogen atoms located in the β-position to the ester group. Typically various additive packages including thermal oxidative stabilizers and chain extension agents are employed in PCT injection-molding formulations.[149]

5.14.4.1.5 Poly(ethylene naphthalate)

Poly(ethylene naphthalate) (PEN) 13 is typically prepared from EG and dimethyl-2,6-naphthalene dicarboxylate (DMN) by a transesterification process since purification of 2,6-naphthalene dicarboxylic acid (NDA) is difficult. PEN is different from PET since its polymer chain possesses condensed aromatic rings – naphthalene group instead of the single ring – TPA. PEN has a repeating unit



13

The fundamental differences resulting in the polymer structure and property as a result of changing the terephthalic units in PET to naphthalate units in PEN have been reviewed.[150] PEN has a higher melting temperature in the range of 250–290 °C and it is harder to crystallize than PET.[151] PEN usually crystallizes at higher temperature and at a slower rate due to the rigid

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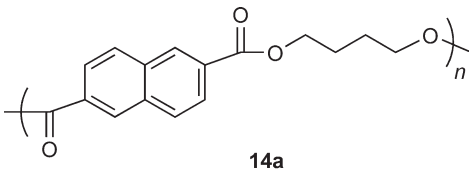
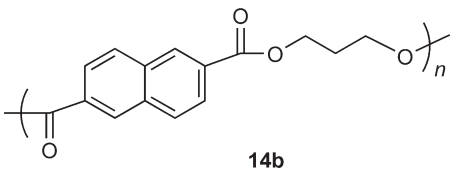
naphthalene ring; therefore, it is necessary to apply more complex conditions of annealing to achieve the suitable crystallization rate. The most important characteristic of PEN is improved stiffness due to the presence of the naphthalene ring. PEN possesses a higher glass transition temperature (about 125 °C) than that of PET (80 °C).[152] PEN is found to exhibit excellent thermal, mechanical, barrier, and chemical resistance properties when compared to PET and PBT.[153] For example, PEN is observed to have superior oxygen barrier properties, which are approximately 5 times higher than those of PET and this higher oxygen barrier renders PEN as an excellent polymer for packaging foods and beverages that are susceptible to oxygen degradation.[152] Currently, PEN homopolymer, copolymers, and blends are being studied in various containers requiring improved barrier properties. The higher heat resistance and excellent solvent resistance properties of biaxially oriented PEN films have made PEN the choice for many applications in photographic films and flexible display applications.[154,155] Multilayered thin films based on PEN have large reflectivity and have seen widespread use in liquid crystal displays.[156]

The SSP processes are still the best methods to achieve high molecular weight PEN. However, the SSP temperatures are typically located in the range of 230–240 °C because of its relatively low reactivity.[157] PET can be modified by 2,6-naphthalene dicarboxylic acid (NDA) to produce amorphous copolymer, but crystallinity can be induced by thermal annealing when the concentration of NDA is low.[158] Since PEN shows strong fluorescence, the fluorescence properties of poly(ethylene terephthalate-co-2,6-naphthalene) were studied.[159] PEN became commercially available from Teijin Ltd., Japan, in 1973. Over the past 35 years there has been an interest in exploiting the higher T_g and higher barrier properties of PEN in container applications; however, these applications are hindered by the expensive nature of DMN. In addition, manufacturing and molding operations are often hindered due to the high processing temperatures required for PEN.

Poly(butylene naphthalene-2,6-dicarboxylate) (PBN) **14a** is a relatively new semicrystalline polyester with excellent chemical resistance, as well as mechanical, thermal, and insulating properties; thus PBN fibers can be applied in many fields. PBN has a T_m of 247 °C and a T_g of 48 °C,[160] and exhibits fast crystallization rates like PBT. The flexibility of the long butylene groups and the interchain interactions between the naphthalene rings result in the improved PBN chain mobility and fast crystallization. However, it is difficult to obtain PBN in amorphous glassy state by cooling from the melt in contrast to PEN.[161]



14a

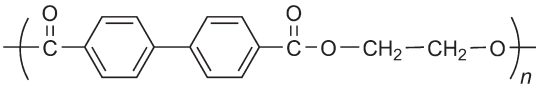


14b

Poly(trimethylene 2,6-naphthalenedicarboxylate) (PTN) **14b** has a T_m of 204 °C and a T_g of 83 °C.[162–164] There have been relatively few studies on this polyester in comparison to other polyesters from commercially available monomers. The preparation of PTN was reported in detail via the polycondensation of DMN with 1,3-propanediol and high molecular weight polymer was obtained.[162] The catalytic reactivity was found to have the following order: Sb(III) < Zr (IV) < Sn(IV) < Ti(IV).[162]

5.14.4.1.6 Poly(ethylene bibenzoate)

4,4′-Biphenyl dicarboxylic acid (BDA) can be synthesized by a selective alkylation[165] and then an oxidation process.[166] A low-cost route to produce BDA from toluene via oxidative coupling, isomerization, fractional crystallization, and final oxidation was reviewed.[167] BDA has been polymerized with various aliphatic diols.[168–174] Polyesters with long-chain aliphatic diols form highly ordered thermotropic smectic mesophases; on the other hand polyesters of BDA with short-chain aliphatic diols have melting points that are very close to the decomposition temperature; poly(ethylene bibenzoate) (PEB) **15** was prepared from BDA and an excess of EG in the existence of titanium isopropoxide and has the following structure:[175]



15

X-ray diffraction studies indicated that PEB melts at about 337 °C to form a mesophase and then changes to an isotropic liquid at 367 °C.[168] When other diacids or diols are copolymerized with PEB, the crystallinity of PEB can be disturbed and this makes the material melt processible.

BDA is also a good modifier for high-performance thermoplastics. It was incorporated into PET to enhance the properties of PET to widen the application opportunities. Introduction of BDA into PET results in a copolymer with an increase in T_g, modulus, strength, and oxygen barrier properties.[158,176,177] The copolyester has a T_g range from 85 to 105 °C depending on the content of BDA (up to 50%). These types of BDA-containing copolyesters could be attractive for applications where high T_g and clarity are important; however, BDA is not produced on commercial scale. When the concentration of BDA is high, the copolymers are highly crystalline and have high crystallization rates from the melt. However, copolymers with high levels of BDA could not be achieved easily because of the high insolubility and intractability of BDA. Thus bis-hydroxyethylbibenzoate (HEB) and oligoethylene bibenzoates were synthesized and employed as comonomers in the PET processes.[175]

BDA was also used to synthesize a series of 'thermotropic liquid crystalline polyesters' with different lengths of flexible spacers in the main chain by the melt polycondensation method.[178] Copolyesters exhibit greater thermal stability of mesophase and higher glass transition temperatures compared to phenyl analogs.[178] Biphenyl-4,4′-dicarbonyl chloride was also polymerized with bis(6-hydroxyhexyl)dimethylsilane in solution to produce a main chain polyester with strong ferroelectric liquid crystalline character.[179] BDA and acetylated

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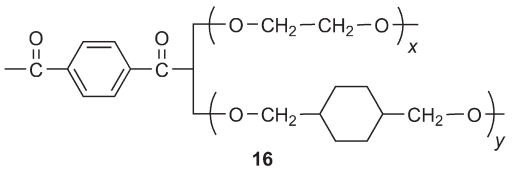
4,4′-biphenydiol (ABD) were polymerized in inert aromatic solvent at temperatures ≤ 300 °C to obtain oligoesters. The polycondensation of biphenyl-4,4′-dicarbonyl chloride with free diphenols in Marlotherm-S at 400 °C proceeds to produce highly crystalline polyesters, which undergo several transitions with increasing temperature (more than 400 °C).[180]

5.14.4.2 Amorphous Copolyesters

Semicrystalline polyesters such as PET, PCT, and PBT can be copolymerized with other glycols or with other diacids to prepare copolyesters with slow crystallization rates. At sufficient comonomer incorporation levels the copolyesters remain amorphous under normal melt processing conditions used in injection molding and extrusion and under use conditions. The most common amorphous copolyesters used in commerce have the abbreviations PETG, PCTG, and PCTA. These important classes of amorphous copolyesters are discussed below.

5.14.4.2.1 Copolyester based on PET with different amounts of CHDM

Poly(ethylene terephthalate) glycol (PETG) **16a** refers to copolyesters based on terephthalic acid and ethylene glycol that are copolymerized or modified with up to 50 mol.% of another glycol (the 'G' in PETG). The most common second diol is CHDM and the PETG name is applied to the copolyesters with enough CHDM content to slow crystallization rates so that the copolyesters remain amorphous under processing conditions. The lower limit is approximately in the 20 mol.% range of CHDM. Lower levels of CHDM in PET lead to crystallization rate modifications that are tuned for controlling crystallization in the stretch blow molding process for bottles and other containers.[181] Therefore, when CHDM is contained in the compositional range from 20 to 50 mol.%, PETGs are typically amorphous and no crystallization peaks are observed in DSC curves.



16

Structure represents PETG **16a** when *x* is the major glycol component; Structure represents PCTG **16b** when *y* is the major glycol component

Clear, tough, and amorphous PETG polyester has been widely accepted in specialty packaging applications because its high clarity and strength are even better than PET and other transparent resins, such as poly(methyl methacrylate).[181] PETG has the largest single application in the heavy gauge sheet market. In the last decade, its trade name Spectar™ based on proprietary manufacturing technology was introduced by Eastman Chemical Company. Spectar™ copolyester possesses excellent color, optical, and physical properties and are extruded into heavy gauge sheeting that is widely used for point-of-purchase displays.[181] A PETG sample based on TPA with about 70 mol.% EG and 30 mol.% CHDM possesses excellent physical properties with a flexural modulus above 2.1 GPa.[181] Although PETG has higher flexural modulus than PCTG, its elongation to break (110%) and notched Izod impact strength are less than PCTG.[181]

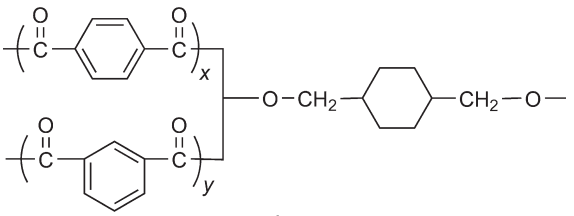
5.14.4.2.2 Copolyester based on PCT with different amounts of ethylene glycol

PCTG **16b** refers to the modification of PCT with ≤50 mol.% EG. The melting points of PCTG drop dramatically when the EG content is increased. Thus inclusion of EG in the PCT backbone slows the crystallization rate and renders these copolyesters amorphous under standard processing conditions. Of course the normally amorphous PCTG copolyester could be intentionally induced to crystallize by a specific heat treatment process.[181]

PCTG copolyesters can be processed into various articles with desirable properties by extrusion or injection molding. Particularly, PCTG copolyester prepared with about 40 mol.% of EG has superior clarity and toughness and is accepted in markets for injection-molding thin-wall medical components. PCTG is well suitable for molding such components due to its excellent resistance to gamma-ray sterilization and its ability to maintain its high elongation to break.[182] A PCTG sample based on TPA with 65 mol.% of CHDM and 35 mol.% of EG exhibits improved toughness when compared to PETG due to the existence of the large amount of CHDM units in the backbone.[181]

5.14.4.2.3 Copolyester based on PCT with different amounts of isophthalic acid

PCTA **17** is an acid-modified PCT copolyester. The most commonly used diacid modifier to prepare PCTA copolyesters is IPA or the dimethyl ester of IPA. PCTA refers to PCT compositions modified with up to 50 mol.% IPA and has the following structure:



17

The structure represents PCTA **17** when $y \leq 50$ mol.% IPA.

As mentioned before, PCT has such a high T_m (up to 295 °C) that higher processing temperature (above 300 °C) is required to process the homopolymer and it results in the occurrence of thermal decomposition.[181] When IPA is incorporated at the low level of 5–10 mol.%, the processing window can be enlarged by lowering the melting point of the polyester while retaining the crystallinity, T_g, and toughness of the PCT homopolymer. At higher IPA incorporation levels, chain crystallization is limited so dramatically that the copolyesters do not crystallize at 35 mol.% of IPA or higher.[183,184]

Amorphous PCTA compositions are transparent and tough and have good hydrolysis and chemical resistance. PCTA can be applied as precision-molded parts and can also be extruded into clear sheeting, pipe, and shaped products.[181] PCTA has an attractive feature, that is, it can be melt processed without extensive pre-drying process. This is a result of the presence of hydrophobic CHDM as the diol in the backbone and absence of hydrophilic EG. PCTA prepared from about 70 mol.% TPA and 30 mol.% IPA has a T_g of 88 °C and

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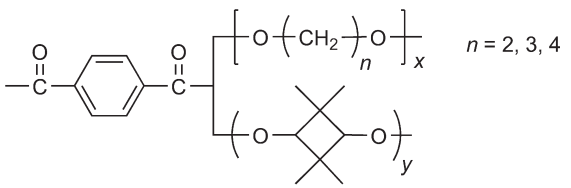
other typical properties are comparable to PETG and PCTG as described in Sections 5.14.4.2.1 and 5.14.4.2.2.[181]

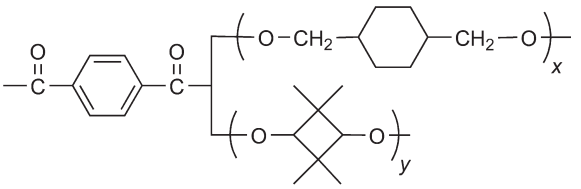
5.14.4.2.4 Polyesters with 2,2,4,4-tetramethyl-1,3-cyclobutanediol units

The monomer TMCBD is another glycol that has been studied extensively as a modifier and property-enhancing glycol for polyesters. There has been considerable work on different polyesters derived from TMCBD by melt polymerization.[33,114–187] Aromatic homopolyesters of TMCBD have been primarily high melting and semicrystalline materials.[188–190] Melting points for the polyesters from DMT and TMCBD, that is, the homopolymers, are 316–319 °C (38/62 *cis*/*trans*),[188] 269–308 °C (*cis*), and >350 °C (*trans*).[33] Kelsey *et al.*[33] synthesized random copolyesters **18** based on DMT, rigid *cis*/*trans*-TMCBD, and flexible aliphatic glycols (two to four carbon atoms) over a range of compositions. The structures of aromatic copolyesters are shown below:



18

The copolyesters prepared from DMT with TMCBD and flexible aliphatic glycols are typically amorphous, transparent materials and soluble in chloroform when the TMCBD (~50/50 *cis*/*trans*) content was 40–90 mol.% of total diols.[33,191,192] Studies show that lower *trans*/*cis* TMCBD isomer ratio may decrease crystallinity. The T_gs are 80–168 °C and dependent on the proportion of rigid TMCBD units. The rigidity of TMCBD unit can decrease the degree of freedom in the copolymers and therefore increase their T_gs. For example, the T_g of a copolyester made from a 78/22 mole ratio of TMCBD/BD with DMT was raised by nearly 100 °C relative to the homopolymer made from BD with DMT.[33] The amorphous TMCBD copolyesters have been found to exhibit excellent physical properties, including high thermal stability, UV stability, clarity, low color, and high T_g (up to 168 °C).[33,192] Furthermore, the highly steric hindrance of the two methyl groups in TMCBD can lead to exceptional hydrolytic stability. Recently, a new family of copolyesters based on PCT modified with TMCBD was commercialized by Eastman Chemical Company with the trade name 'Tritan copolyesters' **19**, which have the following structures:



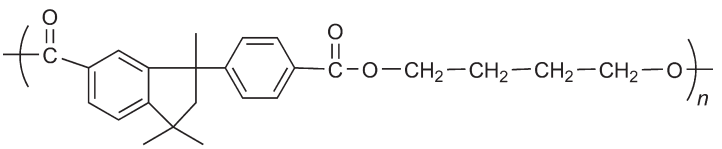
19

These copolyesters have T_gs greater than 100 °C and have found large markets in kitchenware, signs, and so on.[193] Because of health concerns about bisphenol A in bisphenol A polycarbonates, Tritan also has considerable market growth in food container applications. Other high T_g copolyesters, with T_g values in the 200 °C range, prepared from TMCBD and bisphenols with diacid chlorides such as terephthaloyl chloride have been reported.[194] These TMCBD-containing copolyester materials can be used in such applications as lenses, packaging, and compact disks. They also have potential high-temperature outdoor applications due to high impact resistance combined with good weathering resistance.

Tin[188]and lead catalysts have been employed successfully for TMCBD polymerization, although the latter has a tendency to produce gray polymers. Tin compounds like dibutyltin oxide were found to be good catalysts for transesterification of TMCBD with DMT when the flexible co-diol is PDO or BD instead of EG.[33] But it is still not clear why tin catalysts are so much better in these cases than other typical polyester catalysts, such as titanium alkoxides.[33]

5.14.4.2.5 Polyesters with 1,1,3-trimethyl-5-carboxy-3-(4-carboxyphenyl)indan dicarboxylic acid units

1,1,3-Trimethyl-3-(4-carboxyphenyl)-5-carboxyindan dicarboxylic acid (TMCID) has been known for many years and was polymerized with BD to obtain a polyester **20**, which has the following structure:



20

This polyester has much higher glass transition temperature (above 90 °C) than PBT (only 22 °C) and exhibits excellent rigidity.[195] The kinked indan unit in the backbone foils chain packing and results in noncrystalline amorphous structures. In particular the polyesters of TMCID with several norbornane-containing dimethanols possess extremely high T_g, up to 200 °C, which indicates the great effects of chain stiffness on the T_g of these polyesters.[195] The copolyesters derived from the indan (TMCID), DMCD, and tricyclodecanedimethanol were prepared by typical melt polycondensation conditions in the presence of titanium tetraisopropoxide (200–400 ppm) under nitrogen.[196] High temperature (280 °C) and low pressure (10 mmHg) were applied. The obtained indan-containing polyesters have a M_w of

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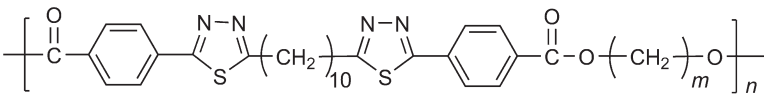
27 000 g mol^{-1} with a polydispersity index (PDI) of 1.90.[196] The indan-containing polyesters can be blended with thermoplastic resins and processed into transparent products.

5.14.4.2.6 Semirigid thermotropic liquid crystalline polyesters

Semirigid thermotropic liquid crystalline aryl–alkyl polyesters **21** were prepared from several aliphatic diols and a twin biphenyl analogue of 1,3,4-thiadiazole having a decamethylene segment in the central part by melt polycondensation.[197] The polyesters have the following structures and form a monotropic nematic phase due to the lateral dipole interaction based on the twin biphenyl analogue of 1,3,4-thiadiazole:



m = 8, 10, 12

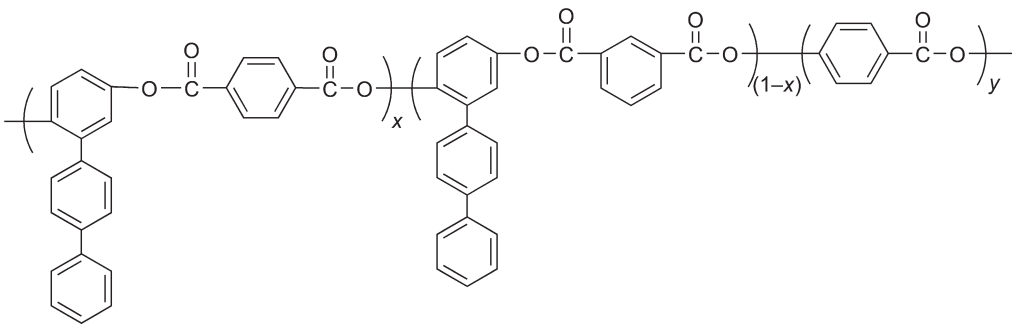
21

5.14.5 All-aromatic Polyesters

All-aromatic polyesters, often termed poly(arylates), have attracted considerable research and commercial interest since they can be the backbones for excellent high-performance polymeric materials. Although the term poly(arylate) generally refers to polyesters that contain all-aromatic groups, more specifically it denotes the composition based on 50/50 TPA/IPA and bisphenol A. These materials were commercialized in the 1970s by Hoechst-Celanese and Unitika and have very high glass transition temperatures at around 180 °C. All-aromatic or highly aromatic polyesters can be divided into two main classes: 'amorphous high T_g materials' such as the TPA/IPA bisphenol A polymer described above and 'liquid crystalline aromatic polyesters' where the structural properties arise from the rigidity and packing capabilities of the aromatic polyester chains.

A homopolymer prepared from *p*-hydroxybenzoic acid (HBA) ester was likely the first all-aromatic polyester and this material was commercialized as Ekonol. It has a T_g over 500 °C and is also highly crystalline and possesses high mechanical strength.[198] Copolymers of PET and HBA were likely the first liquid crystalline polyesters and were prepared by a melt ester exchange process with *p*-acetoxybenzoic acid and PET.[199] The earliest commercial liquid crystalline polyester was based on HBA and 6-hydroxy-2-naphthoic acid (HNA) with a trade name 'Vectra', which is used as a high-tech engineering plastic in various applications, such as electronic and healthcare applications.[200] Investigation of the size and shape of the aromatic units in all-aromatic liquid crystalline polyesters has received considerable research investment.[201] Many different rod-like mesogenic units have been studied enchained in a polyester backbone. The biphenyl unit has been one of the most intensely studied, to establish fundamental structure–property relationships.[202] A detailed discussion of liquid crystalline polyesters is covered in another chapter in this volume.

Since all-aromatic polyesters usually have low solubility and suffer processing difficulties, development of new aromatic polyesters with better solubility at high temperature has been an area of research interest. In order to improve solubility of the macromolecules without excessively sacrificing their high thermal stability, bulky pendent groups can be introduced into polyester backbones. For example, Mallakpour and Kolahdoozan[203] reported a series of new organosoluble, thermally stable aromatic polyesters with pendant aromatic or heteroaromatic rings by direct polycondensation reaction. The introduction of pendent imide rings disturbed the strong interchain interaction and improved the solubility while maintaining good thermal stability. A series of wholly aromatic rigid polyesters and copolyesters **22** containing (4-biphenyl) side groups were also synthesized based on 2,5-dihydroxyterphenyl and 2,5-dicarboxyterphenyl.[204] They have the following structures:



22

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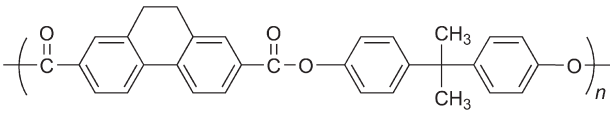
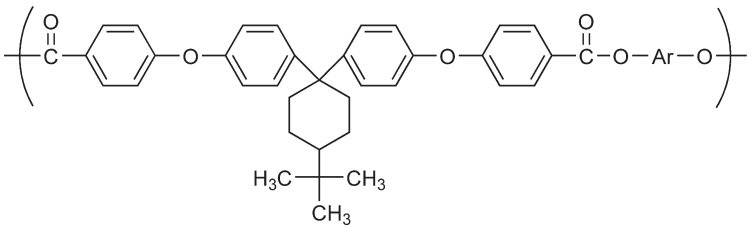
The introduction of these bulky aromatic side groups has enhanced polymer processibility but still retained the thermostability at a high level. Most of these polymers are amorphous with T_gs of 155–170 °C because the chain packing is disrupted by the bulky, rigid (4-biphenyl) group.[204] Another series of wholly aromatic polyesters were prepared from carbonylation–polycondensation of dihalobiphenyls (such as 2,7-dibromo-9,10-dihydrophenanthrene) and bisphenols in the presence of palladium catalyst (Pd-PPh_3). The polyesters possess high solubility and high molecular weights (M_w is higher than 100 000 g mol^{-1});[205] thus transparent casting films were formed. The following structure is one example of these aromatic polyesters:



23

Liaw *et al.* synthesized various soluble cardo (pendent cyclic units along the polymer backbone with one atom in the backbone rendering these cyclic groups perpendicular to the neighboring backbone groups) aromatic polyesters **24** with higher T_gs (up to 197 °C) and better solubility than bisphenol A-based aromatic polyesters.[206]



24

A series of polyarylates based on 1,1,3-trimethyl-3-(4-chloroformylphenyl)indanecarbonyl chloride with various bisphenols were prepared in an organic solvent–aqueous alkaline solution system in the presence of a phase transfer catalyst.[207] These polyarylates are amorphous and exhibit high solubility in organic solvents. Transparent and tough films can be obtained by solution casting and have tensile modulus of 1.2–1.6 GPa. These polyarylates possess T_gs of 205–310 °C and they start to decompose at about 350 °C in air.[207]

Another method to improve the processability and solubility of all-aromatic polyesters is to synthesize 'hyperbranched aromatic polyesters'.[208] In addition to their high thermal stability and good processability, hyperbranched aromatic polyesters have low solution and melt viscosities due to their globular shape with a large amount of functional groups distributed in the internal and external parts of polymers.[209–211] They can be used in blends as rheology modifiers.[212] Recently, a convenient room temperature solution polycondensation was developed to prepare hyperbranched all-aromatic polyesters directly from the commercially available monomer 3,5-dihydroxybenzoic acid in the presence of catalyst 4-(dimethylamino) pyridinium 4-tosylate.[213] When compared to the traditional melt polycondensation, this simple solution polymerization avoids the use of preactivated or protected monomers. Furthermore, the degree of polymerization can be easily controlled by the reaction time. The mild reaction conditions result in completely colorless polyesters with narrow polydispersity.[213]

Most of all-aromatic polyesters are synthesized by acidolysis at high temperature (up to 250 °C) followed by the release of acetic acid.[56] The thermotropic liquid crystalline Vectra is prepared by heating a mixture of HBA and HNA in the presence of acetic anhydride. The acetoxy groups converted from phenolic hydroxyl end groups react with the carboxylic acid end groups to form the ester groups.[200,214,215] Copolyesters based on 2,5-dihydroxyterphenyl diacetate with IPA and TPA were prepared by high-temperature polycondensation in a melt.[204] However, it is preferred to use direct polycondensation of aromatic carboxylic acids and aromatic phenols in solution in the presence of a suitable condensing agent due to the occurrence of some side reactions in melt polymerization. In the last several decades some condensing agents, such as diphenyl chlorophosphate and arylsulfonyl chlorides, have been developed in direct polycondensation reaction.[60,216,217] The Vilsmeier adduct derived from tosyl chloride (TsCl) and DMF in pyridine (Py) has been reported as a good condensing agent for the synthesis of aromatic polyesters with high molecular weights by the direct polycondensation of aromatic dicarboxylic acids and bisphenols.[57,60,203,218–220] Better results were obtained by a two-stage solution copolycondensation of IPA/TPA (50/50) with diols, such as PXG, and several bisphenols using the same condensing agent.[58,221]

5.14.6 Summary

Polyesters and their associated production and processing technologies are constantly changing and still improving based on new research and development and new needs in the marketplace. The fundamental underpinning of this technology has been the mainstay semicrystalline and amorphous polyesters: PET, PBT, PETG, and PCTG. These basic structures are now commodity type polymeric materials. Because of the unique characteristics of the ester bonds, polyesters, especially PET, are leading polymers for recycle and thus sustainability. An everlasting need for higher performance and better properties continues to drive research in the polyester area. For example, new commercial polyesters based on PDO and TMCBD are experiencing fast growth in commercial markets. Polyesters based on sustainable monomers may present future opportunities for growth. It is likely that polyester science and

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technology will remain as important areas of investment and the new and improved polyester materials that result from these investments will enhance the utility of polyesters for today's and tomorrow's societies.

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Biographical Sketches

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5.15 Biodegradable Polyesters

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5.15.1 Introduction

The stability of conventional synthetic polymers like polyolefins to the degrading action of living systems, chemicals, or light is considered a limitation in several areas where they are used for a limited period of time before becoming waste. The importance and relevance of (bio)degradable polymers are further strengthened due to the promising applications in various medical and nonmedical fields like agriculture, medicine, pharmacy, and biomedicine, and also because of their environmentally friendly nature.[1] Many examples are found in the medical, biomedical, and pharmaceutical fields where degradation has brought about some desired effects. For example, biodegradable polymers find application as resorbable sutures, as resorbable plates and screws, as scaffolds for the growth and repair of tissue and organs, and as drug carriers for the delivery of drugs.[2–4] This scenario makes the studies related to the design, synthesis, and properties of degradable polymers extremely important and relevant.

Degradation is a process of polymer chain breakage by the cleavage of bonds between the monomers in the polymer backbone leading to a size reduction. This is characterized by a decrease of molecular weight and mechanical properties with the loss of newly formed monomers and oligomers. The degradation can be brought about by photo, mechanical, thermal, and chemical means besides biodegradation. According to the European Committee for Standardization, a biodegradable polymer is a material in which degradation results from the action of microorganisms with ultimate conversion to water, carbon dioxide and/or methane, and biomass. This could take place, for example, in soil, natural water, human beings, and animals. Generally, high-molecular-weight polymers based on the C–C backbone like vinyl polymers tend to be resistant to hydrolysis, oxidative cleavage, enzymatic attack, and other reactions and are, therefore, not (bio)degradable, whereas heteroatom-containing polymer backbones confer (bio) degradability.[5] Heteroatom-containing polymers include polyesters, polyamides, polycarbonates, polyanhydrides, polyphosphates, and others, and the rate of biodegradation depends upon the type of chemical linkage, crystallinity, morphology, porosity, and other characteristics. A large number of commercially available biodegradable materials as environmentally friendly materials or for medical and nonmedical applications are based on aliphatic polyesters (heterochain macromolecules having carboxylate ester groups (–COO–) in the backbone).[2,3,6–12] Biodegradation is an enzymatically catalyzed hydrolysis of the heterobonds like ester bonds in the polymers. The first step of degradation is a surface erosion process as enzymes cannot penetrate into the polymer bulk, and forming water-soluble intermediates, which then are assimilated by microbial cells and are thereby metabolized. In this chapter, the term biodegradable also includes polymers that are degraded in biological environments by nonenzymatic hydrolysis and the depolymerization intermediates are then finally metabolized by microorganisms or resorbed by the body in the case of medical applications (i.e., bioabsorbable polymers).

This chapter deals with the general introduction of biodegradable polyesters, in particular the aliphatic polyesters made by condensation polymerization, classification of biodegradable polyesters, macromolecular architectures of biodegradable polyesters, and their applications.

5.15.2 Synthetic Routes to Polyesters

In general, the conventional synthesis of polyesters is either by ring-opening polymerization (ROP) of cyclic esters or by condensation polymerization (condensation of the diacids/diacid derivatives with diols) (Scheme 1).

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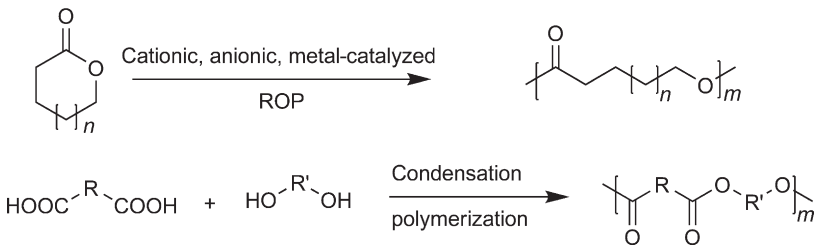


Scheme 1 Conventional synthetic routes to polyesters: ROP of cyclic esters and condensation polymerization.

5.15.2.1 Ring-Opening Polymerization of Cyclic Esters and Polycondensation

A lot of literature is already available, and is still increasing day by day, on the use of different initiator systems like cationic, anionic, and metal catalysts, as well as on the mechanisms of ROP of cyclic esters for the synthesis of aliphatic polyesters.[13–17] Commercially available aliphatic polyesters like polycaprolactone (PCL) and polylactide (PLA) are made by metal-catalyzed (mostly tin octoate) ROP in high molecular weights. Recent advances in the ROP of lactones and related compounds can be seen in detail in review articles.[18,19]

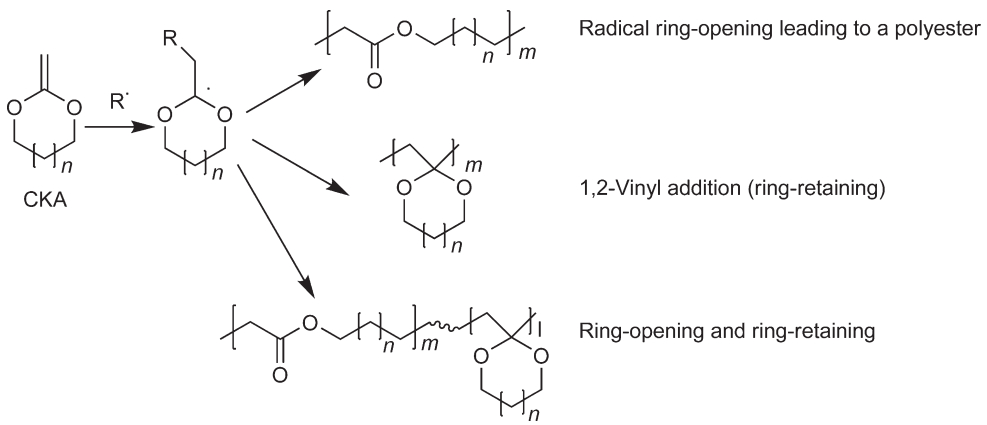
Furthermore, the synthesis of aliphatic polyesters by condensation polymerization is also well explored.[20,21] The corresponding high-molecular-weight polyesters are not accessible by direct condensation of the related carboxylic acids and diols because of the reversibility of the condensation reactions, cyclization reactions, and the high conversion of the reaction required.

5.15.2.2 Radical Ring-Opening Polymerization of Cyclic Ketene Acetals

Another route to the synthesis of polyesters, which is not very well explored, is by radical ring-opening polymerization (RROP) of cyclic ketene acetals (CKAs).[21–25] CKAs are the isomers of the corresponding cyclic lactones and can undergo radical addition at the vinyl double bond with subsequent possibilities of either ring-opening or ring-retaining or a combination of the two (Scheme 2). For such reactions, conventional radical initiators like azobisisobutyronitrile (AIBN), di-*t*-butylperoxide (DTBP), or benzoylperoxide (BPO) are used depending upon the polymerization temperature.

The ring-opening after radical attack gives the polyester with the same structure as from the ring-opening of the corresponding isomeric cyclic ester. For example, the RROP of CKA, 2-methylene-1,3-dioxepane (MDO), gives aliphatic degradable polyester, PCL,[26,27] which is conventionally obtained by metal-catalyzed ring-opening of caprolactone (Scheme 3).

During the free radical reaction of CKAs, the probability of ring-opening over 1,2-vinyl addition reaction depends on the monomer concentration, temperature, ring size, substituents, and other parameters. The driving force for the ring-opening, in general, is the relief of ring strain or the formation of ester linkages as a carbon–oxygen bond is about 40 kcal mol^{-1} more stable than a carbon–carbon double bond.[28] Although the method offers the advantage of using free radical chemistry, low volume shrinkage, and other properties, it could not attract many researchers in the past. Achieving very high-molecular-weight homopolyesters by this route is a little problematic because of backbiting reactions. After the pioneering work of Bailey *et al.*,[28] there was slow progress in this field. Recently, the synthesis of degradable polymers has raised interest in this promising synthetic method. This is the only method that allows the combination of ester units with the C–C backbone of vinyl polymers in a random way to generate a new class of degradable materials poly(vinyl-*co*-ester)s simply by copolymerization of CKAs with the corresponding vinyl monomers. The resulting polymers besides being (bio)degradable could also be useful for a variety of speciality applications as precision materials, adhesives, ionomers, and thermoplastic elastomers.[29–35] The details of chemistry, chances, and limitations



Scheme 2 Different reaction possibilities during RROP of CKAs for the formation of polyesters.

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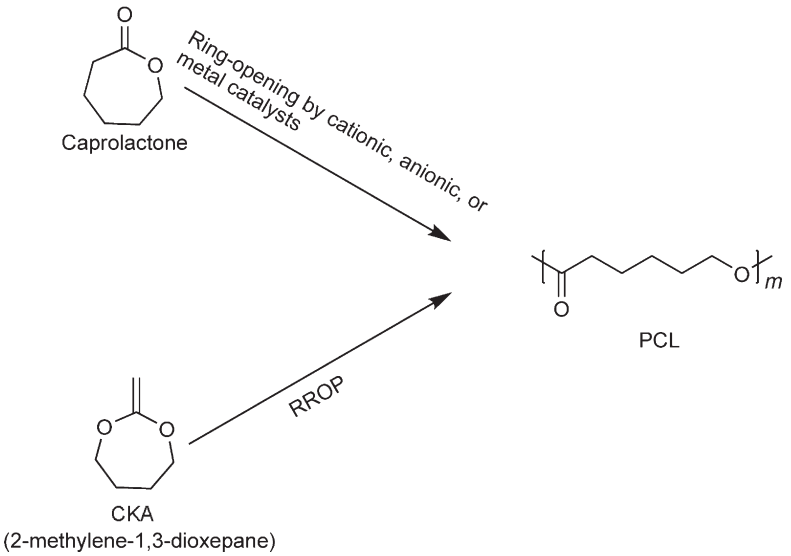


Scheme 3 RROP as an alternative to the synthesis of aliphatic polyesters like PCL.

of this method of generating degradable functional polyesters can be found in a recent review article.[36]

5.15.3 Classification, Biodegradability, and Applications of Polyesters

Aliphatic biodegradable polyesters are classified as natural and synthetic polyesters (Table 1).

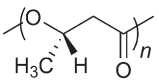
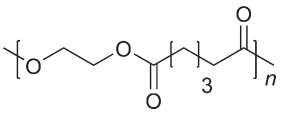
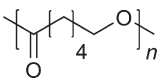
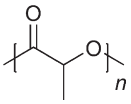
The synthetic polymers could be further classified based on natural building blocks or petrochemical building blocks. The natural polyesters have the advantage of being produced from renewable resources and are mostly low-priced but generally have low reproducibility and batch-to-batch variation in properties. The synthetic polymers based on natural building blocks, on the other hand, are also from renewable resources but show good reproducibility of material properties and structure control.

5.15.3.1 Polyhydroxyalkanoates

Poly(3-hydroxyalkanoate)s (PHAs) are natural polyesters of microbial origin (Scheme 4). The first known PHA was poly(hydroxybutyrate) (PHB) (melting temperature (T_m) = 180 °C, glass transition temperature (T_g) = 5 °C, isolated and characterized by Lemoigne in 1927 from *Bacillus megaterium*).

The cells of *B. megaterium* could contain as much as 44% of their dry weight of PHB depending upon the growth conditions.[37] A historical review of bacterial polyesters is provided by Lenz and Marchessault.[38] The enzyme ketothiolase (1) catalyzes

Table 1 Classification of biodegradable aliphatic polyesters with representative examples

Biodegradable polyester	*Type*	*Representative example*	*Chemical structure*
Natural polyester	Poly(3-hydroxyalkanoate)	Poly(3-hydroxybutyrate)	 Poly((R)-3HB)
Synthetic polyesters	Polycondensates of diols and diacids Poly(alkylene dicarboxylates)	Poly(ethylene adipate)	
	Lactones (poly(ω-hydroxyalkanoates))	Poly(ε-caprolactone)	
Bio-based synthetic polyester	Lactides (poly(α-hydroxy acids))	Poly(lactide)	

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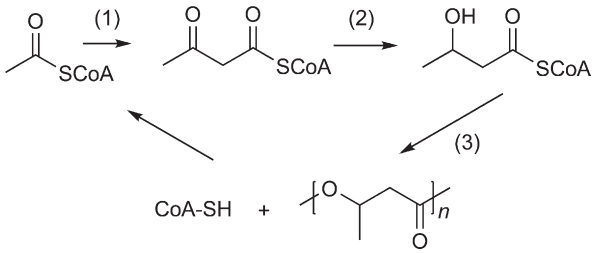
Poly-(*R*)-3-hydroxybutyrate Poly((R)-3HB) Poly-3-hydroxyvalerate (P3HV)

Scheme 4 Chemical structures of PHAs.



Scheme 5 The enzyme ketothiolase (1) catalyzes the dimerization of the coenzyme A derivative of acetic acid, acetyl-CoA, to acetoacetyl-CoA, and a reductase (2) catalyzes its hydrogenation to [*R*]-3-hydroxybutyryl-CoA monomer, which is polymerized to PHB by a synthase (3).

the dimerization of the coenzyme A derivative of acetic acid, acetyl-CoA, to acetoacetyl-CoA, and a reductase (2) catalyzes its hydrogenation to [*R*]-3-hydroxybutyryl-CoA monomer, which is polymerized to PHB by a synthase (3) as shown in Scheme 5.

PHB is a highly crystalline, water-insoluble, chemically inert polymer with poor processability and mechanical properties. Biopol is the commercial PHA product (copolymer of hydroxybutyrate and hydroxyvalerate) developed by ICI and later bought by Zeneca (Great Britain) and then by Monsanto.[39] PHAs vary in their properties like flexibility, crystallinity, and melting points depending upon the physicochemical–biochemical properties of the producing microorganism, the conditions of biosynthesis, and the carbon source. The physical and mechanical properties of bacterial PHA copolymers can be regulated by varying their molecular structure and copolymer compositions. The introduction of hydroxyalkanoate comonomers like hydroxyvalerate into a poly(3-hydroxybutyrate) (P3HB) chain greatly improves its mechanical properties. The polyester derived from the activated sludge is hetero-PHA with components from hydroxybutyric acid, hydroxyvaleric acid, hydroxyhexanoic acid, and hydroxyheptanoic acid.[40] This has more ductility and a low melting point. PHAs can be easily processed from melt or from solution. An interesting thing with PHAs is that they can compete in mechanical properties with polyolefins like polypropylene (PP) and polystyrene (PS) but in addition have better oxygen barrier properties, better resistance to UV light, and better resistance to water and heat. A comparison of physical properties of PHAs with those of some conventional nonbiodegradable and biodegradable polymers like PS, low-density polyethylene (LDPE), PCL, PLA, polyethylene terephthalate (PET), and Ecoflex (polytetramethylene adipate terephthalate) is given in Table 2.[39,41b]

Some of the application areas of PHAs are in the medical field, for example, surgical pins, sutures, wound dressing, blood vessel replacement, and drug carriers, and other industrial applications of PHAs include biodegradable carriers for fungicides, fertilizers, packaging containers, and so on.[41a] PHA biodegrades in different environments. A number of microorganisms such as bacteria and fungi in soil, sludge, and seawater excrete PHA depolymerase to hydrolyze the solid PHA into water-soluble oligomers and monomers and they utilize the resulting products as nutrients within cells.

5.15.3.2 Poly(alkylene dicarboxylates): Homo- and Copolymers

Synthetic polyesters, that is, polycondensates of diols and diacids like poly(alkylene dicarboxylates), are also well studied. Polycondensation of hydroxy acids (A-B monomers) or diacids (A-A) and diols (B-B) does not give high-molecular-weight polymers because of the reversibility of the condensation reaction, backbiting reactions, and the high conversions required. In recent times, new catalysts and heat stabilizers have been developed and researched with an aim to get high-molecular-weight aliphatic polyesters by condensation polymerization. Biodegradable aliphatic polyesters, trademarked 'BIONOLLE' (Showa Highpolymer Co., Ltd., Japan), such as poly(butylene succinate) (PBSu), poly(butylene succinate adipate) copolymer, and poly(ethylene succinate) (PESu) with high molecular weights ranging from several tens of thousands to several hundreds of thousands were invented in 1990 and produced successfully through polycondensation reaction of glycols with aliphatic dicarboxylic acids.[41c] BIONOLLE is a white crystalline thermoplastic with a melting point of about 90–120 °C, a glass transition temperature of about – 45 to – 10 °C, and a density of about 1.25 g cm^{-3}. BIONOLLE has excellent processability, so it can be processed on conventional equipment (commonly used in processing polyolefins) at a temperature of 160–200 °C into various molded products such as injected, extruded, and blown ones. A new grade of BIONOLLE (coded #1900 series), which has a long-chain branch (LCB), high melt tension, and high recrystallization rate, has been developed to enable stretched blown bottles and highly expanded foams to be made easily.

Poly(alkylene dicarboxylates) (Scheme 6) like PBSu, PESu, and poly(ethylene adipate) (PEAd) are well characterized in terms of crystal structure and morphology.[42] Poly(propylene succinate) (PPSu) was the first biodegradable polyester from 1,3-propanediol to be studied.[43] These aliphatic polyesters are biodegradable due to their susceptibility to hydrolysis and are degraded by proteases,[44] α-chymotrypsin,[45] lipases, and esterase.[46]

From the materials point of view, the biodegradability rate, in general, depends upon the type of chemical linkage, molecular weight, hydrophilicity, crystallinity, flexibility, porosity, and morphology of polyesters. The effect of these parameters on biodegradability of polyesters can be seen by the following literature examples. One of the methods of tuning the biodegradability by changing these material parameters is by copolymerization (Scheme 7). Mochizuki *et al.*[47] have studied

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Table 2 Comparison of the properties of biodegradable polyesters and conventional plastics

Property	*PHB (Biopol)*	*PHB-PHV (Biopol)*	*PS*	*LDPE*	*PCL (Tone 787)*	*PLA (Ecopia)*	*PET*	*Ecoflex (polytetramethylene adipate terephthalate)*
Melting point (°C)	140–180	100–190		98–115	59–64	130–180	245–265	108–110
T_g (°C)	0	0–30	70–115	–100	–60	40–70	73–80	–30
Tensile stress at break (MPa)	25–40	25–30	34–50	8–10	4–28	48–53	48–72	22
Elongation at break (%)	6	7–15	1–2.5	15–600	800–1000	30–240	30–300	700
Tensile modulus (MPa)	4000	600–1000	2800–3500	300–500	386–470	3500	2800–4100	100

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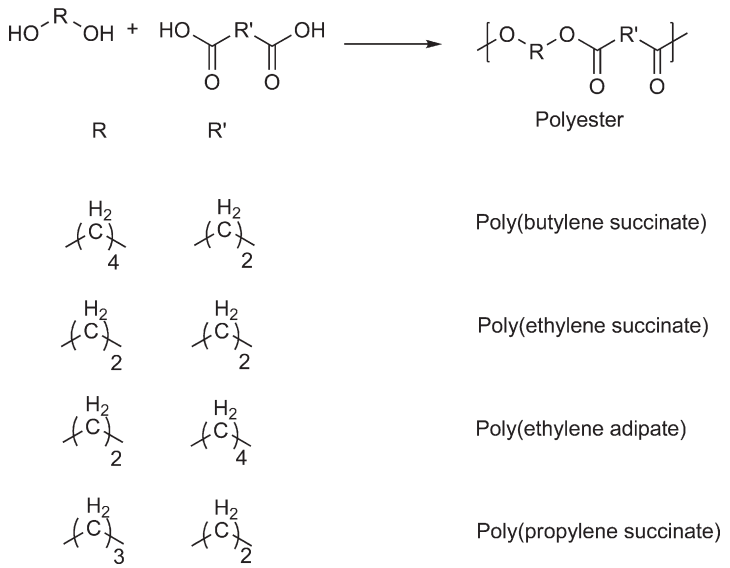
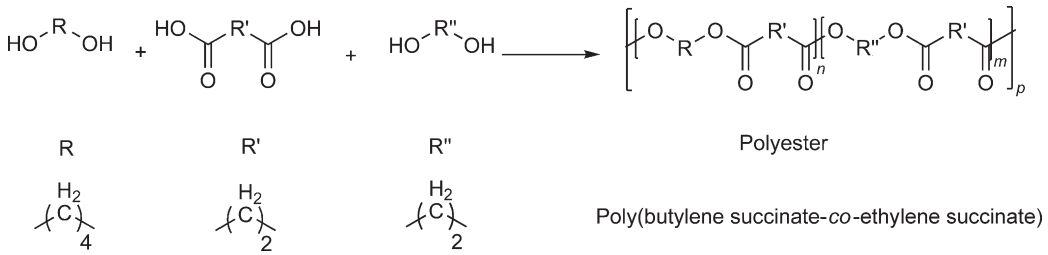


Scheme 6 Some aliphatic polyesters made by polycondensation.

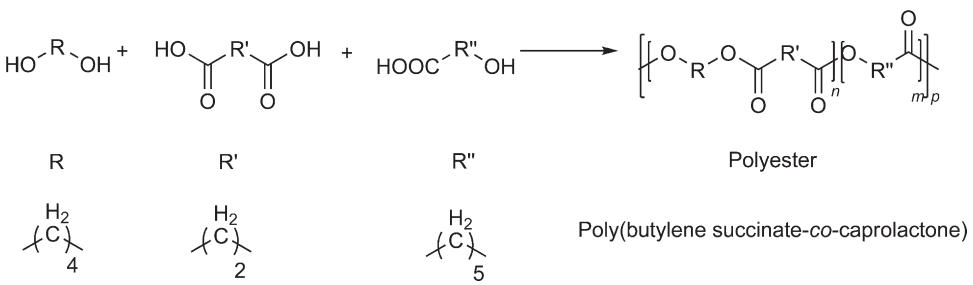


Scheme 7 Chemical structure of copolyesters made by polycondensation of A-A and B-B type of monomers.

the effect of structure upon enzymatic degradation of high-molar-mass poly(butylene succinate-*co*-ethylene succinate).

The hydrolysis rate of the copolymer was higher than that of the corresponding homopolymers with a maximum of degradability (lipase from *Rhizopus arrhizus*) observed for 53 mol.% ethylene succinate (ESu) as it had minimum systemic crystallinity and the enzymatic degradation was highly dependent upon lipase source. Cao *et al.*[48] checked the biodegradability of poly(butylene succinate-*co*-caprolactone) (**Scheme 8**) in compost soil at 30 °C and 95% relative humidity (RH) and showed higher biodegradability of copolymers as compared to the respective homopolymers due to increased flexibility and reduced crystallinity.

On the other hand, for some other copolymers, the effect of lipase source on biodegradability of polyesters was not seen. Rizzarelli *et al.*[49] showed enzymatic hydrolysis of high-molecular-weight random poly(butylene succinate-*co*-butylene sebacate) (P(BSu-*co*-BSe)) and poly(butylene succinate-*co*-butylene adipate) (P(BS-*co*-BA)) by lipase from *Mucor miehei* or from *R. arrhizus* and produced a mixture of water-soluble monomers and co-oligomers. There was no difference in the activity of lipases observed depending upon the source. Bikiaris *et al.*[50] have synthesized poly(alkylene succinates) from succinic acid and aliphatic diols with 2–4 methylene groups by melt polycondensation. These poly(alkylene succinates) are PPSu, PESu, and PBSu. Biodegradability studies of these polyesters



Scheme 8 Aliphatic copolyesters made by polycondensation of A-A/B-B and A-B type of monomers.

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with the same average molecular weight included enzymatic hydrolysis for several days using *Rhizopus delemar* lipase at pH 7.2 and 30 °C. Differential Scanning Calorimetry (DSC) of traces of biodegraded polyesters revealed that hydrolysis affected mainly the amorphous material. The biodegradation rates of the polymers decreased following the order PPSu > PESu ≥ PBSu and it was attributed to the lower crystallinity of PPSu compared to other polyesters, rather than to differences in chemical structure. In general, biodegradability can be followed by following the weight loss, change in the mechanical properties, morphological changes, or structural changes using different spectroscopic methods.

Other petrochemical-based polymers of commercial interest are polyglycolide (PGA) and PCL and their copolymers. These polymers are well studied from the point of view of academics and industry. High-molecular-weight polymers are generally made by ROP of the corresponding cyclic esters. The details of ROP for the synthesis of polyesters can be seen in the review article.[51] The biodegradation of PCL by fungi[52] in different biotic environments and by mixed and pure cultures of bacteria and yeast[53] in seawater[54] has been demonstrated. PLA is produced by ROP of lactide, a cyclic dimer obtained by the fermentation of starch or cellulose. Its mechanical properties are better than those of many other biodegradable and biocompatible polymers as shown in Table 2. Microbial and enzymatic degradation of PLA is well studied. Microbial degradation takes place in two steps. The first step is the nonenzymatic temperature- and humidity-dependent hydrolysis of ester bonds. This is followed by microbial breakdown to oligomers and monomers, producing carbon dioxide and water.[55] These polyesters are considered in detail in other volumes of this compilation and are therefore not dealt further in detail.

5.15.3.3 Poly(aliphatic–aromatic) Copolyesters

In contrast to most aliphatic polyesters, aromatic polyesters like PET or poly(butylene terephthalate) (PBT) provide excellent material properties and, hence, are commercially used for a wide variety of applications like textiles and bottles but are resistant to hydrolysis and microbial attack. Very drastic conditions like sulfuric acid at 150 °C can hydrolyze aromatic polyesters.

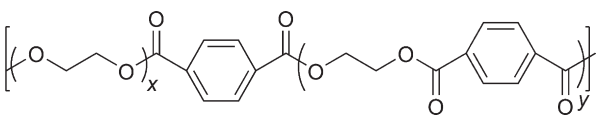
Copolymerization of aliphatic polyesters with aromatic moieties has been tried to improve the balance between degradability and mechanical properties. The ratio of aromatic units with respect to the aliphatic ones is highly important for the balance between degradability and good mechanical properties. Any change in this ratio alters the crystallinity, flexibility, hydrophilicity/hydrophobicity ratio, and therefore the degradability (hydrolytic attack on ester linkages) of the polyesters. For example, the introduction of flexible long poly(ethylene glycol) (PEG) units, that is, replacement of a part of ethylene glycol monomer with PEG during PET synthesis (Scheme 9), led to a hydrolytically and enzymatically degradable (leucine amino peptidase, esterase, α-amylase) aromatic polyester with the degradation starting at ester bonds between PEG and PET segments.[56]

Also, biodegradation catalyzed by enzymes can be achieved in aliphatic–aromatic polyesters. Copolyesters (CPEs) synthesized from aliphatic and aromatic comonomers, such as 1,2-ethanediol, 1,3-propanediol, 1,4-butanediol, sebacic acid, adipic acid, and terephthalic acid, combined in an appropriate range have proven to be biodegradable. The biodegradability for such cases is dependent upon the chemical composition, length and sequence distributions, and crystallinity.[57] The effect of microstructure on biodegradability (soil burial test) could also have significant influence and was studied, for example, by Witt *et al.*[58] for homo-, random, and block copolymers of aliphatic and aromatic polyesters. These polyesters were made by polycondensation of terephthalic acid, adipic acid, sebacic acid, and 1,3-propanediol. A decrease in weight loss with increasing melting points of aliphatic dicarboxylic acids was observed for the homopolyesters synthesized from dicarboxylic acids with carbon chain lengths larger than 2 and 1,3-propanediol. However, the films were brittle and had low melting point, which limited their applicability. For statistical copolymers, from values of the molar fraction approximately larger than 0.3 of terephthalic acid, the melting point and mechanical properties increased but no weight loss was observed. For the same composition and almost similar melting point block copolymer, a significant weight loss was observed as compared to the statistical copolymers. But the studies could not show if the weight loss was due to which block, i.e., aliphatic or aromatic.

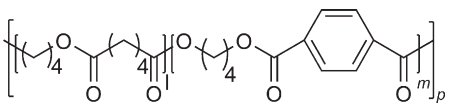
Statistical substitution of 10 mol.% sebacic acid by terephthalic acid during polycondensation of 1,3-propanediol and decanedioic acid (poly(trimethylene decanedioate-*co*-trimethylene terphthalate) (90:10 mol.%)) enhanced the biodegradability due to lowering of melting point. When the fraction of aromatic substituent was increased to 50 mol.%, microbial attack could not be observed.[59] Tokiwa and Suzuki[57] showed the increased susceptibility of lipase (*R. delemar*) with decreased rigidity of the aliphatic–aromatic CPEs. CPEs containing poly(ethylene isophthalate) (PEIP) or poly(diethylene isophthalate) (PDIP) as low-melting-point aromatic polyester were hydrolyzed better than other CPEs.

The combination of terephthalic acid, adipic acid, and 1,4-butanediol turned out to be the most appropriate combination with regard to both material properties and price, and has been commercialized by BASF AG in Germany. The product is being sold under the trade name Ecoflex^{R} (BTA-copolyester) (Scheme 10).

As with other aromatic–aliphatic CPEs, the degradation rate is dependent upon the amount of aromatic moieties. Figure 1 shows the dependence of the degradation rate of



Scheme 9 Structure of PEG/PET copolymers.



Scheme 10 Chemical structure of terephthalic acid-, adipic acid-, and 1,4-butanediol-based copolyester (BTA-copolyester).

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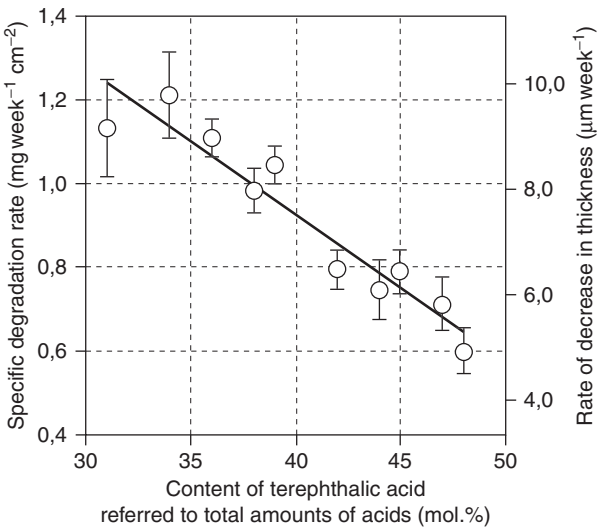

Figure 1 Dependence of the degradation rate (expressed as weight loss per surface area and degradation time) of BTA-copolyesters on terephthalic acid content. Data were obtained from an agar-plate test (mineral salt medium at 60 °C) with BTA films (2.5 cm diameter). The test duration was up to 6 weeks. Reproduced with permission from Müller, R. J.; Kleeberg, I.; Deckwer, W. D. *J. Biotechnol.* **2001**, *86*, 87.[60]

BTA-copolyesters on the content of terephthalic acid.[60] The degradation rate decreased continuously with the increase in aromatic content. Both aromatic and aliphatic oligomers are formed during degradation and the aromatic oligomers with one or two terephthalate units and all monomers are rapidly metabolized by microorganisms.

Although the mechanism of degradation is not entirely clear, that is, if it is enzymatic cleavage or a simple hydrolysis of ester units between two aromatic units, there is no accumulation of oligomeric aromatic units and no adverse ecotoxic effect after composting of BTA-polyesters.

5.15.4 Different Macromolecular Architectures and Speciality Biodegradable Polyesters

5.15.4.1 Star Polyesters

Although many studies have been reported on the synthesis, crystallization, and morphology of polyesters based on star-shaped PCL and PLA by ROP, to the best of our knowledge there are no such examples related to condensation polymerization. Also not much is provided in the literature regarding the systematic comparison of linear and star polymers in terms of degradability.[61] Li and Kissel[62] provided a comparison of degradability profile (phosphate buffer, pH 7.2, 37 °C) of star block copolymers containing a hydrophilic four- or eight-arm branched poly(ethylene oxide) (PEO) central unit and hydrophobic PLA or poly(L-lactide-*co*-glycolide) (PLLG) with those of linear ABA triblock copolymers (**Figure 2**). Compared to the fast erosion of ABA triblock copolymers, star polymers showed a slower degradation and mass erosion in the first 2–3 weeks followed by a fast degradation. Star block copolymers had on an average shorter PLLG arms as compared to the blocks of PLLG in the linear block copolymers as they both had almost similar molecular weight. Water-soluble breakdown products, such as PLLG oligomers and monomers, could be produced after fewer hydrolytic cleavage steps, leading to the fast erosion of the matrix.[62]

Xie *et al.*[63] have compared star-shaped PCL with 1–5 arms with the linear PCL of similar molecular weights and crystal structure for enzymatic (*Pseudomonas cepacia*) degradability (**Figure 3**). Interestingly, enzymatic degradation of star-shaped PCLs was dependent on arm numbers. The biodegradation rate increased with the increase in arm number in the case of 1–3 arms. However, a further increase in arm number from three to five resulted in a decreased biodegradation rate. The authors have proposed two main factors as affecting biodegradation rate, namely, crystallinity and chain mobility. An increase in arm numbers results in decreased arm length (since star-shaped

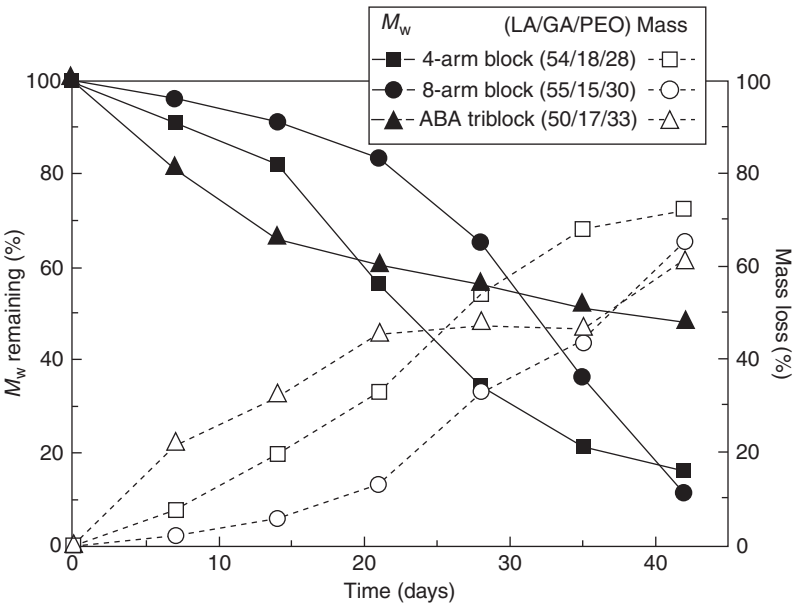

Figure 2 *In vitro* degradation of film specimens from linear and star block copolymers in PBS (pH 7.2) at 37 °C. Reproduced with permission from Li, Y.; Kissel, T. *Polymer* **1998**, *39*, 4421.[62]

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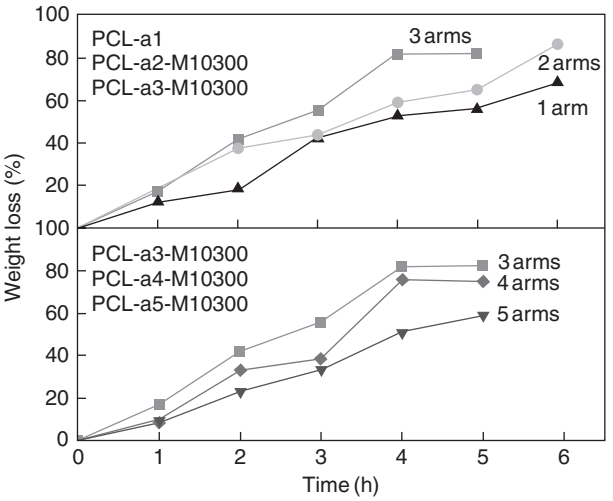

Figure 3 Weight loss of star-shaped PCLs with similar molecular weights (M_n = 10 300) but different arm numbers in the course of enzymatic degradation. Reproduced with permission from Xie, W.; Jiang, N.; Gan, Z. *Macromol. Biosci.* **2008**, *8*, 775.[63]

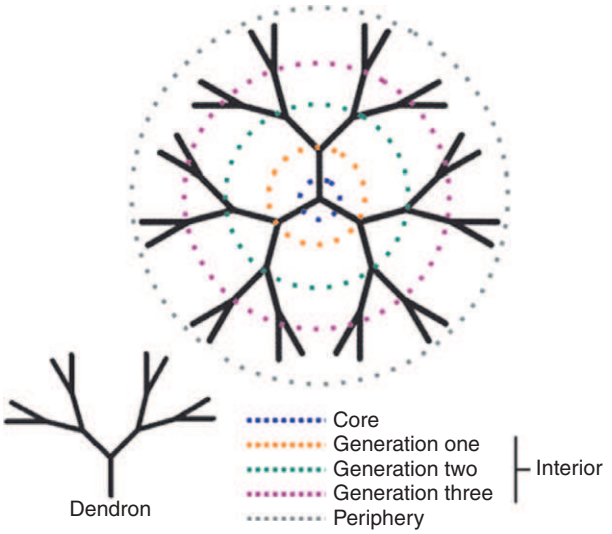

Figure 4 General structure of a dendrimer: a dendrimer and dendron are represented with solid lines. The colored broken lines identify the various key regions of the dendrimer. Reproduced with permission from Lee, C. C.; MacKay, J. A.; Fréchet, J. M. J.; Szoka, F. C. *Nat. Biotechnol.* **2005**, *23*, 1517.[65]

PCLs had same molecular weight (M_n = 10 300)) and therefore decreased crystallinity, which favored enzymatic degradation. However, for star-shaped PCLs with 3–5 arms, even though the crystallinity also decreased, since the arm length is much shorter, the chain mobility of each arm was limited by the center core.

5.15.4.2 Dendrimers and Hyperbranched Polyesters

Dendrimers are globular monodisperse, three-dimensional structures having symmetrical branches emerging from a core. The ester-functionalized dendrimers are highlighted in a review article by Nummelin *et al.*,[64] which mentions vast application areas like adhesives and coatings, catalysts, sensors, lubricants, and viscosity modifiers. Although the synthesis of dendrimers is challenging, time consuming, and expensive, dendrimers could provide an edge over the conventional biodegradable polyesters in many application areas due to their low polydispersity, intercavity for encapsulation of drugs, catalysts, and other materials, and a large number of end functional groups. The basic structure of a general dendrimer is shown in Figure 4.[65]

The first biodegradable polyester-based dendrimer from (*R*)-3-hydroxybutanoic acid (HB) and trimesic acid was reported by Seebach *et al.*[66] The biodegradability of the dendrimers was tested in the presence of various hydrolases. Acid-terminated dendrimers were found to be degradable with zero-order kinetics. Later, many different polyester-based dendrimers and complex dendrimer-based architectures were developed for different purposes. For example, water-soluble and nontoxic polyester dendritic scaffolds based on the monomer 2,2-bis(hydroxymethyl)propanoic acid were evaluated[67] for their suitability as drug carriers (doxorubicin) both *in vitro* and *in vivo*. The results were highly promising in terms of the reduced cytotoxicity of the bound drug and little accumulation in the vital organs. Biodegradable comb-dendritic triblock copolymers based on PEG and poly(L-lactide) (Scheme 11) were made to overcome the general problems of PLA for biomedical applications such as hydrophobicity, poor cell affinity, high crystallinity, and deviation from sustained release profile for drug release applications due to the increase in local acidity.[68] PEG made the system more hydrophilic.

The capability of adsorbing protein increases with the length of poly(L-lactide) (PLLA) arms and no cytotoxicity has been found using rabbit bone marrow stromal cells. Also, the dendrimers attached on both ends of linear polymers (linear-dendritic copolymers) can build supramolecular micelle[69–71] structures and hence are expected to increase the drug payload.

Kim *et al.*[72] introduced linear-dendritic copolymers (820–40 nm in dry state) for the purpose of targeted and sustained drug delivery in response to environmental changes (Scheme 12).

Thermoresponsive-*co*-biodegradable linear-dendritic copolymer has thermoresponsive poly(*N*-isopropylacrylamide) (PNIPAAM), hydrophobic and biodegradable PLA, and hydrophilic cationic poly(L-lysine) dendrons. The polyamine groups of poly(L-lysine) can interact electrostatically with the polyanionic phospholipid cell membranes and, therefore, could increase the delivery of therapeutic agents. PNIPAAM with hydrophobic and hydrophilic units provides an edge in drug delivery by allowing aqueous loading of hydrophilic therapeutic agents at temperatures lower than lower critical solution temperature (LCST), by modulating the mechanism of biodegradation, by decreasing the cytotoxicity of polycations, and by releasing therapeutic agents at different profiles in response to temperature, pH, and other stimuli. The copolymer degraded in 19 days in PBS (pH 7.4) (Figure 5).

Hyperbranched polyesters are special types of dendritic polyesters with irregular and high branching density.[73] In general, hyperbranched polymers are good alternatives to dendrimers bearing in mind the high cost required for dendrimer synthesis. A lot of research has been carried out in the past few years on the synthesis and properties evaluation of hyperbranched polyesters including aliphatic, aromatic, and

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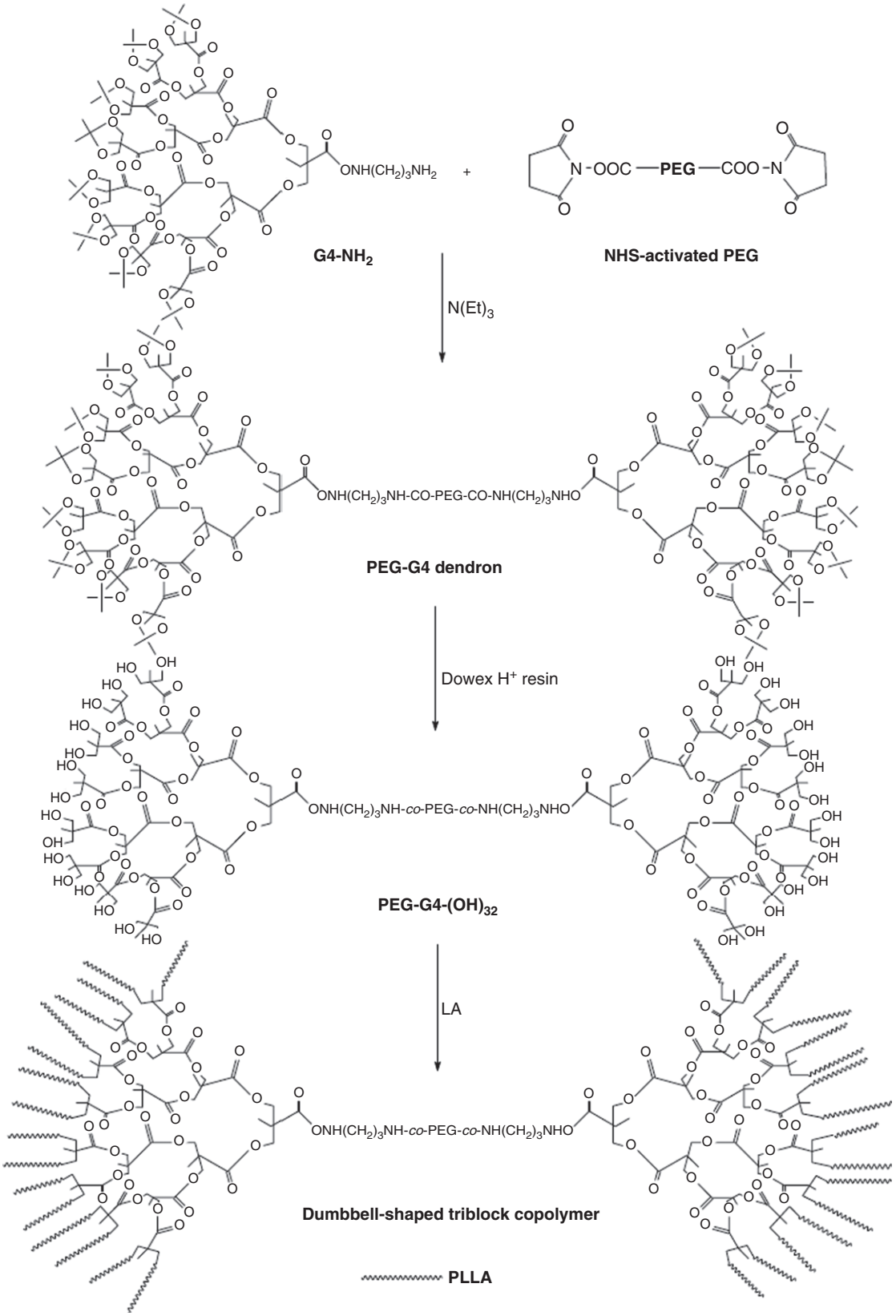

Scheme 11 Synthesis of dumbbell-shaped triblock copolymers. LA, D,L-lactic acid; NHS, N-hydroxysuccinimide. Reproduced with permission from Gong, F.; Cheng, X.; Wang, S.; *et al. Polymer* **2009**, *50*, 2775.[68]

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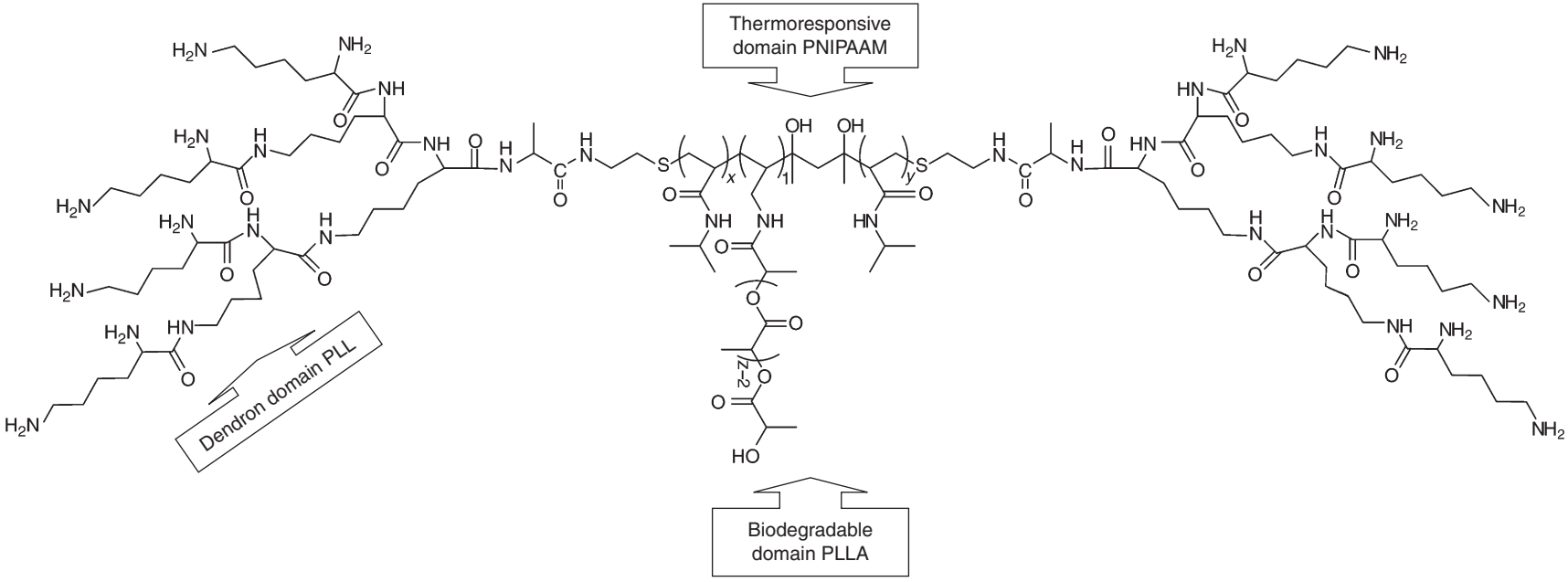

Scheme 12 Biodegradable linear-dendritic copolymer. PLLA, poly(L-lactic acid); PLL, poly(L-lysine). Reproduced with permission from Kim, Y. S.; Gil, E. S.; Lowe, T. L. *Macromolecules* **2006,** *39,* 7805.[72]

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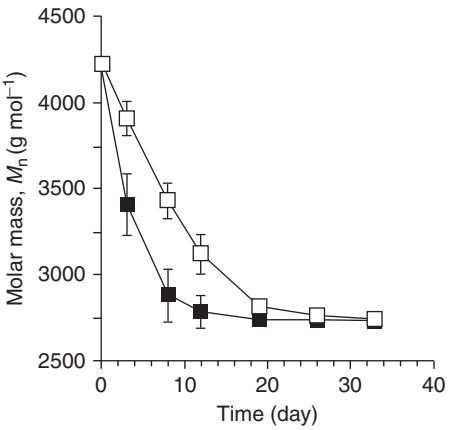

Figure 5 Molar mass of dendrimer against time in PBS (pH 7.4) at 0.1 mg ml^{-1} at temperature below 25 °C (□) and above 37 °C (■), measured by MALDI-TOF. Reproduced with permission from Kim, Y. S.; Gil, E. S.; Lowe, T. L. *Macromolecules* **2006**, *39*, 7805.[72]

aliphatic–aromatic ones. Malmström *et al.*[74] have shown the synthesis of aliphatic hyperbranched polyesters based on 2,2-bis(hydroxymethyl)propionic acid as an AB_x monomer and 2-ethyl-2-(hydroxymethyl)-1,3-propanediol as a core moiety. Although rheological and mechanical properties are studied by them, there is no mention of biodegradability of these hyperbranched polyesters. The commercial hyperbranched polyester Boltorn H20 and H30 (from Perstorp AB, Sweden) is based on the same building block, that is, 2,2-bis(hydroxymethyl)propionic acid.[75] The theoretical core/monomer ratio is 1:12 and 1:28 for H20 and H30, respectively. The H40 (**Figure 6**) has a core/monomer ratio of 1:60.[76,77]

The beauty of dendrimers or hyperbranched polyesters is that the chain end functional groups can be further modified by wet chemistry to achieve special properties. For example, commercially available hyperbranched polyesters (Boltron H) were modified with *t*-amine groups to make use of these nontoxic biodegradable materials as gene delivery systems.[78] The terminal OH groups were modified with diethylaminopropylamine (DEAPA) by carbonyldiimidazole (CDI) chemistry. Degradability and degradation rate were investigated with respect to the degree of amine substitution. The toxicity of all hyperbranched polyesters was generally very low compared to polyethyleneimine (PEI) (a positive standard). Measurements of size and zeta potential showed that small nanocomplexes with a positive zeta potential were formed. The influence of amine substitution on transfection efficiency of the different polymers demonstrated that a certain amine substitution degree was required to achieve transfection efficiency. These carriers provide degradability, very low toxicity, and the ability to transfect cells, which can be influenced by the degree of amine substitution. Kontoyianni *et al.*[76] have functionalized BH40 with PEG chains to get a new water-soluble hyperbranched polymer exhibiting unimolecular micellar properties and effectively encapsulating anticancer drug. The system was shown to be nontoxic and suitable for slow release of drug with complete release in 10 h (**Figure 7**).

BH40-PEG showed enzymatic degradation using Greasex 50L, a lipase capable of degrading ester bonds. The degree of enzymatic degradation was followed by ^{1}H NMR spectroscopy and 53% of ester bonds degraded in 28 h.

Boltorn H20 is also modified to impart amphiphilicity by using succinic anhydride and glycidyl methacrylate and it formed nanoparticles in aqueous solution.[79] The aim of the work was to increase the encapsulation efficacy of a water-insoluble Chinese drug daidzein. The biodegradation of nanoparticles was followed by light scattering studies and showed release of drug over a few days demonstrating the potential of the system as a controlled drug release carrier for hydrophobic compounds (**Figure 8**).

Hyperbranched PCLs were synthesized by Choi and Kwak[80] by melt polycondensation of AB_2 macromonomers, 2,2-bis [ω-hydroxy oligo(caprolactone)methyl]propionic acids having different lengths of PCL segments. Furthermore, hyperbranched aliphatic CPEs have been prepared by the copolymerization of CL and 2,2-bis(hydroxymethyl)butyric acid (AB_2 monomer), catalyzed by $HfCl_4(THF)_2$ and diphenylammonium trifluoromethanesulfonate, respectively.[81] In both cases, a combination of ROP and AB_2 polycondensation occurred. The reaction is also possible under enzymatic catalyses (lipase B).[82] Parzuchowski *et al.*[83] used glycerol-based monomers, {3-[2-hydroxy-1-(hydroxymethyl)ethoxy]propyl} mercaptoacetic acid ethyl ester, for polycondensation, yielding hyperbranched polyesters. The authors showed the degradability of these hyperbranched polyesters only under basic conditions and recommended them for cross-linking polios or building blocks for recyclable molecular systems. Multifunctional hyperbranched aliphatic polyester-based nanoparticles and nanocomposites with properties ranging from magnetic, resonance, antioxidant, and X-ray contrast are also reported.[84] These are based on a new biodegradable hyperbranched polyester based on diethyl malonate with a hydrophobic cavity for the encapsulation of drugs and carboxyl groups on surface, which were further changed to amine, azide, and propargyl, and mediated conjugation of small molecules via click chemistry (**Scheme 13**).

Stumbe and Bruchmann[85] have shown the use of $A_2 + B_3$ system for the formation of aliphatic hyperbranched polyesters starting from adipic acid and glycerol in bulk in the presence of tin catalyst with the advantage of commercial availability of such starting materials in low cost and large amounts as compared to the speciality monomers of the type AB_x (**Scheme 14**).

The first suggestion of this route was actually given by Flory[86] in 1952. Later, Kulshrestha *et al.*[87] used the $A_2 + B_3 + B_3$ approach for enzyme-catalyzed synthesis of hyperbranched aliphatic polyesters. The condensation between adipic acid, 1,8-octanediol, and glycerol was carried out using immobilized CAL-B (Candida antarctica; Novozyme 435). The branching could be systematically varied by changing the reaction time and stoichiometric ratio of B_2 to B_3 in the monomer feed. Unsaturated hyperbranched polyesters were shown by Werry and Fossum[88] based on condensation reaction ($A_2 + B_3$) between glycerol or trimethylolpropane and fumaric acid.

Gao *et al.*[89] have prepared hyperbranched aliphatic polyesters with large numbers of hydroxyl groups in one-pot synthesis of AB-type and CD_n-type monomers ($n \geq 2$) and amino groups imparting water solubility and proposed these polyesters for drug delivery applications. The Michael addition of diethanolamine (CD_2) or *N*-methyl-D-glucamine (CD_5) to methylacrylate (AB) generated ADF_n-type intermediates. The

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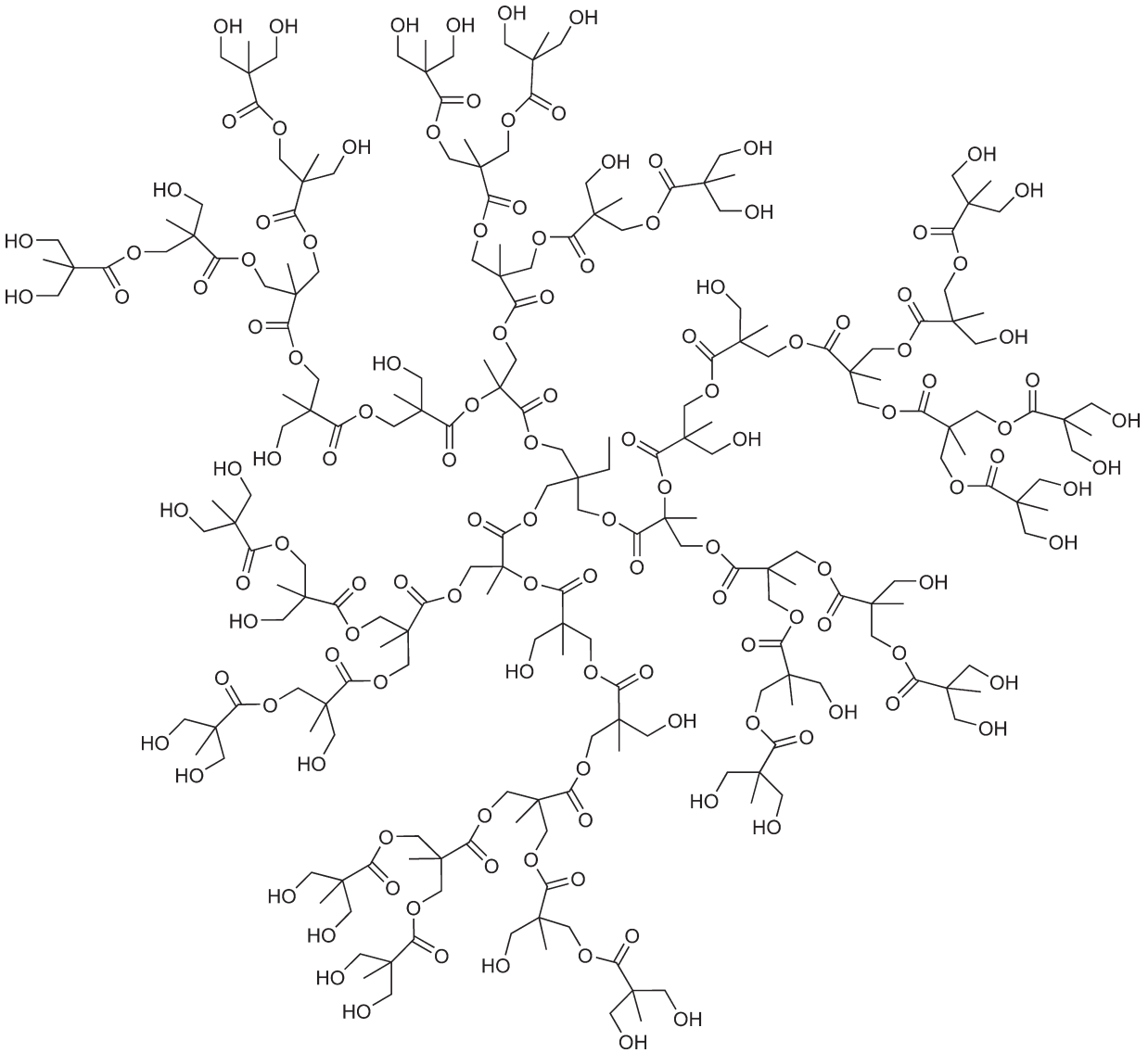

Figure 6 Chemical structure of Boltron H40. Reproduced with permission from Kontoyianni, C.; Sidetatou, Z.; Theodossiou, T.; *et al. Macromol. Biosci.* **2008**, *8*, 871.[76] Copyright Wiley-VCH Verlag GmbH & Co. KGaA.

condensation of these intermediates at high temperatures and in the presence of catalyst gave hyperbranched polyesters (Scheme 15).

Kricheldorf and Behnken[90] have shown the successful formation of soluble hyperbranched polyesters by polycondensation of pentaerythritol (B_4) with dimethylsebacate (A_2) in bulk at high temperatures. Under optimized reaction conditions for the equimolar ratio, the ratio of pentaerythritol to dimethylsebacate of >1 led to the formation of soluble polyesters. Although no biodegradation studies are shown in this work, the resulting hyperbranched polyesters are claimed to be biodegradable.

The literature clearly shows the remarkable progress in the synthesis and use of various hyperbranched polyesters. There are not many efforts to show the biodegradability of these hyperbranched polyesters since they are based on aliphatic ester linkages and hence are assumed to be biodegradable. It would be interesting to compare the biodegradability of linear and hyperbranched polyesters as we know that enzyme-catalyzed degradability is a complex process. First, the binding sites of enzymes make bonds with the substrate through noncovalent interactions (such as hydrophobic) and then catalytic sites facilitate the hydrolysis process. Mallepally *et al.*[91] have initiated such studies and showed the enzymatic degradation of surface-modified hyperbranched polyesters (Boltorn H30) with long-chain fatty acids. The degradation rate is dependent upon the source of the enzyme used for degradation.

5.15.4.3 Physically and Chemically Cross-Linked Biodegradable Polyesters: Shape-Memory Polymers and Elastic Films

As the name says, shape-memory polymers have the capability of remembering their shape and come back to their predefined shape with external stimuli like temperature or light (Figure 9).[92]

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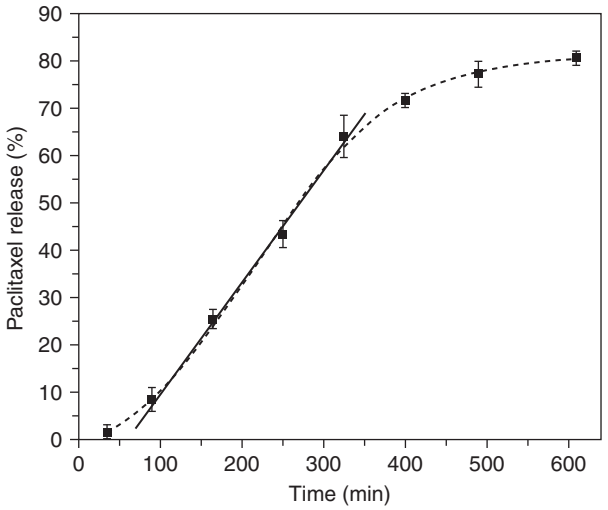

Figure 7 Paclitaxel release from a 30 mg ml^{-1} BH40-PEG solution. Reproduced with permission from Kontoyianni, C.; Sidetatou, Z.; Theodossiou, T.; *et al. Macromol. Biosci.* **2008**, *8*, 871.[76] Copyright Wiley-VCH Verlag GmbH & Co. KGaA.

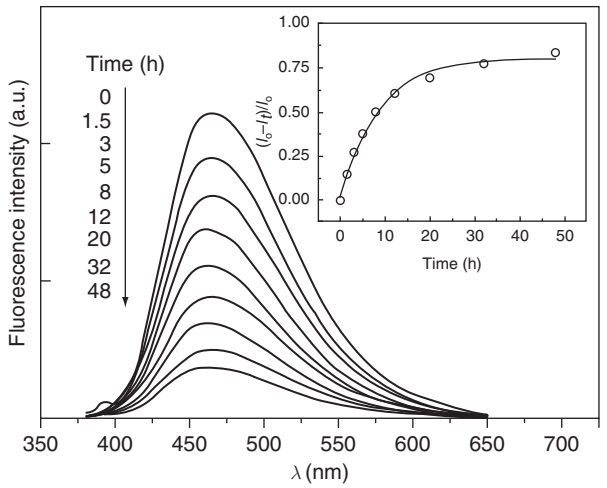

Figure 8 Change of fluorescence intensity of daidzein-loaded nanoparticles and daidzein release kinetics with incubation time. The inset shows the drug release kinetics. Reproduced with permission from Zhou, J.; Shi, W.; Wang, J.; Bo, J. *Macromol. Biosci.* **2005**, *5*, 662.[79] Copyright Wiley-VCH Verlag GmbH & Co. KGaA.

Shape-memory effect is dependent upon the molecular architecture and requires a combination of morphology and specific processing. This is explained in brief to help understand the concept – a polymer is given a permanent shape by conventional processing methods like injection molding, extrusion, and compression molding. Then the polymer is deformed and fixed into a temporary shape by a process that is called programming. External stimulus brings the polymer to the original permanent shape (**Figure 10**). Shape-memory polymers are the most promising candidates for applications like drug delivery, implant materials, and sensors to name a few. The review article by Lendlein and Kelch[93] on this theme is a good reference.

A combination of biodegradability and shape-memory property could lead to many interesting applications in biomedical fields like minimal invasive surgery and sutures. Biodegradable shape-memory polymers could be based on both multiblock copolymers and cross-linked networks. Lendlein and Langer[94] described degradable phase-segregated multiblock copolymers as shape-memory polymers changing their shape with temperature. Oligo(caprolactone)diol was chosen as the switching segment with a melting temperature and crystallizable oligo(*p*-dioxanone) with higher T_m than PCL was the hard segment to provide physical cross-links. The shape-memory property is defined by two important parameters, the strain fixity rate R_f (the ability of the switching segment to fix the mechanical deformation) and the strain recovery rate R_r (the ability of the material to recover its permanent shape). For this system, T_{trans} was 40 °C and R_f and R_r values in the third cycle were 98–99.5% and 98–99%, respectively. The degradation kinetics can be controlled through the composition and relative mass content of the precursor diols.

Gamma radiation cross-linked PCLs with a high cross-linking degree (gel content is higher than 10%) are also shown to have shape-memory effect.[95] T_{trans} in this case was high (about 55 °C) and recovery strains were low. Later Min *et al.*[96] provided a system based on polylactide-*co*-poly (glycolide-*co*-caprolactone) multiblock (PLAGC) copolymers. Depending upon the composition, the transition temperatures around 45 °C could be obtained with R_f and R_r values exceeding 90% depending upon the copolymer composition (**Figure 11**).

Nagata and Kitazima[97] have synthesized shape-memory multiblock copolymers by polycondensation of PCL- diol and PEG with 4,4′-(adipoyldioxy)dicinnamic acid (CAC) dichloride as a chain extender. The resulting photosensitive copolymers were photo-cross-linked by a 400 W high-pressure mercury lamp (λ > 280 nm) to form a network structure. The films with gel content of 57% showed R_f 100% and R_r 88%. The hydrolytic degradation data are shown under physiological conditions (1/15 mol phosphate buffer solution, pH 7.2, 37 °C). A rapid weight loss is observed at an early period followed by slower hydrolysis.

The transition temperature of shape-memory polymers near body temperature could further enhance their application areas and therefore Xue *et al.*[98] proposed some shape-memory polymers based on star poly(ester-urethanes) containing three-arm PCL as the switching segment. Reaction of the PCL-triols with methylene diphenyl 4,4′-diisocyanate (MDI) and 1,6-hexanediol (HD) gave three-arm PCL-based poly (ester-urethanes) (**Scheme 16**). The resulting material showed shape recovery in 10 s at 38 °C with R_f of 91–92% and R_r of 95–99%.

Also for many medical applications it would be advantageous to have amorphous biodegradable shape-memory polymers. Advantages could be homogeneous degradation behavior and transparency. Lendlein *et al.*[92,99] provided the amorphous network of biodegradable shape-memory polymers by coupling star-shaped oligomeric PCL or PLA with diisocyanates. The R_f and R_r values were higher than 90% for all the cycles but T_{trans} was very high (70 °C).

Most of the polyester-based shape-memory polymers are based on PCL/PLA. Cai and Liu[100] have made use of a polycondensation aliphatic polyester, poly(glycerol-sebacate) (PGS), for showing shape-memory properties. The polymer was made in two steps, polycondensation of glycerol and sebacic acid

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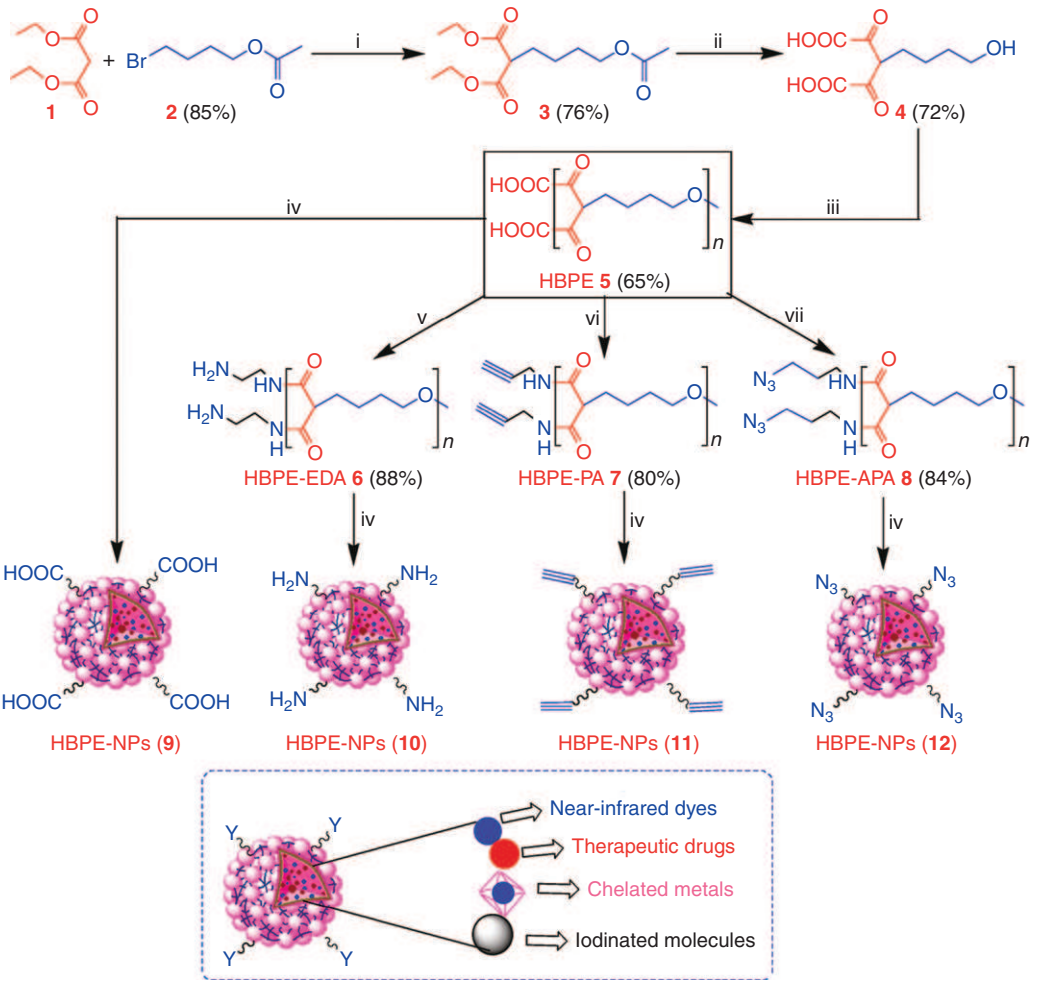

Scheme 13 Schematic representation of the syntheses of functional hyperbranched polyesters (5–8) and hyperbranched polyester nanoparticles (HBPE-NPs, 9–12) using the melt polymerization technique and the solvent diffusion method, repectively. HBPE, Hyperbranched polyester; HBPE-EDA, amine functionalised HBPE; HBPE-PA, alkynated HBPE; HBPE-APA, azidine functionalised HBPE. Reproduced with permission from Santra, S.; Kaittanis, C.; Perez, J. M. *Langmuir* **2010,** *26* (8), 5364.[84]

followed by cross-linking (Scheme 17). It is found that the cross-linked, three-dimensional networks of the PGS acting as fixed phase and the amorphous phase of the PGS acting as reversible phase are the two necessary conditions for PGS with shape-memory behavior. The response temperature of shape memory is dependent on the glass transition temperature of PGS. The PGS polymer had an excellent shape-memory effect (Figure 12), having a shape-memory ratio of above 99.5%.

This system has the disadvantage of a very low switching temperature (10–18 °C) and is, therefore, not suitable for body temperature applications. In an effort to increase the switching temperature further, variation was carried out by making a terpolymer, that is, poly(glycol-glycerol-sebacate), which showed a response temperature around 37 °C.[101]

Wang *et al.*[102] have pointed out the need of having implants that can recover and sustain various deformations when implanted in mechanically dynamic environments in the body besides being biodegradable, soft, and tough. They made a cross-linked polyester with elastomeric properties by polycondensation of glycerol and sebacic acid and subsequent thermal curing (curing is the term generally used in reference to cross-linking of polymers) (Young's modulus 0.282 MPa, ultimate tensile strength >0.5 MPa, rupture strain >267%) (Figure 13).

The process of thermal curing could restrict the application of this biodegradable elastomer system in some areas like drug encapsulation. The most general approach to cross-linked biodegradable elastic films is to functionalize polymers with acryloyl/methacryloyl moieties and their subsequent cross-linking by photo/thermal initiators. Nijst *et al.*[103] also further improvised the system by introducing acrylate moieties as side groups and studying the photocuring behavior (Scheme 18). The photocured system showed *in vitro* biocompatibility as judged by human primary cell adherence and proliferation.

The main advantage of photocuring is that it can be carried out under mild conditions and is also applicable in direct contact with body tissues and a good example is given by Han and Hubbell.[104] They aimed at making biodegradable hydrogel in direct contact with tissues or proteins by photopolymerization using long-wave ultraviolet or visible light. To achieve their aim, macromonomers with PEG central block, extended with oligomers of D,L-lactic acid or glycolic acid terminated with acrylate groups, were synthesized. These undergo gelation under mild conditions. The beauty of the system is

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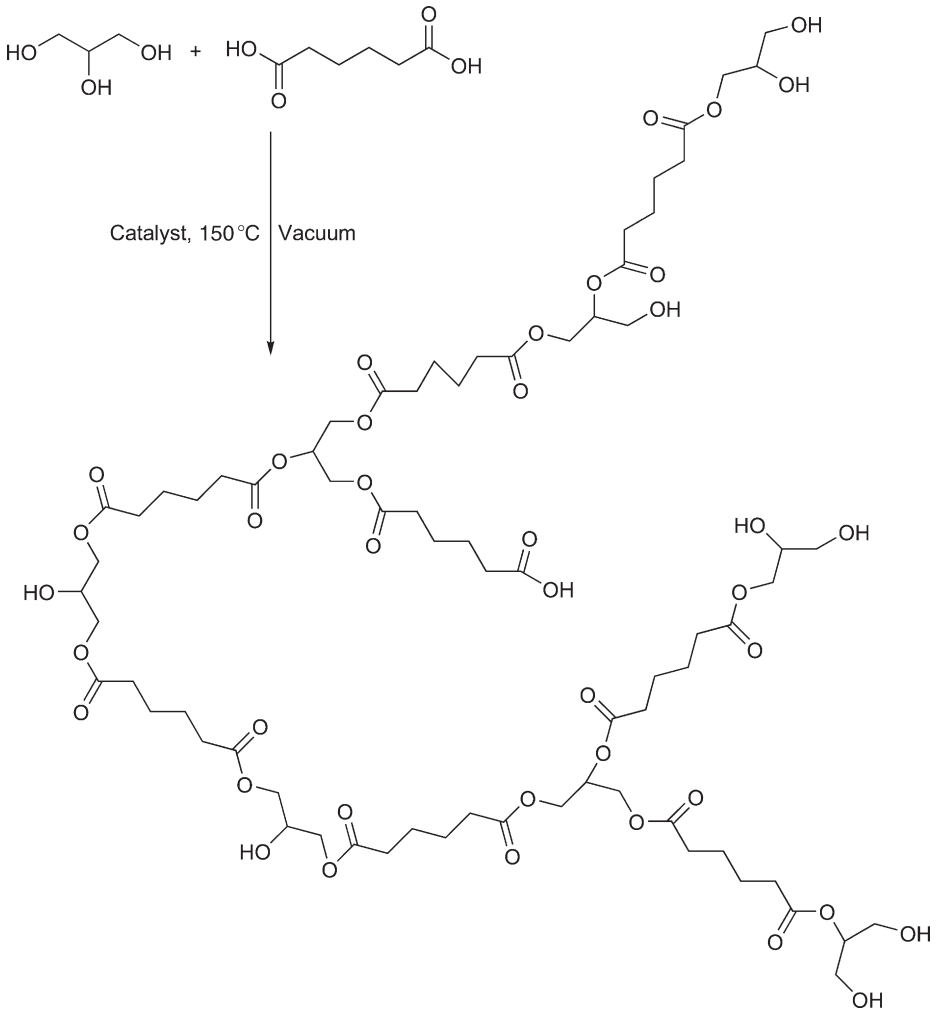

Scheme 14 Reaction scheme for the polycondensation of adipic acid and glycerol. Reproduced with permission from Stumbe, J. F.; Bruchmann, B. *Macromol. Rapid Commun.* **2004**, *25*, 921.[85] Copyright Wiley-VCH Verlag GmbH & Co. KGaA.

that the physical properties and the degradation rate can be easily varied by changing the PEG molecular weight, hydrolyzable comonomers, and the end groups. The gels adhere well to the tissues and also show continuous release of albumin for about 2 months using PEG poly(D-lactide) (PDLA) system. The potential applications are burn dressings, surgical adhesives, and modulators of tissue interactions with other tissues.

Other important polyesters studied as biodegradable elastomers for intended application in tissue engineering are poly(polyol sebacate)s (PPSs), poly(amino alcohol sebacate), and poly(diol-*co*-citrate). PPSs were made by the condensation reaction between sugar alcohols like xylitol and sorbitol and sebacic acid.[105] These thermoset networks exhibited tensile Young's moduli ranging from 0.37 ± 0.08 to 378 ± 33 MPa with maximum elongations at break from $10.90 \pm 1.37\%$ to $205.16 \pm 55.76\%$ and glass transition temperatures ranging from ~7 to 46 °C. The properties can be easily varied by changing the starting polyol monomer. PPS polymers demonstrated similar *in vitro* and *in vivo* biocompatibility compared to poly (*l*-lactic-*co*-glycolic acid) (PLGA). Poly(amino alcohol sebacate)s provide the advantages of prolonged *in vivo* degradation and postfunctionalization of biodegradable elastomers through free amino groups. They are made by polycondensation of, for example, sebacic acid, 1,3-diamino-2-hydroxypropane, and glycerol.[106] The reaction of citric acid with diols like 1,8-octanediol led to the synthesis of poly (octanediol-*co*-citrate) (POC)-type elastomers.[107] The material properties, like mechanical strength, hydrophilicity, degradation rate, and cell affinity, of such elastomers can be easily modified by controlling the monomer ratio and postpolymerization conditions and they can be further grafted by biomolecules. Biodegradable elastomers are of utmost interest as artificial skin, drug delivery agents, and scaffold for tissue engineering. Biodegradable network films with high elongations (225–277%), tensile strength (13 MPa), and Young's modulus (214 MPa) were prepared from trimesic acid and PEG with different molecular weights. Prepolymers were prepared by polycondensation reaction and then postpolymerized at 290 °C to form cross-linked transparent, flexible films. The structure of the polymer is shown in **Scheme 19**.[108]

The degradability studies are carried out with and without enzymes and showed dependence on the amount of PEG present and on the presence of the enzymes (**Figure 14**).

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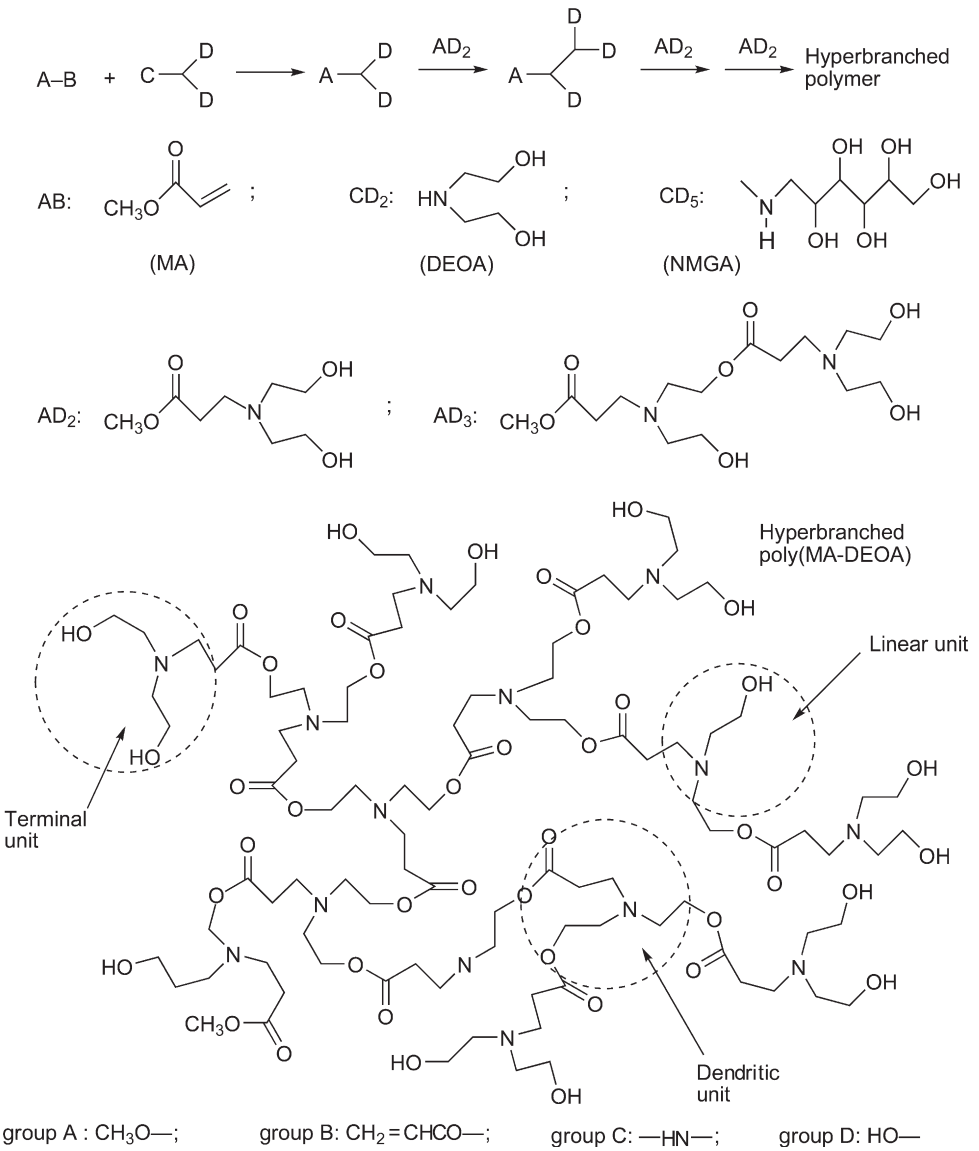

Scheme 15 AB + CD*n* approach to hyperbranched polyesters.[89] MA Methacrylic acid; DEOA Diethanol amine; NMGA N- methyl-D-glucamine

5.15.4.4 Liquid Crystalline Degradable Polyesters

Liquid crystalline polyesters (LCPs) were developed due to their high mechanical properties and processability. They can have liquid-like flow properties and solid-like tensile strengths. Liquid crystallinity in polymers may occur either in solution (lyotropic liquid crystal polymers) or by heating (thermotropic liquid crystal polymers). A number of aromatic LCPs are available that can be spun into high-modulus fibers or can be processed into high-strength articles as compared to simple aromatic polyesters. But these polyesters lack solubility in organic solvents, have very high processing temperatures, and show nonbiodegradability. In order to design LCPs with very good mechanical properties, processability, and biodegradability, an aromatic mesogen with flexible spacer and biodegradability is required. The LCPs based on glycolic acid and 4-hydroxybenzoic acid (HBA) (**Scheme 20**) were made as potential biodegradable LCPs[109a] but had the shortcoming of poor solubility in organic solvents, still high melting point limiting the processability and degradability, and low molecular weights.

Furthermore, one-step polycondensation of glycolic acid, *p*-hydroxybenzoic acid, and 4-hydroxycinnamic acid gave thermotropic LCP (**Scheme 21**).[109b] 4-Hydroxycinnamic acid provided the required balance between the liquid crystallinity and flexibility and biodegradability. The copolymers showed hydrolytic degradability.

Keeping in view the same aims of having high molecular weight, good mechanical properties, and better processability and biodegradability, some other mesogens and spacers were tried. LCPs with biodegradable lactide units were made by the reaction of phenylterephthaloyl dichloride, 2,2′-dimethyl-4,4′-dihydroxybiphenyl, and an oligolactide (**Scheme 22**). There was no mention about the biodegradability tests of the resulting polyesters but they were shown to be biocompatible.[110]

Further variation is to make the system more hydrophilic to influence the processability and biodegradability and,

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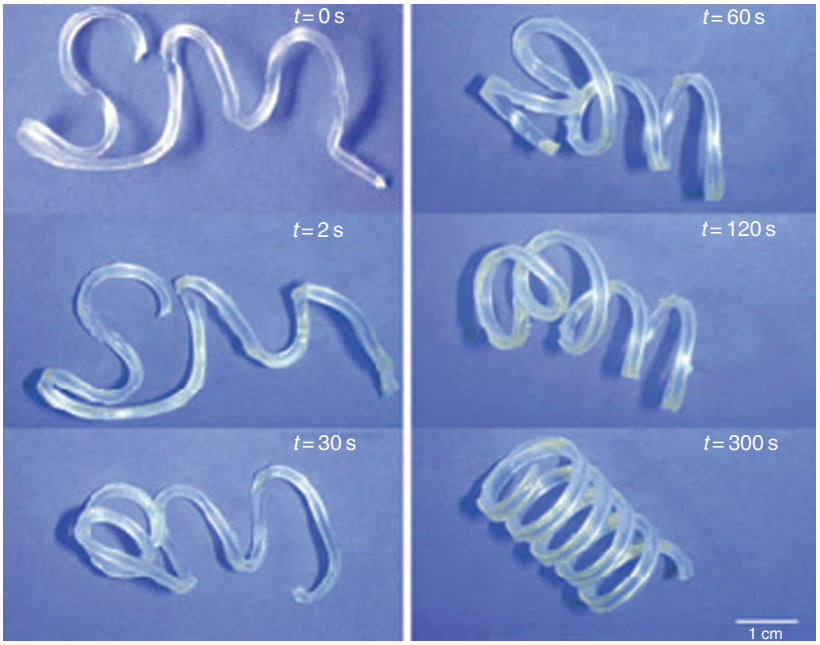

Figure 9 Shape-memory effect for a biodegradable CPE-urethane network. The transition from the temporary shape (SM) to permanent shape (corkscrew) took 300 s at 70 °C. Reproduced with permission from Alteheld, A.; Feng, Y.; Kelch, S.; Lendlein, A. *Angew. Chem. Int. Ed.* **2005**, *44*, 1188.[92] Copyright Wiley-VCH Verlag GmbH & Co. KGaA.

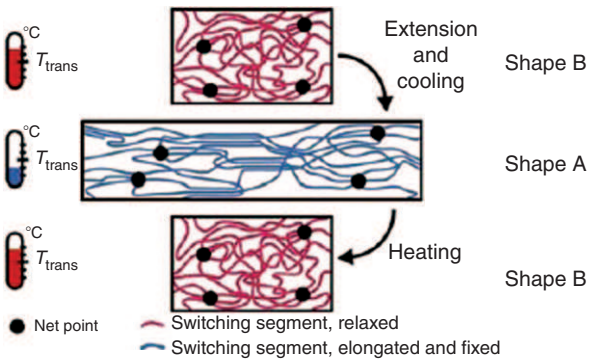

Figure 10 Molecular mechanism of the thermally induced shape-memory effect. T_{trans} = thermal transition temperature related to the switching phase. Reproduced with permission from Lendlein, A.; Kelch, S. *Angew. Chem. Int. Ed.* **2002**, *41*, 2034.[93] Copyright Wiley-VCH Verlag GmbH & Co. KGaA.

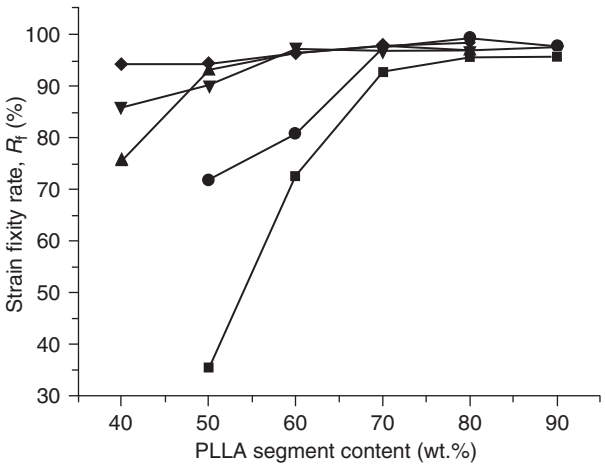

Figure 11 Dependence of strain fixity rate (R_f) of PLAGC copolymer on lengths and contents of PLLA and Poly(glycolide-co-caprolactone) (PGC) segments under 200% elongation (stressed at 45 °C and cooled to room temperature). All the copolymers have a number-average molecular weight of about 90 000. The molecular weights of both PLLA and PGC segments are ■ 2000, ● 4000, ▼ 6000, ▲ 8000, ◆ 10 000. Reproduced with permission from Min, C.; Cui, W.; Bei, J.; Wang, S. *Polym. Adv. Technol.* **2005**, *16*, 608.[96]

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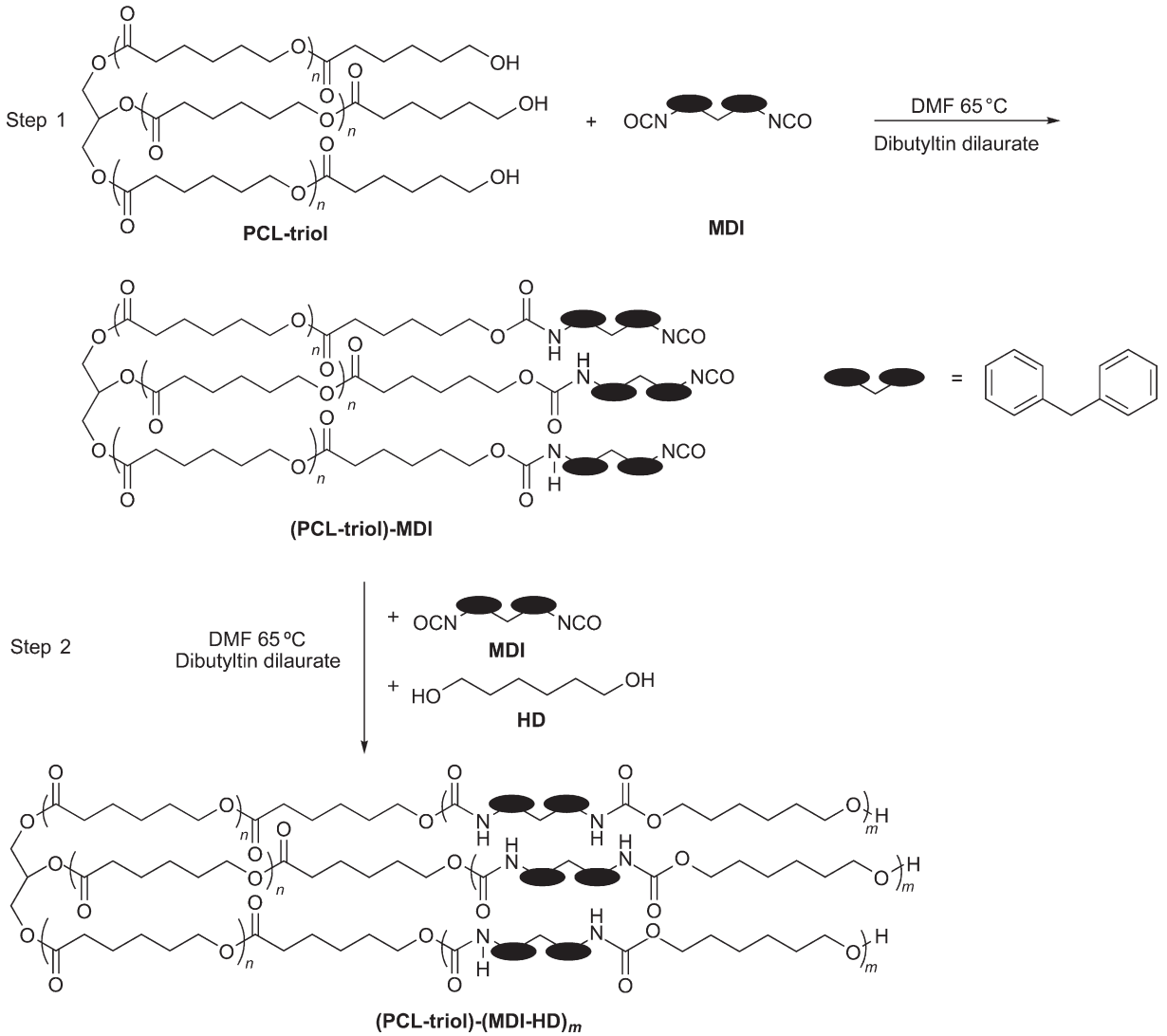
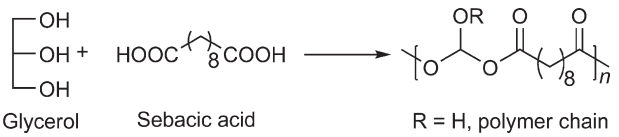


Scheme 16 Synthesis of PCL-PU (polycaprolactone-polyurethane) from PCL-triols, MDI, and HD via two-step reactions. DMF Dimethylformamide. Reproduced with permission from Xue, L.; Dai, S.; Li, Z. *Macromolecules* **2009,** *42,* 964.[98]



Scheme 17 Synthetic scheme for polycondensation of glycerol and sebacic acid. Generation of shape-memory polymers.

therefore, additionally PEG was used. The liquid crystalline biodegradable polyesters made by polycondensation of aromatic diols, diacylchlorides, oligolactides, and PEGs are shown in Scheme 23 and are hydrolytically degradable.[111]

Liquid crystalline terpolyesters of 4-hydroxyphenylacetic acid and 3-(4-hydroxyphenyl)propionic acid with terephthalic acid and 2,6-naphthalene diol (Scheme 24) showed some enzymatic degradability after 60 days (porcine pancreas lipase). The liquid crystalline properties and degradability are dependent upon the copolymer composition.[112]

Thermotropic LCPs made by polycondensation of diacyl chloride derivatives of 4,4′-(terephthaloyldioxy)-di-4-phenylpropionic acid (PTP) and glycols with different numbers of methylene groups showed influence of a number of methylene groups on melting point and isotropization temperature and were hydrolytically degradable under basic conditions (Scheme 25). They showed resistance to hydrolysis.[113]

Du *et al.*[114] have introduced biodegradable-cum-photoactive liquid crystalline CPEs by the melt condensation of ferulic acid (FA), HBA, and D,L-lactic acid (LA) (Scheme 26). The CPE having 45:30:25 molar ratio of FA/HBA/LA showed schlieren texture of nematics at 120 °C and possessed biodegradability in buffer in the presence of the enzyme proteinase K

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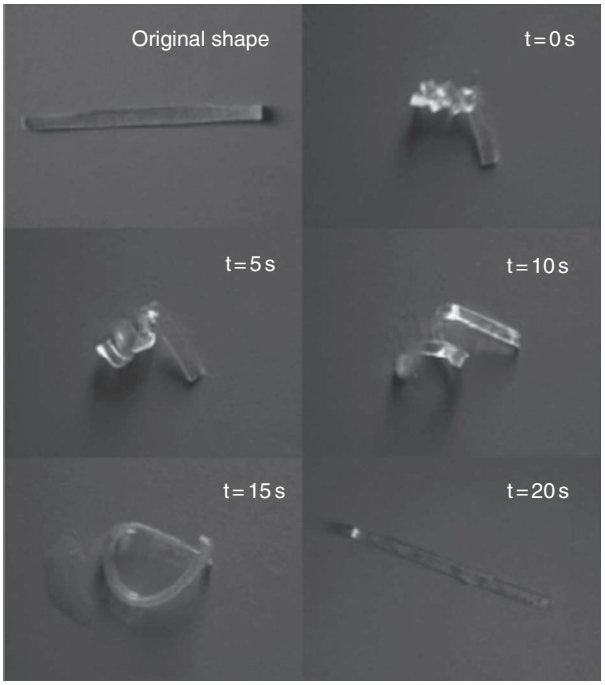


Figure 12 Shape-memory effect of PGS; recovery temperature is 18 °C. Reproduced with permission from Cai, W.; Liu, L. L. *Mater. Lett.* **2008**, *62*, 2171.[100]

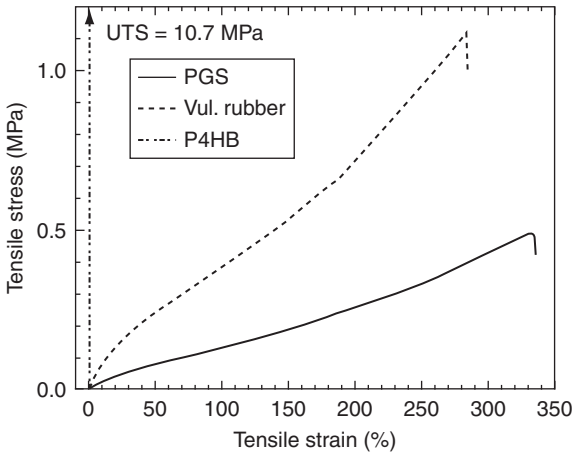
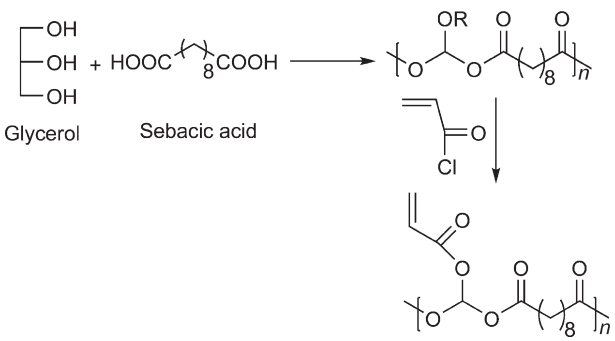


Figure 13 Stress–strain curves of PGS, vulcanized rubber, and P4HB. Both PGS and vulcanized rubber are marked by low modulus and large elongation ratio, indicating elastomeric and tough materials. The high-modulus and low-yield strain (~10%) of poly(4-hydroxybutyrate) P4HB indicates stiffer material. UTS, ultimate tensile strength. Reproduced with permission from Wang, Y.; Ameer, G. A.; Sheppard, B. J.; Langer, R. *Nat. Biotechnol.* **2002**, *20*, 602.[102]



Scheme 18 Synthetic scheme for polycondensation of glycerol and sebacic acid with photo-cross-linkable groups.

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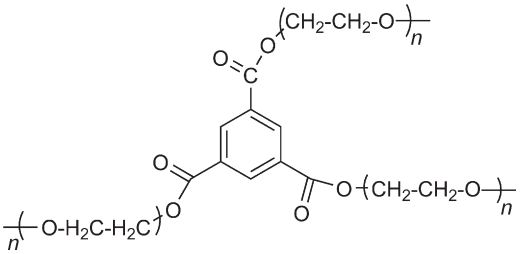


Scheme 19 Chemical structure of polymer prepared from trimesic acid and PEG. Reproduced with permission from Nagata, M.; Sugiura, R.; Sakai, W.; Tsutsumi, N. *J. Appl. Polym. Sci.* **2007**, *106*, 2885.[108]

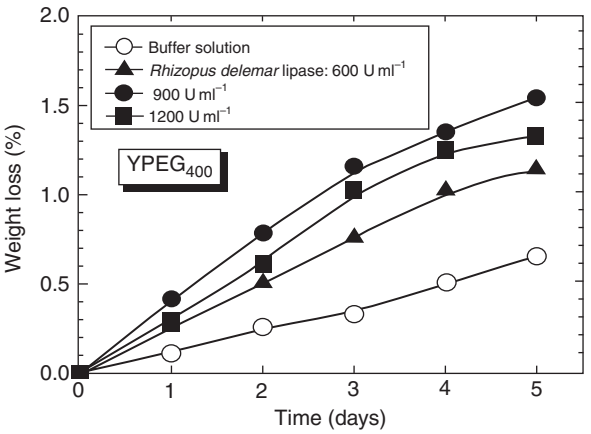
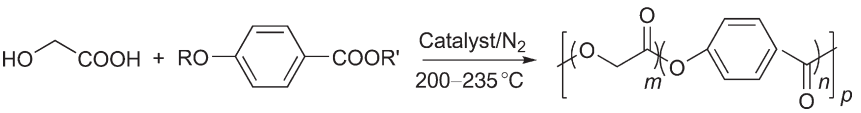
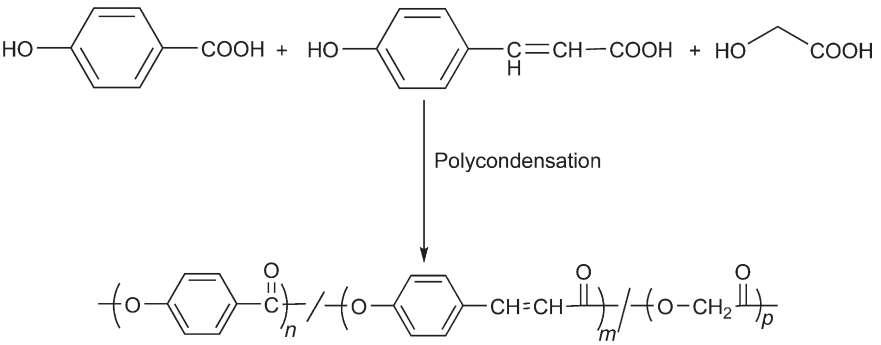


Figure 14 Weight loss against time in a buffer solution with and without *Rhizopus delemar* lipase at 37 °C. Reproduced with permission from Nagata, M.; Sugiura, R.; Sakai, W.; Tsutsumi, N. *J. Appl. Polym. Sci.* **2007**, *106*, 2885.[108]



Scheme 20 LCPs based on glycolic acid and HBA/HBA derivatives.



Scheme 21 LCPs based on glycolic acid, *p*-hydroxybenzoic acid, and 4-hydroxycinnamic acid.

at 37 °C. The degradability behavior with and without enzymes is depicted in Figure 15 showing a significant effect of enzyme on the degradation rate.

5.15.4.5 Polyester-Based Degradable Ionomers

An ion-containing polymer with low mol.% (10–15 mol.%) of ionic units either in the backbone or as pendent groups is called an ionomer. Ionomers show better mechanical and thermal properties than the parent polymer (without ionic moieties) due to ionic aggregation. The reason is the aggregation of ion pairs to form ion multiplets or clusters restricting the mobility of the polymer chain and thereby acting as physical cross-link points. There are few reports on PCL/PLA-based ionomers. They are synthesized by titrating aqueous LiOH, RbOH, CsOH, and KOH with the corresponding polymers with the COOH end groups. Here ionic species are at the chain end and are of very low molecular weights to be of any use. Degradable

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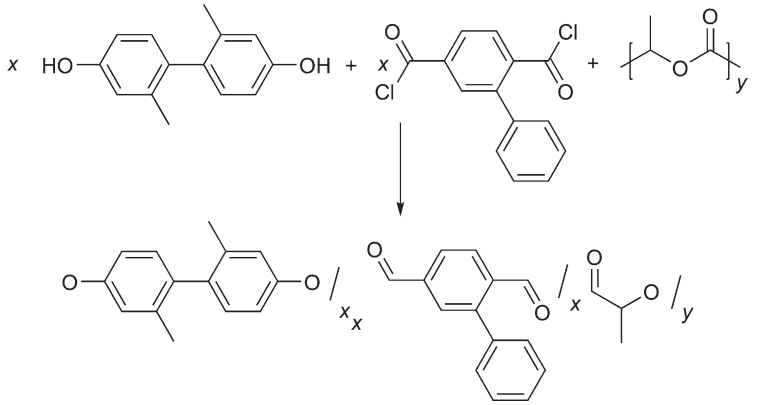
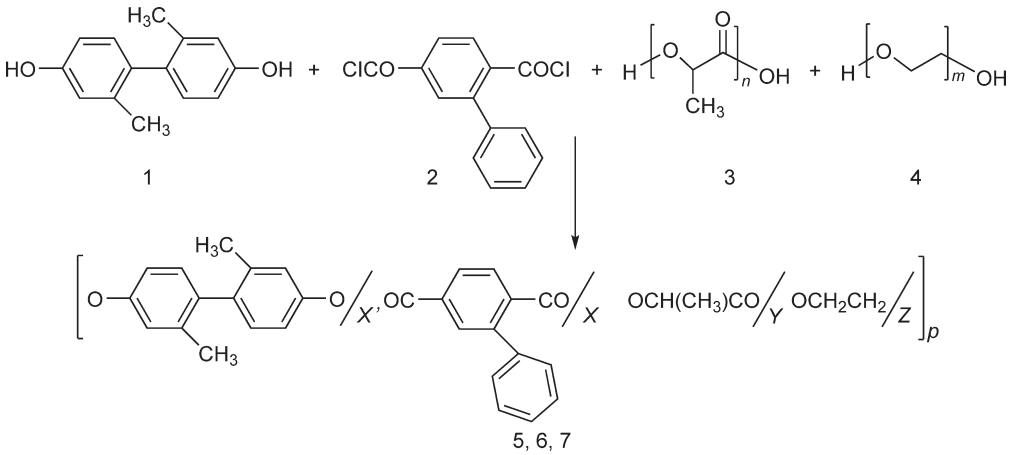
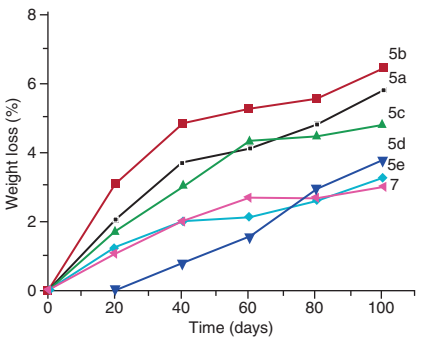


Scheme 22 LCPs having lactide moieties made by polycondensation reaction.



	x	x′	y	z
6	2	2	0	0
7	2	2	1	0
5a	2	1.87	1	1.8
5b	2	1.88	1	1.6
5c	2	1.90	1	1.3
5d	2	1.93	1	0.8
5e	2	1.95	1	0.6



Scheme 23 LCPs having lactide moieties and PEG spacers made by polycondensation reaction. Inset: Hydrolytic degradation of CPEs **5**. Reproduced with permission from Chen, Y.; Wombacher, W.; Wendorff, J. H.; *et al. Biomacromolecules* **2003**, *4*, 974.[111]

aliphatic polyester-based ionomers could also be synthesized by free radical chemistry. Radical terpolymerization of MDO, methyl methacrylate (MMA), and *N,N*-dimethylaminoethyl methacrylate (DMAEMA) followed by quaternization of amine with alkyl bromide leads to an ionomer (Scheme 27).[115]

The small-angle X-ray scattering (SAXS) analysis, transmission electron microscopy (TEM), and dynamic mechanical analysis (DMA) showed ionic aggregates existing in ionomers (Figure 16). Preliminary degradability studies are also carried out in compost and showed highly encouraging results. A 0.1 mm thick ionomer P(MDO-*co*-MMA-*co*-DMAEMA•BrC_2H_5) film containing 40 mol.% MDO and 12 mol.% ion was buried in compost under proper humidity at 60 °C. Visibly degraded holes were found out after 2 weeks, demonstrating the biodegradability of the ionomers.

The polyester-based ionomers with ionic species randomly distributed throughout the polymer chain are also made by polycondensation reaction. The polyester-based ionomers (PBSu with 1–5 mol.% dimethyl 5-sodium sulfoisophthalate) (Scheme 28) were evaluated as biomaterials by Han *et al.*[116]

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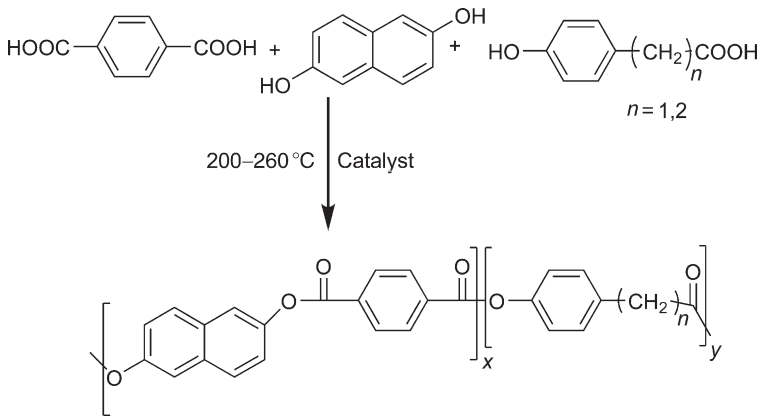
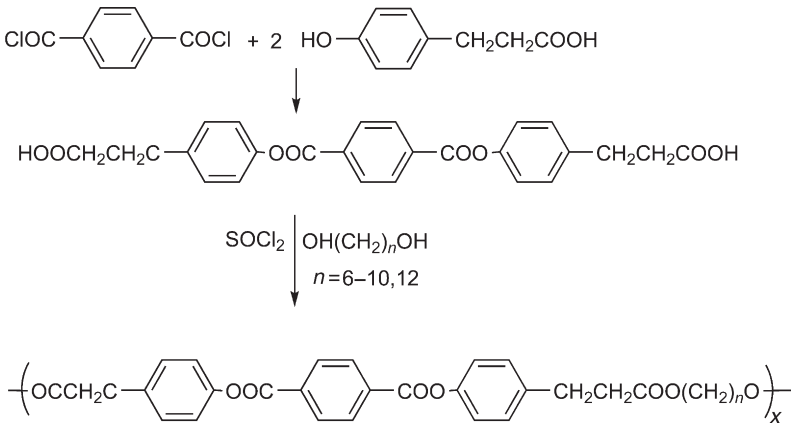


Scheme 24 Chemical structure of LCP made by polycondensation of 4-hydroxyphenylacetic acid and 3-(4-hydroxyphenyl)propionic acid with terephthalic acid and 2,6-naphthalene diol.[112]



Scheme 25 Thermotropic LCPs made by polycondensation of diacyl chloride derivatives of PTP and glycols.

and showed reduced crystallization due to ionic aggregates. Crystallization is one of the major factors affecting degradability and therefore they show promise as biomaterials. The biodegradability increased with the increase in the ionic content due to the increase in hydrophilicity and decrease in crystallinity. The *in vitro* cellular interactions were studied using the human dermal fibroblasts and showed good adhesion and proliferation, indicating the ionomers as potential good biomaterials.

Also, similar polyester ionomers made promising composites with hydroxyapatite (HAP; $Ca_{10}(PO_4)_6(OH)_2$) by binding Ca^{2+} ions effectively and, therefore, serving as active sites allowing HAP crystal to grow on the surfaces of polyester matrix. HAP is similar to inorganic components in bone and is biocompatible.

Furthermore, the clustering of ionic moieties in ionomers is used as fixing points memorizing shape during deformation and shape-memory properties are also shown for poly (oxyethylene-*b*-butylene adipate) ionomers (POBAis). Biodegradable polyester ionomers were prepared by bulk polymerization of adipic acid and mixed monomers of bis(poly (oxyethylene)) sulfonated dimethylfumarate and 1,4-butanediol (Figure 17). The ionomers showed very good dimensional stability above the glass transition temperature region, high storage modulus around 30 °C, and shape recovery rate exceeding 90% (with 2.5 mol.% ionic content), which together made them very promising for use in body temperature environment.[117]

5.15.5 Biodegradable Polyester Nanoparticles

A lot of literature is available on the use of aliphatic polyesters for drug delivery applications. Aqueous suspensions of biodegradable polyesters, mainly PCL, PLA, and copolymers, have been extensively studied for this purpose.[118] Suspensions of polyester nanoparticles are obtained as secondary suspensions, for example, by solvent displacement method, emulsion, double emulsion, and salting out methods. The method selected is dependent on the size and loading efficiency required for different biomedical applications. Biodegradable particle dispersion provides not only the advantage of encapsulation of drug molecules but interestingly a reduction in biodegradation time by a factor of 10^3 for PCL nanoparticles as compared to the film as shown by Gan *et al.*[119]

Only a few studies have reported on the use of condensation polyesters for the formation of aqueous dispersions (nano/microparticles in water) for different aims. Bikiaris *et al.*[120]

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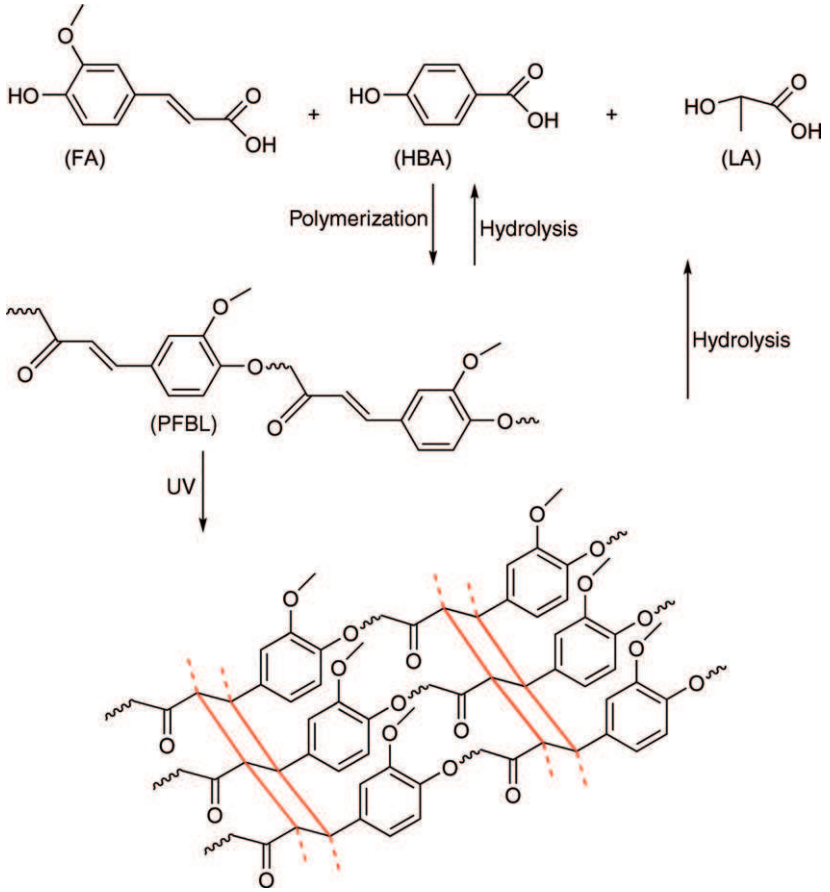

Scheme 26 Synthesis and hydrolysis of CPEs of FA, HBA, and D,L-LA.[114] FA Ferulic acid; HBA 4-hydroxybenzoic acid; LA D,L-lactic acid; PFBL Copolymer of FA, HBA and LA.

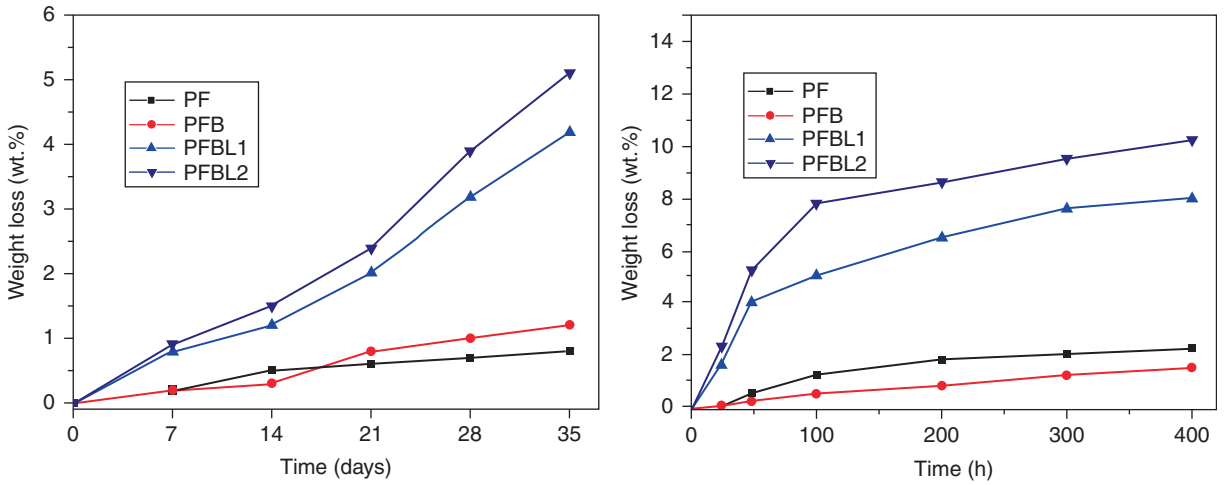

Figure 15 The degradation profiles in phosphate buffer (pH 7.2) at 37 °C: (a) without proteinase K and (b) with 0.2 mg ml^{-1} proteinase K. poly(ferulic acid) (PF); poly(ferulic acid -co-4-hydroxybenzoic acid) (PFB); (poly(ferulic acid-co-4-hydroxybenzoic acid-co-D,L-lactic acid) (PFBL). Reproduced with permission from Du, J.; Fang, Y.; Zheng, Y. *Polymer* **2007**, *48*, 5541.[114]

have shown the use of secondary dispersion of PPSu for the encapsulation of model drug sodium fluvastatin. The nanoparticles in aqueous system were prepared by w/o/w emulsification-solvent evaporation method. Khoee *et al.*[111] have used PEG-PHA-PEG, PEG-polybutylene adipate-PEG, and PEG-PEAd-PEG triblock copolymers made by condensation polymerization (Scheme 29) for the encapsulation of quercetin (anticarcinogenic, allergy inhibitor, and antibacterial agent) and showed a sustained release behavior. PEG-polyester-PEG can self-assemble to form nanosized spheres

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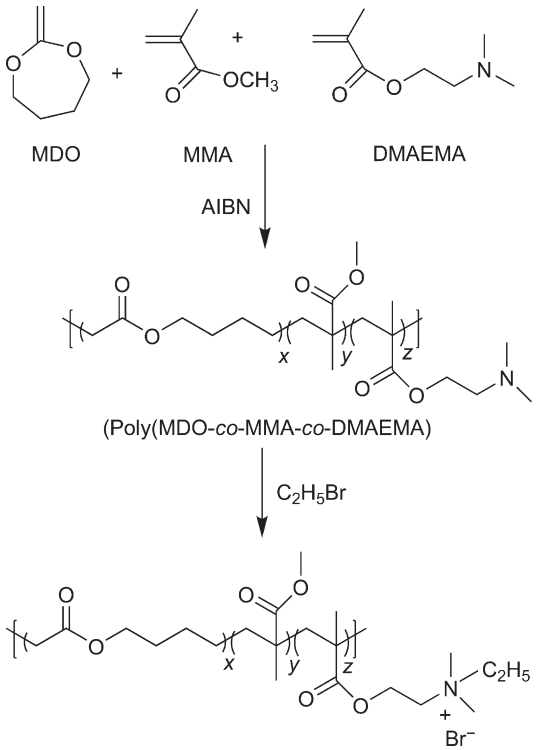

Scheme 27 Synthesis of PCL-based degradable ionomers using free radical chemistry.

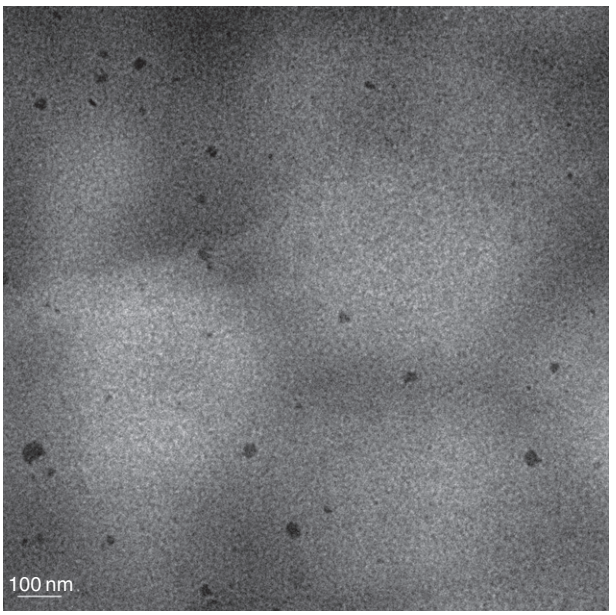

Figure 16 TEM pictures of P(MDO-*co*-MMA-*co*-DMAEMA)•BrC_2H_5 containing 9% ion (40-50-10); sample prepared by film casting on the TEM grid. Reproduced with permission from Ren, L.; Agarwal, S. *Macromolecules* **2009**, *42* (5), 1574.[115]

consisting of a hydrophilic outer shell and a hydrophobic inner core in an aqueous medium that can be used to incorporate lipophilic drugs and release them in a controlled manner.

Interestingly, Kallinteri *et al.*[122] in a highly enzyme-specific reaction prepared a linear polyester with one free pendant hydroxyl group per repeat unit by condensation polymerization of glycerol and divinyladipate and showed it to be a promising drug carrier system.

Polyester nanoparticles can also be made *in situ* during the synthesis, that is, emulsion or miniemulsion polymerization.[123] The process requires water-insoluble monomers and a surfactant. The technique of miniemulsion has the advantage

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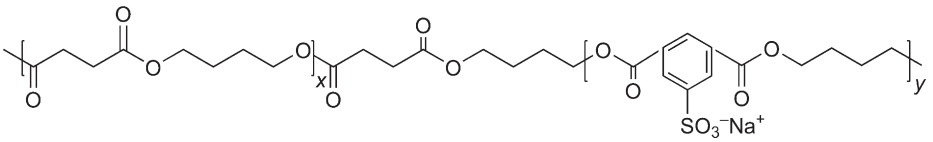


Scheme 28 Chemical structure of polyester-based ionomers based on PBSu with 1–5 mol.% dimethyl 5-sodium sulfoisophthalate units randomly distributed.

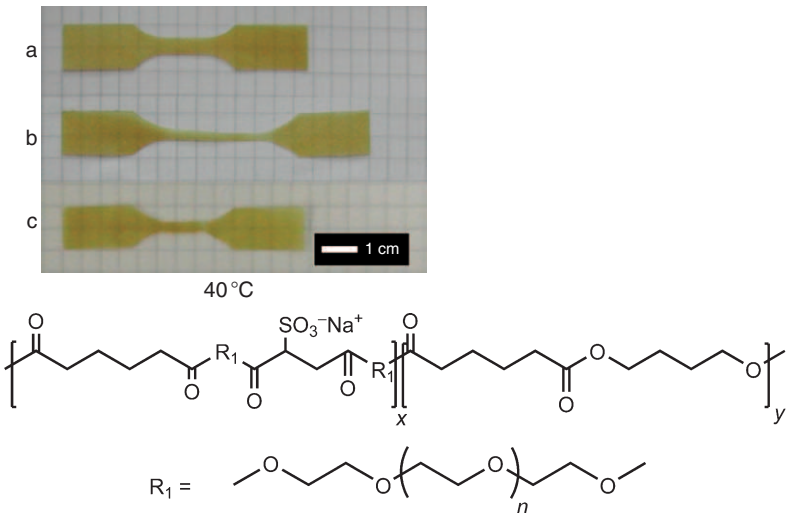
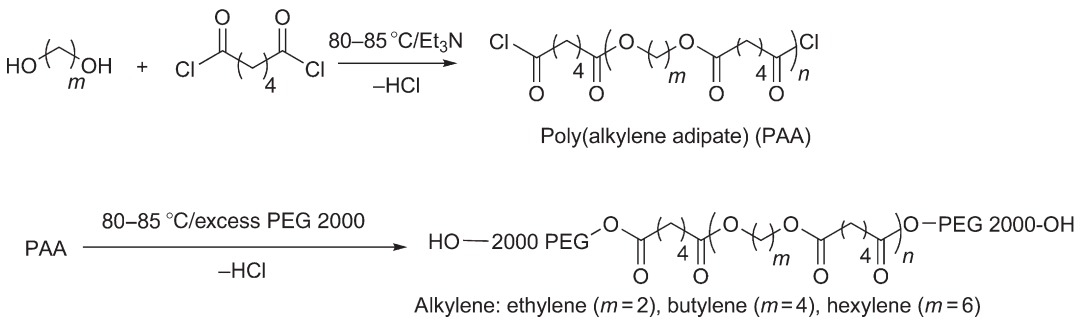


Figure 17 Biodegradable polyester ionomers based on polycondensation of adipic acid and mixed monomers of bis(poly(oxyethylene)) sulfonated dimethylfumarate and 1,4-butanediol and shape recovery: (a) initial state; (b) deformed state; and (c) shape-recovered state. Reproduced with permission from Han, S. I.; Gu, B. H.; Nam, K. H.; *et al. Polymer* **2007**, *48*, 1830.[117]



Scheme 29 Triblock CPEs with PEG as a drug carrier.[121]

of using only water and no organic solvent and gives dispersions with high solid contents. This could be of great importance for many different biomedical applications where organic solvents should be avoided.

5.15.6 Conclusions

Polyesters are an important class of degradable polymers. Some of them are commercialized for different applications and many of them are of only academic interest. Besides conventional step polymerization technique, some other methods have been developed like ROP of cyclic esters and free radical ROP of CKAs for their synthesis to overcome the inherent disadvantages of low molecular weight, property modification, difficulty of processing, and so on. Besides linear polyesters, many new architectures have also been developed for different purposes and in fact showed an edge over linear counterparts for many application areas like catalysis and drug encapsulation. Degradable shape-memory polymers could simplify many of the problems in medicine by providing materials for different applications like minimal invasive surgery and smart sutures. The development that has taken place regarding the use of different forms of polyesters is also significant. There are different methods for making polyester-based degradable nanoparticles. Even polycondensation can be carried out in emulsion/miniemulsion. Thus, there is room for exponential growth in the field of biodegradable polyesters including

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development of new synthetic methods and new architectures, thereby providing a wide spectrum of properties in terms of mechanical and thermal properties with varied degradation rates and also opening new intended application areas.

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5.16 Polycarbonates

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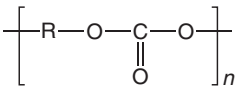
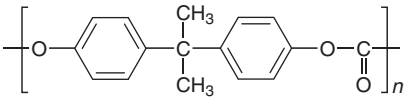
5.16.1 Introduction

Polycarbonates (PCs) are a class of polymers with carbonate linkages. PCs are classified as aliphatic or aromatic PCs, depending on the structure of the R groups. In this chapter, PCs in which the carbonate group is directly connected to an aromatic carbon are defined as aromatic PCs. Others are defined as aliphatic PCs. In 1881, Birnbaum and Lurie first reported the synthesis of PCs by polycondensation of resorcinol.



Thereafter, numerous species of PCs were synthesized. In the 1950s, Schnell and Fox independently found that PCs derived from bisphenol A (BPA, 2,2-bis(*p*-hydroxyphenyl) propane); have excellent performance characteristics such as high heat capability, optical clarity, and extreme toughness. They are extremely useful as engineering plastics and have become one of the most commercially successful classes of synthetic polymers. Millions of tons of BPA-based PCs are currently produced and used every year throughout the world.

Most of the BPA-based PCs have been produced in the phosgene process. The phosgene process has some advantages including easy synthesis, moderate reaction conditions, and excellent properties of products. On the other hand, it also has some drawbacks, such as the usage of highly poisonous phosgene and chlorinated solvents.



In recent years, industries have been developing more environmentally benign synthesis processes without poisonous phosgene and chlorinated solvents, using carbon monoxide or carbon dioxide as alternatives to phosgene, from the viewpoint of green chemistry and protection from the greenhouse effects.

In contrast to aromatic PCs, aliphatic PCs have received less attention from industry because of their moderate properties. However, in recent years, some aliphatic PCs derived from carbon dioxide- and biomass-based materials have been highlighted because of new promising alternatives for the present fossil resource-based plastics.

This chapter mainly describes the synthesis technologies of various PCs – both commercialized and under development. We will also outline the history of PC synthesis, the properties of PCs, and their uses.

5.16.2 Historical Development of PCs

Birnbaum and Lurie first prepared PCs in 1881 via the polycondensation of resorcinol and phosgene in the presence of pyridine.[1] Einhorn extended this phosgene method

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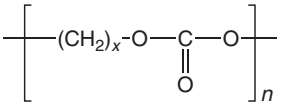
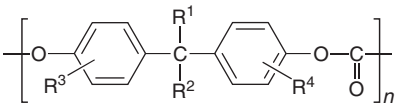
to hydroquinone in 1898.[2] A few years later, Bischoff and Hendenström prepared similar polymers via transesterification between bisphenols and diphenyl carbonate (DPC).[3] These PCs derived from dihydroxy phenols possessed a low molecular weight; were brittle, crystalline, and insoluble in most solvents; and proved difficult for further processing and characterization.

In the early 1930s, Carothers of DuPont (USA) studied the synthesis of various aliphatic PCs via the transesterification of alkyl diol and diethyl carbonate and via the ring-opening polymerization (ROP) of low-molecular-weight cyclic PCs.[4] However, the aliphatic PCs obtained were waxlike solids with low molecular weights and low melting points and did not demonstrate sufficient interesting properties for commercial production.



$x = 3, 4, 5, 6, 10$

In the 1950s, Schnell of Bayer AG (Germany) extensively reexamined the chemistry of aromatic PCs and discovered that PCs derived from 4,4′-dihydroxydiarylalkanes exhibit excellent properties as structural materials. This implies that, unlike aliphatic PCs, these aromatic PCs exhibited unusual and useful properties such as extreme toughness, optical transparency, thermal stability, and solvent resistance.[5] They prepared and examined various types of PCs derived from 4,4′-dihydroxydiarylalkanes.



Among these compounds, the PC prepared from BPA exhibited excellent toughness, thermal stability, and transparency, and the cost of BPA is much lower than other precursors. Bayer started industrial production of BPA-derived PC under the commercial name Makrolon in 1959. At the same time, Fox of General Electric (USA) also independently developed bisphenol-type PCs and commercialized this PC resin under the commercial name Lexan in 1960.[6]

In the beginning of the development of BPA-based PC, both the processes of transesterification using DPC and the phosgene-based interfacial polycondensation were examined. The material obtained in the transesterification process had some drawbacks, such as poor resin color, low thermal stability, low water resistance, and lower molecular weight. Therefore, a majority of the chemical industry has adopted interfacial processes for commercial production.

The interfacial process also has some disadvantages, such as using highly poisonous phosgene and chlorinated solvents and complicated postpolymerization processes among others.

In 1993, GE Plastic Japan developed a new transesterification process.[7] This process, also called a melt process, precedes the transesterification of BPA and DPC under a melt state without any solvents and yields colorless, high-molecular-weight polymers. Since this development, the new transesterification processes, with some variations, have been used as alternatives for the interfacial processes.

Table 1 lists the production capacity and manufacturers of BPA-based PCs in 2009. The officially announced production capacity is over 4000 kton per year worldwide, and the melt process produces more than 22% of the PCs.

As described above, aliphatic PCs have been of little interest because of their modest properties. In 1968, Inoue *et al.* discovered a direct synthesis method for aliphatic PCs by one-step alternating copolymerization of carbon dioxide and cyclic ethers such as propylene oxide (PO).[8] This polymer has garnered much attention from industries partly because of the direct fixation of carbon dioxide, and thus protection from greenhouse gas effects. In recent years, some aliphatic PCs derived from biomass may also serve as alternatives to fossil fuel resources.

5.16.3 Properties and Uses of PCs

5.16.3.1 Aromatic PCs

When the R unit is composed of only one aromatic group, the polymer chain is very rigid and has a very high melting point and viscosity, which makes the processing of the polymer very difficult. On the other hand, when aromatic moieties of R of a polymer are connected with some linkages such as BPA, the polymer becomes softer and suitable for processing under mild conditions.

BPA-based PC has the following useful properties:

1. High thermal stability
   a. A high glass transition temperature: 145–155 °C
   b. A high melting point: 220–230 °C
2. High strength at low temperatures (very strong even at −100 °C)
3. High flame retardancy
4. High weather resistance
5. High impact resistance
6. Significant electrical insulation properties
7. Low water absorbability (< 0.36%)
8. High dimensional stability
9. The largest transparency among the common engineering plastics
10. A high gross yield
11. Easy moldability
12. Ease to paint and decorate
13. Safety in medical and food contact applications.

However, BPA-based PC also has the following flaws:

1. It is slightly decomposed by alkaline solutions
2. It is slightly hydrolyzed when processed at high temperatures without complete drying.

BPA-based PCs are used in a wide range of fields, such as:

1. electrical applications – computer covers, cell phones, support of voltage-carrying components, and insulating separations of electrical elements;
2. optical applications – CDs/DVDs, light covers for automobiles, and glasses;
3. construction – windows, greenhouses, and dome construction;
4. household and consumer articles – kitchen sinks, nursing bottles, and helmets;

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Table 1 Production capacity of polycarbonate (2009: unit 1000 ton yr^{-1})

Manufacturer	*Process site*	*Production capacity*	*Process type*
Mitsubishi Chemical Group			
Mitsubishi Gas Chemical Company, Inc.	Japan	110	Interfacial
Mitsubishi Gas Chemical Company, Inc.[a]	China	80	Interfacial
Mitsubishi Chemical Co.	Japan	80	Melt
Mitsubishi Chemical Co.[b]	China	60	Melt
Thai Polycarbonate Co., Ltd.	Thailand	160	Interfacial
Samyang Kasei Co., Ltd.	Korea	110	Interfacial
Total		600	
Teijin Group			
Teijin Chemicals Ltd.	Japan	120	Interfacial
Teijin Polycarbonate Singapore PTE Ltd.	Singapore	200	Interfacial
Teijin Polycarbonate China Ltd.	China	100	Interfacial
Total		420	
Idemitsu Kosan Group			
Idemitsu Kosan Co., Ltd.	Japan	47	Interfacial
Formosa-Idemitsu Petrochemical (FIPC)	Taiwan	195	Interfacial
Total		242	
Sabic Group			
Sabic	Japan	–	Melt
Sabic	USA	550	Interfacial
Sabic	The Netherlands	200	Interfacial
Sabic	Spain	270	Melt
Total		1020	
Bayer Group			
Bayer	Germany	300	Interfacial
Bayer	Belgium	240	Melt
Bayer	USA	260	Interfacial
Bayer	Thailand	250	Interfacial
Bayer[c]	China	100	Melt
Total		1150	
Dow Chemical Group			
Sumitomo Dow Ltd.	Japan	55	Interfacial
Dow Chemical	USA	75	Interfacial
Dow Chemical	Germany	134	Interfacial
LG–Dow Polycarbonate Ltd.	Korea	170	Interfacial
Total		434	
Others			
Chi Mei–Asahi[d]	Taiwan	150	Melt
Cheil Industries	Korea	65	Interfacial
Honam Petrochemical Co.	Korea	65	Interfacial
PC de Brasil	Brazil	20	Interfacial
OAO Kazanorgsintez (KOS)	Russia	65	Melt
PCCI	Iran	25	Interfacial
Total		390	
Total		4256	

[a]Joint venture (JV) with Mitsubishi Engineering Plastics Co. (MEP).
[b]JV with MEP and SINOPEC.
[c]JV with Shanghai Chlor-Alkali Chemicals.
[d]JV of Asahi Chemical Industry Co., Ltd. and Chi Mei.
This table was made based on an article in *The Chemical Daily*, 29 May 2009, p.1, announcements by manufacturers, and private information by Drs. Okamoto and Ishii of Idemitsu Kosan.

5. medical applications – blood filters, dialyzers, and pacemaker components; and
6. packages – milk/water bottles, food containers, and milk pails.

According to the requirements of a wide variety of usages, researchers have developed numerous species of BPA-based PCs with variations of monomer structures, including variations in molecular weights, the structures

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of the polymer ends, the blends and alloys, and the copolymers.[9]

5.16.3.2 Aliphatic PCs

Since aliphatic PCs derived from aliphatic diols have an elastic structure, they are generally oily or fine crystalline polymers with low melting points at room temperature and generally have low heat resistances and low tensile strengths. These compounds are easily soluble in common organic solvents such as methylene dichloride, chloroform, benzene, acetone, and acetic acid. On the other hand, these polymers are not soluble in alcohols, ethers, or aliphatic hydrocarbons. Many of these polymers are also biodegradable.

In recent years, some researchers have developed a stereoregular polymerization of aliphatic PCs derived from carbon dioxide and epoxides that have improved melting points and mechanical strength. They also generally have low gas permeabilities.

5.16.4 Synthesis of PCs

Polymerization processes for PCs are mainly classified on the basis of the following four methods, according to their starting materials:

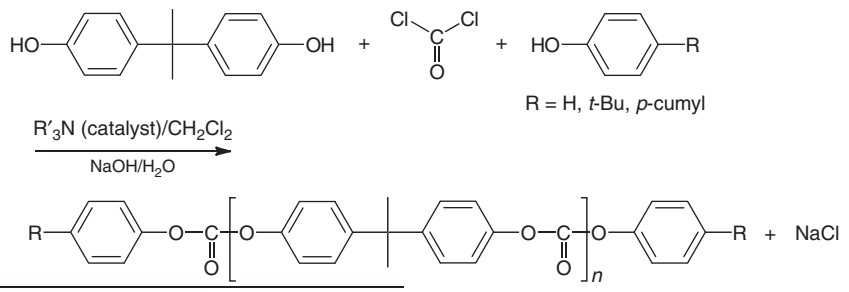
1. Interfacial synthesis process (phosgene process)
2. Transesterification process (melt or solventless process)
3. Oxidative carbonylation process (one-step process)
4. CO_2 process (synthesis process using carbon dioxide or carbonates).

The processes (1), (2), and (3) can be used to produce both aromatic and aliphatic PCs. On the other hand, (4) has been applied only for aliphatic PC synthesis at present.

5.16.5 Interfacial Synthesis Process (Phosgene Process)

Interfacial synthesis processes use carbonyl halides and diols as starting materials. The polymerization is conducted in a binary phase solvent system composed of organic solvent and water and proceeds at the interface between the organic and water phases.

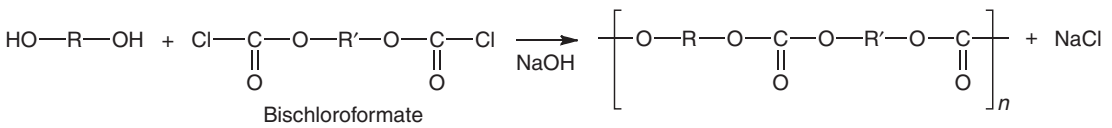
Among the various carbonyl halides, phosgene is the most active, and the reaction between phosgene and aromatic diols like BPA proceeds smoothly even at room temperature and yields high-molecular-weight polymers (eqn [1]).[5b,10]



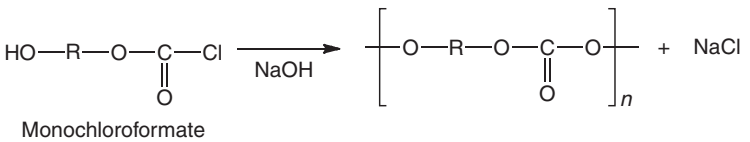
[1]

In the interfacial process, various basic compounds are added as scavengers of hydrogen halides. Sodium hydroxide is the most popular basic compound in the industry, and some other basic organic compounds such as pyridine and amines are also used. A small amount of certain types of phenols is commonly used as a chain stopper to control the molecular weight of the polymer as shown in eqn [1].

Bischloroformates (eqn [2]) and monochloroformates (eqn [3]) of diols are also applicable as carbonyl halides in the polymerization. These methods are used for the preparation of copolymers of PCs.



[2]



[3]

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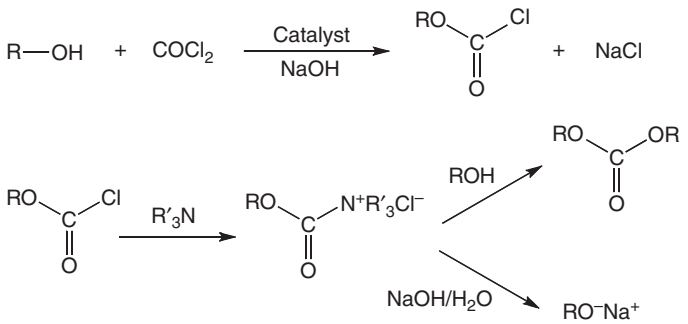
In this polymerization, the tertiary amine catalyzes the polymerization as illustrated in eqn [4].

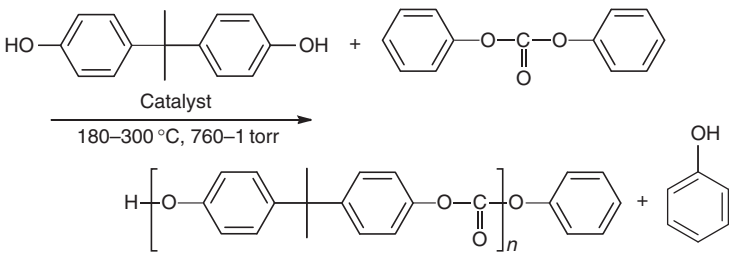


[4]

The interfacial process, especially the phosgene process, readily produces a highly transparent PC with molecular weights of 20 000–150 000. On the other hand, this process uses highly toxic and corrosive phosgene and copious amounts of chlorinated organic solvents (commonly methylene chloride). The usage of the solvent is 10 times the weight of the product. This solvent is water soluble, and thus it also contaminates the wash water. In addition, a small amount of sodium chloride remaining in the polymer may occasionally corrode the recording pits of CDs and DVDs.

5.16.6 Transesterification Synthesis Process (Melt or Solventless Process)

The transesterification synthesis process uses organic carbonate and diols as raw materials and carries out polycondensation by eliminating alcohols (eqn [5]).[5a,11–13] In the BPA-based PC synthesis, DPC is used as the starting organic carbonate. Other organic carbonates, such as dimethyl carbonates, cannot be used because of the limitations of the reaction temperature and the chemical equilibrium.



[5]

Small amounts of alkali metal salts (N, Li, and K) or tetraalkylammonium salts are commonly used as catalysts in this reaction. The polymerization is conducted at 180–300 °C and 760–1 torr for a duration ranging from tens of hours to some days under melt conditions without any solvents in a melt reactor in which phenol begins to be liberated according to the equilibrium as shown in eqn [5].

In general, this process depends on the polymerization level. That is, as the raw materials pass through different reactors, the temperature of the reaction is increased, and the vacuum is set higher in the latter steps in order to remove phenol from the equilibrium to drive the reaction to higher molecular-weight polymers. In the latter stage, the polymer melt becomes viscous, and special equipment, such as film evaporators, multiple vacuum-vented extruders, and helicone reactors, is used to effectively remove phenol. After the polymerization, the melt polymer is directly pelletized.

The transesterification process has various advantages compared to the phosgene process. That is, it does not use poisonous phosgene and hazardous chlorinated solvents. Phenol is the only by-product of this process, and it can be recovered and recycled. The polymer can also be pelletized directly without washing in advance.

However, this process requires much more production energy because of its severe reaction conditions. In addition, the polymer is exposed to high temperature conditions for a long period during the reaction. In the early works on this process, thermal oxidation in the presence of catalysts colored the polymer. Recently, problems such as the coloring and decomposition of the polymer were relatively suppressed because of the following reasons: development of high-performance catalysts such as organic amines (amines, imidazoles) and organic phosphorus compounds (phosphines, phosphonium salts, and phosphates); improvements to the reaction vessel, including better vacuum sealing and the depression of air leakage into the reactor; and the use of pure starting materials.

The solid polycondensation of amorphous PC oligomers developed by Asahi Chemical Industry (Japan) also significantly contributed to the improvement of the quality of the polymers.[14] They first prepared amorphous PC oligomer, 'prepolymer', (molecular weights of 2000–20 000) via the transesterification of BPA and DPC and were then heated the crystallized prepolymer to further polymerize under vacuum or a stream of inert gas. This process produced higher quality PCs applicable even for optical uses.

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In the transesterification methods, the effective preparation of DPC is the key technology to develop an efficient polymerization process. Thus far, various methods of DPC synthesis have been proposed as follows: (1) a phosgene process, (2) a dimethyl carbonate (DMC) transesterification process, (3) a diphenyl oxalate (DPO) decarbonylation process, and (4) an oxidative carbonylation process.

5.16.6.1 Phosgene Process for DPC Synthesis

Phosgene is a very active carbonyl chloride and reacts readily with phenols in the liquid phase in the presence of sodium hydroxide as described in Section 5.16.5 (eqn [6]).[15] This method has been employed in industry from the beginning of PC production. However, there are some disadvantages to this method, such as the usage of highly toxic phosgene and the byproduction of large amounts of sodium chloride.

$$2PhOH + COCl_2 + NaOH \longrightarrow DPC + 2NaCl + H_2O \quad [6]$$

Mitsubishi Chemical (Japan) developed a new synthesis method in which the phosgenation of phenol is carried out without sodium hydroxide (eqn [7]).[16,17] This process produces only hydrogen chloride, which can be recovered and recycled for other uses.

$$2PhOH + COCl_2 \longrightarrow DPC + 2HCl \quad [7]$$

5.16.6.2 DMC Transesterification Process for DPC Synthesis

In the present industry, the most popular method of DPC synthesis is the transesterification of phenol with DMC in the presence of some catalysts similar to the PC synthesis process.

DPC is produced via two-step reactions as shown in eqn [8]. That is, transesterification between phenol and DMC is followed by the disproportionation of methyl phenyl carbonate. Both reactions occur under equilibrium conditions; therefore, the effective removal of methanol from the reactor is essential in order to improve the DPC yield. Since methanol (bp 64.7 °C) and DMC (bp 90 °C) have relatively close boiling points and form an azeotropic mixture, some processes use a reaction–distillation technique to remove methanol from the reactor effectively. The use of catalysts such as Lewis acids (Bu_2SnO, $Ti(OR)_4$, and $Pb(OPh)_2$) and solid acids (SiO_2/Al_2O_3, MoO_3/SiO_2) can accelerate these reactions.

DMC not only is a key intermediate for DPC synthesis but also has a variety of uses, including applications as an organic solvent, an octane booster/antiknock additive for gasoline, and others.[18] The development of an effective synthesis method for DMC is essential to design a highly effective DPC synthesis process. Thus far, researchers have proposed the following various methods for DMC synthesis: (1) phosgenation of methanol, (2) oxidative carbonylation of methanol, (3) carbonylation of methyl nitrate (MN) and decarbonylation of dimethyl oxalate (DMO), and (4) transesterification of cyclic carbonate.

1. Phosgenation of methanol was the most popular method of DMC synthesis before the 1980s (eqn [9]).

$$2CH_3OH + COCl_2 \longrightarrow (CH_3)_2CO + 2HCl \quad [9]$$

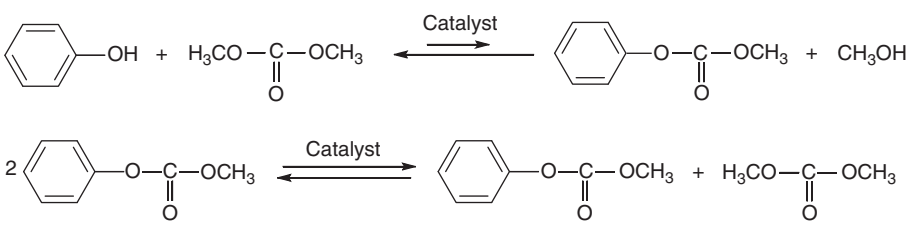
Since the 1980s, researchers, mainly within the chemical industry, have intensively developed non-phosgene routes to DMC synthesis. At present, all of the non-phosgene processes (2)–(4) are utilized in the commercial production of DMC.

2. The oxidative carbonylation of methanol is catalyzed by copper catalysts developed by ENIChem (Italy)[19] and licensed to GE for the DPC manufacturing process (eqn [10]).

$$2CH_3OH + CO + \frac{1}{2}O_2 \xrightarrow{Cu} (CH_3O)_2CO + H_2O \quad [10]$$

Scheme 1 illustrates the general reaction mechanism in the DMC synthesis with copper catalysts. The reaction occurs in the liquid phase. A vapor-phase reaction process was also developed using solid catalysts such as $CuCl_2$ supported on activated carbon. The partial pressure of oxygen is maintained much lower than that of CO to avoid the formation of an explosive mixture of CO and O_2.

3. The methyl nitrate process developed by Ube Industry, Japan, is a variation of the direct methanol oxidative carbonylation process.[20] Methanol is first oxidized to MN with NO and O_2 under mild conditions (2–3 atm, 40 °C) in the absence of a catalyst. The MN is separated from the coproduced water and carbonized by palladium (Pd^{2+}) catalysts in the presence of O_2 to form DMC. The reaction occurs in the gas phase over a heterogeneous catalyst bed. Using palladium metal (Pd^0) catalyst, MN is carbonized to DMO, which can also be converted to DMC (eqn [11]).[21]



[8]

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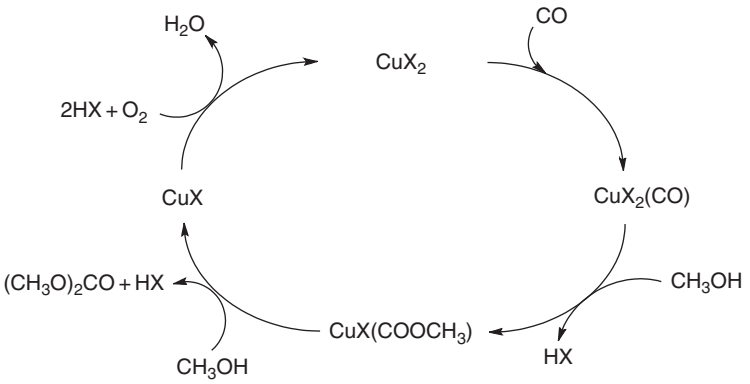


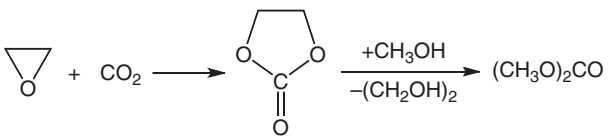
Scheme 1 A general mechanism of DMC sythesis by oxidative carbonylation with copper catalysts.

$$CH_3OH + NO + \frac{1}{2}O_2 \longrightarrow CH_3ONO + H_2O$$

$$CH_3ONO + CO \xrightarrow[-NO]{Pd^{2+}} (CH_3O)_2CO$$

$$CH_3ONO + CO \xrightarrow[-NO]{Pd^{0}} (COOCH_3)_2 \xrightarrow[-CO]{} (CH_3O)_2CO \qquad [11]$$

4. The process of transesterification of cyclic carbonate uses CO_2 and ethylene oxide (EO) as starting materials. That is, CO_2 and EO form ethylene carbonate (EC),[22] then EC is converted to DMC by transesterification with methanol (eqn [12]). Asahi Chemical Industry applied this reaction to develop a new process for BPA-based PC production. The details of this process will be described in 5.16.9.



[12]

5.16.6.3 DPO Decarbonylation Process for DPC Synthesis

This process related to the methyl nitrate process was developed by UBE Industry.[23] Here, methyl nitrate is oxidized to DMO, and then continuously converted to DPO by transesterification with phenol. Decarbonylation converts DPO to DPC in the presence of catalysts composed of Me_4NCl, alkali carbonates, and alkali halides at temperatures around 200–230 °C, as shown in eqn [13].

5.16.6.4 Oxidative Carbonylation Process (One-Step Process) for DPC Synthesis

The direct oxidative carbonylation process, which is also called the one-step process, is a simple and energetically favorable alternative non-phosgene route to DPC synthesis using phenol, carbon monoxide, and oxygen as shown in eqn [14].

$$2PhOH + CO + \frac{1}{2}O_2 \longrightarrow PhOCOOPh + H_2O \qquad [14]$$

The catalytic oxidative carbonylation of phenol to DPC is an analogue to that of methanol to DMC. However, synthesis of DPC is much more difficult than that of DMC due to the higher acidity of phenol. Therefore, one-step DPC technology is not currently used in commercial production.

The development of high-performance catalysts is one of the most important key technologies required to realize this process. If a catalyst with nearly perfect conversion and selectivity for the monomer of a PC could be developed, a one-step process can also be applied for PC synthesis using BPA instead of phenol. Since the pioneering works by Chalk[24] and Hallgren,[25] researchers have proposed various palladium-based catalysts for these syntheses. Details of the oxidative carbonylation of phenol and BPA will be described in 5.16.8.

5.16.7 ROP of Cyclic Oligomers

BPA-based PCs can be prepared via ROP of cyclic oligomers with BPA. It is possible to prepare very high-molecular-weight polymers in a single step.

Schnell first studied the ROP of BPA cyclic oligomers in the early 1960s.[26] However, due to the difficulty in preparing

$$CH_3OH \xrightarrow[-H_2O]{HONO} CH_3ONO \xrightarrow[-NO]{CO} (COOCH_3)_2 \xrightarrow[-CH_3OH]{PhOH} (COOPh)_2 \xrightarrow[-CO]{} PhOCOPh \qquad [13]$$

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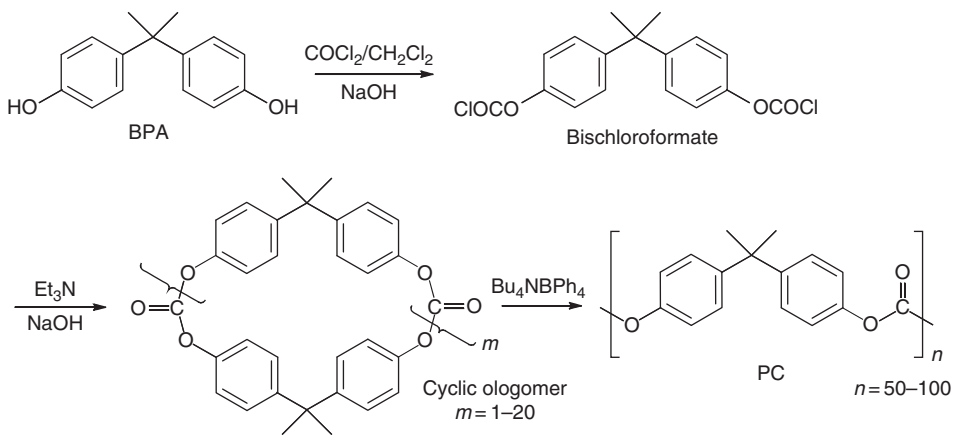
the cyclics and the high melting point of the crystalline BPA cyclic tetramer, further study of the melt polymerization of cyclics was rather difficult. In the early 1990s, Brunelle of GE developed a new method for the preparation of a mixture of cyclic oligomers of BPA.[27] This process utilizes a triethyl amine-catalyzed hydrolysis condensation of BPA bis-chloroformate in a quasi-dilute solution. This method provides an 85–90% yield of a mixture of cyclic oligomers with a degree of polymerization of 2 to about 20. On the other hand, the yields of linear oligomers are very low – less than 0.01%. Because the mixture of cyclics had a wide distribution of molecular weights, the mixture was amorphous, and the melting point was around 200 °C, which was much lower than that of the crystalline cyclic tetramer. Melt polymerization of the cyclic oligomers was carried out at 200–300 °C and yields very high-molecular-weight polymers ($M_w \geq 700\,000$) (eqn [15]). This ROP is driven not by enthalpy but by entropy, which yields the highest molecular weights.



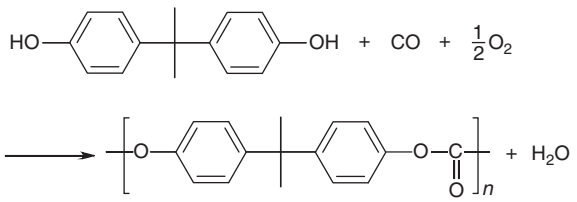
[15]

The reactivity of the BPA cyclic oligomers significantly depends on the size of the cyclics. The cyclic dimer (mp 330–335 °C), which is the smallest cyclic oligomer and has the largest ring strain, exhibits the highest ROP reactivity and gives ultra-high-molecular-weight polymer ($M_w \geq 2\,000\,000$) in the 5 min reaction at 300 °C without any catalysts. Cyclic trimer (mp 345–350 °C) and tetramer (mp 368–372 °C) showed lower reactivity than the cyclic dimer and gave polymers with molecular weights of 1 290 000 (300 °C, 15 min) and 866 000 (300 °C, 120 min), respectively.[28]

Although the process of the ROP of cyclic oligomers is not currently commercialized, this process has some promising applications. The cyclic oligomers have rather low viscosities and rapidly produce very high-molecular-weight resins without the evolution of volatile materials such as water, phenol, or DPC. These characteristics demonstrate that the ROP can be applicable in injection molding processes for easily preparing high-performance resins.

5.16.8 Oxidative Carbonylation Process (One-Step Process)

The oxidative carbonylation synthesis process uses carbon monoxide as a carbonyl source of the carbonate structure of PCs in the presence of small amounts of oxygen as shown in eqn [16]. This reaction is a very simple and energetically favorable alternative candidate for the non-phosgene route to PC and DPC productions.



[16]

Catalytic oxidative carbonylation of phenolic compounds to DPC or PCs is an analogue to that of methanol to DMC. However, because the acidity of phenol is much higher than that of methanol, synthesis of DPC or PCs is much more difficult than that of DMC.

In the mid-1970s, Chalk discovered a stoichiometric carbonylation of *para*-substituted phenols using a catalyst composed of a Group VIIIB element selected from Ru, Rh, Pd, Os, Ir, and Pt.[24] In practice, only Pd exhibited practical activity for further study. Hallgren *et al.* of GE has done pioneering work on this synthesis in the 1980s.[25] They studied the reaction of phenol with CO and O_2 at atmospheric pressure and room temperature using palladium chloride and tertiary amine to produce DPC and arylsalicylate as a by-product. They also tried PC synthesis using BPA under similar reaction conditions and got PC oligomers with molecular weights of 2000–10 000. The palladium salts worked stoichiometrically in these reactions. That is, during the carbonylation of phenol, the palladium atom in the oxidative state is reduced to a metallic state.

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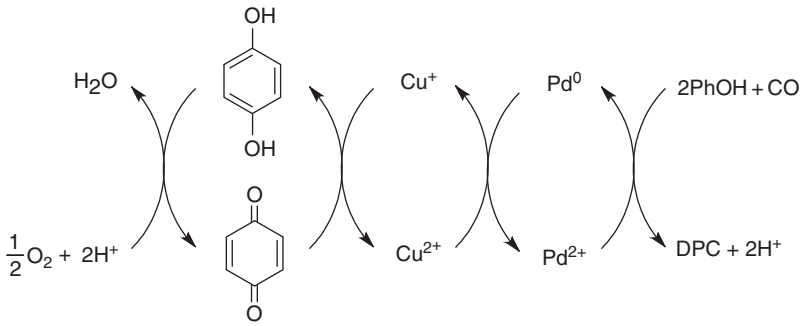

Scheme 2 A proposed redox mechanism of the Pd–Cu–hydroquinone catalyst system.

Therefore, to convert these reactions into a catalytic process, a reoxidation mechanism of the reduced Pd to regenerate the active palladium species is required. As reoxidation cocatalysts, inorganic metal salts such as Cu, Mn, and Pb compounds were used. Organic redox reagents such as hydroquinone were also occasionally used together with inorganic redox reagents to accelerate the reaction. Scheme 2 shows a proposed redox mechanism of the Pd–Cu–hydroquinone catalyst system.

In addition, the oxidative carbonylation of phenols is an equilibrium reaction, and to improve the yield of carbonates, it is essential to remove the byproduced water from the reaction system effectively.[29]

Thus far, researchers have proposed various catalyst systems, mainly for DPC synthesis. Many of these catalysts were composed of palladium compounds and inorganic redox cocatalysts. Some of them contained hydroquinones, quaternary ammonium salts, and phosphonium halide salts and/or desiccants in addition to these metallic elements. Quaternary ammonium salts and phosphonium halides activate the phenoxide ions.

As a palladium source, palladium halides ($PdCl_2$, $PdBr_2$), Pd $(OAc)_2$, carbonyl complexes (Pd(CO)Cl), palladium complexes, giant palladium clusters, and palladium metal or compounds supported on some solid, such as activated carbon, silica gel, and organic resin (cross-linked polystyrene), were examined. As inorganic redox cocatalysts, salts and compounds of copper, vanadium, manganese, lead, and cerium were tested. As quaternary ammonium salts or phosphonium halide salts, pyridines (pyridine, terpyridine), tetraalkyl ammonium halides (Bu_4NBr), and phosphonium halides ($(Ph_3P{=})_2NBr$) were tested.

These catalysts were tested mainly in the DPC synthesis. By using these catalysts, the charged phenol was converted to DPC in a maximum yield of about 80%. Some of these catalysts were applied to polymer synthesis using BPA. Takeuchi *et al.* determined that the palladium complexes with 2-substituted bipyridine-type ligands or carbine-type ligands illustrated in Figure 1 have high activities in the oxidative carbonylation of BPA and discovered some high-performance multicomponent catalysts composed of a Pd complex, a Mn or Ce complex as an inorganic redox cocatalyst (Mn, Ce), hydroquinone as an organic redox cocatalyst, quaternary amine (n-Bu_4NBr) or phosphonium halide ($(Ph_3P{=})_2NBr$), and a molecular sieve as a desiccant. These catalysts exhibited high activities (Pd turnover number >10 000) and produced high-molecular-weight PCs in a good yield (M_w: 12 000–24 000) in a one-step reaction under the reaction conditions of P(CO) 6.0 MPa and $P(O_2)$ 0.3 MPa at 100 °C. These palladium complexes supported on solid polystyrene or some clays such as hydrotalcite also show high catalytic activities, which enable the recycled use of the catalyst. This reaction requires some solvents, such as methylene chloride. They also reported that some nonhalogenated solvents such as propylene carbonate also worked as a good solvent for PC in the reaction.[30]

5.16.9 CO_2 Process (Synthesis Process Using Carbon Dioxide or Carbonates)

Carbon dioxide is the most fundamental carbon resource on Earth, and vast quantities of CO_2 are exhausted every day worldwide. Carbon dioxide is a readily available, cheap, nonflammable, nontoxic, and renewable substance. Technologies for the chemical utilization of CO_2 have been extensively developed, not only for innovating new materials but also for environmental issues.

Carbon dioxide has the potential to be a monomer in PC synthesis as a carbonyl source. Thus far, researchers have proposed the following reactions: (1) PC synthesis via cyclic carbonate transesterification, (2) copolymerization of CO_2 with cyclic ethers, and (3) polycondensation of CO_2 with aliphatic dihalides. Other carbonate compounds are also available for PC syntheses.

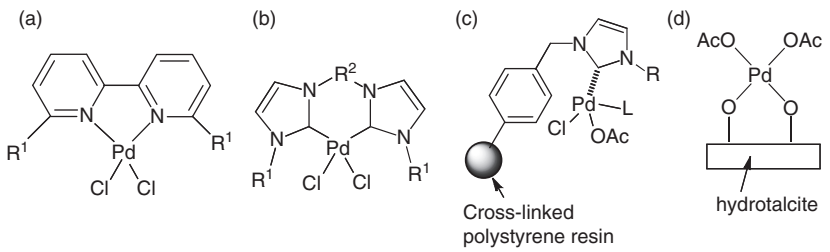

Figure 1 Palladium catalysts for DPC and PC syntheses by oxidative carbonylation of phenol and BPA. (a) Pd–bipyridine complex, (b) Pd–carbene complex, (c) Pd–complex supported on polystyrene, (d) Pd–complex supported on hydrotalcite.

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5.16.9.1 PC Synthesis Via Cyclic Carbonate Transesterification

Some cyclic ethers, such as epoxides and oxetanes, readily form cyclic carbonates with CO_2. For example, EO and CO_2 readily form EC under mild conditions as described in Section 5.16.6.

Asahi Chemical Industry developed a new process for PC synthesis.[31] This process is one of the transesterification processes between DPC and BPA described in Section 5.16.6. In this process, DMC, an intermediate of DPC, is prepared via the transesterification of EC and methanol, and EC forms from EO and CO_2 as shown in **Scheme 3**.

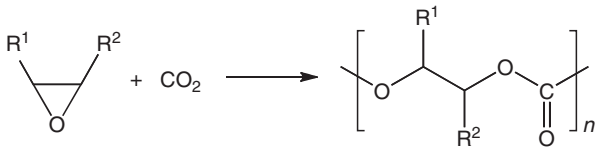
This process was originally designed in combination with an ethylene glycol (EG) preparation process via the oxidation of ethylene. That is, in the ethylene oxidation step, only one atom of an oxygen molecule is used to form EO, and the other atom remains on the surface of the silver-based epoxidation catalyst. To restore the catalytic activity, ethylene is used to remove this oxygen atom from the surface, producing a large quantity of CO_2. Asahi Kasei's process utilizes this CO_2 and EO to prepare EC. The EC is converted to DMC with methanol then to DPC with phenol; the compound is then converted to PC prepolymer and finally to a high-molecular-weight PC, all via consecutive transesterifications.

This process is characterized as an environmentally benign method with non-phosgene and non-chlorinated organic solvents. In addition, the PC obtained in this process possesses good transparency by applying solid polycondensation of the PC prepolymer at the final stage. This process also provides dry EG as the by-product in the transesterification step of EC and methanol.

This is the first process using CO_2 as a starting material for polymer synthesis and has already been commercialized by Asahi-Chi Mei in Taiwan in 2002.

5.16.9.2 Copolymerization of CO_2 and Cyclic Ethers

In 1968, Inoue *et al.* reported a direct copolymerization of carbon dioxide and epoxides in the presence of zinc catalysts as shown in eqn [17].[32] This process is the first example of incorporating CO_2 directly in the main chain of a polymer.

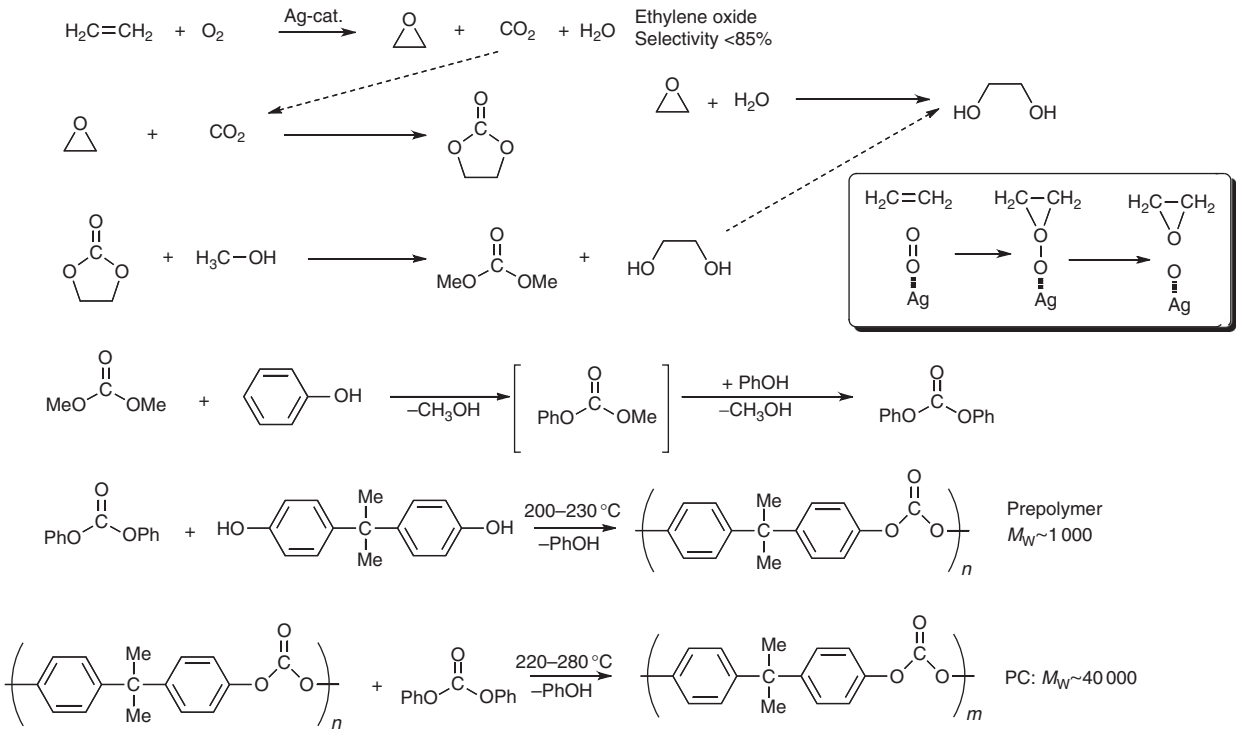


[17]

The zinc catalyst was prepared by the equimolar reaction of diethylzinc and water. The polymerization was carried out in an autoclave using PO, pressurized CO_2 (5.0 MPa), dioxane as a solvent, and the catalyst at room temperature for 1 day. The obtained polymer has a sufficiently high molecular weight of 50 000–150 000 and exhibits an alternating structure of CO_2 and EO.

Since this discovery, the copolymerization of CO_2 was extended to other epoxides, such as EO, PO, butene oxide, styrene oxide, and cyclohexene oxide (CHO).

Oxetane, a four-membered cyclic ether, also copolymerizes with CO_2. In the presence of a catalyst composed of triethyl aluminum, water, and acetyl acetone, researchers obtained a copolymer composed of a mixture of PC and polyether linkages.[33] A catalyst composed of organotin halide and a Lewis base gave an alternating copolymer of CO_2 and oxetane (eqn [18]).[34] On the other hand, the $ZnEt_2$–H_2O catalyst yielded no polymers at all. Cyclic ethers larger than five-membered rings have no copolymerization activities with CO_2.



Scheme 3 PC sythesis via transesterification of CO_2–derived cyclic carbonate

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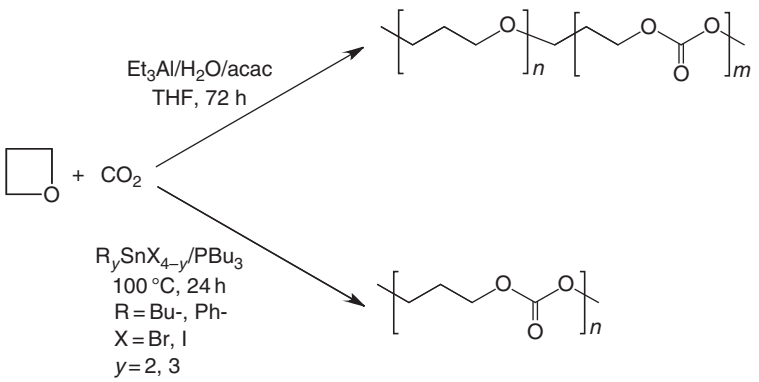


[18]

Other than the $ZnEt_2$–H_2O catalyst, other organozinc and organoaluminum compounds exhibited catalytic activities in the CO_2-alternating copolymerization. Compounds of chromium, cobalt, manganese, and nickel and rare earth metals such as neodymium, lanthanide, and yttrium also function as good catalysts.

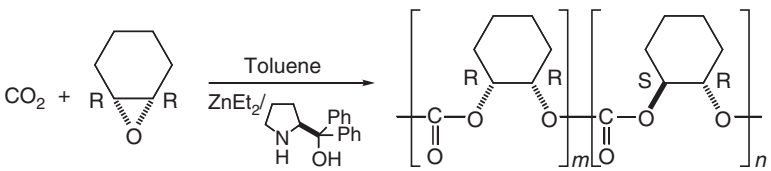
A Chinese company reportedly began commercial production of the CO_2-derived polypropylene carbonate (PPC) as a plasticizer/additive for rubber, thermoplastics, and surfactants using multicomponent catalysts based on zinc and rare earth metals in 2007.

The alternating copolymerization of CO_2 and epoxides is considered via the alternating repetition of the addition of CO_2 and epoxide to the active terminal of the growing polymer. During the copolymerization, epoxide is occasionally incorporated in the chain repeatedly, forming ether linkages and inducing deviations from the alternation of the monomers. Five-membered cyclic carbonate, a one-to-one cyclic adduct of CO_2 and epoxide, is occasionally byproduced by the backbiting of the growing terminal end. **Scheme 4** illustrates the mechanism of the alternating copolymerization of CO_2 and epoxide in the presence of zinc catalyst.

Glass transition temperatures (T_g) of PPC and poly(cyclohexene carbonate) are 30–40 °C and 110–120 °C, respectively. The T_g of the copolymer of PO, CHO, and CO_2 can be arbitrarily controlled between 50 and 100 °C by modifying the mole ratio of PO and CHO in the copolymer.[35] Most of the alternating copolymers composed of CO_2 and epoxides are quantitatively pyrolyzed to cyclic carbonate, such as propylene carbonate, at 200–250 °C. Poly(ethylene carbonate) and PPC exhibit biodegradability.[36]

Most of the aliphatic PCs derived from CO_2 and epoxide are amorphous, and have very low tensile strengths and very low heat resistances. Therefore, these polymers are still far from practical use. Some efforts have been made to improve their properties, including stereoregulation of the alternating polymers, blends with other polymers, and others.

Nozaki *et al.*[37] and Coates *et al.*[38] reported the stereoregulation of the alternating copolymerization of CO_2 with CHO, cyclopentene oxide, and PPO using a catalyst of $ZnEt_2$–chiral amino alcohol such as the (*S*)-α,αα,α-diphenylpyrrolidine-2-yl-methanol system (eqn [19]) and a chiral zinc complex (eqn [20]), respectively.



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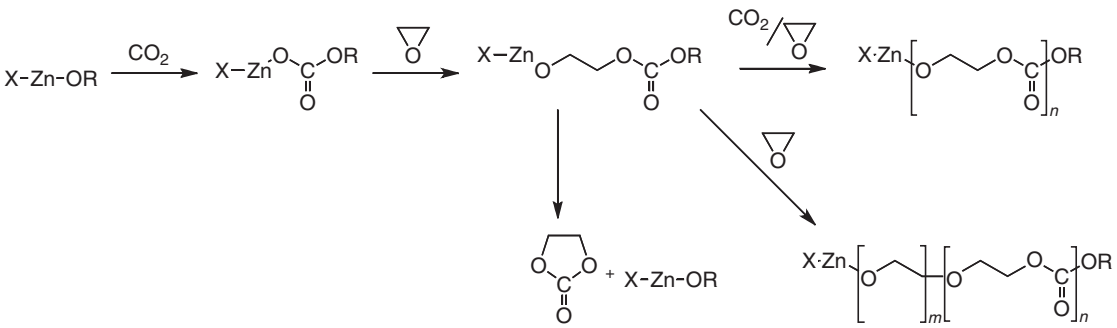

Scheme 4 Alternating copolymerization of CO_2 and epoxide and related side reactions.

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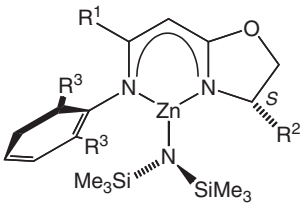


R^1 = Me, CF_3, Pr^i
R^2 = *(R)*–Ph, *(S)*–Pr^i, *(S)*–Bu^t
R^3 = Et, Pr^i

[20]

Shimizu *et al.* reported that the modulus and tensile strength of the polymer blend of PPC and poly(methyl methacrylate) (PMMA) were significantly improved by the addition of a small amount of poly(vinyl acetate) (PVAc). The polymer blend of PPC/PMMA/PVAc (70/30/5) exhibits higher tensile strength, elastic modulus, and storage modulus than low-density polyethylene (LDPE).[39]

5.16.9.3 Polycondensation of CO_2 or Alkaline Carbonates with Aliphatic Dihalides

Some organic dihalides, such as aliphatic dibromides and *p*-xylene dibromide, condense with potassium carbonate in the presence of phase-transfer catalysts, such as crown ether, to form PCs as shown in eqn [21].[40]

This polymerization is applicable only for aliphatic dihalides, not for aromatics. This reaction occurs in a solid–liquid binary phase. Crown ethers such as 18-crown-6 are commonly used as phase-transfer catalysts in this reaction and yield PCs with molecular weights of around 10 000.

Similar to potassium carbonate, organic dicarbonate salts formed by carbon dioxide and potassium salts of a diphenolic compound also react with organic dihalides and prepared PCs (eqn [22]).[41]

5.16.9.4 ROP of Cyclic Carbonates

Carothers *et al.* reported the synthesis of aliphatic PCs via the ROP of cyclic carbonates in the presence of base catalysts (eqn [23]). The polymer obtained had a low molecular weight of at most several thousands.[4a]

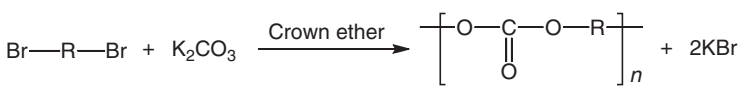
Some other aliphatic cyclic orthocarbonates (spiro-orthocarbonates) such as 18,10,19,20-tetraoxatrispiro-[5.2.2.5.2.2]heneicosane and 3,9-dimethylene-1,5,7,11-tetraoxaspiro[5.5]undecane easily produce PCs as shown in eqns [24] and [25]. These polymerizations proceed in cationic or radical ROPs by use of initiators such as Lewis acids (e.g., boron trichloride and stannic chloride) and di-*t*-butyl peroxide, respectively.[42]

This ROP occurs with essentially zero shrinkage or with some expansion. Therefore, these polymers are applicable for precision coatings, high strength adhesives, prestressed castings, and dental fillings.

5.16.10 Conclusion

BPA-based PCs are one of the most successful synthetic polymers in industry because of their excellent properties. Most of the PCs have been produced by the interfacial process using poisonous phosgene. The recent trend for 'Green Chemistry' has gradually changed the production to more environmentally benign process such as melt process. Other synthesis methods using CO and CO_2 as the carbonyl source also attract the interest of researchers' as greener chemistry. However, the phosgene process will be used in the future because it gives high-quality PCs very easily, and enables fine tuning of the molecular structure of polymer chain.

Although aliphatic PCs have been out of the spotlight, PCs prepared of CO_2 and biomass materials are expected as the materials of the next generations. The future of PCs appears to be very bright.



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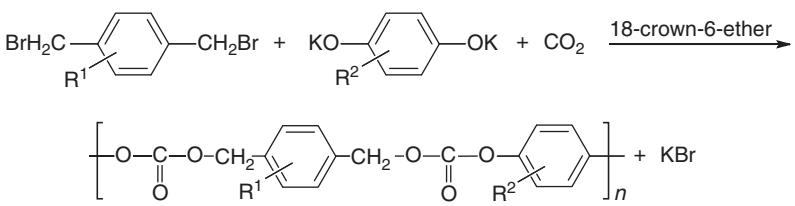

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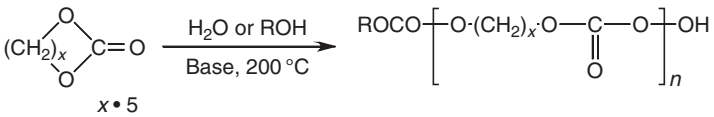

[23]

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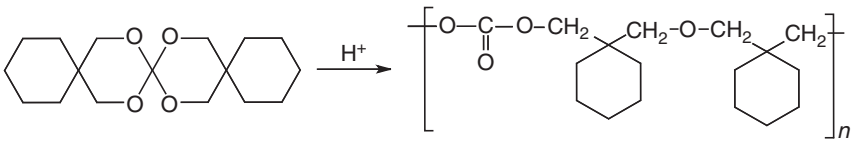

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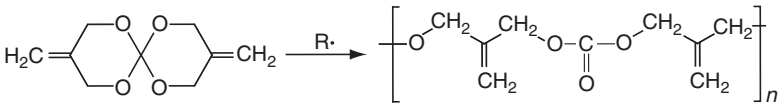

[25]

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Biographical Sketch

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5.17 Aromatic Polyethers, Polyetherketones, Polysulfides, and Polysulfones

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5.17.1 Introduction

Aromatic-based polymers are a very important group of industrial high-performance engineering materials – principally due to their significant advantages over aliphatic polymers for engineering and other high-performance applications, such as greater thermal and oxidative stability, better solvent resistance, lower flammability, and higher strength. The general structure

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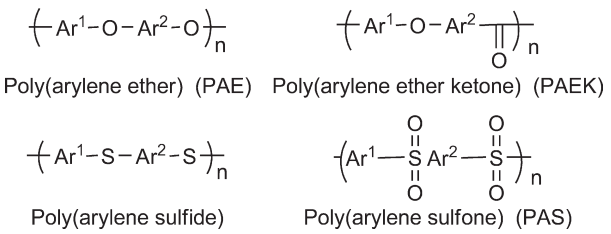

Figure 1 Typical repeat unit structures of poly(arylene ether), poly(arylene ether ketone), poly(arylene sulfide), and poly(arylene sulfone).

of aromatic-based polymers may be written as $-Ar^1-X-Ar^2-Y-$, where Ar^i's are aromatic moieties and X and Y are bridging units, which may not necessarily be the same. Ar^i's are normally phenyl, naphthyl, or even higher aromatics, substituted or unsubstituted. The bridging units (X and Y) may be an ether, ester, ketone, sulfone, sulfide, amide, imide, and so on, and may be *ortho*, *meta*, or *para* linked. A variety of polymer structures are possible by constituting various combinations of aromatic moieties, bridging units, and substitution positions. Each of these combinations generates a unique polymer structure possessing its own characteristics in terms of synthesis mechanism, morphology, thermal and mechanical properties, and many other aspects.

Rather than being an exhaustive survey describing the various types of aromatic polymers that have been reported, this chapter will focus on those aromatic polymers where the linking groups are ether, ether ketone, sulfone, and sulfide, as illustrated in Figure 1. Using specific published examples for illustration, this chapter will present an overview of the general synthetic routes, associated properties, and recent developments concerning these four high-performance polymer families.

5.17.2 Poly(arylene ether)s

Aromatic polyethers, also known as poly(arylene ether)s (PAEs) or poly(phenylene oxide)s (PPOs), are a class of high-performance thermoplastic engineering copolymers with good thermo-oxidative stability and mechanical properties. By simply incorporating –O– linkages in poly(*p*-phenylene), we can totally change the nature of the polymer so that it becomes readily processable well below the degradation temperature – in comparison to poly(*p*-phenylene), which degrades before melting. The aryl C–O–C linkage has a lower rotation barrier, lower excluded volume, and decreased Van der Waals interaction forces compared to the aromatic C–C bond, which makes the backbone highly flexible and thus lowers the glass transition temperature (T_g). It has also been suggested that the low barrier to rotation of the aromatic ether bond provides a mechanism for energy dispersion, which explains the improved toughness and impact resistance observed for this type of materials.[1] In addition, aromatic ether linkages (Ar^1-O-Ar^2) are stabilized through resonance, as illustrated in Figure 2 for diphenyl ether, which renders good thermal and mechanical properties.

In this section, PAEs containing only aryl C–O functional links in their backbone will be discussed in terms of synthesis, properties, and some applications. Other aromatic polyethers, that is, poly(arylene ether ketone)s (PAEKs), poly(arylene ether sulfone)s, poly(thio ether)s, or poly(arylene sulfide)s will be reviewed in subsequent sections of 5.17.3, 5.17.4 and 5.17.5, respectively.

5.17.2.1 General Synthesis Approaches

5.17.2.1.1 Oxidative coupling polymerization

The first commercial wholly aromatic polyether, PPO (PPO®), or more specifically, poly(2,6-dimethyl-1,4-phenylene oxide), was discovered by Hay *et al.*[2] over a half century ago and was later commercialized by General Electric[3] (now SABIC Innovative Plastics) and AKZO.[4] This compound represents an example of synthesizing a phenolic functional polymer with high molecular weight via oxidative coupling polymerization. This process involves the room temperature oxidative coupling of 2,6-dimethylphenol (DMP) in the presence of stoichiometric amounts of oxygen (oxidant), catalyzed by CuCl and an amine ligand, such as *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) or pyridine. Oxidative coupling reactions can occur via the formation of either a C–O bond, which leads to the high-molecular-weight polymer, or a C–C bond that gives rise to small dimeric molecules (Figure 3). How to maximize the C–O coupling rather than C–C coupling is the most important issue in the oxidative polymerization of phenols. In fact, the failure of phenol itself to afford a useful product under the same conditions led to the study of oxidative coupling on the substituted phenols and the subsequent development of PPO®.

The mechanisms associated with the oxidative coupling selectivity of phenols have been extensively studied by many researchers.[5–14] Among the various proposed mechanisms, the free radical process has been found to be effective. This process involves the formation of aryloxy radicals by the oxidation of the phenol with the oxidized form of the copper–amine complex, followed by enolization.[15] This mechanism is shown in Figure 4. By continuing the process of oxidation, which involves the coordination of aryloxy radicals with copper complex, radical coupling, dissociation, and enolization, we can eventually achieve a high-molecular-weight polymer. By means of electron spin resonance (ESR) spectroscopy measurements,[13,14] free radical species have been detected during the oxidation of substituted phenols. This suggests that coupling via the coordinated phenoxy radicals may mainly lead to C–O coupling and thus high-molecular-weight polymers. In essence, the oxidative polymerization of phenols more closely resembles a step-growth polymerization than a chain reaction process.

The C–O/C–C coupling selectivity and molecular weight of polymers obtained via oxidative coupling are both greatly

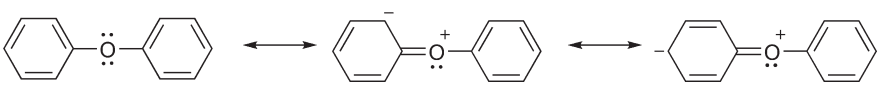

Figure 2 Resonance stabilization in arylene ethers.

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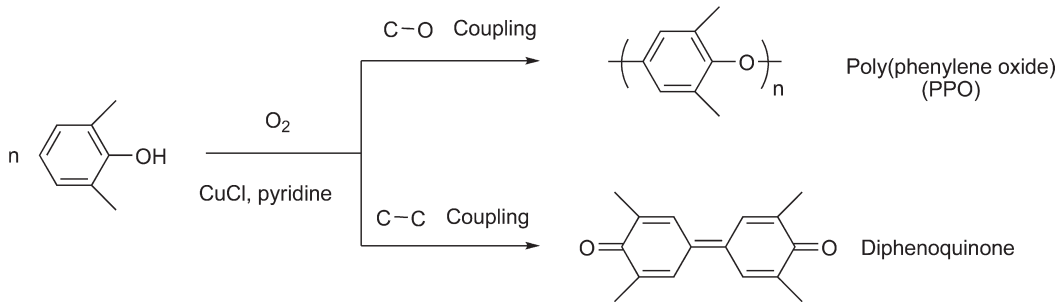

Figure 3 Oxidative coupling of 2,6-dimethylphenol.

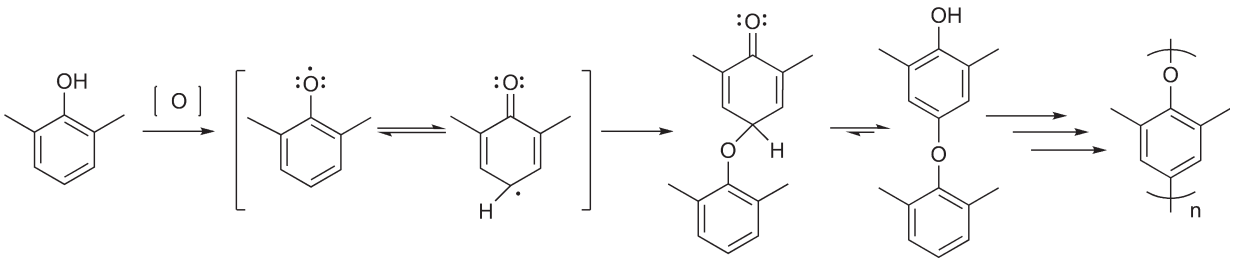

Figure 4 Free radical mechanism of oxidative polymerization.

dependent on the chemical structure of the phenol monomers, that is, the type of substituents, as well as the position of substitution. The oxidation potential of phenols is reduced by alkyl substitution and increased by electron withdrawing substituents. It has been shown that 2,6-disubstituted phenols without substitution at the *para* position polymerize the most easily via an oxidative reaction. However, when the substituents are large and bulky (e.g., *t*-butyl and isopropyl), no polymers can form due to steric hindrance, and the coupled diphenoquinone product forms in high yield via C–C coupling. When both substituents are electron withdrawing groups, such as chloro or nitro, no oxidation can occur due to the high oxidation potential of these types of substituted phenols. When one substituent is chloro and the other is methyl, a branched polymer can form due to a chloro-displacement reaction.[16]

Transition metal catalysts such as copper or a manganese compound combined with amine ligands are the main catalyst systems used in the oxidative polymerization of phenols. The type, composition, and concentration of the oxidizing system can affect the reaction rate, selectivity, and product quality. In general, copper halide salts are typically used with amine ligands, such as diamines, oligomeric amines, and even polymeric amines, which can solubilize the metal salt and increase the PH, thus reducing the oxidation potential of the phenol monomers. It is generally observed that an excess of amine relative to metal salt leads to the predominance of C–O bond formation, thereby affording the expected PAE structure. Since copper–amine complex catalysts are very susceptible to hydrolysis, a desiccant is usually added to the reaction mixture to avoid hydrolysis as a result of the water generated during the polymerization. (Excellent summaries concerning catalysts for oxidative polymerization can be found in the literature.[17,18]) The polymerization occurs in an organic solvent. Aromatic solvents such as benzene, toluene, xylene, and *o*-dichlorobenzene are the preferred solvents, although some halogenated hydrocarbons like tetrachloromethane, trichloromethane, dichloromethane, 1,2-dichloroethane, and trichloroethylene can also be utilized.

In general, compared with other synthetic methods, the catalytic oxidative polymerization of phenols has significant advantages over other methods, such as the ability to utilize halogen-free monomers, the use of moderate reaction temperatures, and the production of water as by-product. Catalytic oxidative polymerization, therefore, is considered to be a clean process for the synthesis of phenolic functional polymers. A number of comprehensive reports have been issued describing the oxidative polymerization of phenols,[16,19,20] which provide excellent insights into the chronological development of this methodology, as well as detail representative examples of some structural variations that have been achieved.

5.17.2.1.2 Nucleophilic aromatic substitution

The most practical method for preparing PAEs employs the nucleophilic aromatic substitution (S_NAr) process, which has greatly advanced PAEs for a variety of commercial applications. The S_NAr mechanism typically involves two steps: (1) nucleophilic attack, followed by (2) aromatic substitution between the activated aromatic ring and the phenol (or metal phenolates),[21] as illustrated in Figure 5. In the first step, the nucleophile (phenol or metal phenolate) attacks the carbon atom of the activated C–X bond, resulting in a resonance-stabilized intermediate, often termed the Meisenheimer complex.[22] The second step involves the departure of the leaving group. Typical leaving groups are fluorine, chlorine, and nitro groups. The first step is generally considered to be the rate-determining step, which is supported by the fact that in spite of the strength of the C–F bond, the order of reactivity for the halogens was found to be F >> Cl > Br > I. This suggests that the rate-determining step does not involve the departure of the leaving group. Therefore, reactivity is greatly dependent on the

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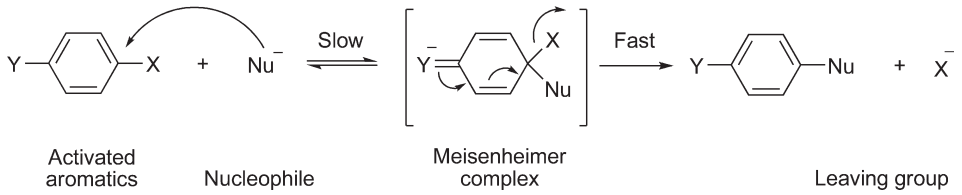

Figure 5 Nucleophilic aromatic substitution (S_NAr) mechanism.

electronegative substituents through inductive electron-withdrawing effects. Isolation of the Meisenheimer salts during polymerization further supports this suggested mechanism.

The first subcategory of the S_NAr polymerization method for affording PAEs is known as polyetherification, which involves a carbonate-mediated process between phenols with activated aromatic halides. Specifically, an aryl ether link (C–O) is formed by the nucleophilic polycondensation of phenols with activated aromatic dihalides; alternatively, this can be achieved with a single halo-aromatic phenol monomer in the presence of a base like potassium carbonate (Figure 6). The halogenated aromatics are activated by the presence of pendant electron-withdrawing substituents. Conversely, electron donating groups such as an amine or a methoxy can decrease the stability of the Meisenheimer intermediate, thus hindering the substitution. Effective activating groups include carbonyl and sulfonyl groups, which lead to PAEKs and poly(arylene sulfone)s, respectively, as will be discussed later in this chapter. Other electron-withdrawing substituents such as acetylene,[23] ethylene,[24] benzoyl,[25,26] perfluoroalkylene,[27] phosphine oxides,[28] and azino[29] have been reported to afford high-molecular-weight PAEs.

The second subcategory, the S_NAr polymerization method for affording PAEs, involves the aromatic nucleophilic polycondensation of diphenols with activated aromatic dinitro compounds.[30–32] An example of synthesizing PAEs from nitro-substituted monomers is illustrated in Figure 7. In this method, the properly activated nitro groups are displaced readily, although it produces a reactive nitrite ion as a by-product that causes side reactions at elevated temperature. High-molecular-weight polymers can be obtained for several homo- and copolymers.

Third, the synthesis of certain PAEs from perfluorinated aromatic compounds with bisphenolates has been studied under solid–liquid phase transfer conditions.[33,34] It was reported that hexafluorobenzene (HFB) could undergo a 1,4-disubstitution with model mono nucleophiles, thereby affording linear soluble polymers with certain bisphenols and aromatic dimercaptans. An example polymerization of HFB with bisphenol A is shown in Figure 8. The polymerization

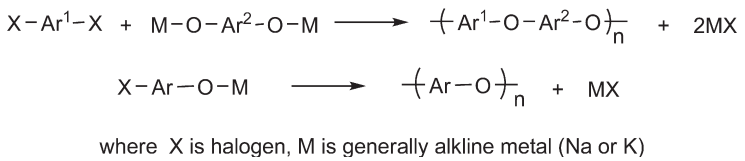

Figure 6 Nucleophilic aromatic substitution (S_NAr) of phenols with activated aromatic halides.

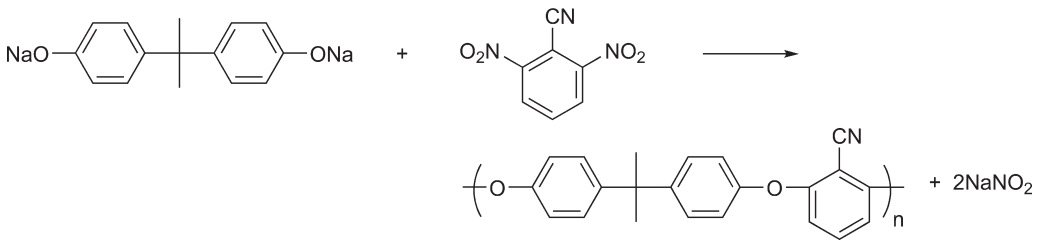

Figure 7 Nucleophilic aromatic substitution (S_NAr) of phenols with activated aromatic dinitro monomers.

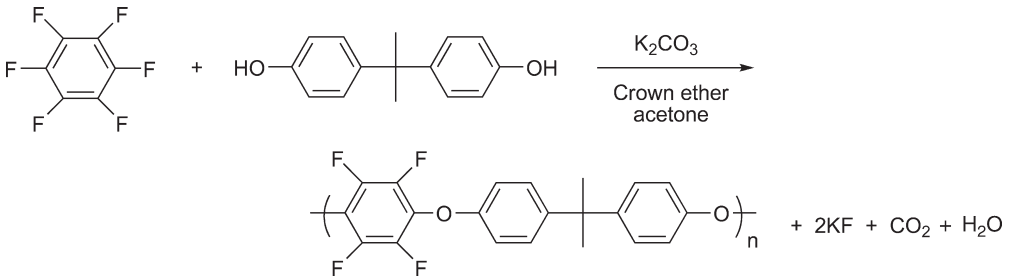

Figure 8 Synthesis of poly(arylene ether) via phase transfer catalysis.

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was effectively catalyzed in the presence of crown ethers, which resulted in high-molecular-weight polymers. It should be noted that no polymers were obtained in the absence of the crown ethers. The catalytic effect was most pronounced in solvents of intermediate polarity, such as acetone, but not in nonpolar solvents such as chlorobenzene. In addition, polymerization reactivity can also be favorably affected by trace amounts of water. Other perfluorinated bisaryl monomers have also been studied for their reactivity, including perfluorobiphenyl (PFB), perfluorobenzophenone, and perfluorophenylsulfide. However, only PFB polymerized with bisphenol A and 4,4′-dimercaptodiphenyl ether could afford soluble, high-molecular-weight polymers, in comparison to the other monomers that produced insoluble or low-molecular-weight products.

Using phase-transfer-catalyzed S_NAr polymerization, Jayakannan *et al.*[35] reported the synthesis of well-defined telechelic PPOs from 4-bromo-2,6-dimethylphenol and biphenolic compounds. The composition analysis via ^1H NMR revealed that 2,6-dihydroxynaphthalene was highly reactive, whereas 4,4′-biphenol was nonreactive in the polymerization process.

Another example of using fluorinated monomer in the synthesis of PPO was reported by Kim *et al.*[36] The self-polymerization of potassium 4-fluoro-3-(trifluoromethyl) phenolate was conducted via S_NAr reaction resulting in the trifluoromethylated PPOs. It was also reported that by introducing an appropriate initiator at the chain end, atom transfer radical polymerization (ATRP) of the trifluoromethylated PPOs could be conducted with styrene and methyl methacrylate, yielding well-defined rod-coil block copolymers.

Silylated diphenols have also been reported to undergo S_NAr polymerization with activated aromatic dihalides to afford high-molecular-weight PAEs.[37] Several aromatic dihalides have been polymerized by this method. The highest molecular weight polymers obtained via this process have employed benzonitrile systems, as shown in **Figure 9**. One possible advantage of this method over the use of free bisphenols is that water is not formed during the polymerization, which could be beneficial for the polymerization of monomers with hydrolyzable groups. The polymerization of silylated diphenols with activated aromatic dihalides to produce poly (ether ketone)s (PEKs) and poly(ether sulfone)s (PESs) has also been reported and will be discussed later.

In addition to the aforementioned typical activating groups such as halogens, heterocyclic rings that do not possess very strong electron-withdrawing capabilities, such as imide,[38] quinoxalines,[39,40] oxadiazole,[41] benzoxazoles,[42–44] thiazoles,[45,46] and benzimidazole,[47] have been demonstrated to be effective as well in activating halides toward S_NAr for the synthesis of PAEs. The common characteristic of all these heterocyclic activating groups is that they are electron withdrawing and are located in the *para* position relative to the aryl halide, which activates the electrophilic position by decreasing the electron density at the *ipso* carbon atom. In addition, these heterocyclic rings usually have a site of unsaturation, which can stabilize the negative charge developed in the displacement through resonance to a heteroatom (O, N, or S) involving the formation of a Meisenheimer complex. The detailed synthesis of PAEs with heterocyclic rings is discussed in Section 5.17.2.2.1.

In addition to the strength of the activating groups, many other factors impact the kinetics of S_NAr reaction. These include the nucleophilicity of the attacking nucleophiles, the electronegativity of the leaving groups, alkali metal and phenolate formation, and the nature of the reaction solvent. The reaction rate generally increases as the strength of the nucleophile (i.e., nucleophilicity) increases. The overall approximate order of nucleophilicity has been determined to be[48] $ArS^- > RO^- > R_2NH > ArO^- > OH^- > ArNH_2 > NH_3 > I^- > Br^- > Cl^- > H_2O > ROH$. The trends for the leaving groups are quite different from common nucleophilic substitution, which is due to the fact that the decomposition of the Meisenheimer intermediate is not the rate-determining step. The leaving group trends for S_NAr substitutions have been reported to have the order[49,50] $F^- > NO_2^- > {}^-SOPh > Cl^- > Br^- \sim I^- > {}^-OAr > {}^-OR > {}^-SR$. With respect to alkali metals, potassium phenolates are generally used in order to achieve an acceptable reaction rate, high molecular weight, and good linearity. In practice, either potassium salt or a mixture of potassium and sodium salts has been used. Solvent choice is relatively limited due to the multiple requirements in S_NAr reactions, such as reaction temperature and solvating properties. Not only does the solvent need to dissolve the reactants, the alkali metal salt, and the resulting polymers, but it should also be able to enhance the rate of substitution in nucleophilic reactions.

In general, the S_NAr approach for the synthesis of PAEs is more easily achieved with some reactive functional groups, which makes it possible to synthesize reactive group end-capped polymers and functional polymers using functional monomers. The resulting polymers generally have well-defined structures, which is advantageous. However, this method requires a high reaction temperature and the removal of salt by-products. In addition, nucleophilic reactions are very susceptible to monomer impurities and are very dependent on stoichiometry to obtain high molecular weight and good polydispersity of polymers. Therefore, the high cost of such

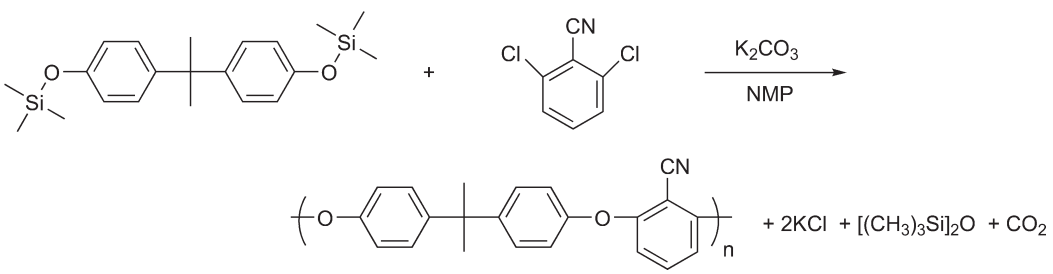

Figure 9 Synthesis of poly(arylene ether) from silylated diphenol.

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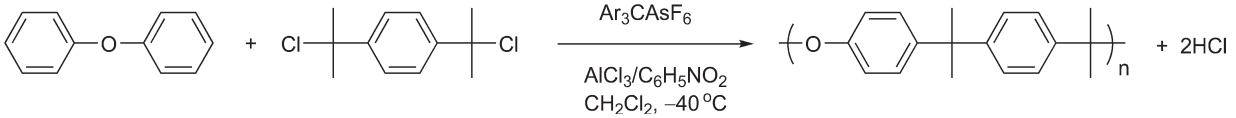

Figure 10 Synthesis of poly(arylene ether) via electrophilic aromatic substitution reaction.

monomers is one of the main disadvantages of the nucleophilic substitution route.

5.17.2.1.3 Electrophilic aromatic substitution using Friedel–Crafts catalysts

Another route for producing PAEs is via the formation of an ether link by an electrophilic condensation reaction, which involves adapting well-known Friedel–Crafts catalysts such as $AlCl_3$, $FeCl_3$, $SbCl_5$, $AlBr_3$, and BF_3. This process employs the polyalkylation of aromatic ethers as indicated in Figure 10.

This type of polycondensation proceeds well with a variety of bis(chloroisopropyl) compounds, such as *p*-bis-(2-chloroisopropyl)benzene,[51] but is limited to electron-rich aromatic compounds such as naphthalene, aromatic ethers, sulfides, and amines. Aromatics such as diphenyl sulfone and benzophenone, however, do not undergo alkylation successfully. Catalyst concentrations of 1–15 mol.% generally afford high yields of the polyalkylation polymers. Compared to the nucleophilic route, the electrophilic substitution route uses less-expensive monomers, and polymerizations may be conducted at temperatures lower than 100 °C. However, the extremely limited choice of suitable solvents and problems with disposing the reaction residues make this route less attractive.

Given the fact that the electrophilic substitution route for synthesizing PAEs is quite limited, a detailed discussion of the mechanisms for this type of reaction, the factors affecting it and its applicability will be covered in the synthesis sections of PAEKs and poly(arylene sulfone)s.

5.17.2.1.4 Other synthetic routes to poly(arylene ether)s

5.17.2.1.4(i) Enzyme-catalyzed oxidative polymerization

There has been significant interest in oxidative polymerizations catalyzed by enzymes ('enzymatic polymerizations') as a new methodology of polymer synthesis. Enzyme-catalyzed oxidative polymerizations (EOPs) represent a new approach for producing new polymers with high reactivity for generating free radicals from phenols. It has been shown that oxidative polymerization of phenols can be catalyzed by oxidoreductase enzymes such as peroxidase, oxidase, or oxygenase. Peroxidases such as horseradish peroxidase (HRP) and soybean peroxidase (SBP) are hemoproteins having an Fe-containing porphyrin-type structure as the active site, which can then catalyze the coupling of a number of phenol and aniline derivatives using H_2O_2 as the oxidant, liberating small molecules like water and carbon dioxide.

The first attempt to use HRP and H_2O_2 as catalysts for the polymerization of phenols is ascribed to Klibanov *et al.*[52] in 1983, who were able to remove phenols from coal-conversion wastewater solutions. In this study, the oxidative polymerization of phenols afforded water-insoluble, low-molecular-weight polymers from solution. In a subsequent study, several polyphenols with high molecular weights of up to 26 000 g mol^{-1} were synthesized by Dordick *et al.*[53] using EOP in aqueous organic solvents. The use of a mixture of a buffer with a water-miscible organic solvent, such as 1,4-dioxane, acetone, and *N*,*N*-dimethylformamide (DMF), was found to be very important for the synthesis of various polymers with higher molecular weights – due to the fact that many phenolic polymers are insoluble in water. Following that, Kobayashi and co-workers conducted an HRP-catalyzed oxidative polymerization of phenol, the simplest and the most important phenolic compound, in a 1,4-dioxane/buffer solvent. As a result, a new family of resins was produced.[54,55] Later on, a number of enzyme-catalyzed polymerizations of functionally substituted phenols were conducted, resulted in many structural varieties in polyphenols.[56–60]

Laccase, an oxidase enzyme, has also been used as a catalyst for the oxidative polymerization of different phenolics. This compound oxidizes substrates using oxygen as an oxidant. The laccase–O_2 catalytic system was reported to show a similar reactivity to HRP in the oxidative polymerization of phenol monomers. For instance, under acidic conditions, the laccase-catalyzed polymerization of 2,6-dimethylphenol in a mixture of an acetone buffer produced high-molecular-weight poly(2,6-dimethylphenol), indicating successful phenylene coupling.[61] Additionally, using laccase with O_2 in an aqueous organic solvent, syringic acid (a monomer known to be very difficult to polymerize by metal complex catalysts), was successfully polymerized, which involved eliminations of carbon dioxide and hydrogen from the monomer (Figure 11).[62]

Although oxidoreductase enzymes are effective in catalyzing oxidative polymerization, they are more expensive than conventional copper–amine catalysts, which prevent the industrial application of these enzymes. As a cheaper catalyst system, Fe(salen), a *N*,*N*′-bis(salicylidene)ethylenediamino iron complex, was designed by Kobayashi and co-workers.[63] It was found to be a peroxidase model catalyst that could mimic the function of a peroxidase for the oxidative polymerization of phenols with H_2O_2 (Figure 12). Some important polymers were produced using an Fe(salen) catalyst with O_2 or H_2O_2, such as high-molecular-weight poly(2,6-difluoro-1,4-phenylene oxide).[64,65] An interesting study on the oxidative cross-coupling reaction between phenolic polymer and phenol-containing cellulose was conducted in a medium of Fe-salen/H_2O_2 and pyridine producing the hybrid polymer.[66]

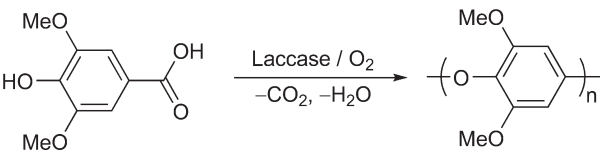

Figure 11 Laccase–O_2-catalyzed oxidative polymerization of syringic acid.

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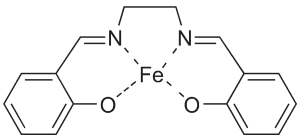

Figure 12 Structure of Fe(salen) complex.

Despite some successful examples of oxidative polymerizations of phenols using enzyme catalysts, there are still a number of problems to be addressed before EOP can be widely used for industrial applications, such as the catalytic activities of enzymes in nonaqueous media. In addition, for some enzymatic oxidative polymerization reactions, the enzyme may remain in the final product, thereby negatively affecting certain desirable properties. Moreover, the high cost of enzymes is still an obvious disadvantage.

5.17.2.1.4(ii) Ullman polycondensation

The Ullman reaction has long been known as a method for synthesizing aromatic ethers by the reaction of a phenol with an aromatic halide in the presence of a copper compound as a catalyst. It is a variation of the nucleophilic substitution reaction in that the halogenated aromatics are not activated by electron withdrawing groups; it is a phenolic salt that reacts with the halides. By using nonactivated aromatic halides as well as halophenols in the synthesis of PAEs, the Ullman reaction provides a way of producing many polymer structures that are not available via the conventional nucleophilic substitution route. The Ullman coupling approach to PPO was explored very early by Stamatoff, though it was not commercially developed.[67] Decades later, Jurek and McGrath[68] have reexplored this approach for preparing simple PPO and other PAEs from nonactivated aromatic dihalides. In an Ullman condensation, bromine compounds are the favored reactants.[4,68–70] For example, PAE was prepared via the Ullman coupling of bisphenol sodium salt and dibromoarylene in the presence of a copper catalyst as shown in the accompanying scheme (**Figure 13**). Mechanism studies on Ullman couplings concluded that Cu^+ ions coordinate with the π system of the aromatic halides, thereby facilitating the cleavage of carbon–halogen bonds. In this sense, Ullman condensation is essentially an S_NAr.

Via Ullman polycondensation, In and Kim[71] synthesized bromo-terminated hyperbranched PPO (HPPOs) from a simple AB_2-type monomer, 3,5-dibromophenol. The hyperbranched polymer was amorphous and showed good solubility and high thermal stability. By modifying the bromo end groups via lithiation and subsequent carbon dioxide treatment, the produced the carboxylate-terminated HPPOs can act as unimolecular micelle in aqueous solution. More recently, Zhang *et al.*[72] reported the synthesis of HPPOs with phenolic terminal groups from 4-bromo-4,4′-dihydroxytriphenylmethane via a modified Ullmann reaction. The sulfolane–NaOH system at higher temperature led to more rapid polymerization, higher molecular weight and lower degree of branching (DB). By modifying the peripheral hydroxyl groups of the HPPOs, hyperbranched polymers with a variety of functional chain ends can be synthesized, which show significant differences in solubility.

Although a number of very high-molecular-weight polymers have been prepared through this method, there are several major disadvantages of the Ullman condensation route. These include poor reproducibility, the need for brominated monomers, and the difficulty of removing copper salts.

5.17.2.1.4(iii) Ion-radical coupling polymerization

In traditional oxidative coupling polymerization, it is believed that chain growth occurs via the coupling of phenoxy radicals, as described previously. It has also been shown that coupling reactions in the synthesis of PAEs can proceed via ion-radical coupling mechanisms, namely, either an anion-radical or a cation-radical intermediate formed during reaction.

5.17.2.1.4(iii)(a) Anion-radical polymerization In the presence of catalytic amounts of an oxidative initiator, such as lead oxide, potassium ferricyanide, or even air, the synthesis of PAEs from bromophenols proceeds via a anion-radical intermediate ($S_{RN}1'$ mechanism).[73–75] In this case, the polymer chain is extended via the addition of a phenoxy radical to a phenolate anion. More recently, the utilization of the phase transfer catalysis (PTC) system has been shown to lead to well-defined PPOs with controllable molecular weights and functionality.[76] By using various end-blocking phenols, such as 2,4,6-trimethylphenol[77] or isphenol A-type phenols[78] as a chain-initiating phenol, functional PPO oligomers have been obtained with well-controlled molecular weights, with either single phenolic end groups that can be further functionalized or two phenolic chain ends.

5.17.2.1.4(iii)(b) Cation-radical polymerization The cation-radical polymerization, or Scholl reaction, of bis(1-naphthoxy)aryls was also shown to produce high-molecular-weight aromatic polyethers by Percec and co-workers.[79] The particular examples that have been used to demonstrate this polymerization reaction include the synthesis and polymerization of 4,4′-bis(1-naphthoxy)biphenyl, 2,2′-bis(l-naphthoxy)biphenyl, 3,3′-bis(1-naphthoxy)biphenyl, and 1,3-bis(1-naphthoxy)benzene in nitrobenzene with $FeCl_3$ as the oxidant. PAEs with number average molecular weights of up to 90 500 g mol^{-1} have been obtained.

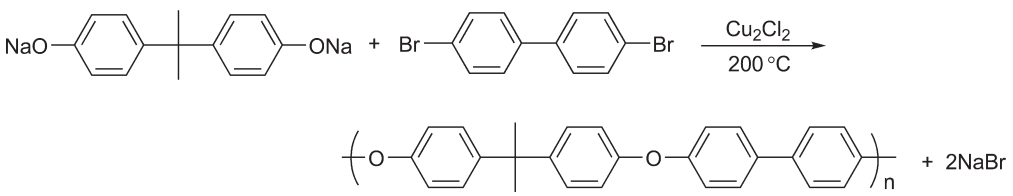

Figure 13 Ullman condensation of bisphenol sodium salt and dibromoarylene.

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5.17.2.2 Other Functionalized Poly(arylene ether)s

5.17.2.2.1 Poly(arylene ether)s containing heterocyclic rings

In general, PAEs containing heterocyclic rings in their backbones have been prepared via one of two approaches: (1) from monomers containing a heterocyclic ring, either on aromatic dihalide monomers or on diphenol monomers; (2) by chemical modification of suitable precursor polymers. Both the types of PAEs are characterized by high glass transition temperatures and high thermal stabilities. Some selected heterocycle-containing PAEs are discussed below.

5.17.2.2.1(i) Poly(arylene ether oxadiazole)s

A general method for the preparation of poly(arylene ether oxadiazoles) from heterocycle-containing monomers was developed by Hedrick and Twieg.[43] The polymerizations were based on an oxadiazole-activated halo or nitro displacement with phenoxides. Analogous to the conventional activating groups (i.e., sulfone and ketone), the oxadiazole heterocycle was found to be sufficiently electron withdrawing to activate halo and nitro substituents toward S_NAr. Halo- or nitro-substituted 2,5-diphenyloxadiazole monomers were synthesized by cyclization of the symmetrical bishydrazides, which were then polycondensed with various bisphenols under standard conditions, such as in *N*-methyl-2-pyrrolidone (NMP)–*N*-cyclohexyl-2-pyrrolidone (CHP) solvent mixtures at 180 °C, as shown in **Figure 14**. High-molecular-weight polymers with glass transition temperatures of around 200 °C were obtained by the described synthetic procedures. The thermal stability for the resulting polymers was good, with decomposition temperatures in the 450 °C range, which is just below the temperature range of other heterocycle-containing polymers. The poly(arylene ether oxadiazole)s showed limited solubility in common organic solvents, as expected, but films could be readily fabricated directly from the polymer melt. The 2,5-fluoro-diphenyloxadiazole monomer was also used by the researchers to synthesize the diamines, in which 2,5-fluoro-diphenyloxadiazole was mixed with 4,4′-oxydianilines (ODAs), and polymer chains were extended with pyromellitic dianhydride (PMDA), yielding thermally stable imide–arylene ether oxadiazole copolymers.[80]

Connell and co-workers[41] also reported a reverse procedure in the synthesis of poly(arylene ether oxadizaoles), in which an oxadiazole-containing bisphenol monomer was polycondensed with a broad variety of fluoro monomers, such as DFDPS and DFBP. The same research group also reported the synthesis of an analogous series of PAEs from the triazole diphenol.

5.17.2.2.1(ii) Poly(arylene ether oxazole)s and poly(arylene ether thiazole)s

In most synthesis of poly(arylene ether oxazole)s and poly (arylene ether thiazole)s, fluoro monomers were utilized for reactivity considerations.[45,81–83] The polymerization proceeded via the normal nucleophilic aromatic replacement of the halogen atoms by phenolate groups, such as bisphenol A or other commercial diphenols, in combination with K_2CO_3. The best reaction media were found to be NMP and 1,3-dimethyl-pyrimidinone-2.

Maier and Hecht[45] reported the synthesis of poly(arylene ether thiazole)s via the nucleophilic displacement of the fluorine atoms on the thiazole rings with bisphenols or silylated bisphenols, as shown in **Figure 15**. The trifluoromethyl-substituted bis(thiazole) monomers containing two thiazole rings with the 4-(trifluoromethyl)-5-fluoro substitution pattern were prepared from aromatic terephthalic acid dithioamide and hexafluoroacetone in three reaction steps. However, the fluorine atoms on the thiazole rings were much less reactive for nucleophilic displacement than the fluorine atoms in similar

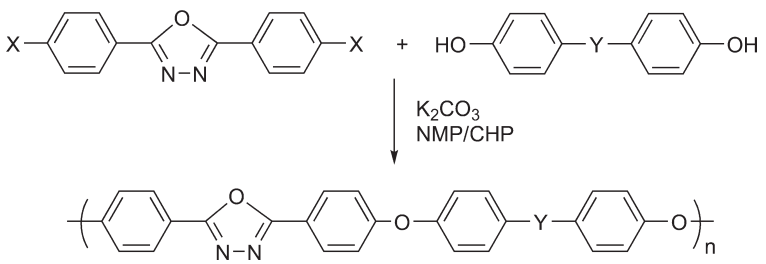

Figure 14 Synthesis of poly(arylene ether oxadiazole).

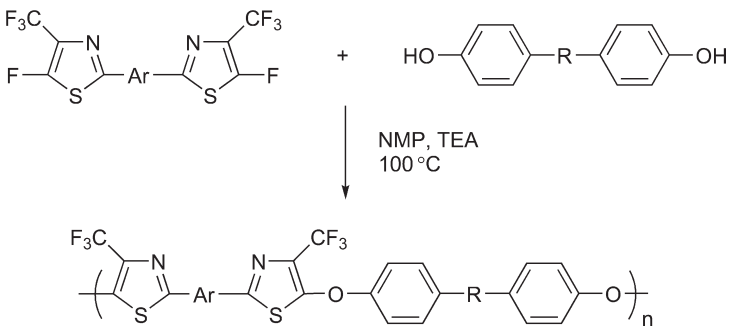

Figure 15 Synthesis of poly(arylene ether thiazole).

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oxazole rings. They circumvented this effect by using silylated bisphenol monomers and cesium fluoride as catalyst. Using the silylated bisphenols, polymers with high molecular weights of up to 78 500 g mol^{-1} were obtained.

Poly(arylene ether thiazole)s are amorphous with glass transition temperatures ranging between 169 and 217 °C, depending on the structure of the repeating unit (*meta* or *para* linkage to the benzene ring). The T_g's of the thiazole polymers were 26–32 degrees higher than those of the corresponding oxazole polymers and they were less soluble than oxazole polymers. The thiazole rings exhibited a much higher decomposition temperature than the oxazole rings. It was stated that the most possible reason for this increased thermal stability is the more pronounced aromatic character of sulfur-based hetero aromatic rings as compared to oxygen-based systems.

The synthesis of poly(arylene ether oxazole)s was similar to the thiazole-containing PAEs as reported by different groups via S_NAr approach.[81–83] Different fluoro-substituted monomers containing oxazole rings were prepared. These bis (oxazole) monomers containing two activated fluorine atoms differed in the number and position of trifluoromethyl substituents at the phenyl rings, as shown in Figure 16. Poly(arylene ether oxazole)s were synthesized by nucleophilic displacement of 2,5-bis(4-fluorophenyl)oxazole monomer with bisphenols. Most of the resultant poly(arylene ether oxazole)s were reported to be amorphous with few exceptions and their glass transition temperatures were in the range from 136 to 191 °C, depending on the structure of the bisphenol monomers. Oxazole PAEs were soluble in a number of common organic solvents due to their amorphous nature. However, some of the polymers exhibited an unexpected instability at high temperatures possibly due to the interactions between the trifluoromethyl substituents and the oxygen-based hetero aromatic rings.

Polyethers containing benzoxazole[42,44] or benzothiazole[46,84] rings on their backbone have also been reported. In most studies, electrophilic fluoro monomers containing benzoxazole or benzothiazole moieties were used in combination with diphenols to incorporate the heterocyclic rings into the polymer chains (Figure 17). A reverse process was also reported using the polymerization between benzoxazole- or benzothiazole-containing diphenol monomers (replacing the F atoms with hydroxyl groups in Figure 17) and aromatic dihalides.[44]

5.17.2.2.1(iii) Poly(arylene ether benzimidazole)s

The synthesis of PAEs containing benzimidazole rings was reported by Twieg and co-workers[47] in an attempt to improve the solubility and processibility of polybenzimidazoles (PBIs) by the incorporation of aryl ether linkages into the starting monomers. It was found that 2-(4-fluorophenyl)-benzimidazoles could be activated toward S_NAr with phenoxides since the benzimidazole ring stabilized the negative charge that was developed in the transition state of a Meisenheimer complex, analogous to conventional activating groups such as sulfone and carbonyl groups. The dihalo bibenzimidazole monomers, such as 2,2′-bis(4-fluorophenyl)-6,6′-bibenzimidazole, were prepared separately, which were then polymerized with bisphenols in aprotic dipolar solvents in the presence of K_2CO_3 (Figure 18). Polymers were obtained with high molecular weights and the glass transition temperatures ranged from 220 to 250 °C. The resulting PBIs showed good thermal stability as expected and could be processed from solution.

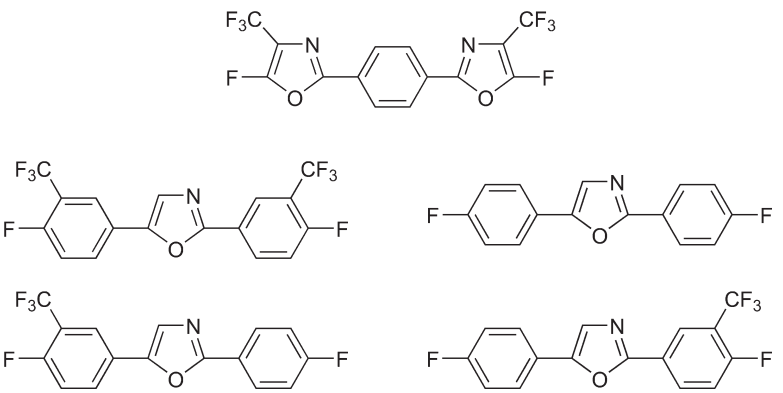

Figure 16 Chemical structures of some difluoro bis(oxazole) monomers.

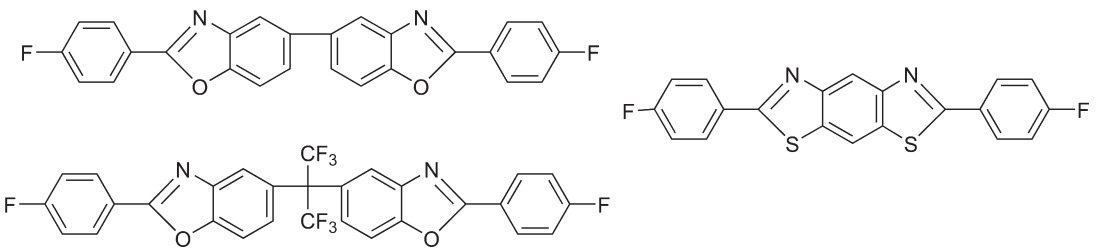

Figure 17 Chemical structures of monomers containing benzoxazole or benzothiazole moieties.

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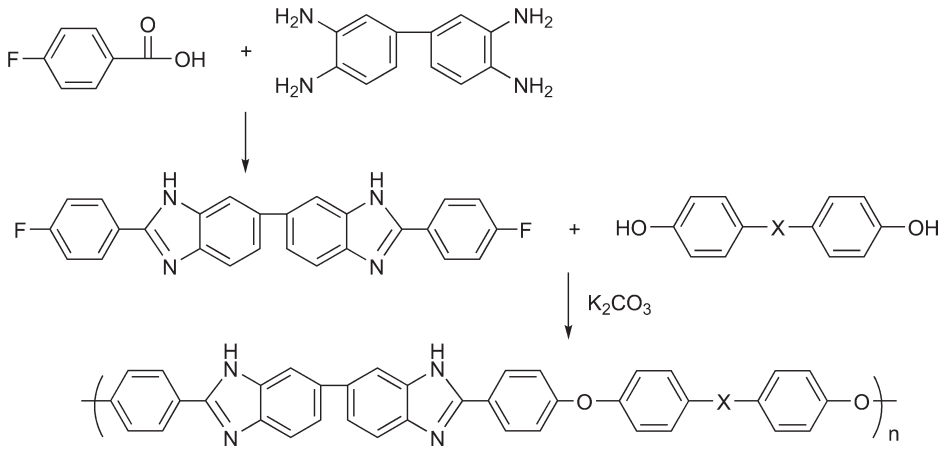

Figure 18 Synthesis of poly(arylene ether benzimidazole).

5.17.2.2.1(iv) Poly(arylene ether azine)s and poly(arylene ether quinoxaline)s

Alternatively, PAEs with heterocyclic pendant rings have been prepared by chemical modification of precursor polymers, particularly PAEKs derived from phthaloyl bisfluorobenzene.[85–87] Using a variety of catalysts, PAEs with various heterocyclic pendant rings were obtained via an intramolecular ring-closure reaction of the 1,2-dibenzoylbenzene moiety in the polyketone polymer chains. As shown in **Figure 19**, the tertiary amine-catalyzed condensation with benzyl amine yielded the poly (isoquinoline ether)s, whereas condensation with hydrazine produced the poly(phthalazine)s. Both polymers were amorphous with high glass transition temperatures.

5.17.2.2.2 Crosslinked and graft poly(arylene ether)s

Several publications report the synthesis of PAE oligomers with functional end groups that are capable of forming networks or hyperbranched structures. Gao and Hay[88] reported the synthesis of thermally curable PAE oligomers containing the diphenylethylene moiety. The diphenylethynene functionality was introduced in either diphenol or dihalide monomers before polymerization. As shown in **Figure 20**, a normal nucleophilic aromatic displacement reaction utilized these monomers with dihalides or diphenolates, respectively. The resulting polymers containing diphenylethylene moiety were thermally cured by heating at 320 °C without using any catalysts. Since no volatile by-products evolved during the curing reaction, 'void free' polymer structures were obtained. Another approach to introduce vinyl functionality was reported,[89] in which mono-dispersed vinyl-terminated oligoethers were synthesized from bisphenol A and 4-chloromethyl styrene as tetravalent comonomers for radical crosslinking with various vinyl monomers.

More recently, Ueda *et al.*[90–92] reported an efficient oxidative coupling polymerization for the synthesis of thermosetting

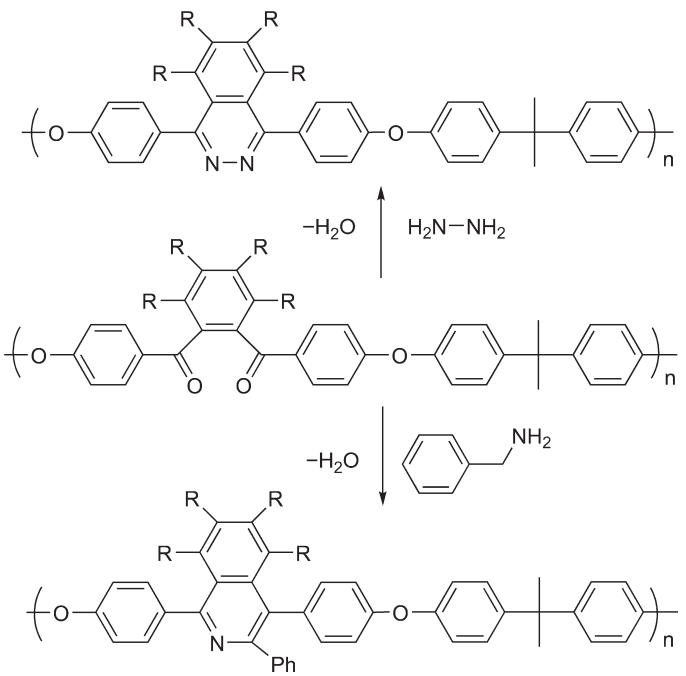

Figure 19 Chemical modification of poly(arylene ether ketone) to afford poly(arylene ether azine) (top) and poly(quinoline ether) (bottom).

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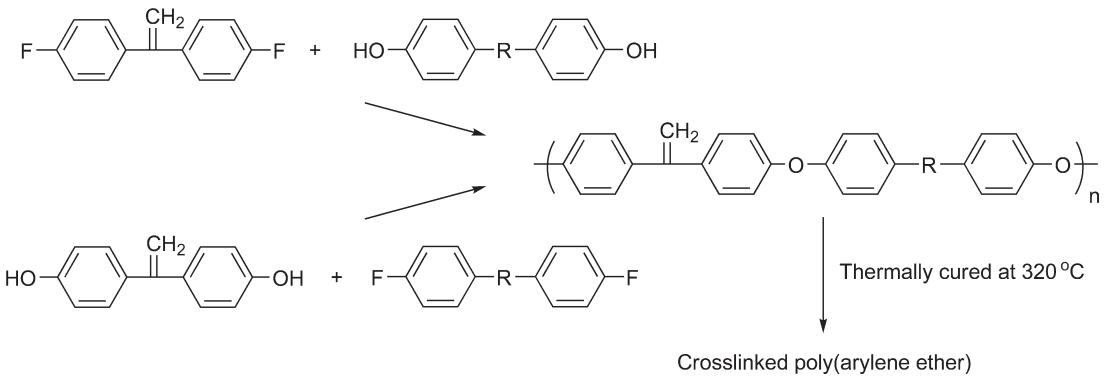

Figure 20 Synthesis of crosslinkable poly(arylene ether) oligomer containing ethylene moiety.

PPOs. The crosslinkable aromatic copolyethers containing allyl moieties were prepared from the oxidative copolymerization of 2-allyl-6-methylphenol (AMP) and 2,6-dimethylphenol using copper–amine complex (TMEDA) as catalysts in a heterogeneous system of water and toluene (**Figure 21**). The resulting thermosetting copolymers exhibited excellent dielectric properties which made them potential materials for applications in high-speed and high-frequency printed circuit boards.

The synthesis of PPOs grafted with Nylon was reported by Chao *et al.*[93] A commercial PPO was reacted with phenyl acrylate, *p*-substituted phenyl acrylates, and diphenyl fumarate in an extruder or in solution. The reaction products were used as coinitiators or promoters of anionic polymerizations of ε-caprolactam to afford Nylon-grafted PPOs.

5.17.2.3 Properties and Applications

In spite of the extensive studies in the design and synthesis of new PAEs, very few of them are used singly and even fewer are successfully introduced to the commercial market. PPO®, or more precisely poly(2,6-dimethyl,1,4-phenylene oxide)), is the first commercialized aromatic polyether and is still being used in many applications. PPO crystallizes only with difficulty and behaves essentially as an amorphous polymer during melt processing. It is soluble in solvents such as chloroform, benzene, and toluene. However, poly(phenylene ether) resins usually are difficult to process by extrusion or injection molding because of their high glass transition temperatures. At a temperature of 300–350 °C, the viscosity remains quite high. PPO has a T_g of 208 °C and must be melt processed at very high temperatures. Therefore, it is difficult to avoid oxidative degradation (autoxidation of benzylic methyl groups and phenolic end groups) during melt processing which can result in deterioration of the properties of molded parts. The commercial solution to this problem has been the introduction of blends of PPO with other resins. The first discovery that PPO had unusual blending properties is ascribed to the work of Boldebuck,[94] who reported that PPO was completely miscible with polystyrene and poly(diphenyl siloxane). This finding later led to a series of commercial products, that is, Noryl® resins, which are the homogeneous blends of PPO and polystyrene with glass transition temperatures between those of the two homopolymers ranging from 88 to 208 °C with increasing amount of PPO from 0 to 100 wt.%.[95] Noryl®, therefore, is a family of resins with a wide range of properties as a function of the relative amounts of PPO and polystyrene present in the blends. Since the processing temperatures of the blends are much lower than pure PPO, the oxidative degradation problem during processing is also significantly alleviated. In addition, the blends of PPO with polystyrene maintain many of the useful properties of PPO while improving some of the properties of polystyrene such as impact strength.[95] Besides polystyrene, blends of PPO with other polymer materials have been reported subsequently that have targeted modification of resin properties or improved processibility. Gowan[96] showed that blending small amounts of polyethylene with PPO increased the impact strength and the solvent craze resistance, which led to a commercial product. It was also found that by adding small amounts of Nylon to PPO the flow properties of polyamide could be improved.[97] Other polymeric materials, like polysulfone,[98] polyacrylates,[99] silicone,[100] polysulfide,[101] and PVC[102] were also reported to afford useful blends with PPO resulting in improved properties. More recently, heterogeneous blends of PPO with Nylon and polyesters have been introduced, but a discussion of this topic is beyond the scope of this chapter.

Since poly(phenylene ether)-based polymers are lightweight and exhibit excellent impact resistance when compared with metal or glass, the resins, or modified versions therein, have been employed in a variety of fields, namely, automobile body panels,[103] adhesives in electronic applications,[104] gas separation membranes,[105,106] and polymer

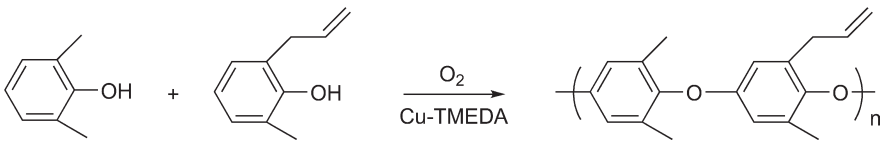

Figure 21 Synthesis of allyl-poly(arylene ether) copolymer via oxidative coupling (m:n = 9:1).

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electrolyte membranes.[107,108] Particularly, poly(phenylene ether) exhibits high dielectric strength. Thus, it can be used as a polymeric electrets,[109] which shows an better charge storage behavior than that of cellular poly(propylene) and poly(ether imide).

5.17.3 Poly(arylene ether ketone)s

Aromatic ketone polymers, sometimes referred to as poly(arylene ether ketone)s, belong to the class of high-performance engineering thermoplastics, which contain both ether groups and ketone groups in the polymer backbone. Commercialized PAEKs are mostly semicrystalline polymers. By changing the number and relative positions of the ether and ketone linkages, there are several varieties of this type of polymers covering a wide range of glass transition temperatures and melting values. The basic repeating structures of some of the PAEKs that are of greatest commercial interest are illustrated in Figure 22. The acronyms depicted in E's and K's refer to the arrangement of ether and ketone groups in the repeat units of the polymers. It should be noted that the aromatic groups in the ketone polymers that have been commercialized are all 1,4-phenylene moieties and that all are not still commercially available.

A major intrinsic property of wholly aromatic PAEKs is that many of them are crystalline or semicrystalline polymers, which results in many desirable properties such as solvent resistance, flame resistance, low wear rate, abrasion resistance, and high strength. However, these advantages come at a cost. Due to their crystallinity, PAEKs are much less soluble in the usual reaction solvents, which makes them more difficult to synthesize.

5.17.3.1 General Synthesis Approaches

5.17.3.1.1 Electrophilic aromatic substitution

5.17.3.1.1(i) Condensation of carboxylic acid chlorides with aromatic ethers using $AlCl_3$

The first fully aromatic PEKs were prepared via electrophilic aromatic substitution approach by Bonner[110] at DuPont in 1962. The aromatic poly(ether ketone ketone)s (PEKKs) were obtained from copolymerization of diphenyl ether with iso- and terephthaloyl chlorides in the presence of a Friedel–Crafts catalyst, aluminum chloride using nitrobenzene as the solvent (Figure 23).

However, only very low-molecular-weight polymers were obtained under above conditions due to the insolubility problem of the growing chains during polymerization. Similar problem was also encountered in the self-polycondensation of *p*-phenoxybenzoyl chloride using methylene chloride as solvent,[111] although some success in obtaining moderately high-molecular-weight polymers was achieved using solutions of $AlCl_3$ in polyphosphoric acid (PPA).[112] Attempts have also been taken to use large excess amount of $AlCl_3$ to solubilize ketone polymers by complexing with carbonyl groups. However, side reactions led to structural complexity, like *ortho*-acylation and alkylation of aromatic polymer chains, which adversely affected the melt processibility due to the difficulties associated with removal and disposal of large amount of $AlCl_3$ in polymer products.

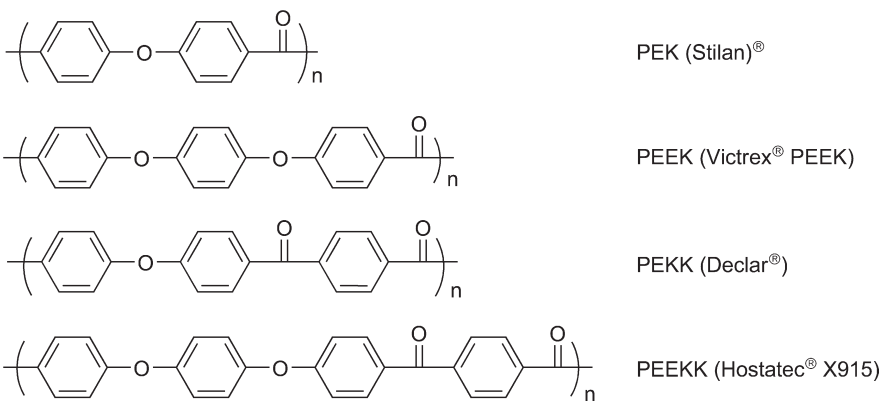

Figure 22 Basic backbone structures of some commercial PAEKs.

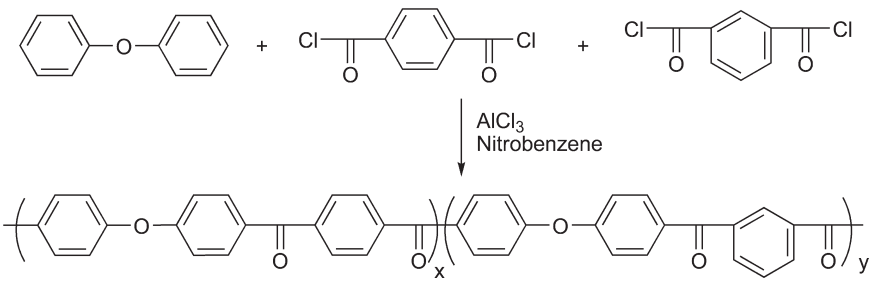

Figure 23 Synthesis of PEKK via electrophilic aromatic substitution catalyzed by $AlCl_3$.

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Later improved processes in the use of $AlCl_3$ for the synthesis of cleaner and higher-molecular-weight aromatic PEKs have been reported by researchers at Raychem and DuPont, respectively. Jansons *et al.* at Raychem[113–115] utilized a Lewis base as 'a controlling agent' with $AlCl_3$ and obtained substantially linear, high-molecular-weight, melt-processible polymers. Both inorganic Lewis base such as NaCl and LiCl, and an organic Lewis base such as dimethyl formamide (DMF) and pyridine have been reported to be effective in the polymerization. Similarly, PEK with inherent viscosity of 1.37 dl g^{-1} was synthesized from *p*-phenoxybenzoyl chloride by Fukawa and Tanabe[116] in the presence of excess $AlCl_3$ and phenyl ether end-capping agent in a solution of DMF in methylene chloride. In all the above-mentioned attempts, $AlCl_3$ was used in an amount equal to one equivalent per equivalent of carbonyl groups present, plus a catalytic amount of about 0.3 equivalents per equivalent of acid halides. It was preferable to use about 0.5 equivalents of Lewis base per equivalent of acid halides to fully promote complexation. The presence of Lewis base was claimed to reduce side reactions like polymer branching and alkylation by solvents such as methylene chloride. Furthermore, the Lewis base enhanced the solubility of growing polymers in the reaction media by forming complexes with $AlCl_3$, therefore allowing polymerization to proceed to high molecular weight.

Structurally ordered PEKK copolymers were prepared by Gay *et al.*[117] at DuPont with a higher degree of crystallization and more rapid crystallization behavior than the corresponding random polyetherketones. The perfectly alternating PEKK copolymer was synthesized from diphenyl ether with iso- and terephthaloyl chlorides in the presence of $AlCl_3$ and *o*-dichlorobenzene via a two-step process as shown in **Figure 24**. Rather than feeding all the monomers at the onset of polymerization as done by Bonner (**Figure 23**), initially, only one acid chloride was introduced to the diphenyl ether, which was then subsequently polymerized with the other acid chloride to form the ordered PEKK polymer with alternating *meta* and *ortho* phenylene linkages. This process is believed to be the basis of the commercial PEKK product line of Declar® introduced by DuPont in 1988. This perfectly alternating copolymer of *meta* and *ortho* phenylene group exhibited a high T_g of 166 °C and a relatively low T_m of 330 °C, which is desirable for melt processing and high-heat deformation resistance.

Copolymers of PEKK and poly(ether ether ketone ketone) (PEEKK) containing naphthalene moieties and pendant cyano groups were prepared by Cai *et al.*[118] via electrophilic Friedel–Crafts solution polycondensation. The copolymers were prepared through copolycondensation of terephthaloyl chloride with varying mole proportions of diphenyl ether and 2,6-bis (β-naphthoxy)benzonitrile using 1,2-dichloroethane as solvent and NMP as Lewis base in the presence of anhydrous $AlCl_3$. The crystallinity and melting temperatures of the copolymers were found to be dependent on the relative feeding ratio of comonomers.

5.17.3.1.1(ii) Condensation reactions using strong acids

Another feasible approach to address the insolubility problem of PAEKs when using Friedel–Crafts catalysts is to conduct the polymerization in strong acids such as hydrogen fluoride (HF). It was found that HF was an excellent solvent for this family of polymers probably due to the fact that it could effectively protonate the carbonyl group, thus reducing the tendency of the growing polymer to crystallize. Tough PEKs with very high molecular weights (IV = 1.33 dl g^{-1}) were synthesized from *p*-phenoxybenzoyl chloride by Marks[119] using HF in conjunction with equimolar quantities of BF_3 as catalyst/reagent (**Figure 25**).

This technology was commercialized by Raychem[120] later to produce a semicrystalline commercial PEK, known as Stilan®, for its applications in insulation of electrical wiring. Preferably large excess of boron trifluoride (2–3 moles per mole of acid chloride groups) and HF (2–10 moles per mole of boron trifuoride) were used to afford high-molecular-weight polymers. Carboxylic acids and their esters were also claimed to be able to polymerize using this process. However, there are obvious problems in applying this process on the industrial scale since HF is exceedingly corrosive and toxic. Therefore, the manufacture of the Stilan® PEK by this route was discontinued due to the hazards involved in handling liquid HF acid. Some other strong acid media, such as trifluoromethanesulfonic acid (TFMSA, CF_3SO_3H), have been introduced to catalyze the polycondensation of carboxylic acid with activated phenyl ether.

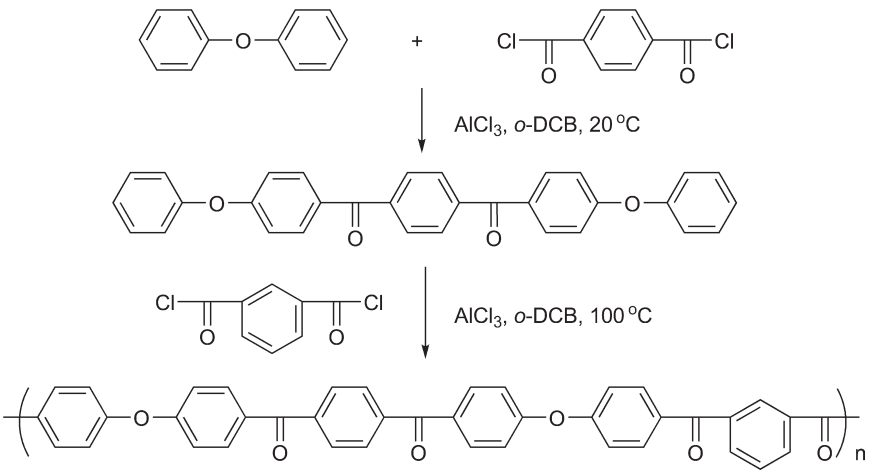

Figure 24 Synthesis of ordered PEKK via two-step process.

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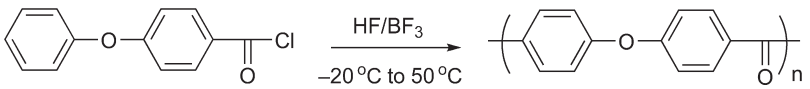

Figure 25 Synthesis of PEK using HF/BF_3 as catalyst/reagent.

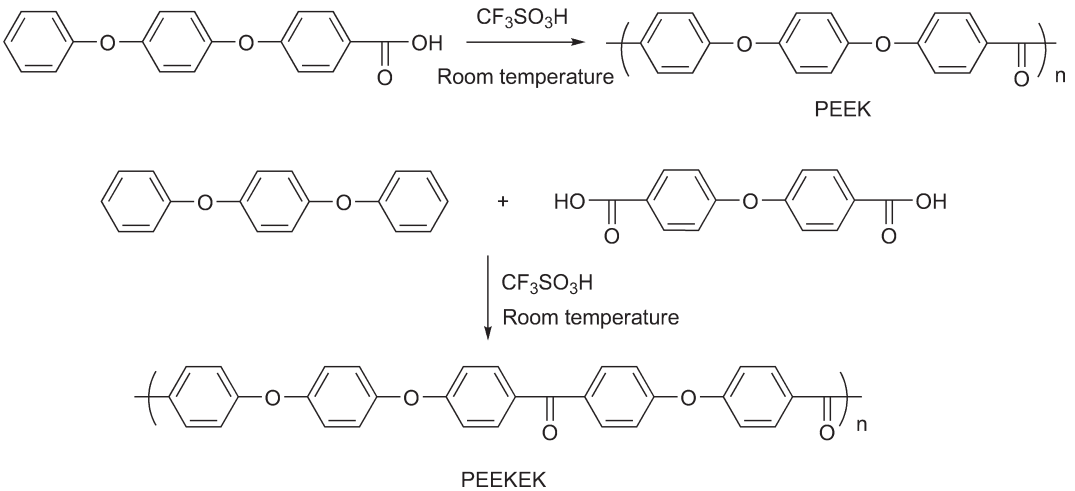

Figure 26 Synthesis of PEEK and PEEKEK using trifluoromethanesulfonic acid (TFMSA) as catalyst/solvent.

The direct polymerization of carboxylic acids with aromatic ethers is advantageous since it obviates the need to prepare acid chloride. On the other hand, acids are generally less reactive than acid chlorides, therefore more vigorous reaction conditions are required. High-molecular-weight polymers, poly(ether ether ketone) (PEEK) and PEEKEK, were produced by Rose using TFMSA[121] (**Figure 26**).

Attempt of replacing CF_3SO_3H with the less-expensive CH_3SO_3H, however, failed to yield high-molecular-weight PAEKs. In addition, since the monomers react as protonated species in the strong acid media, some limitations were encountered. It was found that electron withdrawing groups *para* to a carboxyl group inhibited acylation in TFMSA and the aromatic ether monomer must have at least three benzene rings and no carbonyl groups. For example, 4-phenoxybenzoic acid, as well as diphenoxybenzophenone, did not give polymers under above conditions. Later, some of these limitations were overcome by adding phosphorous pentachloride with the TFMSA and high-molecular-weight polymers ($IV = 1.19–1.93\ dl\ g^{-1}$) were produced.[121] It is possible that acid chloride-reactive intermediates were formed *in situ* due to the presence of phosphorous pentachloride. Some success of using phosphorous pentoxide as the dehydrating agent was also reported to be able to produce very high-molecular-weight polymers from phenoxybenzoic acids.[122] However, strong acid systems in general are not very attractive in the synthesis of PAEKs for industrial applications due to the harsh reaction conditions and high cost.

5.17.3.1.1(iii) Condensation of diphenyl ether with phosgene and its derivatives

In order to lower the process cost, PAEKs, particularly PEK, have also been prepared by reacting aromatic ethers with phosgene ($COCl_2$) in an aprotic solvent using anhydrous Group II metals as catalysts (**Figure 27**). An obvious economical source of the ether linkage in electrophilic polymerization is diphenyl ether, which is readily available at low cost. However, it has proved difficult to obtain high-molecular-weight polymers from this monomer via other methods. Several groups[113,123] have attempted to develop the synthetic route of polymerizing diphenyl ether with phosgene using various catalytic systems such as HF/BF_3, $AlCl_3/LiCl$, and $TFMSA/AlCl_3$. However, commercialization of this route has not been successful.

An alternative way to use phosgene in the synthesis of PEK is to use its derivatives such as thio- or dithiocarbonic acids.[124] It was reported that alkyl thiochloroformates and dialkyl dithiocarbonates were effective substitutes for phosgene in producing high-molecular-weight PEK and PEEK in the HF/BF_3 reaction/catalyst systems.

5.17.3.1.2 Nucleophilic aromatic substitution

Compared with the electrophilic aromatic substitution approach, the S_NAr approach generally affords polymers with well-defined structures, although higher reaction temperatures are required. Therefore, it is more facile to control the structures of the polymers via the S_NAr approach. In addition, it is more tolerable to some reactive functional groups, which makes it possible to synthesize functional polymers from functional

Figure 27 Synthesis of PEK using phosgene as comonomer.

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monomers and prepolymers end-capped with reactive functional groups.

5.17.3.1.2(i) Condensation of diphenols and activated aromatic dihalides

The S_NAr reaction for the synthesis of PAEKs generally involves aromatic dihalides and aromatic diphenols or bisphenolates. The first successful attempt to synthesize PEEK by polycondensation of bisphenolate with activated aromatic dihalide was reported by Johnson *et al.*[125] using dimethyl sulfoxide (DMSO) as solvent and NaOH as base. Again, high-molecular-weight polymer was not obtained because of premature crystallization and precipitation of the growing polymers. Later, Attwood and Rose *et al.*[126,127] discovered that diphenyl sulfone was a unique solvent for aromatic PEKs. This finding led to the success in obtaining very high-molecular-weight polymers from bisphenolates and activated aromatic dihalides. An example synthesis of PEK via S_NAr approach is shown in **Figure 28**.

In general, bisphenolates, mostly potassium bisphenolates, are prepared and isolated in separate processes, which require very careful control of the base stoichiometry during the phenolate preparation and its subsequent reaction with the dihalides. The reactivity of phenolates derived from alkali metal cations follows the order of Cs > K > Na > Li. Considering the cost–reactivity factor, potassium is usually preferred. Since carbonyl is a relatively weak electron-withdrawing group for activating aromatic halides, in most cases, the use of highly reactive (but expensive) difluoro aromatic compounds is necessary to afford high-molecular-weight polymers since fluorine is much more reactive toward phenoxide than chloro when both are activated by a ketone group. Less-reactive dichloro monomers always failed to produce high-molecular-weight polymers, partially due to the side reactions such as single-electron transfer reaction. Another obvious disadvantage of this approach is that the polymerization was conducted near the melting point of the polymer in order to maintain solubility. Therefore, side reactions such as ether–ether exchange and bond cleavage became significant at high reaction temperatures.

Attempts to improve the above approach by directly polymerizing bisphenols rather than bisphenolates with activated dihalides have been reported. This 'carbonate process' has proved to be extremely useful for the preparation of aromatic ethers. In contrast to the bisphenolates approach, no separate procedures are necessary in the carbonate approach to prepare the anhydrous bisphenolates. In addition, bisphenolates are insoluble in organic solvents and are very sensitive to air oxidation resulting in colored by-products that adversely affect product quality. On the other hand, in the carbonate process, monophenolates are first formed which react rapidly giving growing polyether chains that have enhanced solubility in the reaction medium. This is particularly true of phenolates derived from hydroquinone, a monomer used in the commercial synthesis of Victrex® PEEK.[128] High-molecular-weight PEEKs were prepared from 4,4′-difluorobenzophenone and hydroquinone in diphenyl sulfone with a slight excess of potassium carbonate, as shown in **Figure 29**. A programmed stepwise increase in reaction temperatures was used for these polymerizations in order to maintain the growing, crystallizable polymer chains in reaction solutions. The molecular weight of PEEK can be controlled by using excess of the fluoro monomer.

PAEK oligomers have been prepared and utilized to make Kadel® products that have similar structure to PEEK.[129] As shown in the synthesis of PEEK (**Figure 29**), potassium fluoride is formed in the polymerization, which is a strong base and can induce degradative ether interchange reactions at high polymerization temperatures. A solution to prevent the polymer degradation was reported in a later patent[130] stating that addition of an alkali salt, such as lithium chloride, at the terminal polymerization conditions could stop the polymerization and stabilize the polymer against degradation. Alkali earth salts such as magnesium chloride are also reported to be effective.

To lower the process cost, attempts to replace expensive fluoro monomers with activated chloro monomers have been reported. Fukawa *et al.*[131] successfully prepared

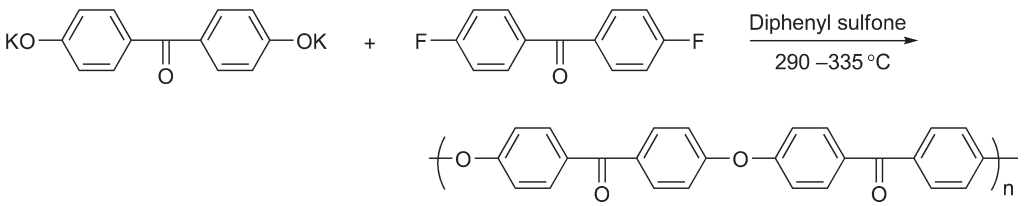

Figure 28 Synthesis of PEK via nucleophilic aromatic substitution from bisphenolate and activated aromatic dihalide.

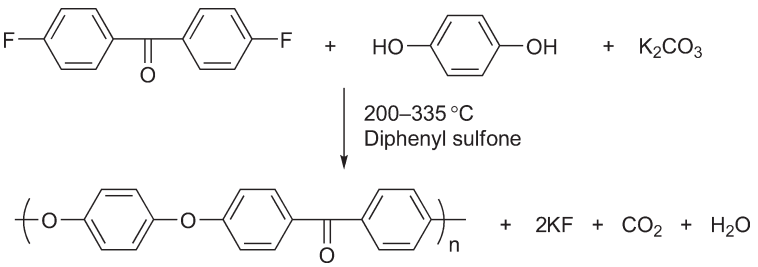

Figure 29 Synthesis of PEEK via carbonate process from hydroquinone and 4,4′-difluorobenzophenone.

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high-molecular-weight PEK (IV = 1.15 dl g^{-1}) from the reaction of 4,4′-dichlorobenzophenone (DCBP) with sodium carbonate in the presence of SiO_2–$CuCl_2$ catalyst via a silylated approach. The polymerization was conducted in diphenyl sulfone at high temperatures (2 h at 280 °C, 1 h at 300 °C, and then 1 h at 320 °C). It was proposed that the silyl ether formed by the reaction of DCBP and the silanol on the surface of silica was the intermediate of the etherification. Using fluoride as a promoting agent, Hoffman *et al.*[132] reported the synthesis of high-molecular-weight PEK from the reaction of DCBP within a significantly reduced reaction time. Potassium fluoride or a mixture of potassium fluoride and *N*-neopentyl-4-(dialkylamino)-pyridinium chlorides were used as catalysts to promote the polymer-forming nucleophilic displacement reaction in PEK synthesis.

5.17.3.1.2(ii) 'Masked' diphenols and activated aromatic dihalides

Under neutral conditions, an excellent alternative for the preparation of PAEs is to use silylated or 'masked' bisphenols in the presence of cesium fluoride, replacing the bisphenolate salts. Kricheldorf and Bier[133] developed this method and used trimethylsilylated bisphenols to react with activated difluoro aromatic monomers, such as DFBP. The polymerizations were catalyzed by catalytic mounts of cesium fluoride to afford high-molecular-weight PAEKs. S_NAr was still the mechanism. An example polymerization of silylated bisphenol A with DFBP is shown in **Figure 30**.

The most effective amount of cesium fluoride catalyst was found to be about 0.1 wt.% of the monomers in this approach. Therefore, all anions that form insoluble cesium salts (such as chloride ions) must not be present during the reaction. This could be a disadvantage since the silylation of the bisphenols required the use of chlorotrimethylsilane and triethylamine in boiling toluene. Extreme care must be taken because amine hydrochlorides, a product of the silylation reaction, could contaminate the silylated bisphenols. Similarly to the use of silylated bisphenols, Wang *et al.*[134] utilized carbamate derivatives as 'masked' bisphenols to polymerize with ketone-activated dihalides. The carbamate groups were readily cleaved in the presence of $KHCO_3/K_2CO_3$ at 155–165 °C generating the potassium phenolate *in situ*. In the presence of activated bis(arylfluoride)s, high-molecular-weight polymers were obtained within relatively short reaction time.

A major advantage of the 'masked' bisphenols approach developed by Kricheldorf *et al.* is that the polymers were prepared in the melt without solvent so that purification of the polymer from solvents or metal salts was not required and the molten polymers could be processed directly. Additionally, transetherifications were not found during the course of the polymerization. A wide range of PAEs, including PAEKs,[133] poly(arylene sulfone)s,[135] poly(arylene ether pyridine)s,[136] and poly(arylene ether benzonitrile)s,[137] have been prepared using this approach. However, the utility of this approach for the synthesis of crystalline PEEK is limited due to the crystallization-induced insolubility problem. Most of the PAEKs that have been synthesized via this approach have been amorphous.[133]

5.17.3.1.2(iii) Soluble (amorphous) precursors approach

An important issue in the synthesis of PAEKs is the early precipitation of the crystallizable growing polymer chains from the reaction mixture during polymerization. The insolubility and high melting temperatures of crystalline PAEKs make the processing difficult as well. A novel strategy to address this issue is to synthesize soluble, low-melting-point precursor polymers, which can be easily transformed into the desired PAEKs by removing the solubilizing groups or converting them to ketone groups. Several soluble precursors approaches have been reported including the use of monomers with bulky substitutions,[138,139] poly(ketal ketone) precursors,[140,141] poly(ketimine) precursors,[142–144] poly(amino nitrile) precursors,[145] and poly(ether thiolketal) precursor.[146]

The introduction of bulky substitutions on the polymer backbone can reduce crystallization or even suppress crystallization of a polymer, thereby improving its solubility substantially. Thus, synthesis of soluble high-molecular-weight precursors with removable substituents provides a strategy for preparing crystalline aromatic PEKs with high molecular weights. The pendent soluble moieties can be introduced onto either the diphenol monomers or the activated aromatic dihalides. McGrath *et al.*[138] were among the first to introduce the bulky *tert*-butyl groups in the polyketone backbones and the resulting PEEK was quite soluble in aprotic dipolar solvents. The PEEK precursors were prepared under mild reaction conditions at 170 °C. The polymer precursors were converted to PEEK in the presence of Lewis acid catalyst $AlCl_3$ via a Retro Friedel–Crafts alkylation. Approximately only 50% of the *tert*-butyl substitutes were removed due to the insolubility of the product in the solvent used. Later, *tert*-butyl- and phenyl-substituted PAEKs were prepared by Risse and Sogah,[139] which were highly soluble in common solvents like chloroform, tetrahydrofuran (THF), and toluene. It was also shown that using a strong Lewis acid CF_3SO_3H as both the catalyst and the reaction medium, complete cleavage of bulky

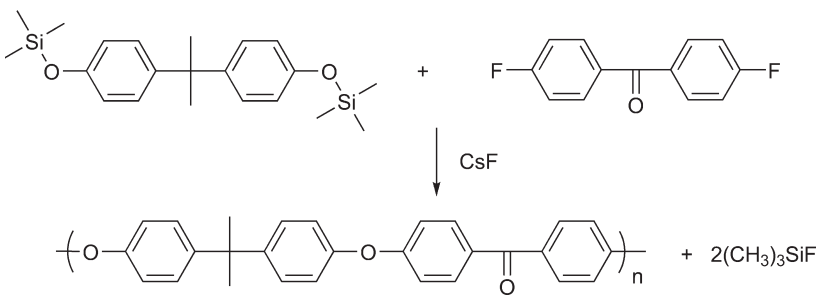

Figure 30 Synthesis of poly(arylene ether ketone) from 'masked' bisphenol and activated dihalide.

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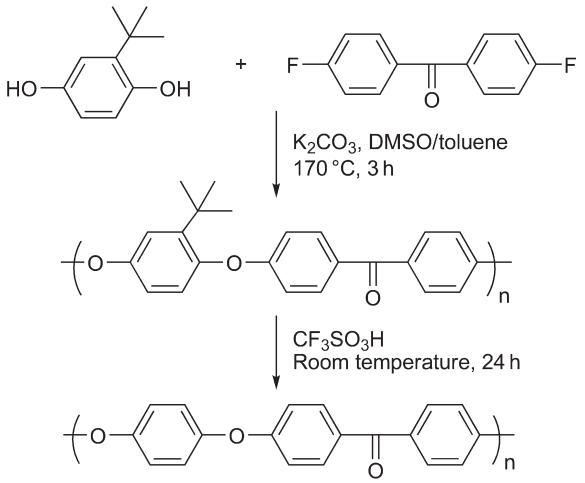

Figure 31 Synthesis of PEEK from soluble *tert*-butyl containing poly (arylene ether ketone) precursor.

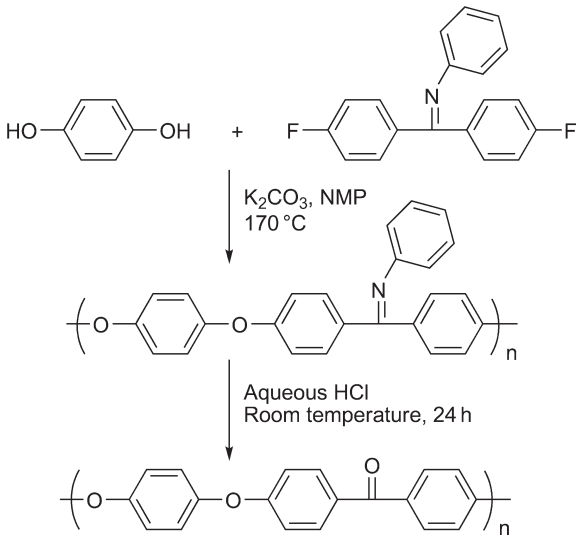

Figure 33 Synthesis of PEEK from soluble poly(arylene ether ether ketimine) precursor.

substitutes could be achieved in the presence of a *tert*-butyl group acceptor such as toluene (**Figure 31**).

A synthetic route for preparing so-called 'defect-free' PAEKs from amorphous poly(ketal ketone)s was developed by Kelsey *et al.*[140] In their work, an amorphous high-molecular-weight precursor, poly(ketal ketone), was first prepared by nucleophilic displacement polycondensation of an cyclic acetal monomer of 4,4′-dihydroxybenzophenone (DHBP) with DFBP in DMAc at 150 °C or sulfolane at 220 °C (**Figure 32**). The soluble amorphous poly(ketal ketone) was then quantitatively converted to high-molecular-weight, crystalline, insoluble PEK by acid-catalyzed hydrolysis under heterogeneous conditions. Due to relatively low reaction temperature, PEK prepared by this route had minimal defect structures ('defect-free') and thus possessed higher crystallinity and a higher glass transition temperature, rendering better physical and mechanical properties than its counterparts prepared by other routes.

Ketimine groups have also been used to protect ketone groups to produce high-molecular-weight soluble poly(arylene ether ketimine), which can be used as precursors to afford corresponding PAEKs.[142–144] As shown in **Figure 33**, the starting monomer DFBP was converted into difluorophenyl ketimine, which was copolymerized with a bisphenol to prepare the soluble prepolymer of poly(arylene ether ether ketimine). The polymerization proceeded smoothly at 170 °C in NMP. Fine powders of PEEK were obtained via hydrolyzing the resulting soluble poly(arylene ether ether ketimine) with dilute acid or methanol. The biphenol-based ketimine modified PEEKs have also been prepared via the same approach. The thermal properties of the PEEK prepared via this approach resembled those of commercial PEEK samples. Compared with the PEEK prepared from bulky group-substituted precursors, carbonyl functionalized polyketones can be converted to the target polyketones under relatively mild conditions.

More recently, Colquhoun *et al.*[146] reported that crystalline aromatic PEKs such as PEEK may be cleanly and reversibly derivatized by dithioketalization of the carbonyl groups with 1,2-ethanedithiol or 1,3-propanedithiol under strong acid conditions (**Figure 34**). Unlike their parent polymers, the resulting 1,3-dithiolane and 1,3-dithiane polymers are hydrolytically stable, amorphous, and readily soluble in organic solvents

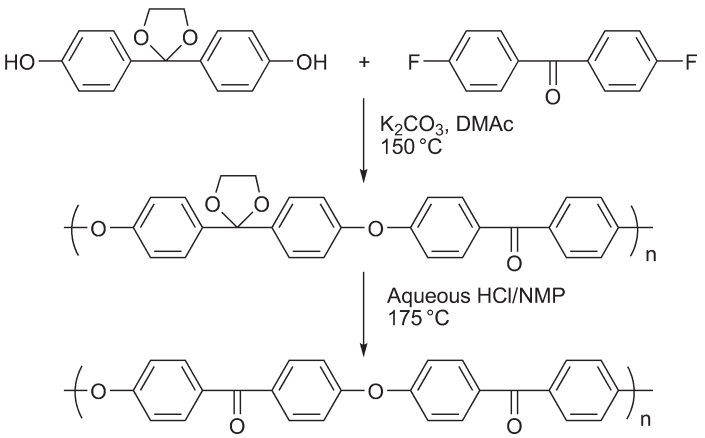

Figure 32 Synthesis of PEK from soluble poly(ketal ketone) precursor.

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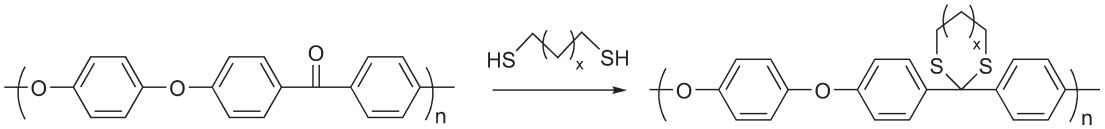

Figure 34 Synthesis of soluble poly(arylene ether ether dithiolane) from PEEK.

such as chloroform and THF. It was reported that these poly (dithiolketal)s could be quantitatively deprotected to regenerate the starting PEKs.

5.17.3.1.3 Other synthetic routes to poly(arylene ether ketone)s

5.17.3.1.3(i) Ring-opening polymerization

Ring-opening polymerization (ROP) has been applied primarily to the synthesis of aliphatic polyethers, such as poly (ethylene oxide)s. In recent years, ROP routes for the preparation of engineering thermoplastics have received a great deal of attention. ROP has obvious advantages in processing technologies, for example, reactive injection molding, over preformed high-molecular-weight polymers due to the low melt viscosity of the cyclic oligomers (cyclomers). The injection–molded cyclomers can be readily transformed to high-molecular-weight polymers without the release of volatiles. Furthermore, this approach is better suited for the fabrication of fiber-reinforced thermoplastic composites because of the potentially improved consolidation and fiber-wetting properties of the low-molecular-weight cyclomers.

Colquhoun *et al.*[147,148] first reported the ROP of macrocyclic aromatic ether ketone oligomers through nickel (0)-catalyzed coupling of aryl dihalides under *pseudo* high dilution conditions. The macrocyclic biaryl structure was characterized using single-crystal X-ray analysis. Since the ether linkages were activated by *para*-carbonyl groups, rapid ROP in the presence of nucleophilic initiators, such as fluoride or phenoxide ions, gave high-molecular-weight, tough, semicrystalline PEKs. However, earlier attempts via this route gave only low yields (less than 50%) of cyclomers and required rather high polymerization temperatures. Later, Chen *et al.*[149–151] prepared PEEK single-size macrocycles and macrocyclic oligomer mixtures via both S_NAr and Friedel–Crafts acylation approaches. ROP was initiated by a catalytic amount of nucleophiles, such as CsF or potassium salts of phenoxides. However, control of ROP is generally difficult and complete conversion of the macromonomers is very difficult to achieve. In addition, under some circumstances, melting points of the cyclics or cyclic mixtures are too high for practical ROP. One way to circumvent this problem may be achieved by preparing low-melting-point or even amorphous oligomers. Chan *et al.*[152] developed an alternative method for preparing PAEKs via using 1,2-dibenzoylbenzene to promote cyclomer formation. The resulting cyclomers were readily polymerizable via ROP to yield high-molecular-weight polymers. However, this approach resulted in relatively broad molecular weight distribution (reflective of branching) and incomplete conversion even at high temperatures. A more recent approach, toward so-called isoPEK, utilized dilution methods to generate mixtures of cyclic oligomers via the self-condensation of 4-fluoro-3-hydroxybenzophenone.[153] High conversion of the cyclomers to corresponding high-molecular-weight polymers was obtained when potassium (or cesium) 4-benzoylphenolate was used.

5.17.3.1.3(ii) Cation-radical polymerization (Scholl reaction)

High-molecular-weight PAEKs have been successfully prepared from ketone-containing dinaphthoxy monomers via the Scholl reaction (**Figure 35**).[154] The Scholl reaction can be depicted as the elimination of two aryl hydrogen atoms by the formation of an aryl–aryl bond and is generally catalyzed by Friedel–Crafts catalysts. Ferric chloride ($FeCl_3$) was found to be the preferred catalyst and was used at a 4:1 molar ratio to the monomer. The polymerizations were conducted in nitrobenzene at room temperature. The di(1-naphthyl) ethers of aromatic derivatives were considered to exhibit lower nucleophilicity and higher oxidation potential than the 1-naphthoxy groups and the polymerization apparently followed a 'reactive intermediate polycondensation' mechanism.

5.17.3.1.3(iii) Ullman polymerization

As mentioned previously, the Ullman polymerization is a variation of the nucleophilic substitution reaction where a phenolic salt reacts with the halide. The ease of halogen displacement under Ullman conditions was found to be the reverse of that observed for nucleophilic substitution reaction, that is, I > Br > Cl >> F. Since the reactive halides such as bromine compounds are very expensive, there has been no incentive to use the Ullman polymerization for the preparation of PEKs from activated aromatic dihalides. Only low-molecular-weight polymer was obtained from the reaction of 4,4′-dichlorobenzophenone with the disodium salt of bisphenol A in DMSO at 153 °C catalyzed by cuprous oxide.[155] Poor reproducibility, the need for expensive brominated monomers and the difficulty of removing copper salts are the major disadvantages of this reaction.

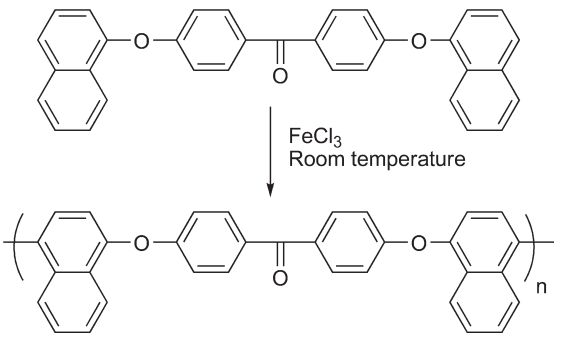

Figure 35 Synthesis of poly(arylene ether ketone) via Scholl reaction.

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5.17.3.1.3(iv) Metal-catalyzed polymerization

Metal promoted coupling of aryl dihalides is one of the newer and more novel methods for the preparation of PAEKs. However, a limitation is imposed on the scope of this method due to the crystalline nature of PAEKs because relatively moderate polymerization temperatures are optimum for this method meanwhile high reaction temperatures are necessary to keep growing polymer chains from precipitation. Furthermore, high-molecular-weight polymers can only be obtained when polymerization can proceed in homogeneous media.

Nickel(0) promoted coupling of *meta*-positioned dihalides was reported to be a successful means of generating high-molecular-weight PAEKs (IV = 0.87 dl g^{-1} in concentrated sulfuric acid) when polymerization was conducted at 90 °C in DMAc (**Figure 36**).[156] However, only low-molecular-weight polymers from the *para*-substituted monomers were obtained because of the precipitation of the resulting polymers. The optimum molar ratios of nickel chloride, triphenyl phosphine, zinc, and 2,2′-bipyridine to the monomer were reported to be 0.05, 0.1, 3.1, and 0.05, respectively.

Palladium-based catalysts have also been reported to be successful in catalyzing coupling reactions to prepare high-molecular-weight PAEKs.[157,158] The highest molecular weight polymers were obtained when palladium–triphenylarsine catalysts ($Pd[As(C_6H_5)_3]_2Cl_2$) were used instead of the analogous phosphine-based catalysts ($Pd[P(C_6H_5)_3]_2Cl_2$). The former catalysts were considered to possess an optimum balance between reactivity and thermal stability.

5.17.3.2 Other Functionalized Poly(arylene ether ketone)s

Without sacrificing the excellent physical and other properties of PAEKs, chemical modification of these polymers have been developed to target particular applications. Generally, there are two approaches to obtain functional polymers. One is to chemically modify the preformed polymers. Another is to use functionalized monomers in the polymerization to afford the functional polymers. Direct chemical modification on the preformed polymers, particularly on commercially available polymers, is more convenient and quite economic to achieve polymer functionalization. However, the extent of chemical modification is generally hard to control and side reactions may occur since the modifications occur on the activated rings, which may deteriorate thermal stability of the polymers. Modification of monomers is fundamentally different from modification of polymer in that it makes possible the control of the molecular structure, such as degree of functionalization and the location of functionality. Therefore, more chemical modification options are possible by using the approach of modifying monomers, although more synthetic challenges may arise.

5.17.3.2.1 Sulfonated poly(arylene ether ketone)s

Sulfonated PAEKs, particularly sulfonated PEEK (SPEEK), have attracted much attention recently in the applications of proton exchange membrane fuel cells (PEMFCs) due to their good properties under fuel cell conditions. Sulfonation enhances the acidity and hydrophilicity of PAEKs, which facilitates proton conduction in the presence of water. At 100% sulfonation, SPEEK can dissolve in water implying its high hydrophilicity.[159]

In concentrated sulfuric acid solution (99–100%), PEEK was sulfonated to an equilibrium degree of one $-SO_3H$ per structural repeat unit within less than 1 day.[160,161] The resulting sulfonated polymer structures were confirmed by Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopies, as was the quantitative increase in molecular weight. In addition, sulfonation was found to occur exclusively on the phenyl rings, which are surrounded by the two ether linkages (**Figure 37**). The other phenyl rings were deactivated by the neighboring ketones. This statement is also supported by the observation that PEK molecules remained unsulfonated under the same conditions since no activated phenyl rings were available for sulfonation.

Other than the commonly known concentrated sulfuric acid, chlorosulfonic acid, pure or complexed sulfur trioxide, acetyl sulfate, and methane sulfonic acid[160,162–164] have been shown to sulfonate PEEK effectively. Sulfonated polymers can be prepared in various forms depending on different sulfonation method, such as free acid form ($-SO_3H$), salt form ($-SO_3^-Na^+$), esters ($-SO_2R$), and various derivatives. It has been shown that sulfonation is greatly hindered with decreasing ether group content in the PEK chain, that is, the ease of sulfonation follows the order of: PEEK > PEEKK/PEK > PEKEKK.[165] However, it is difficult in most cases to

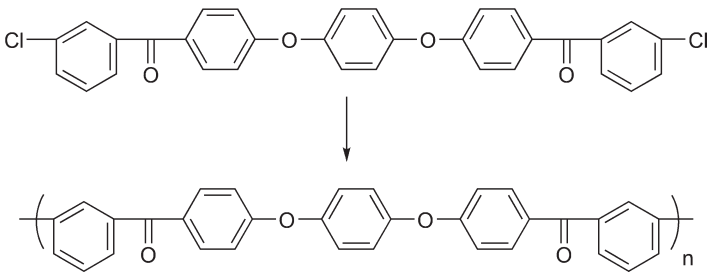

Figure 36 Nickel(0)-catalyzed polymerization of poly(arylene ether ketone).

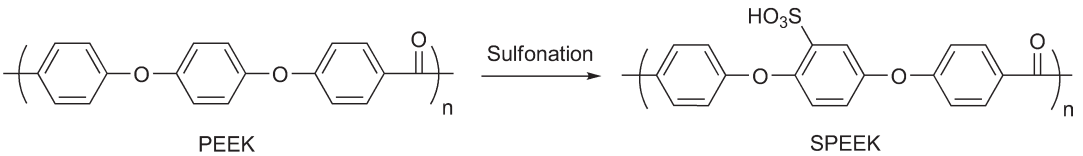

Figure 37 Sulfonation of PEEK.

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achieve degrees of sulfonation (DS) greater than 1.0 per repeat unit due to insolubility and side reactions such as interchain crosslinking and degradation. Marvel *et al.*[166,167] reported that extensive degradation and crosslinking of the polymers occurred when sulfur trioxide–triethyl phosphate complex was used as sulfonating agent. Chlorosulfonic acid was more satisfactory, but some degradation still occurred. Sulfonation of PEEK in H_2SO_4 (< 100%) is considered to be low in degradation and crosslinking reactions. It has been suggested that the presence of water decomposes pyrosulphonate intermediates to inter- and intramolecular sulfone crosslinks. In general, the DS of PEEK (30–100%) can be controlled by the reaction time and temperature. Some polyetherketones, such as PEEKK and PEEK, can be functionalized by electrophilic sulfonation with sulfuric acid and were at one point commercialized by Hoechst-Aventis.

The sulfonated ionic PEEKs exhibit modified properties from original PEEKs. For example, sulfonation alters the nature of chain packing, thus drastically reduces the crystallizability of PEEKs. However, T_g increases with sulfonation due to increased intermolecular interactions. With a DS of 0.72 (the concentration of $-SO_3H$ group per repeat unit of PEEK), a fully amorphous polymer with a high T_g of 206 °C was obtained,[161] which was more than 60 degrees higher than the unsulfonated PEEK. It was also found out that sulfonation decreased the thermo-oxidative stability of PEEK significantly and that poorer melt processibility also resulted. In recent research,[168–172] it has been shown that SPEEK is promising for fuel cell applications (both direct methanol fuel cell (DMFC) and PEMFC) as it possesses good thermal stability, mechanical strength, and adequate conductivity.

5.17.3.2.2 Hyperbranched poly(arylene ether ketone)s

Hyperbranched polymers generally have low melt and intrinsic viscosities (IVs) compared with corresponding linear polymers, which are beneficial for polymer processing. In addition, the presence of large number of functional chain end groups in hyperbranched macromolecules has also been shown to dramatically affect physical properties such as the glass transition temperature, solubility, and chemical reactivity. Conceptually, the DB ranges between 0 for a perfect linear molecule and 1 for a perfect dendritic molecule.

Miller *et al.*[173] reported the first synthesis of hyperbranched PAEKs from 3,5-bis(4-fluorobenzoyl)phenol via S_NAr. The resulting polymer was a hyperbranched analog of isoPEK (**Figure 38**).

Alternatively, by revising an AB_2-type monomer, 3,5-difluoro-4-hydroxybenzophenone, Hawker *et al.*[174] prepared an A_2B-type monomer, 3,5-dihydroxy-4-fluorobenzophenone. Polymerization of these two monomers afforded the same internal linkages but with different terminal groups in the hyperbranched PAEKs. The A_2B-type monomer when polymerized yielded hyperbranched polyethers with phenolic instead of fluoro end groups (**Figure 39**). This reversal had a considerable influence on both their reactivities and the physical properties of the resulting polymers such as solubility and glass transition temperatures. Higher-molecular-weight polymer ($M_n = 95\,kg\,mol^{-1}$) was obtained from A_2B-type monomer than that from AB_2-type monomer ($M_n = 20\,kg\,mol^{-1}$), although the polymerizations proceeded under the same typical S_NAr conditions. This is due to the fact that the fluoro aromatic nucleus in AB_2-type monomer was not as active as in A_2B-type monomer toward an S_NAr-type displacement by virtue of the carbonyl group being in the *meta* position. The DB was also different for these two hyperbranched PEEK analogues, which ranged from 14% for the phenolic-terminated polymer to 49% for the fluoro-terminated polymer. Morikawa[175] further modified the above AB_2-type monomer by introducing various number of phenyl units. It was found that with increasing the number of phenyl units in the monomers, the resulting branched polymers could be from amorphous to semicrystalline with increased T_g's.

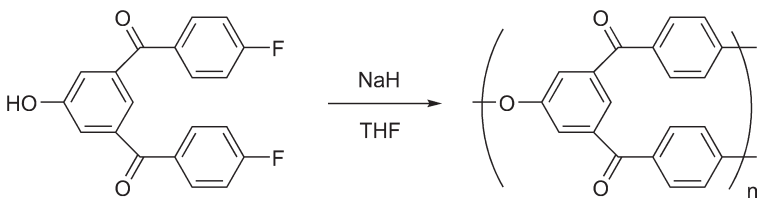

Figure 38 Synthesis of hyperbranched poly(arylene ether ketone).

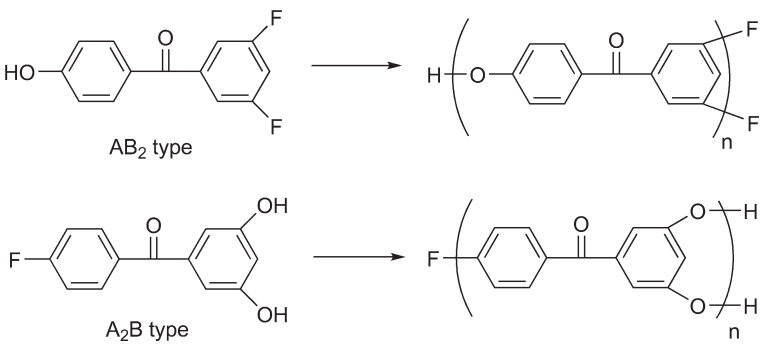

Figure 39 Hyperbranched PEKs synthesized from AB_2-type and A_2B-type monomers.

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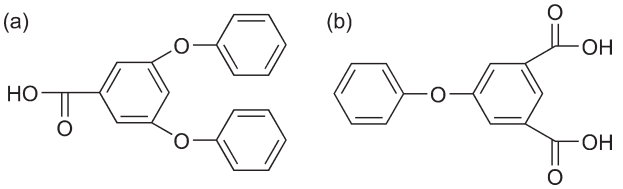

Figure 40 Monomers for the synthesis of hyperbranched PEKs via electrophilic aromatic substitution: a) 3,5-diphenoxybenzoic acid; b) 5-phenoxyisophthalic acid.

Electrophilic aromatic substitution approach has also been used to prepare the hyperbranched PEKs by Shu *et al.*[176,177] In their work, two monomers, 3,5-diphenoxybenzoic acid (a) and 5-phenoxyisophthalic acid (b), were prepared (**Figure 40**), which were then polymerized in mixture of phosphorus pentoxide and methanesulfonic acid *via* an electrophilic aromatic substitution. The reaction temperature for the latter monomer (120 °C) was higher than that for the former monomer (90 °C) due to its poorer solubility. The DB for these polymers was about 55%. The phenoxy groups at the chain ends of the hyperbranched PEK were highly reactive for further electrophilic aromatic substitution with various carboxylic acids. The carboxylic acid groups at the chain ends were also readily converted to a variety of functional groups. Physical properties, such as the glass transition temperature and the solubility of the hyperbranched PEKs, depended heavily on the nature of the chain ends. An ammonium salt form of carboxylic-terminated PEKs was soluble in water and was demonstrated to form unimolecular micelles.

More recently, polymerization of $A_3 + B_2$ monomers was reported by Choi *et al.*[178] to synthesize hyperbranched PEKs without forming crosslinked products. The polymer-forming process based on Friedel–Crafts reaction was kinetically controlled by the solubility difference of monomers in the viscous hydrophilic reaction medium, poly(phosphoric acid) (PPA)/phosphorus pentoxide (P_2O_5). It was stated that the gelation was avoided by automatic and slow feeding of the hydrophobic monomer into the hydrophilic and viscous reaction medium.

5.17.3.2.3 Graft poly(arylene ether ketone)s

Very few graft copolymers based on PAEKs have been reported because of their high chemical inertness. Klapper *et al.*[179] reported grafting polystyrene or polyisoprene onto the PEEKK by anionic deactivation (**Figure 41**). Carbonyl groups on the PEEKK backbone were attacked by the polystyrene or polyisoprene anion (M_n about 3 k), resulting in a 'comb-type' PEEKK-*g*-polystyrene or PEEKK-*g*-polyisoprene, respectively. The high reactivity of the backbone carbonyl groups and the smooth grafting via nucleophilic attack provided graft copolymers with a defined structure. However, only about 30% of the carbonyl groups were modified due to steric hindrance. If the molar ratio of poly(styryllithium) or poly (isoprenelithium) versus PEEKK was kept below the maximum grafting limit resulted from steric hindrance, one could control the degree of grafting thus the properties of the graft copolymers.

Later, the same group[180] modified an amine-functionalized PAEKs by polycondensation between carboxy-terminated oligo-benzamides and benzoyl chloride. The graft polymers showed different thermal and mechanical behaviors, depending on the length and chemical nature of the side chain. Grafting oligo-benzamides increased the T_g of the polymer control, while grafting benzoyl group decreased T_g. Young's modulus increased linearly with the length of the oligo-benzamideside chain introduced. These results indicated that hydrogen bonding of the side chains played a crucial role in the improvement of the polymer properties.

5.17.3.2.4 Crosslinked poly(arylene ether ketone)s

Crosslinked PAEKs have been developed to produce thermally stable elastomers for high-temperature (>200 °C) applications such as O-rings and sealants in petrochemical and automotive industries. Introduction of covalent crosslinks into a semicrystalline PEEK matrix is expected to disrupt the

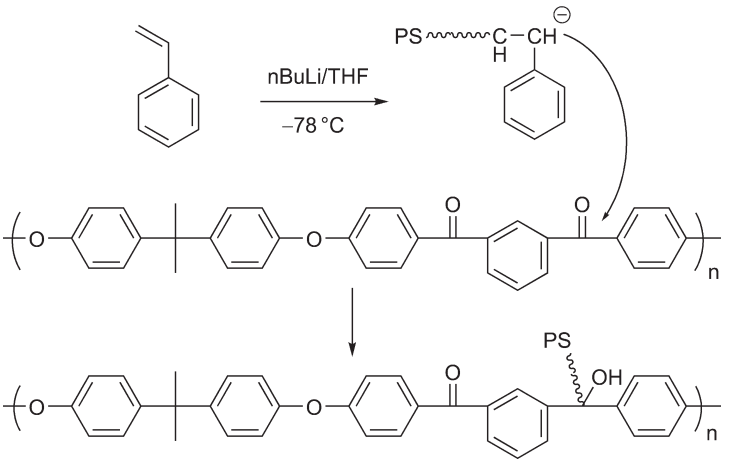

Figure 41 Grafting of polystyrene onto PEEKK via anionic deactivation.

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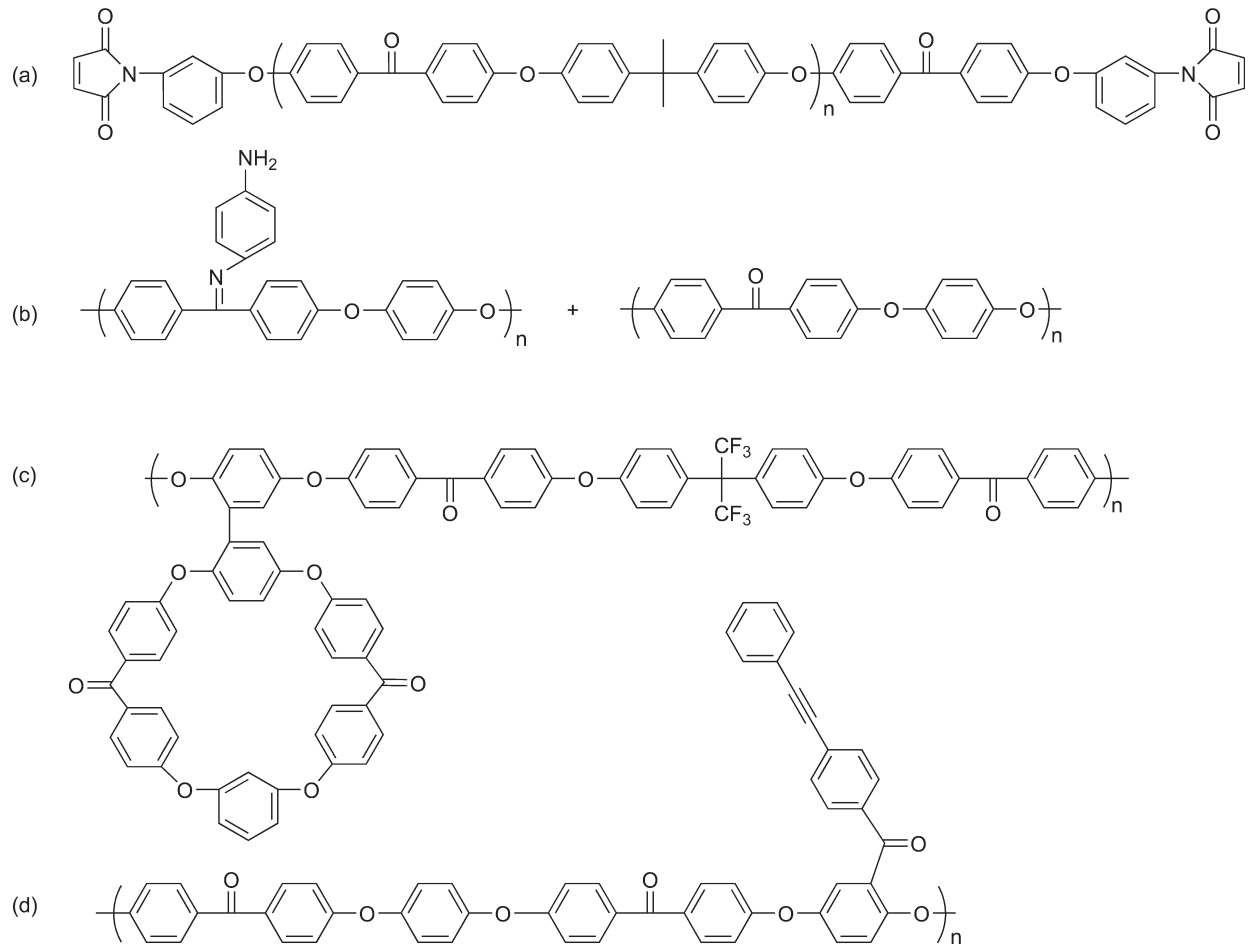

Figure 42 Chemical structures of several crosslinkable poly(arylene ether ketone) oligomers.

crystallinity resulting in amorphous and crosslinked polymers that could exhibit rubbery properties at high temperatures. Several crosslinking approaches have been used to prepare fully aromatic thermosetting PEKs, such as using elemental sulfur,[181] imide end-group crosslinking,[182] (phenyl)ethynyl moieties,[183,184] the formation of imines with aromatic diamines,[185,186] crosslinking from unsaturated norbornene unit,[187] and crosslinking from a macrocyclic pendant.[188] Chemical structures of some of the reported crosslinkable PAEK oligomers are shown in **Figure 42**.

Hedrick *et al.*[182] reported the synthesis of thermally curable PAEKs from maleimide-end-capped bisphenol A-based oligomers. The cured polymers possessed T_g's of around 160 °C. The moduli and elongation to break of the new elastomers at higher temperatures were comparable to an unfilled polydimethylsiloxane (PDMS) rubber, and the thermal stability was considered exceptional. Thermal curing of PAEK oligomers with unsaturated functionality was also employed in preparing thermosetting PAEKs. Ethynyl- or phenylethynyl-containing oligomers have been reported. Li *et al.*[184] synthesized a series of crosslinkable PAEKs containing pendant phenylethynyl moieties by polymerizing a phenylethynyl-modified phenol monomer with hydroquinone and DFBP by means of aromatic nucleophilic substitution. The cured polymers exhibited high T_g's together with excellent thermal stability. Jeong *et al.*[183] developed crosslinked sulfonated PAEKs for applications in proton exchange membranes (PEMs). Crosslinkable sulfonated PAEK copolymers were synthesized with a crosslinking agent (3-ethynylphenol) at the chain end. The ethynyl moiety formed a benzene ring after upon heating and subsequently, a chemically crosslinked network structure was formed. The T_g's of the crosslinked membranes were determined to be in the range from 208 to 258 °C. Improved PEM properties were observed from these crosslinked sulfonated PAEKs, namely, good thermal stability, low water uptake, and high proton conductivity. More recently, Chen *et al.*[187] reported the synthesis of crosslinkable PEEKK copolymers containing unsaturated norbornene unit for proton-conducting membrane application. It was reported that crosslinking through the double bond in norbornene unit reduced both the methanol permeability and methanol uptake.

Moderately crosslinked PEEKs (less than 10% crosslinking) were prepared by Yurchenko *et al.*[186] via a two-stage procedure involving an aromatic imine structure. Rigid crosslinks based on aromatic imines were synthetically introduced into PEEK matrix resulting in various degrees of crosslinking. All crosslinked materials showed surprising resistance to hot oily, acidic and basic media, as well as

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excellent thermal stability. Furthermore, these materials were more rubbery at high temperature than commercial thermoplastic Victrex® 151G.

Another important study to prepare crosslinked PAEKs is based on the ring-opening reaction of macrocycles. As mentioned before, an important advantage of macrocycle-based technology is that starting materials can be polymerized without by-products, and may be processed at much lower temperatures allowing the use of reactive processing techniques (injection molding and melt extrusion) to transform cyclic oligomers directly into commercial objects. Yue *et al.*[188] reported the synthesis and curing of PAEKs bearing crosslinkable macrocyclic pendants. The crosslinking reaction of copolymers occurred by ring-opening reaction driven by entropy. The cured copolymers showed much higher glass transition temperatures, excellent thermal stability, and better mechanical strength.

5.17.3.2.5 Block and segmented copolymers

In order to combine the most desirable properties of PAEKs and other aromatic polymers, block and segmented copolymers have been developed to accommodate specific applications. Generally, the block and segmented copolymers can be prepared by reacting functional group-terminated oligomers with other functional oligomers or monomers.

Poly(arylene ether ketone sulfone) copolymers are among the most popular block copolymers that are being actively investigated,[189–191] especially in the PEMFC applications.[192–195] With highly sulfonated hydrophilic blocks, sulfonated poly(arylene ether sulfone ketone) (SPESK) multiblock copolymer membranes showed high proton conductivity even at low relative humidity (RH). The high local concentration of sulfonic acid groups within the hydrophilic blocks enhanced phase separation between the hydrophobic and hydrophilic blocks.

McGrath *et al.*[196,197] reported the synthesis of the segmented copolymers of PAEKs and PDMS. The materials displayed two T_g's of around −130 and 145 °C, indicating strong phase separation, which was also evidenced from transmission electron microscopy (TEM) studies. The PEEK-*block*-PDMS copolymers showed some special properties that were highly correlated to the structures. Similarly Corfield *et al.*[198] synthesized PEEK-PDMS block copolymers from the condensation of dimethylamino-terminated PDMS and hydroxyl-terminated PEEK oligomers in 1-chloronapthalene. Phase separation of the block copolymers occurred even at very short segment length ($M_n < 4000$). A depression in the crystallinity of both the PEEK and PDMS phases in the block copolymer was also observed.

Segmented block copolymers of imide aryl ether ketone were synthesized by Hedrick *et al.*[199] The block copolymers were prepared via a two-step process. Two aryl ether ketone blocks were incorporated; the first was an amorphous block derived from bisphenol A and the second block was a semicrystalline PEEK prepared from a soluble and amorphous ketimine precursor. The blocks of PEEK oligomers with M_n range of 6000–12 000 g mol^{-1} were coreacted with 4,4′-oxydianiline and PMDA in NMP in the presence of *N*-methylmorphiline. Clear films with high moduli were obtained by solution casting and subsequent thermal curing. Multiphase morphologies were observed from those films.

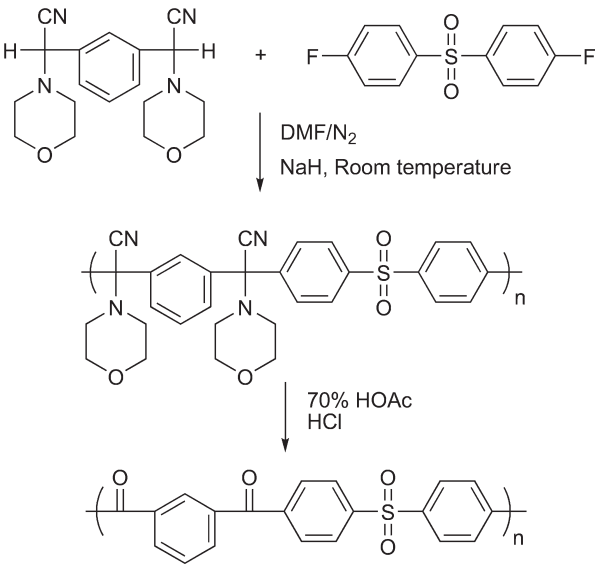

Figure 43 Synthesis of poly(ketone ketone sulfone) copolymer via polyaminonitrile precursor.

Pandya *et al.*[145] developed an approach to prepare poly (arylene ketone sulfone) copolymers via soluble poly(aminonitrile)s. Bis(α-aminonitrile) monomers were prepared from aromatic dihalides in high yield by Strecker synthesis. The conjugate bases of the α-aminonitriles were selective and powerful nucleophiles, which could displace activated halides, forming a C–C bond. As shown in Figure 43, polycondensation of isophthalaminonitrile with DFBPS was conducted in anhydrous DMF at room temperature using NaH as the base yielding a soluble high-molecular-weight polyaminonitrile. Subsequent hydrolysis of the polyaminonitrile under acidic conditions regenerated the carbonyl moiety resulting in the corresponding PEKs that was otherwise difficult to synthesize. This approach has been applied to the synthesis of a series of highly ketone-containing polyketones with or without ether linkages. Polymers prepared via this route were crystalline and had very high T_g's and T_m's.

5.17.3.3 Properties and Applications

As highly aromatic semicrystalline thermoplastics, aromatic ketone polymers exhibit unique set of outstanding properties that are unparalleled by other high-performance polymers, although they have the highest unit price. For examples, outstanding high-temperature performance, unique combination of strength, stiffness, impact resistance and elongation, good resistance to virtually all organic chemicals, good electrical, and insulating properties are some of their attractive characteristics that justify their high prices. Another major advantage for being used as high temperature and composite matrix is theirs low flammability and very low smoke and toxic gas emission.

Aromatic PEKs have melting points (T_m) greater than 330 °C, and their service temperatures may exceed 260 °C.

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For example, PEEK can be used long term up to 250 °C even in hot water or steam. It has been shown that T_g and T_m of these polymers can be tuned by simply changing the number and relative positions of ether and ketone linkages as illustrated in Table 1. As the number of ketone groups increases (from PEEK, PEEKK, PEK to PEKK), the T_g of the polymer rises since both backbone rigidity and degree of polarity increase. Meanwhile, the degree of crystallinity increases and the polymers become more resistant to solvent attack. For practical applications, it is necessary to keep the right balance between T_g, T_m, T_d, crystallinity, solvent resistance, and other properties to assure their feasibility in both synthesis and processing (Table 1).

Because of their unique set of outstanding properties, aromatic ketone polymers have found increasing uses in many critical applications in industrial, transportation, electronic, and medical markets. Subsequently some selected topics will be discussed in detail.

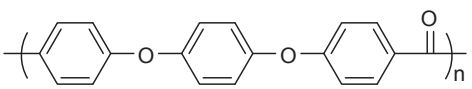
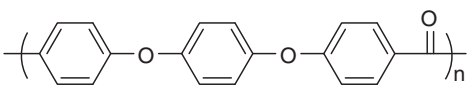
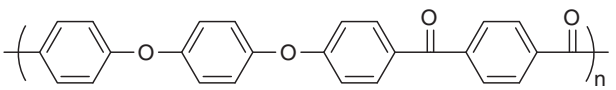
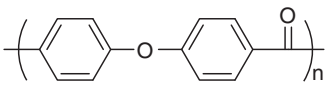
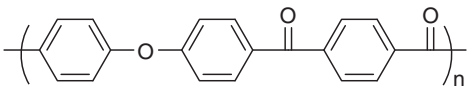
Due to their outstanding chemical resistance and good thermal and mechanical properties, PAEKs are attractive materials for porous membrane in filtration and purification applications, such as filtration of wastewater, preparation of ultrapure water in medical, pharmaceutical, or food applications, including removal of microorganisms and protein filtration. With extremely limited solubility, PEEK membranes are mostly obtained from solutions of concentrated sulfuric acid. To avoid undesired sulfonation, which deteriorates some desired properties of PEEK, less-concentrated sulfuric acid solutions and some nonsulfonating acid solvents, such as methanesulfonic acid and TFMSA, have been used.[202] It has also been reported that some high-boiling-point solvents such as benzophenone and 1-chloronaphthalene and plasticizers dissolved the PEEK at elevated temperatures.[203] The porous membrane was formed by removing the organic polar solvents or the plasticizers via dissolution into a low boiling solvent. Another approach to prepare membranes utilizes the thermally induced phase separation (TIPS) process.[204] TIPS is a process where the polymer is dissolved in a solvent in which the solubility of the polymer in this solvent is temperature dependent. The polymer–solvent blend is extruded or cast at elevated temperatures. Upon cooling, a polymer-rich phase separates from the solvent. The solvent is then removed from the phase-separated blend by leaching.

Another membrane application of aromatic ketone polymers is that their sulfonated polymers can be used as PEMs in fuel cells. As mentioned before, upon sulfonation, SPEEK exhibits proton conductivity. Considered as good candidates for fuel cell applications, sulfonated PAEKs-based membranes show a good chemical and mechanical stability, high proton conductivity, a reduced methanol permeability, and a lower cost with respect to a Nafion® membrane. Various sulfonated PAEKs have been described in literature.[171,205,206] More recently, multiblock copolymers of poly(arylene ether sulfone ketone)s consisting of hydrophobic and a hydrophilic blocks have been developed to further improve the proton conductivity, which will be covered in the section of poly(arylene sulfone)s.

5.17.4 Poly(arylene sulfone)s

Major changes in properties of aromatic polymers result from simply changing the linking groups. By changing from a ketone to a sulfone linking group, many fundamental changes to the polymer properties are produced. For example, the double-bond character of the C–S link restricts chain rotation and consequently enhances chain rigidity, leading to an increase in T_g and amorphous feature instead of crystalline structure in ketone polymers.

Table 1 Structure–property relationships in aromatic ketone polymers[200,201]

Simplified polymer repeat unit	*Name*	*T_g (°C)*	*T_m (°C)*
	PEEK	143	335
	PEEK	167	416
	PEEKK	154	358–365
	PEK	154	365
	PEKK	165–175	384

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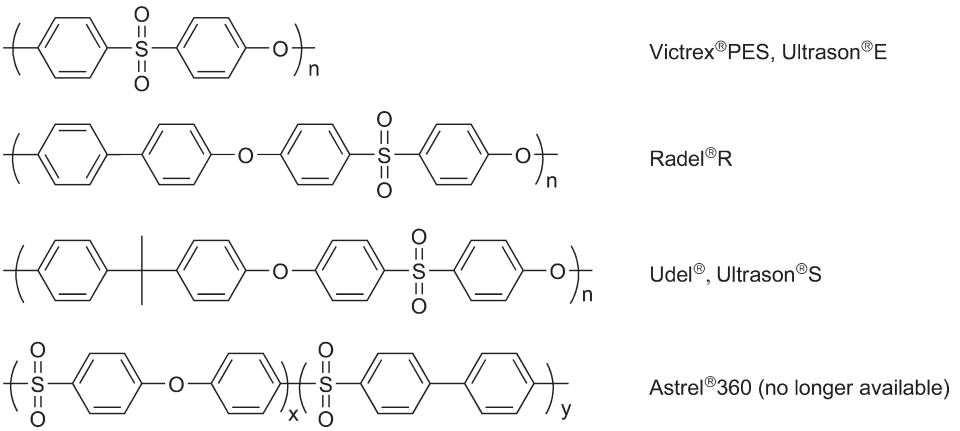

Figure 44 Basic backbone structures of some commercial poly(arylene ether sulfone)s.

Aromatic PESs were discovered independently, by Union Carbide (Udel® polysulfone) and 3M (Astrel® polysulfone) and by Imperial Chemical Industries (ICI) (Victrex® polysulfone) in the United Kingdom, though different synthetic methods were used. Astrel® was prepared by polysulfonylation in the presence of Friedel–Crafts catalyst via electrophilic substitution, while the other two were prepared by polyetherification in which the ether linkages were formed by nucleophilic displacement reactions. The basic repeating structures of some commercial poly(arylene ether sulfone)s are illustrated in Figure 44.

5.17.4.1 General Synthesis Approaches

The main synthetic routes to poly(arylene ether sulfone)s (PAES) are analogous to those used for the corresponding PAEKs, including S_NAr, electrophilic substitution, and other synthetic routes.

5.17.4.1.1 Nucleophilic aromatic substitution

A broad range of poly(arylene ether sulfone)s can be prepared by the nucleophilic aromatic polycondensation of an aromatic dihydroxy compound with a bis-(halophenyl) sulfone (Figure 45). In S_NAr-type reactions, the sulfonyl group is more effective than the carbonyl group in activating the aromatic dihalides and accelerating the nucleophilic substitution due to the fact that the former is more electronegative in nature.

5.17.4.1.1(i) Diphenols and activated aromatic dihalides

4,4′-Dichlorodiphenyl sulfone (DCDPS) is the workhorse monomer for the synthesis of commercial poly(arylene ether sulfone) products via the S_NAr method. Johnson *et al.*[125] reported the first synthesis of poly(arylene ether sulfone) from DCDPS and bisphenol A, which represents a good example for general synthesis of PESs, either in laboratory scale or in industrial scale. This polymer, now referred to as Polysulfone was commercialized in 1965. In this so-called 'caustic process', bisphenol A was first converted to a soluble disodium bisphenolate A salt by reacting with sodium hydroxide (molar ratio of 1:2) in DMSO/chlorobenzene with azeotropic removal of the water condensate. Then an equal molar amount of DCDPS was added in chlorobenzene under anhydrous conditions and the polycondensation was allowed to proceed at 160 °C for over 1 h to afford high-molecular-weight polymers. Chlorobenzene is added to the viscous polymer solution during cooling, since it is a solvent at room temperature and facilitates precipitation of the salts (Figure 46). This process is now commonly referred to as the 'caustic process', which is a 'textbook' example of condensation or step-growth polymerization. For experimental purposes, it can be desirable to use the more reactive difluorodiphenyl sulfone (DFDPS) rather than DCDPS. However, the utilization of DFDPS is very limited due to the high cost of fluoro monomer.

As mentioned before, nucleophilic displacement of a halogen from activated systems most commonly occurs via a two-step addition–elimination mechanism. The first step, the formation of a resonance-stabilized intermediate – Meisenheimer complex – is usually the rate-determining step. Therefore, the nucleophilicity of the derived bisphenolate anions and their thermal stability are the two key parameters in the caustic process determining the kinetics of polymerization. Electron donating substituents *para* to the phenolate group enhance nucleophilicity whereas electron withdrawing

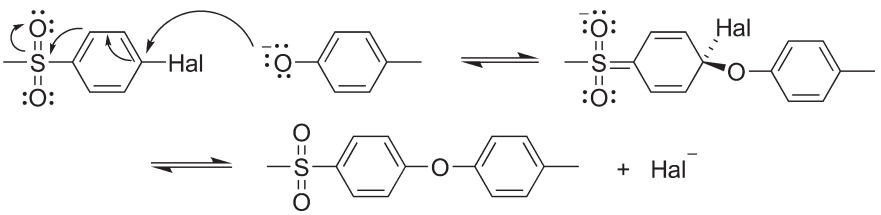

Figure 45 Synthesis of poly(arylene ether sulfone) via nucleophilic aromatic substitution (S_NAr).

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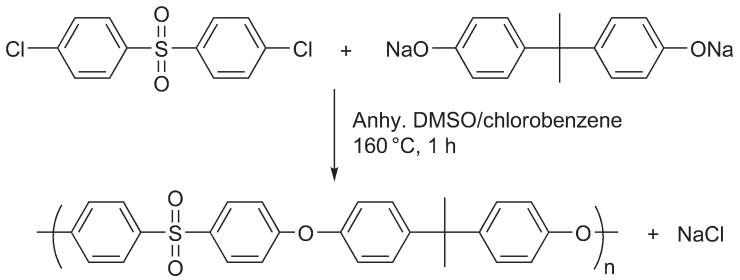

Figure 46 Synthesis of bisphenol A polysulfone via nucleophilic aromatic substitution.

groups decrease nucleophilicity and thus reactivity. For example, bisphenol A with an alkylidene connecting group yielded very high-molecular-weight polymers with DCDPS in an hour, while Bisphenol S with the sulfonyl connecting group gave only low-molecular-weight polymers even after 10 h.[200] To maintain the thermal stability of the phenoxide anions, the polymerization should always be conducted below a certain temperature limit and under air-free and anhydrous conditions. Although the decomposition of the Meisenheimer intermediate is not the rate-determining step, the easiness of activation of the aromatic halo groups by electron withdrawing groups is also essential for a successful polymerization. The reactivity of the activated halides has been studied extensively[22,200,207,208] by measuring ^{1}H, ^{13}C, and ^{19}F NMR chemical shifts. It has been shown that the nucleophilic substitution reaction only proceeds in the halides with *ortho* or *para* positions substituted by strong electron-withdrawing groups. Therefore, ^{1}H NMR chemical shift data of the protons *ortho* or *para* to the electron withdrawing group can be used to determine the reactivity of the monomer indirectly.208 ^{13}C NMR and ^{19}F NMR can be used to probe the chemical shift at the actual site of nucleophilic reaction. In general, lower chemical shifts correlate with lower monomer reactivity. In addition, the relative effectiveness of the group activating the halogen has been found to be in the order of $-NO_2 \sim -SO_2 > -CO- > -N{=}N-$ according to their relative electronegativity. Therefore, varying the combination of halogen and the activating group gives a variety of choices of monomers from which to choose for a polymerization. For example, a fluoro monomer activated by a carbonyl group may be preferable to a sulfone-activated chloro monomer. Besides the monomers, other polymerization conditions, like solvent and choice of base, should also be considered.

Instead of using bisphenolate salts that require separate processes for their preparation and dehydration, the use of alkali metal carbonates as bases has been developed for the synthesis of poly(arylene ether sulfone)s. This so-called 'carbonate process' is advantageous especially when some hydroquinone or biphenol salts are insoluble. Furthermore, a strict stoichiometric amount of base in preparing the salts is required to obtain high-molecular-weight polymers in the above-mentioned 'caustic process'. Moreover, the strong base may undesirably hydrolyze the dihalides to afford deactivated diphenolates, which upsets the stoichiometry. Clendinning *et al.*[209] reported the first use of potassium carbonate or bicarbonate in these reactions instead of the strong base potassium hydroxides. Formation of high-molecular-weight polymers without precipitation of salts was achievable even those alkali metal bisphenol salts were not soluble. Due to this feature and others, the carbonate process is now the preferred method in preparing new and/or small samples of poly(arylene ether sulfone)s. The commercial aromatic PES of Victrex® PES by ICI is believed to be produced from DCDPS and Bisphenol S by the carbonate process. McGrath and coworkers[210–212] were the first to systematically study the use of the weak base K_2CO_3 instead of strong base to obtain phenolate salts. K_2CO_3 was found to be better than Na_2CO_3 because it is a stronger base and has higher solubility in the reaction media. Additionally, the resulting potassium phenoxides are more reactive. The proposed mechanism for the carbonate process is illustrated in **Figure 47**. It is postulated that the potassium monophenate and potassium bicarbonate are formed in the first step. The monophenate salt then reacts with the dihalo monomer to initiate chain growth. The potassium bicarbonate disproportionates to potassium carbonate producing water and carbon dioxide. Therefore, an azeotrope-forming solvent should be included in the polymerization to remove the water.

The same considerations about the bisphenol and dihalide monomers that were discussed earlier in the caustic process also apply to the carbonate process. Aprotic polar solvents have to be used since they are often good solvents for both monomers (including phenolates) and resulting polymers. In addition, they can also stabilize the Meisenheimer intermediates. Common aprotic polar solvents, such as DMSO, *N*,*N*′-dimethyl acetamide (DMAc), *N*,*N*′-dimethyl formamide (DMF), NMP, and CHP, have been used. This approach makes it fairly easy to control the molecular weights and the end groups. Additionally, the precise amount of weak base is not extremely critical for achieving high molecular weights, as long as it is in excess. But it should be mentioned that the kinetics of these reactions are slower than the strong base method.

5.17.4.1.1(ii) Diphenols and activated aromatic dinitros

Activated aromatic dinitro monomers can also be used to polymerize with bisphenolates to yield poly(arylene ether sulfone)s. Typical process chemistry of the synthesis is shown in the accompanying **Figure 48**.

Imai *et al.*[213] prepared the synthesis of poly(arylene ether sulfone)s from nitro-substituted dichlorosulfone and bisphenol in the presence of potassium fluoride without use of alkali at any stage of the reaction (**Figure 49**). The essential feature of this type of polycondensations is that at least 500 mol.% of KF based on bisphenol is required to produce

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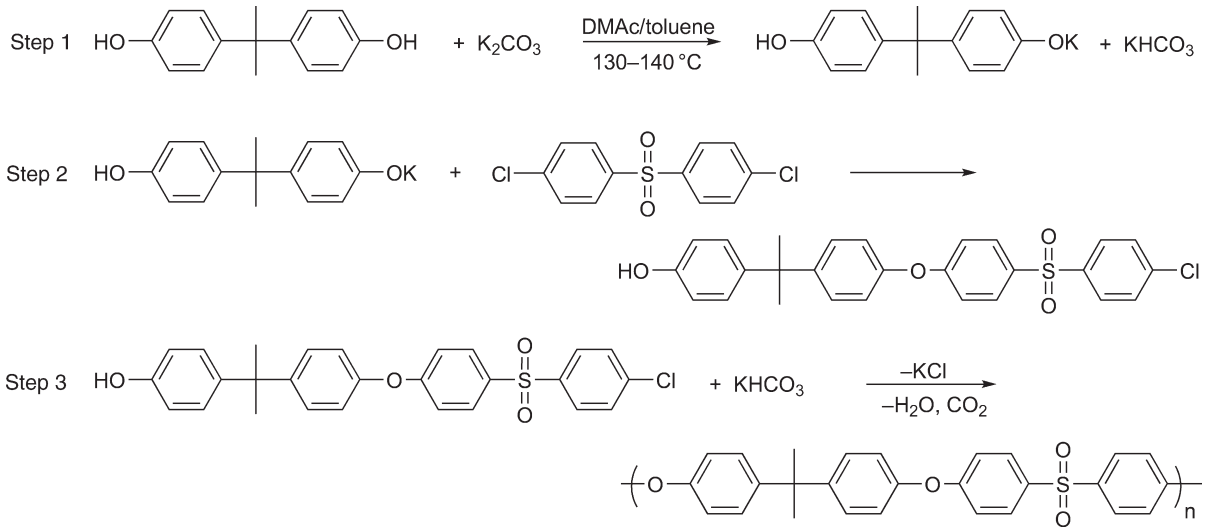

Figure 47 Synthesis of poly(arylene ether sulfone) via carbonate process.

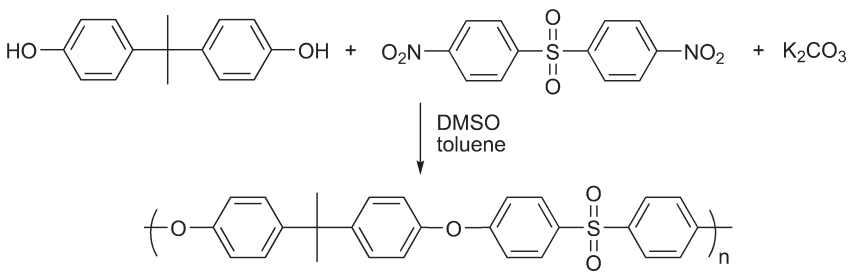

Figure 48 Synthesis of poly(arylene ether sulfone) from activated aromatic dinitro monomer.

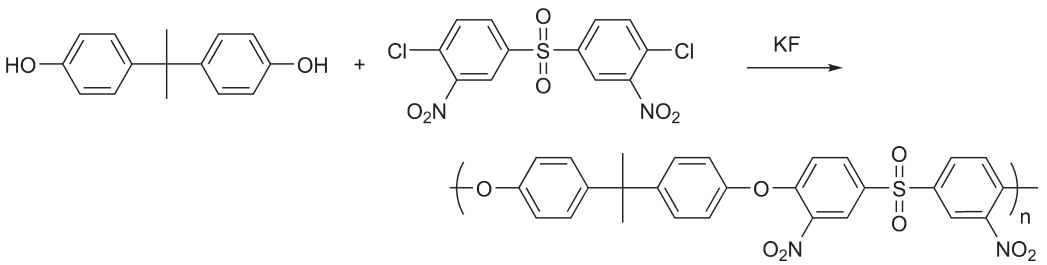

Figure 49 Synthesis of poly(arylene ether sulfone) from nitro-substituted monomer.

high-molecular-weight polymers. It is believed that the fluoride anion forms a very strong hydrogen bond to the hydroxyl group of the bisphenol, resulting in an increase of the nucleophilicity of the latter that is sufficient to enable it to attack the aromatic dichloride. However, the use of nitro monomers offers no advantage over the halo monomers considering the cost and availability. In addition, the release of nitrite ion into the polymerization may adversely affect the product quality such as color.

5.17.4.1.1(iii) Silylated bisphenols with activated aromatic dihalides

While most of the polymers have been synthesized by solution polymerization through nucleophilic substitution, Kricheldorf *et al.*[37,133,135] reported that melt or solvent free polymerizations can be achieved by reacting bis(trimethylsilyl ether)s of various bisphenols with bis(4-fluorophenyl) sulfone (**Figure 50**). It is referred to as the 'silyl method'. This idea came from well-known reactions on trimethylsilylated ethers, esters, and so on that were performed with fluoride-catalyzed desilylation in the presence of KF, CsF, or $(C_4H_9)_4NF$.[214] In the synthesis of poly(arylene ether sulfone), a bisphenol was first silylated using hexamethyldisilazane or chlorotrimethylsilane/triethylamine and purified by distillation. Then the silylated bisphenol was polymerized with DFDPS in bulk using a catalytic amount of CsF. The product can be directly processed without further purification since the highly volatile fluorotrimethylsilane is the only by-product and the catalytic amount of CsF does not deteriorate the mechanical properties of the final products. In addition, the removal of the volatile fluorotrimethylsilane by-product further drives the reaction to yield

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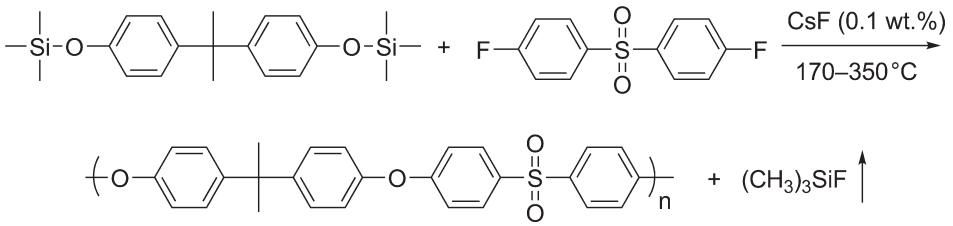

Figure 50 Synthesis of poly(arylene ether sulfone) from silylated bisphenol and activated dihalide.

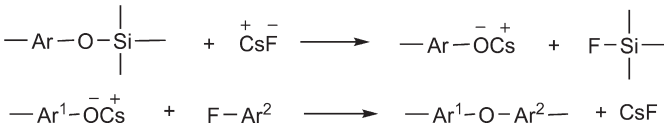

Figure 51 Mechanism of silyl ether displacement.

high molecular weight. No halogen-substituted diphenols can be used since the ether exchange reactions may occur.

A proposed mechanism for silyl ether displacement is shown in Figure 51. It is believed that the polymerization is initiated by fluoride ion attack on the *o*-trimethylsilyl group to generate a phenoxide anion in the first step. Following that, the phenolate anion attacks the activated fluoro monomer to generate an ether bond. Catalyst type and concentration are crucial for this reaction. Reaction temperatures required for this polymerization vary with the nucleophilicity of the phenolate anion since it is an essentially polyetherification method. For example, silylated bisphenol A polymerized at 220–230 °C while silylated bisphenol S required 300 °C.

Unfortunately, this method is only suitable for fluorinated monomers like DFDPS. Using chloro monomers generally affords low molecular weight since DCDPS is not reactive enough under these reaction conditions. However, the activated dichloro compounds were successfully polymerized in NMP or DMAc when an equimolar amount of potassium carbonate was used.[37]

5.17.4.1.1(iv) Phase transfer catalysis method

Since its introduction around 1965, PTC has become a well-established technique in organic chemistry.[215] In polymer chemistry, PTC approach has also shown its potential to offer economic advantages over the traditional solution process, which require no solvent purification and no polymer isolation and purification.

The synthesis of poly(arylene ether sulfone)s under solid–liquid phase transfer or interfacial conditions have been developed using phase transfer catalysts like quaternary ammonium salts and crown ethers. High conversion in nonactivated displacement reactions were obtained at lower temperature and shorter reaction time. Quaternary ammonium salts, such as tetrabutyl ammonium chloride, cetyl trimethyl ammonium chloride, and crown ethers including 15-crown-5 (15-C), dibenzo-18-crown-6 (DB-18-C), and dicyclohexyl-18-crown-6 (DC-18-C) have been used as phase transfer catalysts. In most reports,[216–220] crown ether catalysts have been used in solid–liquid reaction systems of a bifunctional nucleophile with a bifunctional electrophile as well as monomer species carrying both types of functional groups. It is believed that crown ethers form stable complexes with metal cations and provide highly reactive unsolvated anions by increasing the dissociation of ion pairs. Phase-transfer-catalyzed aromatic nucleophilic displacement reaction has shown that phenolate could displace halogen from activated, and relatively nonactivated aryl halides quantitatively at temperatures from 25 to 80 °C in several hours to give PAEs. There are several synthetic advantages associated with PTC method, such as (1) the phenolate anion is less solvated in the organic phase, the displacement rate is thus enhanced and less depressed by steric effects, resulting in exclusive formation of ether product; (2) only the aqueous phase is basic, protecting the halide and ether from destruction through hydrolysis; and (3) stoichiometric quantities of ammonium salt are not necessary.

5.17.4.1.2 Electrophilic aromatic substitution using Friedel–Crafts catalysts

Replacing the polyacylation process with polysulfonylation, poly(arylene ether sulfone)s have been successfully prepared via Friedel–Crafts-catalyzed polymerization of phenoxyaroyl- and phenoxyarenesulfonyl halide. One of the first commercial poly(arylene ether sulfone)s, Astrel®360, was prepared by 3M using polysulfonylation technique as shown in Figure 52.[200] Astrel®360 was a

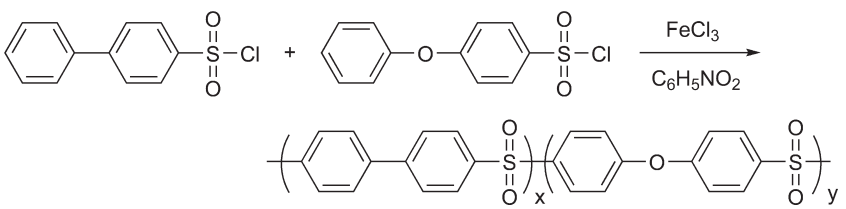

Figure 52 Synthesis of Astrel®360 poly(arylene ether sulfone).

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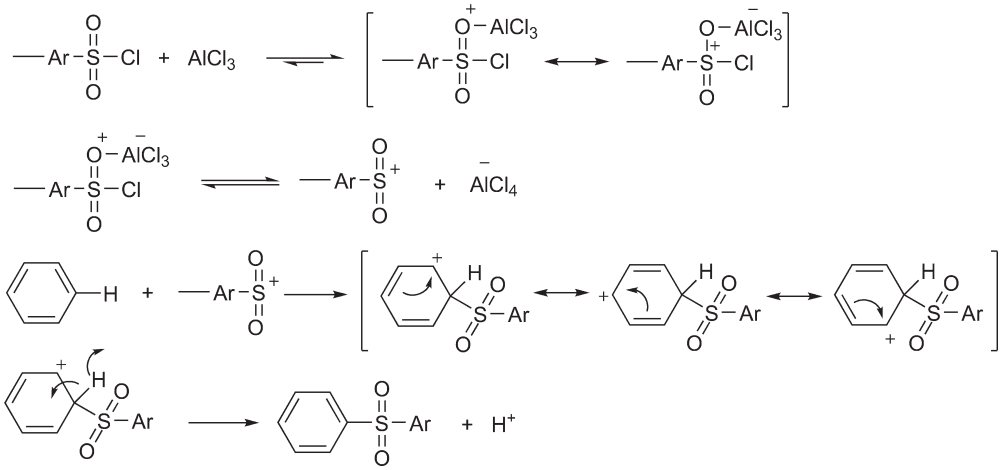

Figure 53 Mechanism for Friedel–Crafts sulfonylation.

copolymer containing the indicated repeat units in a ratio of x:y of about 60:40 to 70:30. However, the production of Astrel®360 was discontinued in 1976 due to the difficulties in melt fabricating the polymers and the availability of other poly(arylene ether sulfone)s prepared by nucleophilic polyetherification methods.

All of the electrophilic substitution reactions are based on the attack of electron-deficient species on an aromatic ring. The sulfonylation mechanism involves two steps, as shown in Figure 53. The electron-deficient species, sulfonylium cation $ArSO_2^+$, attacks the carbon on the aromatic nucleus to generate an intermediate complex, which subsequently decomposes to afford the final product by eliminating a proton. It is postulated that the effective sulfonylating agent is the sulfonylium salt generated by action of the Lewis acid catalyst on the sulfonyl halide. Friedel–Crafts catalysts, such as $AlCl_3$, $FeCl_3$, $SbCl_5$, $AlBr_3$, and BF_3, are all effective for the sulfonylation by arenesulfonyl halides.

Poly(arylene ether sulfone)s can be synthesized by two different polysulfonylation reaction routes: condensation of a nucleophilic monomer with a electrophilic monomer (AA- and BB-type monomers) or self-condensation of monomers containing both functional groups (AB-type monomer). The source of electron-deficient species is derived from the corresponding sulfonyl chlorides or the free sulfonic acids.

5.17.4.1.2(i) Condensation of aromatic sulfonyl chloride monomers

At about the same time that Astrel® was developed, ICI group developed the synthesis of Victrex® Polyethersulfone via polysulfonylation.[200,221] Both one- and two-monomer routes to PES have been developed (Figure 54). Although the polymers prepared from these different routes had the same nominal repeat unit, two-monomer route was preferred for commercialization considering the monomer availability. However, the polymers from this route were not as tough as those from the one-monomer route, possibly due to branching and/or generation of non-*para* isomers.

In some very early research, stoichiometric amounts of $AlCl_3$ were used in the polymerization. However, only small amounts of Lewis acid is now used as catalyst in the Friedel–Crafts reaction of sulfonyl chlorides with aromatic compounds, which is in contrast to the analogous acylation reactions requiring large amount of catalyst. High-molecular-weight polymers can be achieved via polysulfonylation at elevated temperatures with low concentration of the Lewis acids. For example, arenesulfonyl chlorides reacted smoothly in the molten state at 120–140 °C with aromatics in the presence of 1–5 mol.% of $FeCl_3$ (or $SbCl_5$, $InCl_3$, iron (II) or iron (III) acetylacetonate (acetyacetone is 2,4-pentanedione), or $BiCl_3$), giving the corresponding sulfones with high yields in a few hours.[155,222] Polysulfonylation can be conducted in bulk followed by a powder sintering operation to produce high molecular weight.

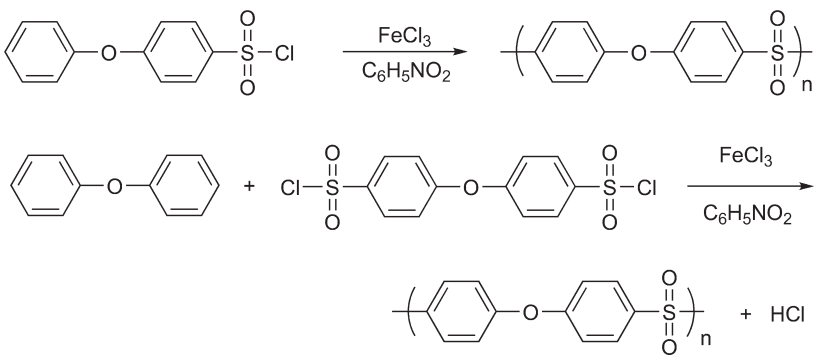

Figure 54 Polysulfonylation via one- and two-monomer routes.

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The final reaction temperatures were from 150 to 320 °C under nitrogen, and vacuum eventually was applied to remove HCl.[155] Since sulfonyl chlorides decompose above 250 °C via a radical mechanism, the best reaction temperature range was determined to be from 230 to 250 °C.[223] However, the polymers prepared by this approach were insoluble due to crosslinking side reactions. Therefore, polymerization in solution is preferred, which produces soluble high-molecular-weight polymers. However, the major disadvantages of this approach are the need for an expensive inert reaction medium and side reactions such as *ortho*-substitution and branching of the nucleophilic monomer. In addition, all the metal halide catalysts need to be removed, since even small amounts of catalyst residue deteriorate the thermal stability and electrical and other properties.

Extensive studies have been conducted to determine the exact chemical structure of PESs prepared by different polysulfonylation methods. It was found by NMR studies[223,224] that self-polymerization of monosulfonyl chlorides (AB-type monomers) gave less than 0.7% of the branched product. However, significant amount of branching (up to 20%) was observed in the two-monomer route, which explained the more brittle materials from the two-monomer route.[225] It is clear that self-polymerization of *p*-phenoxybenzensulfonyl chloride occurs only by substitution on rings that are linked via oxygen to rings containing sulfone group, that is, sulfonylation of rings occurs exclusively in the *para* position resulting in a linear and regular structure. Conversely, in the sulfonylation of a combination of AA- and BB-type monomers, two or more activated aromatic hydrogens are commonly present in the reacting molecules. Thus, structural irregularities can occur due to possible sulfonylation at various phenyl ring positions, disulfonylations on one aromatic nucleus, as well as side reactions directly promoted by the Friedel–Crafts catalyst, giving a substantial amount of branching. This is actually the most fundamental reason why S_NAr routes are preferred over electrophilic routes for the synthesis of PAEs. In addition, the stoichiometry is not affected by vaporization in self–polycondensation, which is critical in polycondensation. However, high reaction temperatures are normally needed in the self-polymerization route since the sulfonyl group is a strong deactivating group for further sulfonylation.

5.17.4.1.2(ii) Condensation of free aromatic sulfonic acid monomers (arenesulfonic acids)

Sulfonic acid monomers can also be used to prepare poly(arylene ether sulfone)s, using typical strong acids as catalyst, such as $(CF_3CO)_2O$, polyphosphoric acid (PPA), $MeSO_3H–P_2O_5$ mixture, and CF_3SO_3H. In this type of polycondensation, a disulfonic acid is formed *in situ* from diphenyl ether, which subsequently polymerizes with diphenyl ether giving a low-molecular-weight prepolymer. Further dehydration of these prepolymers can give high molecular weight at 240 °C in strong acid like polyphosphoric acid. However, the presence of free sulfonic acid groups makes the polymers unstable in the melt due to possible crosslinking. Only low-molecular-weight polymers are obtained from diphenyl ether and 4,4′-oxybenzenedisulfonic acid.[226] Later high-molecular-weight soluble polymer was obtained via a one-step sulfonation/polymerization of diphenyl ether using tungstic or molybdic acids as catalysts (Figure 55).[227]

Several other dehydration media can also be used to polymerize sulfonic acids or their alkali metal salts. For example, $MeSO_3H–P_2O_5$ mixtures was reported to be a desirable dehydrating media in producing the best quality of PESs from sulfonic acid polymerization of diphenyl ether with 4,4′-oxybenzenedisulfonic acid.[227]

5.17.4.1.3 Other synthetic routes to poly(arylene sulfone)s

5.17.4.1.3(i) Cation-radical polymerization (Scholl reaction)

Via the Scholl reaction, high-molecular-weight poly(arylene ether sulfone)s have been successfully prepared from the sulfone-containing diphenoxy monomers.[154,228] The catalysts, solvents, and reaction conditions are essentially the same as detailed above for the synthesis of PAEKs. An example synthesis is shown in Figure 56.

The mechanism of Scholl reaction in the synthesis of PAEs is generally accepted as a cation-radical polymerization.[79] Initiation consists of a one-electron oxidation of the monomer by the $FeCl_3$ to form a cation radical at one of the naphthoxy groups. Most of the reported successful polymerizations using this chemistry have been with monomers that contain naphthoxy groups, which may be due to their ease of being oxidized in the initiation step. Both electrophilic and radical propagation steps have been proposed in termination resulting from the cation radical combining with the counter anion or a fragment of it to form a dead chain end.

5.17.4.1.3(ii) Ring-opening polymerization

A new synthetic strategy involving the synthesis and ROP of sulfone-containing macrocyclic oligomers has been developed

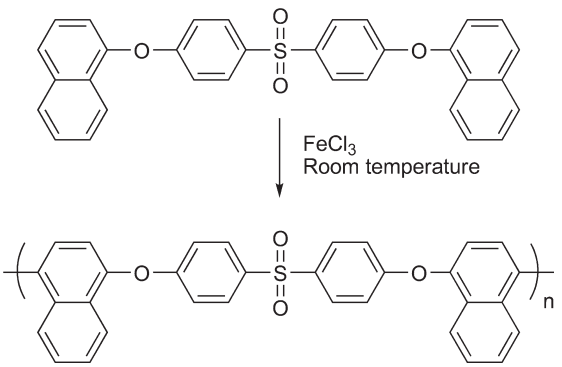

Figure 56 Synthesis of poly(arylene ether sulfone) via Scholl reaction.

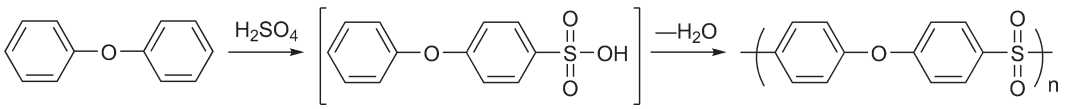

Figure 55 Sulfonation/polycondensation of diphenyl ether to poly(arylene ether sulfone).

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over the past 15 years. As mentioned before, ROP offers several advantages over traditional polycondensation technologies in that it is a bulk polymerization without large amounts of salts and solvents. In addition, low melt viscosities of the cyclomers make the processing easier than the preformed high-molecular-weight polymers. Furthermore, sequential copolymerization with other cyclic monomers can yield a variety of multiblock copolymers. While these advantages that have been realized on a laboratory scale, the main problem of the ROP approach is the synthesis of the macrocyclic monomers/oligomers when large quantities are needed.

Macrocyclic ether sulfone oligomers can be prepared in different ways. A comprehensive review on the synthetic strategies and properties of various cyclic polymers is available.[229] An example of the macro oligomer synthesized from spiroindane bisphenol and 4,4′-difluorodiphenyl sulfone (DFDPS) was reported by Cella *et al.*[230,231] The polymerization of the cyclomers was rapid when conducted in the melt and catalyzed by the disodium salt of bisphenol A, giving polymer with a molecular weight of 80 000 in 15 min (**Figure 57**). However, since these polymers can be synthesized directly by traditional methods, ROP route is only advantageous when used in conjunction with a fabrication method such as reaction injection molding (RIM).

The use of silylation of the diphenols can reduce the risk of oxidation and allow for polycondensation in bulk or in concentrated solutions. A typical polycondensation involving silylated 4-tertbutylcatechol and DFDPS was reported by Kricheldorf *et al.*[232] (**Figure 58**). The cyclics in the product were detectable up to 27 kg mol^{-1} with no linear chains. Similar results were obtained in the polycondensation of free or silylated bisphenol A with DFDPS.[233]

5.17.4.1.3(iii) Chemical modification of precursor polymers

The synthesis of poly(arylene ether sulfone)s by the catalyzed thermal decomposition of polycarbonates has been reported in a patent.[234] As described in the patent, poly(arylene ether sulfone) was obtained by heating the polycarbonate of Bisphenol S at 250–280 °C in a catalytic amount of the potassium salt of Bisphenol S with simultaneous evolution of carbon dioxide (**Figure 59**). The reaction of sulfone-activated aromatic dihalides with bisphenol A polycarbonate in NMP and K_2CO_3 at 150–165 °C also gave poly(arylene ether sulfone)s.[235] However, the practical utility of this method is very limited since the desired polymer can be made directly and more cleanly via traditional synthetic methods.

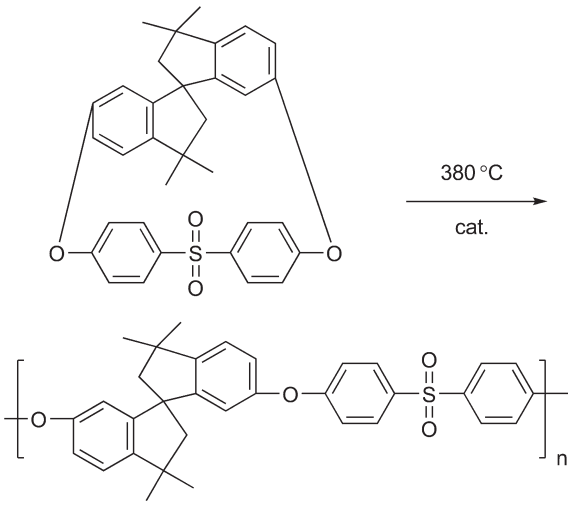

Figure 57 Ring-opening polymerization of cyclic ether sulfone oligomer.

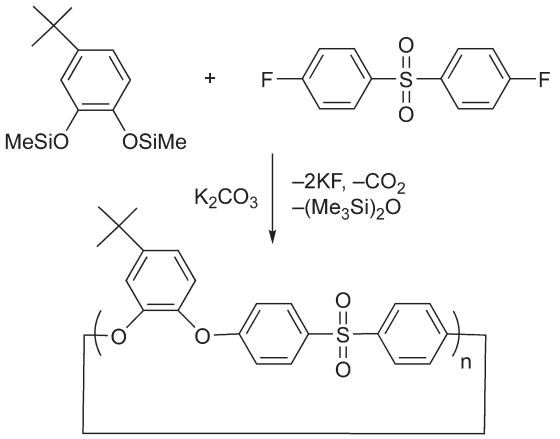

Figure 58 Synthesis of cyclic poly(arylene ether sulfone) via polycondensation of silylated diphenol with DFDPS.

5.17.4.1.3(iv) Metal-catalyzed polymerization

Metal-catalyzed polymerization offers an alternate pathway to polymer synthesis that can be prepared by other methods. Nickel(0)-catalyzed polymerization of aryl dichlorides was developed for the synthesis of Radel R® polysulfone,[236–238] a product prepared commercially by S_NAr method. The nickel(0)-catalyzed polymerization (**Figure 60**) was performed in a anhydrous, aprotic solvent using catalytic amount of nickel(0) (less than 2 mol.% of aryl dichloride), with a large amount of triphenylphosphine ligand and excess zinc metal at moderate temperature (70 °C). Some catalysts such as sodium bromide could accelerate the reaction. The good solubility of the monomers and the obtained polymer in the reaction medium was critical for achieving high-molecular-weight products. In addition, any functional substituents on the monomers must be inert toward the metal catalysts. For example, nitro groups were not tolerated in nickel(0)–zinc catalyst system.[236] Polysulfone with moderate molecular weight was obtained via palladium-catalyzed cross-coupling of bifunctional tin reagents with aromatic dihalides.[239] A major disadvantage of metal-catalyzed polymerization is the necessity of removal of the catalysts from the final products.

5.17.4.2 Other Functionalized Poly(arylene ether sulfone)s

5.17.4.2.1 Sulfonated poly(arylene ether sulfone)s

Poly(arylene ether sulfone)s are hydrophobic. For their applications in membrane technology, especially PEMs in fuel cells, it would be desirable to raise their water affinity. One effective method to increase the water affinity or hydrophilicity is sulfonation. There are generally two ways to introduce sulfonated groups in polymers: postsulfonation of

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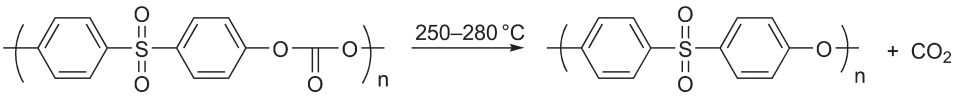

Figure 59 Synthesis of PES from thermal decomposition of polycarbonate.

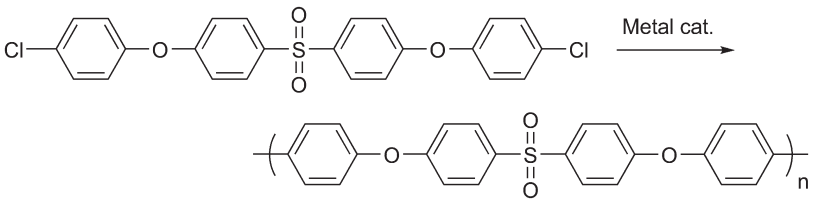

Figure 60 Synthesis of Radel® R poly(ether sulfone) via nickel(0) catalyst system.

preformed polymers using sulfonating agents such as sulfuric acid and use of sulfonated monomers for polymerization.

Sulfonation of preformed commercial poly(arylene ether sulfone)s using sulfonating agents is quite straightforward and has found potential applications in preparing PEMs. Udel® and Radel® R are the two commercial poly(arylene ether sulfone)s produced by Solvay Advanced Polymers that can be chemically modified via sulfonation. Depending on the sulfonation mechanism, sulfonating agents can be categorized into three groups, namely, electrophilic agents (sulfuric acid, chlorosulfonic acid, etc.), nucleophlic agents (sulfites, hydrogen sulfites, sulfur dioxide, etc.), and radically reacting agents (sulfuryl chloride, SO_2–Cl_2 mixture, etc.). In electrophilic substitution, the sulfonated groups are introduced at the *ortho* position of the ether group of the diphenoxy unit.[240–242] In nucleophilic mechanism, the substitution occurs at the *ortho* position of the phenyl sulfone moiety[243,244] (Figure 61). It was found that increasing the reactivity of the sulfonating agents did not influence the DS but the stability of the polymer chains. Furthermore, the precise control of sulfonation location and high DS (disulfonation) are very hard to achieve since the sulfonic acid group is usually restricted to the activated position on the aromatic rings. For example, in the case of the bisphenol A-based systems, no more than one sulfonic acid group per repeat unit could be achieved.[245]

The alternate way to prepare sulfonated polysulfones is via copolymerization of the sulfonated monomers. Rather than postsulfonation, the starting monomers are sulfonated prior to polycondensation reactions. Therefore, the DS of the polymers can be easily controlled by simply varying the feeding ratio of unsulfonated monomer to the sulfonated monomer. This sulfonated monomer was first reported by Robeson *et al.*,[246] in which it primarily was of interest for its flame retarding properties. Later, a general procedure of the synthesis and purification of sulfonated DCDPS monomer was reported by Ueda *et al.*,[247] which was further modified by McGrath and co-workers to afford disulfonated-4,4′-dichlorodiphenyl sulfone (SDCDPS) with high purity,[248,249] as shown in Figure 62. The monomer grade SDCDPS has been successfully scaled up by this procedure, by Akron Polymer Systems, Inc.

The design and synthesis of various sulfonated copoly(ether sulfone)s via polycondensation of SDCDPS with other unsulfonated monomers have been extensively explored by the McGrath research group,[195,250–257] particularly to address their applications in PEMFCs and water purification membranes. The directly copolymerized sulfonated poly(arylene ether sulfone)s were prepared under very similar reaction conditions to those employed for the synthesis of unsulfonated

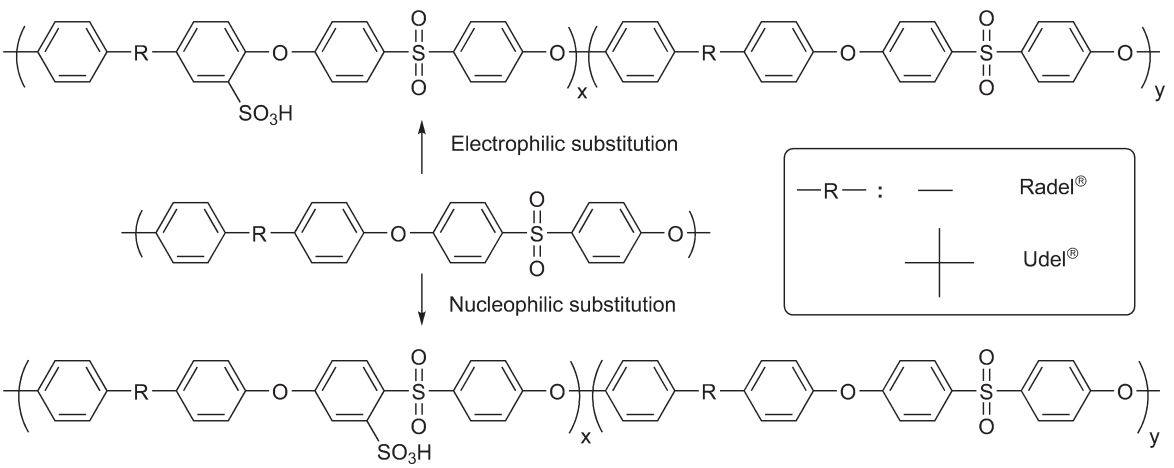

Figure 61 Sulfonation of poly(arylene ether sulfone)s via different substitution routes.

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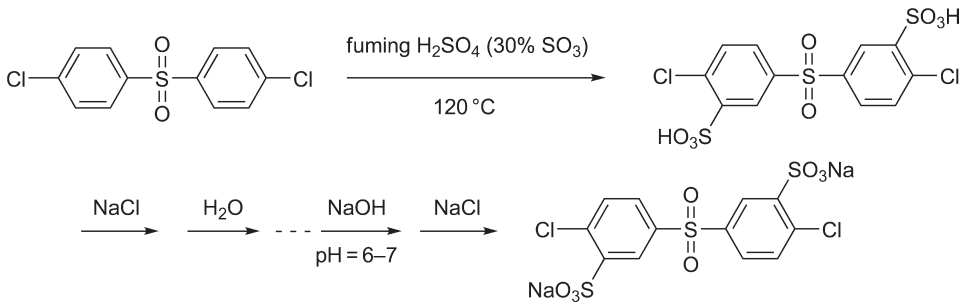

Figure 62 Synthesis of 3,3′-disulfonated-4,4′-dichlorodiphenylsulfone (SDCDPS) and its sodium salt.

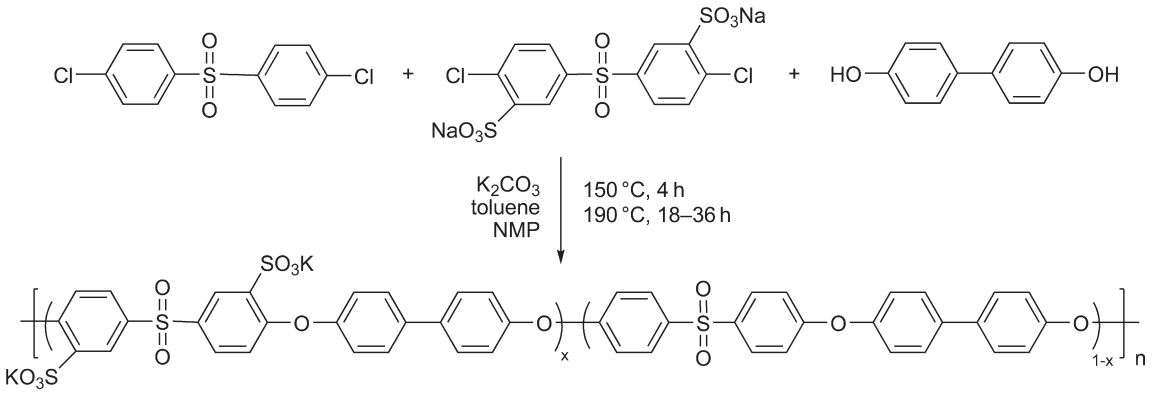

Figure 63 Synthesis of sulfonated poly(arylene ether sulfone) from disulfonated DCDPS.

poly(arylene ether sulfone)s using the carbonate or weak base (K_2CO_3) process. Only moderately higher reaction temperatures and longer times were needed to obtain high-molecular-weight copolymers due to the sterically decreased activity of the disulfonated dihalide monomer. An example synthesis of sulfonated poly(arylene ether sulfone) copolymer in its salt form is shown in Figure 63. Acid form copolymers could be obtained by acidification of salt form polymers in sulfuric acid solution.

Comparing the postsulfonation route and the direct polycondensation of sulfonated monomer route, the main advantage of the chemical modification route lies in its use of commercial high-performance polymers since they are readily available and should be low cost. However, some drawbacks are obvious related to this route, such as no control on the location and DS, possible chain breakings during sulfonation. By using the sulfonated monomer route, all these disadvantages can be easily avoided. The only possible concern is the relatively high cost associated with the synthesis and purification of the disulfonated monomers.

5.17.4.2.2 Crosslinked poly(arylene ether sulfone)s

The crosslinked poly(arylene ether sulfone)s can be obtained in two approaches, namely, physical crosslinking via ionic interactions, and chemical crosslinking via covalent bonding. Membranes formed from crosslinked poly(arylene ether sulfone)s are mostly used as potential PEMs in fuel cell applications due to their limited water swelling ratio even with very high DS.

Ionomers, such as sulfonated polysulfone, can be physically crosslinked via ionic interactions, when sulfonated polysulfones are neutralized by polymers containing basic units. The strength of these acid–base complexes strongly depends on the strength of the respective acid and base. Ionically crosslinked membranes were prepared by blending the selected basically modified polysulfones with the sulfonated polysulfones,[258–260] as shown in Figure 64. The presence of pyridinium ions in the blends containing grafted pyridine unites was confirmed by FTIR spectroscopy. It was reported that the thermal decomposition temperature of the blends was above 300 °C in inert atmosphere, which was even higher than that for the covalently crosslinked membranes.[260]

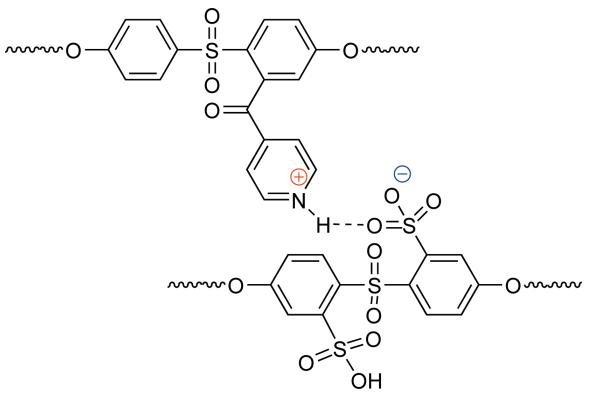

Figure 64 Physically crosslinked poly(arylene ether sulfone)s via the formation of acid-base complexes.

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In general, the thermal stability of the ionomers depends on the DS, crosslink density, the presence of impurities, and measurement conditions. Membranes prepared from these blends were evaluated in both hydrogen fuel cells and DMFCs with promising results. Membranes formed from the ionically crosslinked blends were more mechanically flexible than the covalently crosslinked ionomers. However, at temperatures above 70 °C, these membranes swelled excessively in water due to weakening of the ionic interactions.

In order to limit the water swelling of the sulfonated polysulfones and maintain their dimension stability at relatively high temperatures, chemically crosslinked PESs were also prepared by Kerres *et al.*[261] The covalently bonded crosslinks were introduced by either disproportionation of sulfonic acid units or S-alkylation of sulfonate units using α,ω-dihalogen alkanes.[262,263] The covalently crosslinked membranes showed decomposition temperatures at around 250 °C in N_2 and limited swelling in water at temperatures below 90 °C. More recently, crosslinked highly sulfonated PESs have been developed by Paul *et al.*,[264] which showed potential applications in H_2/O_2 fuel cell membranes. Chemical crosslinking of acetylenic-end-capped polysulfone and polyketone oligomers was described by Delfort *et al.*[265,266] Thermo-oxidative stable networks were obtained upon thermal cure of these oligomers.

5.17.4.2.3 Reactive poly(arylene ether sulfone) oligomers for epoxy toughening

Extensive studies on the reactive poly(arylene ether sulfone) oligomers for the toughening of epoxy networks have been conducted by McGrath and co-workers.[267–271] Traditionally, epoxy resins are toughened by the incorporation of an elastomeric component, such as butadiene-acrylonitrile oligomers, acrylates elastomers, and siloxane oligomers. However, the improvement in the fracture toughness by the incorporation of these rubber modifiers has usually come at the expense of the bulk properties and especially the modulus. A better improvement in the overall properties of the epoxy resins without significant loss in the modulus was reported by McGrath *et al.*, where reactive bisphenol A polysulfone oligomers were used as the network modifier. In their work, both phenolic hydroxyl-terminated PES oligomers[267,268] and aminophenyl-terminated PSF oligomers[271] have been synthesized as toughening agents. A general procedure of preparing the PES-modified epoxy resin networks is shown in Figure 65.

Morphology and mechanical properties of the PES-modified epoxy resins were investigated as a function of the variations of the PES oligomers, such as molecular weight, solubility parameters, and loadings. As a function of composition, SEM studies showed the formation of two-phase structures in the PES-modified epoxy networks (Figure 66).[271] At low loadings

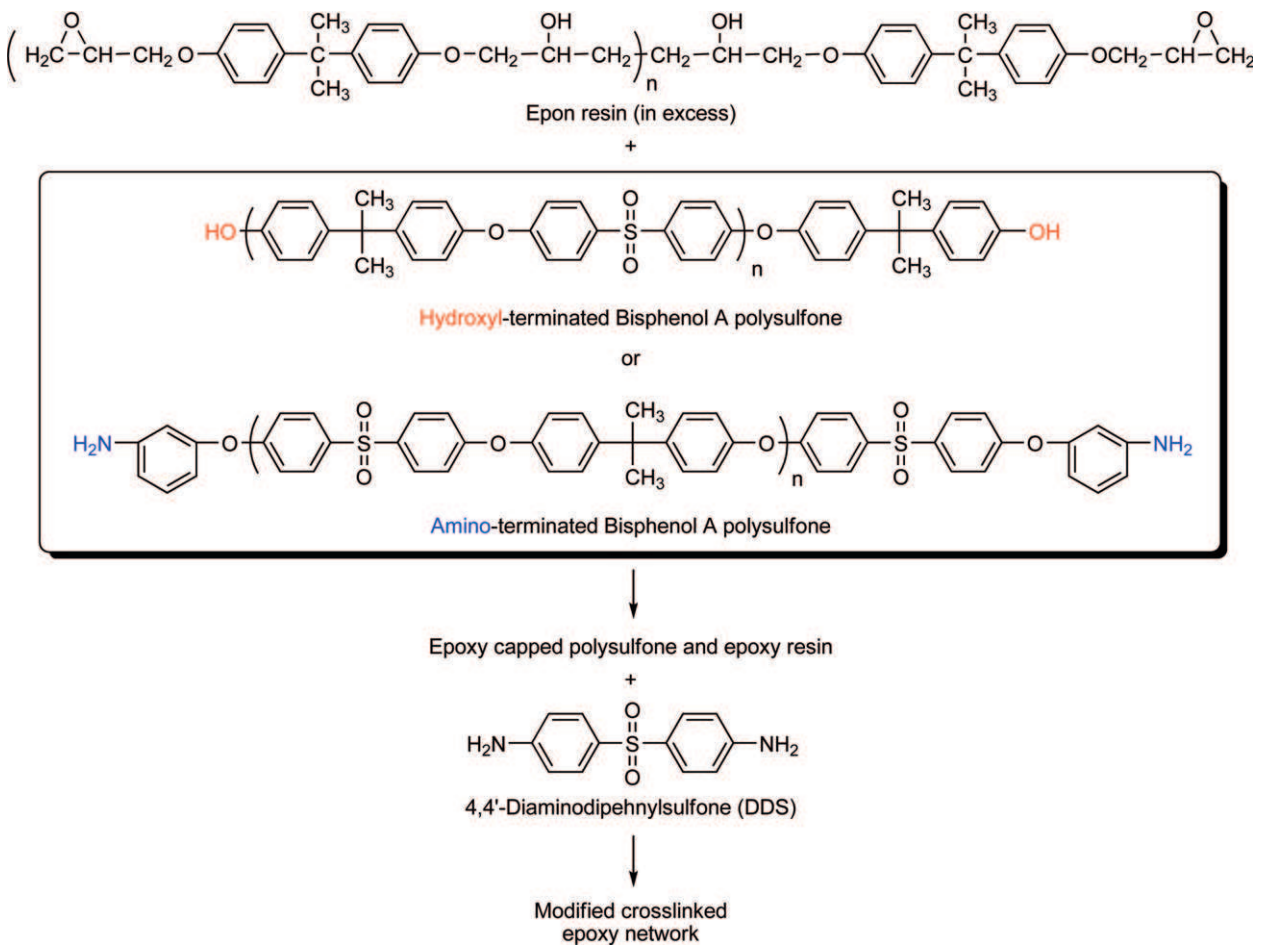

Figure 65 Preparation of reactive polysulfone-modified epoxy networks.

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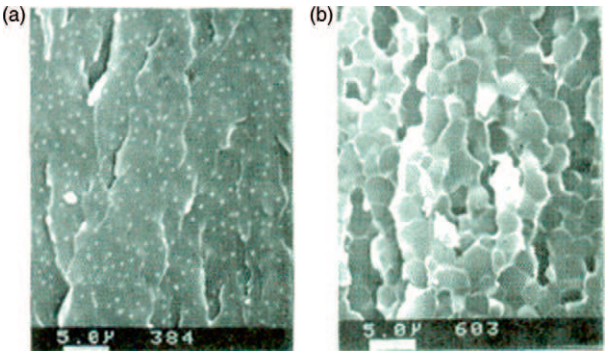

Figure 66 Two-phase structures as a function of reactive PES oligomers loading (left: 10 wt.% 15K PES, right: 25 wt,% 15K PES).[271]

(10–15%), a two-phase structure was formed with ductile PES particles (~0.1–0.6 μm) dispersed in the continuous epoxy matrix. However, at higher thermoplastic content, phase inversion occurred, in which PES continuous morphology with deformed honeycomb-like epoxy spheres developed.

Fracture toughness measurements showed a remarkable increase in K_{IC} or G_{IC} values (plane strain fracture toughness) of the reactive PES-modified networks over that of control, without significant loss in the modulus (Figure 67).[271] As shown, the modified epoxy resins showed greater improvement in fracture toughness with higher loadings of PES oligomers and higher molecular weights. Only slowly increase in the toughness was observed at low loadings and short oligomers due to the discrete PES morphology as shown in Figure 66. It seemed to suggest that the PES continuous phase formed at high loading levels of reactive PES oligomers is desirable for highly improved fracture toughness due to the ductile thermoplastic-like fracture.

Using micro-Raman spectroscopy, van Overbeke *et al.*[272] reported the studies of curing and phase separation phenomena in epoxy-copolyethersulfone blends. Local characterization of the thermoplastic PES content and the epoxide conversion was performed in the different phases by micro-Raman spectroscopy. The evolution of PES content with cure time was followed in both phases and the experimentally determined coexistence curves were reported, relating the epoxide conversion to the thermoplastic content in the coexisting phases.

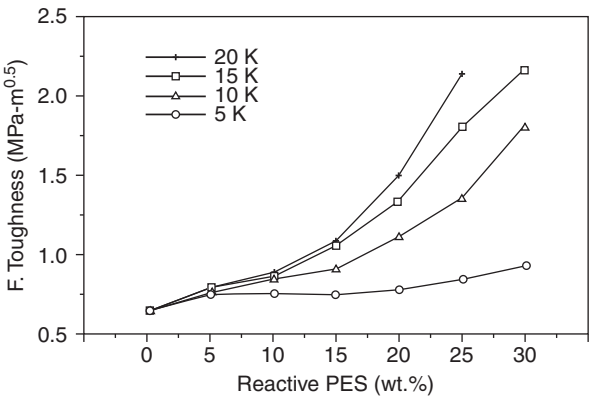

Figure 67 Fracture toughness of reactive PES toughened epoxy resins as a function of oligomer molecular weight and loading.

More recently, Chisari *et al.*[273] reported the synthesis of reactive PES oligomers with various reactive chain ends from the hydroxyl- and amino-ended PES oligomers. It was stated that these modified reactive PES oligomer have potential applications both in the chain extension of low-molecular-weight thermoplastics and in the preparation of well-defined block copolymers.

5.17.4.2.4 Block copolymers

Generally, aromatic polyether multiblock copolymers are synthesized by an S_NAr reaction between hydroxyl-ended oligomers and halogen-ended oligomers. However, when chloride end-capped oligomers are used, the reaction must be conducted at high temperatures, in which an ether–ether exchange reaction[274] could lead to randomized polymer sequences without the formation of multiblock copolymers. To address this problem, McGrath and co-workers used highly reactive fluorine end-capped oligomers instead of chloride end-capped ones, and successfully prepared sulfonated multiblock poly (arylene ether sulfone) copolymers under milder conditions.[251,253] Multifunctional decafluorobiphenyl (DFBP) or HFB was introduced as the functional chain ends in hydrophobic blocks, which provided high reactivity in coupling reactions at low reaction temperature to afford multiblock hydrophilic–hydrophobic copolymers (Figure 68). Similarly, Nakabayashi *et al.*[274] used decafluorobiphenyl (DFBP) as a chain extender in the coupling reaction between hydroxyl end-capped unsulfonated PESs oligomers and hydroxyl end-capped sulfonated oligomers.

Random and block copolymers of polyketone and polysulfone have been developed in order to produce a highly desirable thermoplastic composite combining the desirable properties of both polymers, such as excellent solvent resistance and ease of prepregging. Wu *et al.*[275] synthesized a number of random and segmented poly(arylene ether ketone sulfone) copolymers. The resulting polymers were found to be either amorphous with a T_g from 20 to 60 °C higher than that of PEEK or crystalline with higher T_g but lower T_m than those of PEEK. Particularly, a segmented polymer made from the copolymerization of biphenol-based polysulfone oligomers with bisphenol and DFBP (21:35:44 in weight proportions) was found to be semicrystalline with T_g of 181 °C and T_m of 387 °C. As expected, these copolymers were found to be solvent resistant and ductile.

Block copolymers of PAEK-poly(arylene ether sulfone) have been synthesized by Kricheldorf and Brier[277] via the silylated monomer approach. In their work, the block copolymers were produced via the bulk polycondensation between trimethylsilylated diphenols and activated difluoro aromatic compounds using CsF as a catalyst. Other researchers[276,277] have used an etherification reaction between a phenolate-ended poly(arylene ether sulfone) and a fluorine-ended PAEK to afford block copolymers. However, PES and PEK polymers are known to undergo transetherifications at high temperatures in the presence of nucleophiles such as phenolate, which can lead to molecular weight decrease and/or molecular rearrangement. In order to avoid this problem, Bourgeois *et al.*[189] proposed an alternative synthetic approach, in which oligomers of PEK and PES were synthesized with carefully controlled end-group functionality, which were then coupled together to form block copolymers.

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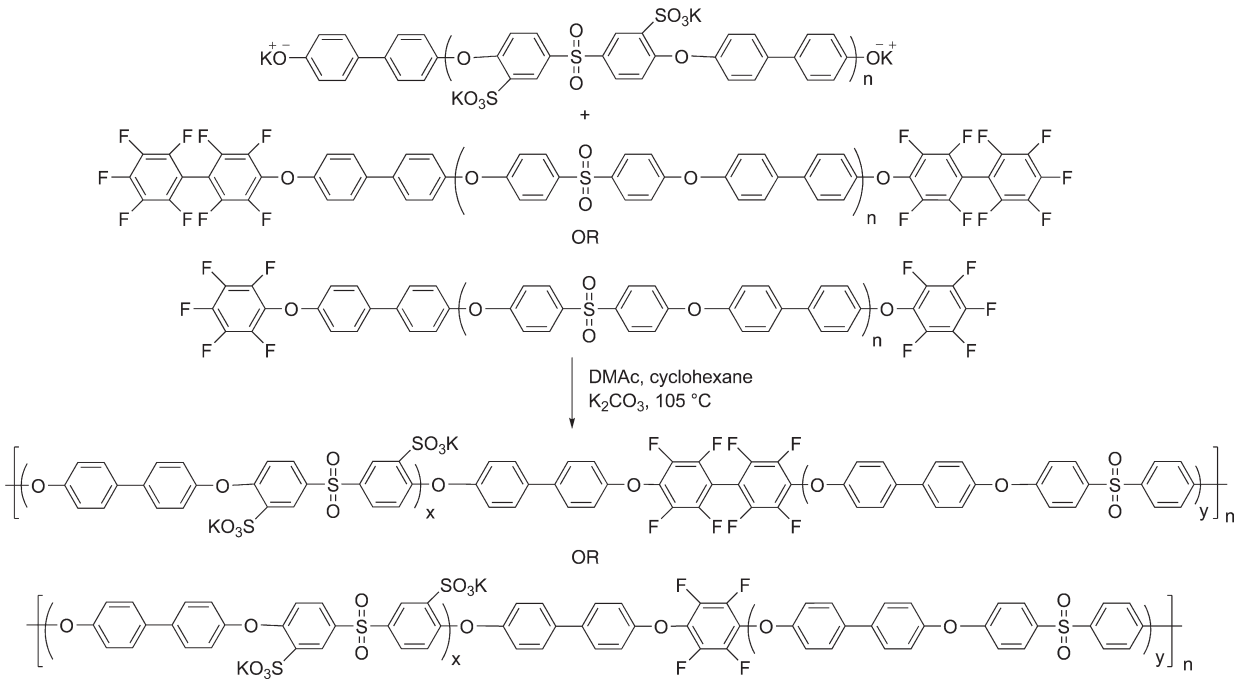

Figure 68 Synthesis of segmented sulfonated multiblock poly(arylene ether sulfone) copolymers with different linkage groups.

In his approach, poly(arylene ether sulfone) and PAEK oligomers were carefully functionalized with anhydride and amine chain ends, respectively. Reaction of the amine-terminated PEK with the anhydride-terminated PES resulted in the PEK-PES-PEK block copolymers with significantly different properties from the component homopolymers (**Figure 69**). It was demonstrated that the block copolymers retained the T_g advantage of the PES block while maintaining a processing temperature below 400 °C and some of the crystallinity of the PEK block could be utilized to achieve solvent resistance. In principle, the most attractive properties of both polymers could be obtained from the block copolymers, although the rate of crystallization of the PEK was slow owing to its partial miscibility with the PES.

Several research groups prepared polysulfone-*co*-polyamides and polysulfone-*co*-polyimides block copolymers. The ether-sulfone oligomers were prepared with primary amine end groups using aminophenol as end-capping agents.[278,279] These amine-terminated ether-sulfone oligomers were polycondensed with various dicarboxylic acid dichlorides to yield polysulfone-*co*-polyamides,[280] or with dianhydrides yielding polysulfone-*co*-polyimides.[281] For preparation of polysulfone-*co*-polyamides, the inverse approach was also employed,[282] in which ether-sulfone oligomers were end-capped with carboxylic acids and polycondensed with various aromatic diamines via the triphenylphosphite pyridine method. These multiblock copolymers showed phase separation, while random block copolymers showed a single-phase morphology. The polyimide greatly enhanced the mechanical properties of the PES, although the block copolymers were insoluble in organic solvents.

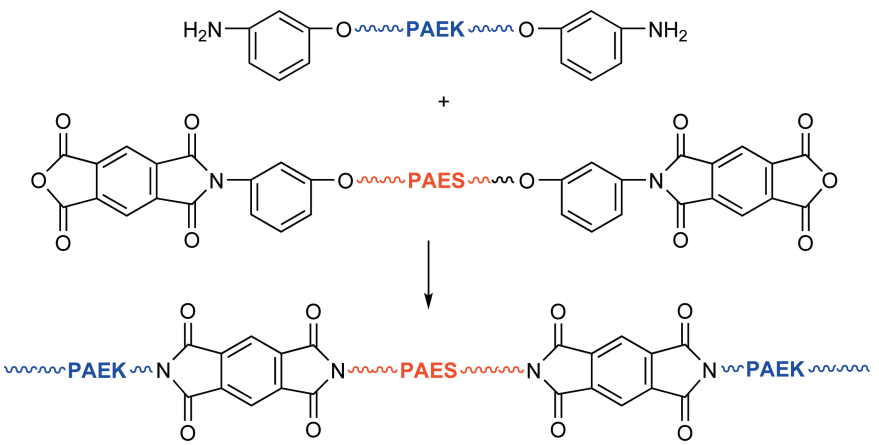

Figure 69 Synthesis of PEK-PES-PEK block copolymers.

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Multiblock copolymers consisting of poly(arylene ether sulfone) and poly(dimethylsiloxane) (PDMS) were prepared by several groups for various applications, including photosensitive materials.[283,284] The block copolymers were prepared from hydroxyl-terminated PES oligomers and diethylamine-terminated siloxane oligomers. The poly(ether sulfone disilane) copolymers were obtained using the same approach from a bis(diethylamino)disilane. Grafting of polysiloxane blocks onto bisphenol A-based PES was reported.[285] In this approach, the Si-H end group of polysiloxane was added onto the pendant vinyl group of polysulfone, which was lithiated and functionalized with chlorodimethylvinylsilane.

5.17.4.3 Properties and Applications

In spite of the fact that most poly(arylene ether sulfone)s are linear and exhibit a symmetrical chain structure, they are all principally noncrystallizable, that is, amorphous, in contrast to wholly aromatic PAEKs. This morphology difference between the PEKs and PESs is attributed to the disruption in chain packing due to the steric hindrance of the sulfone groups and the difference between the valence angles of the chain links.

Since the discovery of the synthesis of poly(arylene sulfone)s in the early 1960s, the influence of the diphenylene sulfone group on the properties of resins have been intensively investigated. Since the sulfur atom in the sulfone groups is in its highest state of oxidation, the sulfone group tends to draw electrons from the adjacent benzene rings, exhibiting strong electronegative characteristics, which lead to a delocalization of π-electrons from the aromatic rings. This highly resonant structure resists any tendency to lose electrons to an oxidizing agent and imparts high strength to the chemical bonds, which explains the extraordinary thermo-oxidative resistance and rigidity of the poly(arylene sulfone)s. The resonance effect between *para* linkages in PES is shown in **Figure 70**. Since there is only one resonance form in *meta*-linked PESs, they show lower chain rigidity, hence lower T_g's than the *para*-linked polysulfones. It is apparent, therefore, that the T_g value is influenced by the increases in chain rigidity resulting from the polarity of sulfone linkages. To give a more quantitative description, simply changing the ketone link in PEK to the sulfone link to form PES, increases the T_g from 154 to 223 °C and changes the polymer morphology from semicrystalline to amorphous. Similarly, changing the ketone linkage in PEEK for a sulfone linkage raises the T_g from 143 to 217 °C along with the disappearance of crystallinity.

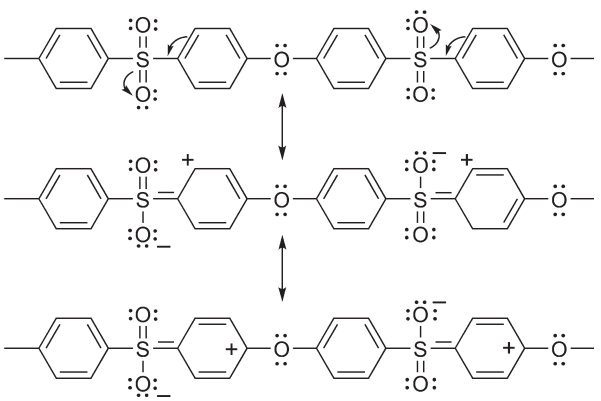

Figure 70 Electron withdrawing (resonance) effect in poly(arylene ether sulfone).

Dynamic mechanical characteristics of eight title poly(arylene sulfone)s have been studied thoroughly by Robeson *et al.*[286] The results showed that polymers containing side chains exhibited higher brittleness than polymers without side chains, and that water absorption did not affect the relative rating for the brittle–ductile behavior. Water absorption increased the resolution of a mechanical loss transition at – 100 °C for only the polymers containing SO_2 groups, suggesting that this transition for the dry polymers is not due to the SO_2 moiety as hypothesized by previous workers, but due to the aryl ether link.

A study of the thermal behavior of aromatic polyethers based on ether, sulfone, and ketone linkages is reported by Carlier *et al.*[287] A group contribution principle based on a concept of 'percentage rigid chain length (PRCL)' was deduced. In this theory, a value of 100% rigidity is ascribed to the S–C bonds on both sides of the SO_2 group (i.e., completely restricted rotation), 33% rigidity to the O–C link next to the ketone group (i.e., partial restricted rotation), and 0% rigidity to the C–O links on both sides of the ether group (i.e., unrestricted rotation). The calculated PRCL values were reported for a range of poly(arylene ether sulfone)s and were correlated with the thermal values (T_g and T_m) reported in the literature. A linear relationship between the T_g values and calculated PRCL values was obtained for all the sulfone- and ketone-type polymers under studies. This simple linear correlation provided a very useful guidance for the design of new polymers by predicting the T_g of any polymers based on phenyl, ether, sulfone, ketone, and direct phenyl–phenyl links.

Commercially available polysulfone products are generally prepared from the halogenated monomer 4,4′-dichlorodiphenylsulfone (DCDPS) with various bisphenols or biphenols via the carbonate process. These commercial polysulfones have structural similarities and differ mainly in processibility, heat-deflection temperature, toughness, and chemical resistance. T_g's of these polysulfones can range from 180 to 270 °C. In general, PES is thermally stable up to 400 °C. It is processed in the melt at 350–380 °C and can be molded at 140–200 °C without degradation, particularly if designed with nonreactive end groups. Because of their high-temperature performance, excellent mechanical properties, inherent flame retardance, good insulation properties, and relatively good environmental resistance, the poly(arylene ether sulfone)s have found wide applications in electrical engineering areas and the automotive and medical industries. Some selected topics of their applications will be discussed in detail.

Aromatic polysulfones have high oxygen indices and low smoke emission on burning. They are inherently self-extinguishing materials owing to their highly aromatic character. It has been shown that during pyrolysis, the sulfide groups are formed in the condensed phase from PES through the reduction of sulfone groups by hydrogen radicals, which increases the flame retardancy of PES.[288]

Among the wide field of applications of poly(arylene ether sulfone)s, the most widespread use is in membrane technology, such as desalination membranes, fuel cell membranes (both H_2/O_2-type and direct-methanol-type fuel cells), and carbon membranes. There are many patents on the use of

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films and hollow fibers of poly(arylene ether sulfone)s, and particularly the sulfonated PES copolymers, as membranes. Sulfonated PES has been shown to possess desirable mechanical and physical properties for use as a reverse osmosis desalination membrane, such as excellent resistance to oxidants, high tolerance to chlorine exposure, and a wide pH range of operation.[289–293] More recently, there are growing interests in applying sulfonated PES copolymers in fuel cell membrane applications as alternative materials to Nafion®. These aromatic ionomers sulfonated in the *ortho* position of an ether and a sulfone are very promising materials for use in both PEMFCs and DMFCs due to their low methanol permeability. Sulfonated PAESs are good candidates for substitution, due to their good acid and thermal oxidative stabilities, high glass transition temperatures, and excellent mechanical strength. As mentioned in Section 5.17.4.2.1, the ionic sulfonated groups can be introduced in PESs through either chemical modification of preformed commercial polysulfones (Udel® and Radel® R) or direct copolymerization of disulfonated monomer SDCDPS. The DS (percentage of monomer units sulfonated) directly determines the ion exchange capacity (IEC), thus the water uptake and proton conductivity. In this sense, the direct synthesis from a sulfonated monomer is more advantageous than the postsulfonation approach in which it can easily and precisely control the DS. The morphology of the PEM membranes was found to greatly influence the proton conduction behavior as well, especially under partially hydrated conditions. It is believed that the unique nanophase-separated morphologies with well-connected continuous hydrophilic domains are formed in the multiblock hydrophilic–hydrophobic copolymers, which greatly facilitates the proton conduction. Multiblock copolymers synthesized by coupling fully disulfonated poly(arylene ether sulfone) hydrophilic blocks with different types of hydrophobic blocks have been largely developed by McGrath group.[254,294–304] Various engineering materials have been used as the hydrophobic blocks to provide dimensional and mechanical stability, such as polysulfone, polyimide, polyketone, polybenzophenone, and polybenzimidazole. These multiblock copolymers showed comparable proton conductivities with Nafion® products.

5.17.5 Poly(arylene sulfide)s

Poly(arylene sulfide)s or poly(phenylene sulfide)s (PPSs) are polymers composed of a series of alternating aromatic rings and sulfur atoms. They possess similar chemical structure in repeating units with simple poly(phenylene ether), by replacing the oxygen atoms with sulfur atoms. Therefore, they are also called poly(arylene thioether)s as analogues to PAEs. Chemical structure of the repeat unit for the simplest poly (arylene sulfide) is shown in Figure 71. Poly(arylene sulfide)s are versatile high-quality engineering plastics and particularly useful as matrix of composites containing glass fiber, carbon fiber, and electroconductive particles.

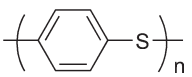

Figure 71 Repeat unit structure of the simplest poly(arylene sulfide).

Poly(arylene sulfide)s should not be confused with another type of polymers of poly(sulfide)s, in that the term 'poly' in poly(sulfide)s refers directly to the sulfide linkage, that is, $-S_n-$, as well as to a polymer. These types of polymers are more rubber-like and are used in a completely different field of application, for example, additives for elastomers, antioxidants for lubricating oils, insecticides, germicides, and as an additive to diesel fuels to improve the octane number and ignition qualities of these fuels.[305] The synthesis of this type of polymers is not covered in this section.

5.17.5.1 General Synthesis Approaches

Aromatic polysulfide, or PPS, was arguably first discovered by Friedel and Crafts back in 1888,[306] and was prepared from the reaction between benzene and elemental sulfur in the presence of aluminum chloride. However, only low-molecular-weight products were obtained and the reaction was very difficult to control since it was highly exothermic. Similar procedures were used by other scientists at the turn of the century. For example, Deuss[307] obtained similar products by reacting thiophenol with aluminum chloride. Glass and Reid[308] obtained a resinous product by heating benzene with sulfur at 350 °C. In all cases, however, ill-defined polymers were obtained, and the presence of many by-products, such as thiophenol, phenyl sulfide, phenyl disulfide, and thianthrene, resulted in very low polymer yields.[309] Moreover, the polymers that were prepared in this manner contained more than one sulfur atom per repeat unit as later reported by Macallum.[310] Macallum developed the process involving reacting elemental sulfur, sodium carbonate, and dichlorobenzene at 275–300 °C, in the melt, in a sealed vessel. Although the polymerization reaction was highly exothermic and difficult to control, the pioneer work of Macallum's sparked an interest in the synthesis of PPS and triggered a series of investigations that eventually led to the commercial production of PPS. In 1967, Edmonds and Hill[311] of Phillips Petroleum developed a method for producing semicrystalline PPS through the copolymerization of *p*-dichlorobenzene and sodium sulfide. The commercial production of PPS started in 1972 and was reviewed by Geibel *et al.*[312]

5.17.5.1.1 Nucleophilic aromatic substitution approach

Edmonds and Hill[311] first developed a commercially feasible synthetic route for PPS via S_NAr approach. The process involved the polycondensation of *p*-dichlorobenzene with sodium sulfide or sodium hydrosulfide/sodium hydroxide in N-methyl-2-pyrrolidinone (NMP) at 260 °C and elevated pressure. Due to its good efficiency and feasibility, the S_NAr approach has been mostly used in the synthesis of PPS.

Although several mechanisms of the polymerization were proposed, such as $S_{RN}1$ mechanism involving aromatic radical anions and radical-cation mechanism, it has been well accepted that the chain growth steps are exclusively based on the S_NAr mechanism involving a Meisenheimer complex as the transitional state and sodium chloride as a by-product.[313] A general scheme of S_NAr mechanism for the synthesis of PPS is shown in Figure 72. The scheme depicts the initiation reaction of an inorganic sulfide with the monomer, *p*-dichlorobenzene, followed by the beginning of polymer chain growth as the product of initiation reacts with additional *p*-dichlorobenzene.

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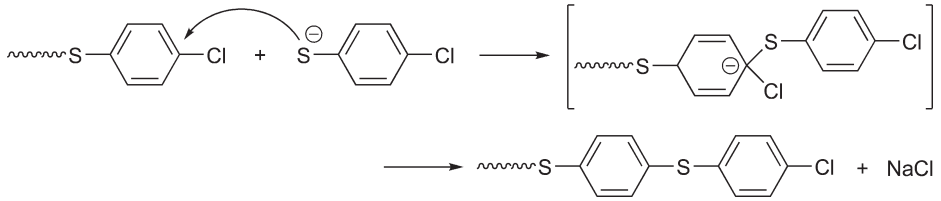

Figure 72 S_NAr mechanism for the synthesis of poly(phenylene sulfide) (PPS).

These reactions may be extended to include the reaction of sodium sulfide and sodium *p*-chlorobenzenethiolate with chlorophenyl end groups on polymeric species. As mentioned before in the synthesis of PAEs, the formation of the Meisenheimer complex is the rate-determining step.

5.17.5.1.1(i) Polycondensation of aromatic dihalides and sodium sulfide (Na_2S)

PPS with the simplest repeat unit structure was synthesized based on the polycondensation of *p*-dichlorobenzene and sodium sulfide in a polar solvent under heat.[311] The chemistry is describeded in **Figure 73**. Though the chemistry seems simple, there are four principal steps involved in practical processes to obtain the good quality products: (1) preparation of sodium sulfide from aqueous sodium hydrosulfide and caustic in a polar solvent; (2) dehydration of sodium sulfide stream; (3) production of PPS from dichlorobenzene and sodium sulfide; and (4) recovery of polymer and removal of by-product, NaCl.

However, this polymerization does not seem to exhibit classic condensation polymerization behavior.[313–315] That is, polymers of higher molecular weight than predicted by the Carother's equation are produced at low conversions[314] and even at unequal *p*-dichlorobenzene to Na_2S ratios.[315] This behavior was rationalized by Fahey and Ash[313] as a natural consequence of the sensitivity of the S_NAr mechanism to the substituents on the aryl chloride, and to the nucleophilicity of the sulfur anion for each individual growth step. Most of the growth steps have rate constants higher than that for the initial condensation of the monomers. More specifically, the enhanced activating ability of a *para* sulfur substituent, relative to chlorine, provides the driving force for developing high-molecular-weight polymer at low initial monomer conversions.

Since the starting materials are relatively inexpensive, commercialization of this polymer became feasible. Polymer produced in this process was a linear polymer with a molecular weight in the range of 15 000–20 000, resulting in a moderate degree of mechanical strength. The polymerization process was further refined at Phillips and the product later was sold under the tradename of Ryton® Polyphenylene Sulfide. It was discovered by the same group of researchers that the as-produced moderate molecular weight polymers could be converted into a much tougher material by simple thermal treatment in oxygen or air.[316] When the molten polymer was subjected to heat in the presence of air, the melt became dark and gelled and solidified very quickly, resulting in a crosslinked material that was insoluble in all organic solvents tested, even at elevated temperatures. Although the mechanism of this curing process has not been completely understood, obviously there are both polymer chain extension and crosslinking taking place in the curing process, which results from several possible reactions such as oxidative crosslinking, disproportionation of phenylene sulfide, and thermal crosslinking. The cured polymers were much stronger, tougher, and easier to process by injection or compression molding than the as-produced virgin polymers, but were no longer thermoplastics.

There are several major factors that influence the reaction rate and product quality in the above polycondensation process, such as dehydration of sodium sulfide, catalyst, and solvent. It is important to eliminate the water of the hydrated sodium sulfide to certain degree for producing a proper 'sulfidizing' agent. Incomplete dehydration results in a lower reaction rate and more undesired by-products, while too little water would lead to a high reaction rate with unfavorable side reactions. In practice, the optimal water content is 0.8–1.2 mole per mole of alkali metal sulfide throughout the polymerization. Another problem that is encountered during the dehydration process is that hydrogen sulfide, an environmentally harmful substance, escapes from the reaction system. Besides environmental demands to capture the escaped harmful H_2S, the loss of H_2S causes a problem in that it destroys the stoichiometric balance between the alkali metal sulfide and the dichloro aromatic compound since the amount of the alkali metal sulfide varies in an uncontrolled manner. Therefore, the amount of H_2S produced in the dehydration step should be analyzed precisely to fully define the amount of sulfur present in the reaction vessel. In addition, the polymerization rate can be accelerated by the proper choice of catalysts. Suitable polymerization catalysts are organic metal carboxylates. Considering the cost and efficiency, sodium acetate is a preferred catalyst since it is cheap and moderately soluble in the polymerization system.[317] Other types of catalysts include organic sulfoxide compounds, cyclic amine compounds, and *N*-heteroaromatic compounds. In addition, achieving a high-molecular-weight polymer also depends on the use of NMP as the reaction medium. In fact, the ability of the NMP solvent to facilitate S_NAr processes by dissociating ion pairs is well documented.[318–320] The special qualities that NMP brings to this process go well beyond that of a conventional solvent. Fahey and Ash[313] reported that a chemical reaction occurs between

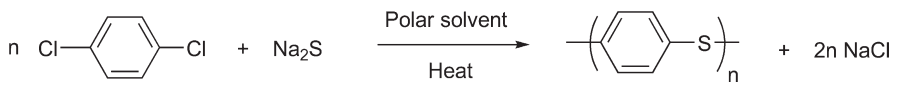

Figure 73 Synthesis of poly(phenylene sulfide) via polycondensation of aromatic dihalides and sodium sulphide.

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hydrated Na_2S and NMP at elevated temperatures, yielding an isolable product with the empirical formula $Na_2S \cdot NMP \cdot H_2O$. It was clearly revealed by NMR that NMP ring is hydrolytically opened to yield a mixture of sodium 4-(N-methylamino)-butanoate (SMAB) and sodium hydrosulfide in equal mole. SMAB is considered to both solubilize NaSH and act as a proton acceptor.

A new synthetic process was developed later by Campbell,[321] in which high-molecular-weight PPS (M_n = 35 000–65 000) were obtained directly during polymerization without the postcuring process. The new process involved the use of an alkali metal carboxylate as a polymerization modifier and eliminated the need of curing process in the above-mentioned conventional process to obtain high molecular weight. It has been reported that an soluble polymer with even higher molecular weight of 200 000 could be prepared by the incorporation of a very small amount of a 1,2,4-trichlorobenzene as a comonomer into the polymerization recipe. The mechanism of Campbell's reaction was traditionally considered to be a nucleophilic substitution. Instead, Heitz *et al.*[12,322] have proposed a one-electron-transfer process, with radical cations as reactive intermediates. However, the general characteristics and responses to reaction variables for this mechanism have not yet been firmly established.

A more recent example of using S_NAr polymerization to synthesize poly(arylene sulfide)s was reported by Robb and Knauss[323] Poly(thianthrene phenylene sulfide) and poly (thianthrene sulfide) containing the thermally stable thianthrene group were synthesized from the activated monomer 2,7-difluorothianthrene with bis-thiophenoxide and sulfide nucleophiles. The corporation of thianthrene group afforded a variety of potentially useful material properties, such as excellent thermal and thermooxidative characteristics.

5.17.5.1.1(ii) Self-condensation of halogen-substituted *p*-thiophenoxide

The self-condensations of monomers such as copper *p*-bromothiophenoxide or sodium *p*-chlorobenzenethiolate were reported by Lenz and co-workers at Dow (**Figure 74**).[324] On the basis of model compound studies, they concluded that the self-condensations of those monomers followed the mechanism of S_NAr as well.

However, some researchers debated that the reactions, instead, followed the radical-cation mechanism ($S_{RN}1$) based on the evidence of organic free radicals and Cu^{2+} presented throughout the polymerization detected by ESR spectroscopy.[325–327] The proposed mechanism involves three steps: (1) single-electron transfer from the thiolate to the initiator to form an aryl radical and a Cu^{2+} ion; (2) growth of the chain by radical-anion coupling; and (3) expulsion of bromide with formation of a new terminal aryl radical. Propagation proceeds by sequential coupling of the monomeric thiolate sulfur atoms to the terminal aryl radicals of growing chains, each coupling step being followed by the loss of a bromide ion in order to regenerate the chain carrier. In accordance with $S_{NR}1$ reactions, the loss of a bromide ion can be expected to be the rate-determining step. These reactions were conducted at 200–250 °C in the solid state or in a reaction media such as pyridine, which provided a linear PPS material. However, considerable difficulty was encountered in removing the salt by-product of copper bromide from polymers, which prevented the attempted scale-up of this process for commercialization. A process using a lithium salt instead of the sodium salt has attracted attention as a process for overcoming this problem, since lithium chloride is soluble in many of the aprotic organic solvents, such as NMP. However, lithium is far more expensive than sodium, so it is essential to recover and reuse the lithium, which increases the cost as well.

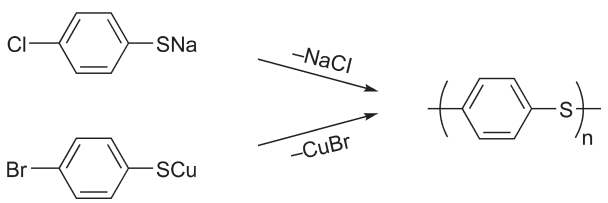

Figure 74 Self-condensation of halogen-substituted *p*-thiophenoxide.

Hay and co-workers[328,329] reported the synthesis of PPS via a self-polymerization of 4-bromobenzenethiol in the presence of a free radical initiator, which was conducted in *m*-terphenyl solution at 270 °C. Different initiators were used to influence the polymerization reaction, such as bis-(4-bromophenyl) disulfide, cyclic disulfide oligomer, diphenyl disulfide, 2,2′-dithiolbis(benzothiazole), and elemental sulfur. Based on the T_g and T_c of the products, using bis-(4-bromophenyl) disulfide as an initiator gave the best results. The polymerization follows the free radical mechanism as well. The bromine radicals here play a key role in propagating the chain reaction by reacting with the thiol group to generate HBr and the thiophenoxy radical. The oligomeric radicals formed can then react further to yield PPS. This novel process produces PPS without the formation of any salt. Instead, HBr is formed as the sole side product. However, this process has the drawback of producing relatively low-molecular-weight polymers.

5.17.5.1.1(iii) Nitro-displacement reaction

In the S_NAr reaction, leaving groups should be properly activated at *para* or *ortho* position by electron withdrawing groups that can stabilize the intermediates during the reaction. Fluorine and chlorine groups are typical leaving groups in the S_NAr reactions as detailed above. Recently, In and Kim[71] reported a nitro-displacement reaction for the synthesis of poly(arylene sulfide) in which a dinitro monomer was reacted with aromatic dithiols with nitro groups as the leaving groups. Due to the fact that the reactive nitrite ions may cause severe side reactions at elevated temperatures, trifluoromethyl groups were usually introduced onto the dinitro monomer, which were considered effective activating groups for the nucleophilic nitro-displacement reactions, even at relatively high temperatures due to inertness of perfluoroalkyl groups to nitrite ions. The nitro-displacement reaction has been successfully conducted with monomers of high reactivity, such as 4,4′-dinitro-3,3′-bis(trifluoromethyl)biphenyl, activated by *o*-trifluoromethyl groups. Complete exclusion of oxygen was also critical for the successful polymerization without the formation of disulfides. Polymerization of the perfluoroalkyl-activated dinitro monomer with various aromatic dithiols is shown in **Figure 75**. The resulting trifluoromethyl-substituted poly(arylene thioether)s were

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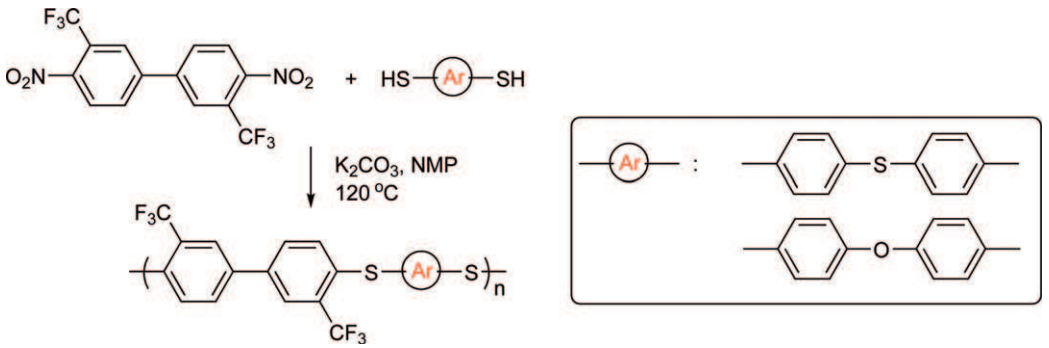

Figure 75 Synthesis of poly(arylene sulfide) via nitro-displacement reaction.

amorphous, soluble in common organic solvents, and showed superior thermal properties compared to commercial PPS.

5.17.5.1.2 Polycondensation of diaryl disulfides

5.17.5.1.2(i) Oxidative polymerization of diaryl disulfides

A group of Japanese researchers reported several studies dealing with the oxidative polycondensation of diaryl disulfides[330–333] using various oxidizing agents via a cationic mechanism. It was reported that diphenyl disulfide was used as a monomer and reacted with an oxidizing agent, which cleaved the S–S bond and easily polymerized to a linear PPS by electrical or chemical oxidation at room temperature and atmospheric pressure. Therefore, the oxidative polymerization approach avoided the high reaction temperature and pressure used in the conventional synthesis process and no by-product of salt was formed which might degrade PPS properties such as electrical performance and moldability. A general scheme of oxidative polymerization of disulfides is shown in Figure 76, where R is the substituent on the benzene rings of disulfide.

A cationic mechanism was proposed for the oxidative polymerization of diaryl disulfides by the researchers based on model compound reactions. In most cases of oxidative polymerization, the diphenyl disulfide was activated in the form of a sulfenium ion by an oxidizing agent such as $SbCl_5$. Instead of a free sulfenium cation, a stabilized form was proposed as the active intermediate in the polymerization, which electrophilically reacted with the *para* position of the benzene ring to yield linear PPS by cleaving the S–S bond. The proposed mechanism is schemed in Figure 77.

Several oxidation agents and catalysts were utilized in oxidative polymerization of diaryl disulfides, such as $SbCl_5$,[332] 2,3-dichloro-4,5-dicyanobenzoquinone (DDQ),[331,333,334] 1,4-benzoquinone, and O_2/vanadium oxide.[330] The oxidative polymerization not only is an efficient synthetic approach for poly(arylene sulfide), but also is applicable to the synthesis of substituted poly(arylene sulfide)s. A broad variety of substituted diphenyl disulfides were used as monomers. For example, ethyl groups were introduced in diphenyl disulfide at the *meta* position of the benzene ring to improve the

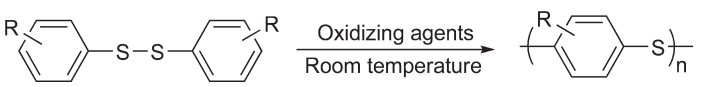

Figure 76 Synthesis of poly(phenylene sulfide) via oxidative polymerization of diaryl disulfide.

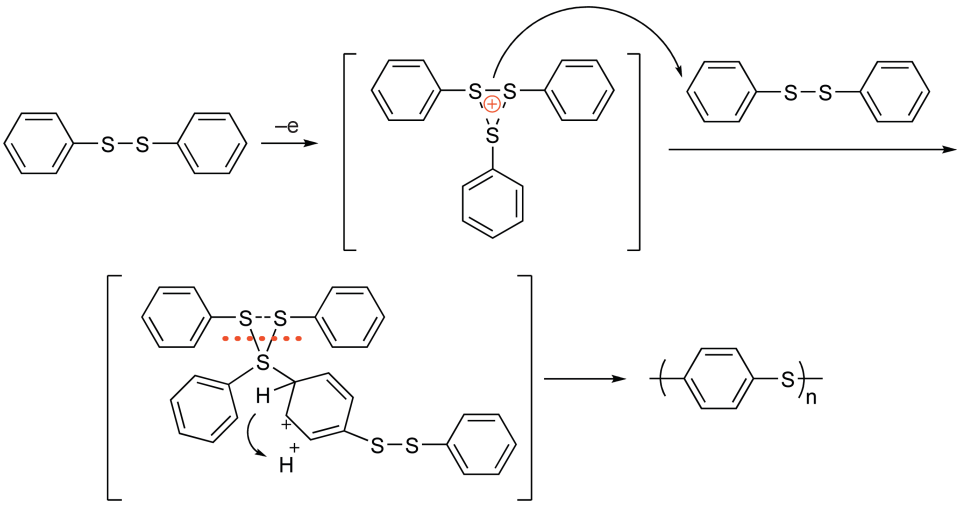

Figure 77 Cationic mechanism of oxidative polymerization of diaryl disulfide.

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solubility of the polymer.[333] Poly(2,6-dimethylphenylene sulfide) with its high molecular weight and melting point was formed through the oxidative polymerization with DDQ in high monomer feed concentration.

5.17.5.1.2(ii) Thermal polymerization (thermolysis) of bis (4-halophenyl) disulfides

Hay and co-workers[335,336] reported a thermal polymerization of bis(4-halophenyl) disulfide to produce linear, high-molecular-weight poly(*p*-phenylene sulfide)s in high yields. The bis(4-iodophenyl) disulfide was prepared by the reaction of potassium iodide with the diazonium salt generated from 4-aminophenyl disulfide with sodium nitrite. Polymerizations were conducted in diphenyl ether at temperatures of 230–270 °C, yielding high-molecular-weight PPSs in high yields along with elemental iodine. Polymers were obtained in high yields as off-white or pale yellow solids with melting points ranging from 270 to 282 °C. The polymerization takes place readily at about 230 °C, as evidenced by the formation of iodine. The completion of the polymerization was indicated by the cessation of iodine evolution. It should be noted that the degree of polymerization was very temperature dependent. With increase in the reaction temperature, the required reaction time shortened dramatically and the degree of polymerization increased significantly. It was reported that poly(arylene sulfide)s could also be prepared from the thermolysis of bis (4-bromophenyl) disulfide and bis(4-chlorophenyl) disulfide if an equivalent amount of iodide ions were present. The thermolysis of diaryl disulfides follows a free radical mechanism, as shown in Figure 78. The polymerization of bis-(4-iodophenyl) disulfide would be expected to proceed initially by thermal homolysis of the disulfide bond to the corresponding thiophenoxy radical. Analogous to the quinone-ketal mechanisms, the thiophenoxy radical could then dimerize to give a dithioquinone ketal, which could subsequently rearrange to dimeric thiophenoxy radical, with the release of iodine radical affording iodine. The removal of the by-product iodine is the driving force for the polymerization, as was the case for the melt reaction of sulfur with iodobenzene.

5.17.5.1.3 Ring-opening polymerization of cyclic oligomers

ROP of the cyclic sulfide oligomers was reported as a new approach to the synthesis of high-molecular-weight PPS. Both macrocyclic sulfides containing C–S–C bonds and macrocyclic disulfides containing C–S–S–C bonds have been prepared as the precursors of ROP.

5.17.5.1.3(i) Ring-opening polymerization of cyclic monosulfides

Hay and co-workers[337–342] explored various synthetic methods for the preparation of the cyclic sulfide oligomers as the precursors for ROP. Two examples of the synthesis of cyclic sulfide oligomers are illustrated in Figure 79. The first approach to prepare sulfide cyclic oligomers was based on the reduction of cyclic sulfoxide oligomers by means of oxalyl chloride. The cyclic sulfoxide oligomers were synthesized via a normal nucleophilic substitution reaction between 4,4′-difluorodiphenhylsulfoxide with a diphenol. The second approach was based on the thermal redox rearrangement of copper 4-bromothiophenolate. All the reactions were conducted at high dilution to favor the formation of small macrocycles. The ROPs of these cyclic sulfide oligomers, that is, transformation of macrocyclic oligomers to linear high-molecular-weight polymers, were conducted either in bulk or in *m*-terphenyl at temperatures higher than 300 °C. The reactions were initiated by elemental sulfur or diphenyl sulfide. The researchers proposed a free radical ring polymerization mechanism. It was stated that a disulfide linkage in the cyclic oligomers might be formed by reactions of the sulfide linkage with elemental sulfur. The disulfide moiety formed then underwent thermolysis to form thiyl radical(s) which initiate the free radical ROP. The free radical nature of the polymerization was confirmed by ESR spectroscopy analysis, which showed free radical signals.

5.17.5.1.3(ii) Ring-opening polymerization of cyclic disulfides

Another type of cylcomer suitable for ROP to prepare poly(arylene sulfide)s are macrocyclic disulfides. The macrocylic disulfides were all reported to be prepared by copper–amine-catalyzed oxidative coupling of aromatic dithiols with oxygen under high dilution, although some variations in the synthesis might be used.[341–345] Similar to the ROP of cyclic monosulfide, the ring-opening reactions of cyclic disulfides were conducted in bulk or in diphenyl ether, but at a much

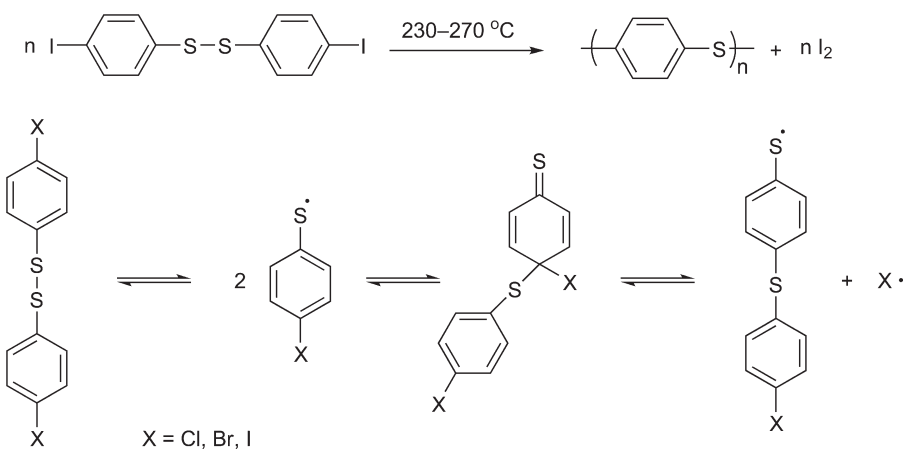

Figure 78 Thermolysis of bis-(4-halophenyl)disulfide and a reaction mechanism.

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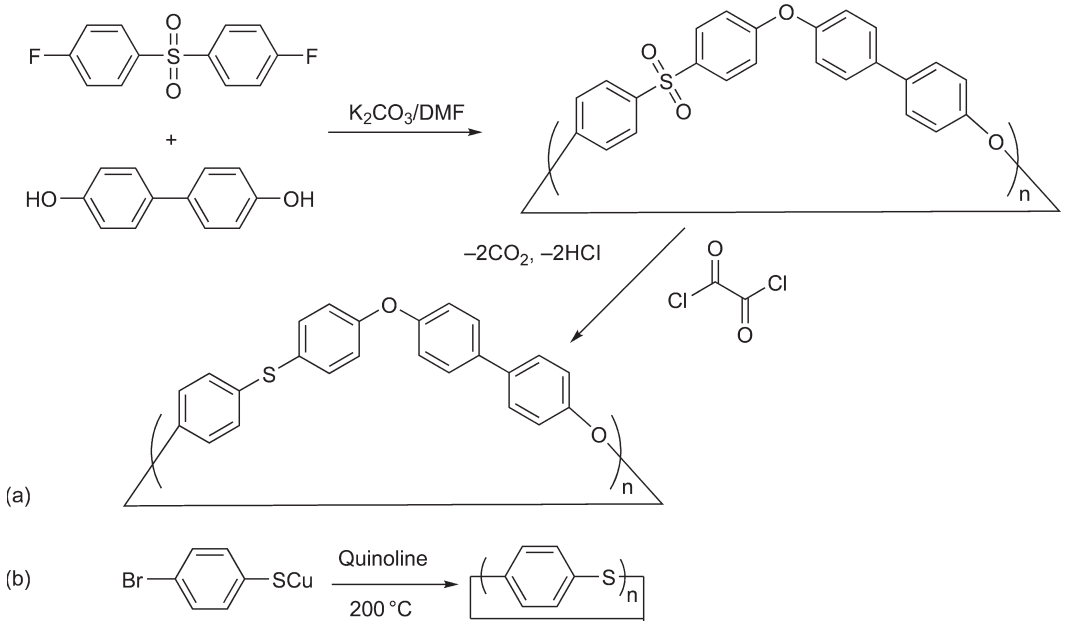

Figure 79 Synthesis of macrocyclic arylene sulfide oligomers via different methods.

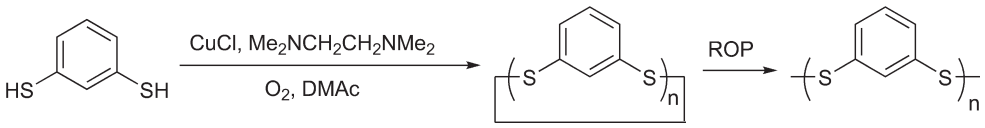

Figure 80 Synthesis of macrocyclic aryl disulfide and its ring-opening polymerization.

lower temperatures between 150 and 250 °C to avoid considerable side reactions at higher temperatures. A typical synthesis of a cyclic disulfide oligomer and its ROP is shown in Figure 80.

A particular interesting copolymerization between the macrocyclic disulfides and dibromo- or diiodoaromats in the presence of KI was reported.[341–343] In the synthesis of cyclic oligomer, DMAc was found to be the most effective solvent, due to the fact that both the reactants and resulting products remain soluble. Cuprous chloride and TMEDA were used as the copper salt and amine ligand, respectively. The cyclic arylene disulfide oligomers then underwent melt ROP with the *p*-diiodobenzene in diphenyl ether to yield high-molecular-weight poly(arylene sulfide)s (Figure 81) by a free radical mechanism.[343] It was found that upon heating, a radical redox process between S–S and C–I bonds occurred, resulting in polysulfides along with free iodine. Potassium iodide serves as a reductant for the bromine atoms that suppress the side reactions caused by the reactive bromine radical. The resultant PPSs possessed a regular sequence of both aromatic moieties as shown in Figure 81. PPS was also prepared by reacting the

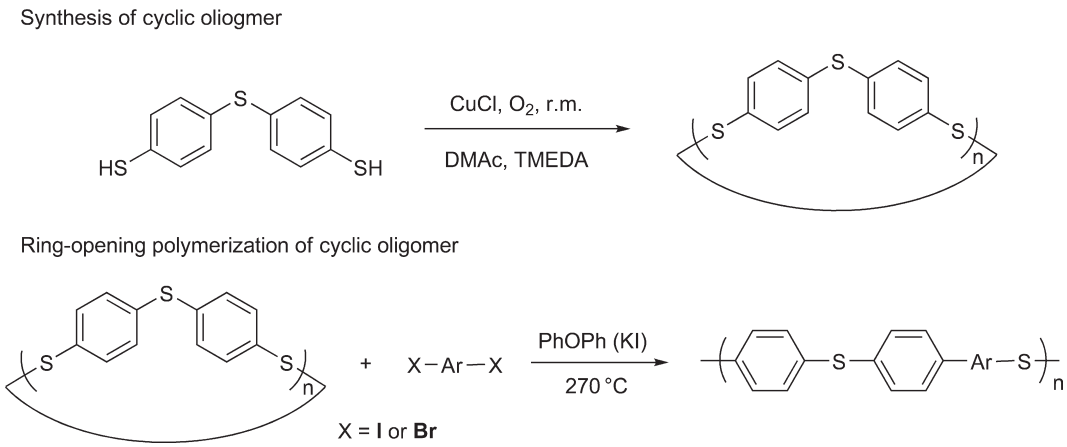

Figure 81 Synthesis of cyclic aromatic sulfide oligomer and its thermal copolymerization with dihalo aromatic compounds.

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cyclic sulfide oligomer with *p*-dibromobenzene in the presence of potassium iodide.[341] In addition, copolymerization of cyclic arylene disulfide oligomers with elemental sulfur was also reported. The melt copolymerization reactions gave high-molecular-weight rubbery polysulfanes with up to seven sulfur linkages.

Both thermal homopolymerization of cyclic monosulfides and copolymerization of cyclic disulfides produced high-molecular-weight soluble polymers. Generally speaking, synthesis and ROP of cyclic sulfide/disulfide oligomers proved to be a versatile approach to the preparation of high-molecular-weight PPS homopolymers and copolymers.

5.17.5.1.4 Polymer precursor approach

As discussed in the synthesis of PAEKs, one way to circumvent the need for some specialized synthetic conditions, such as high reaction temperatures or insoluble polymer during polymerization, is through the preparation of soluble precursor polymers, which can be subsequently converted to the crystallizable structures quantitatively in postpolymerization reactions.

Yamamoto *et al.*[346,347] synthesized high-molecular-weight PPS via the soluble precursor of poly(sulfonium cation) under mild conditions using a sulfoxide acid system. Figure 82 shows that the polymerization proceeds through an electrophilic reaction. The protonated sulfoxide, methylhydroxyphenyl sulfonium cation, is an active species that electrophilically attacks the phenyl ring of the monomer to yield a sulfonium cation of the dimer, accompanied by the elimination of water. Therefore, the reaction was influenced by the acidity of the mixture. Strong protonic acid such as TFMSA is highly effective for the formation of the sulfonium cation, unlike weaker acids such as CH_3COOH or CF_3COOH, which do not promote the electrophilic reaction. The polycation, poly(methyl[4-(phenylthio)phenyl] sulfonium trifluoromethanesulfonate) (PPST), is soluble in common solvents such as acetonitrile, acetone, dimethyl sulfoxide, and formic acid. To convert PPST to PPS, the demethylation was conducted using pyridine as a nucleophile. However, besides the lower melting point, another drawback associated with this method is the requirement for a high concentration of strong acids.

Wilkes *et al.*[348,349] reported that poly(arylene sulfide)s could be prepared via a polysulfone precursor approach. In their approach, poly(arylene ether ether sulfide)s were obtained by the reduction of the corresponding poly(arylene ether ether sulfoxide)s under certain conditions, as shown in Figure 83. In the first step, 4,4′-difluorodiphenylsulfoxide was copolymerized in combination with hydroquinone or 4,4′-dihydroxybiphenyl using the conventional aromatic nucleophilic substitution reaction. The resulting poly(arylene ether ether sulfoxide)s were then reduced in tetrachloroethane by means of oxalylchloride and tetrabutylammonium fluoride. The reduction provided quantitative conversion of sulfoxide to sulfide within seconds. It was also noted that by controlling the reduction process of converting sulfoxide to sulfide, the materials could be prepared in the form of micrometer-size particles. The mechanism of this reduction was proposed to be a two-step process. In the first step, the somewhat nucleophilic sulfoxide oxygen displaced a chloride from oxalyl chloride to produce an unstable intermediate complex. Then iodide attacked either at the sulfur or at the remaining chloride. Attack at either position caused the evolution of carbon monoxide and carbon dioxide, and the sulfur was rapidly reduced.

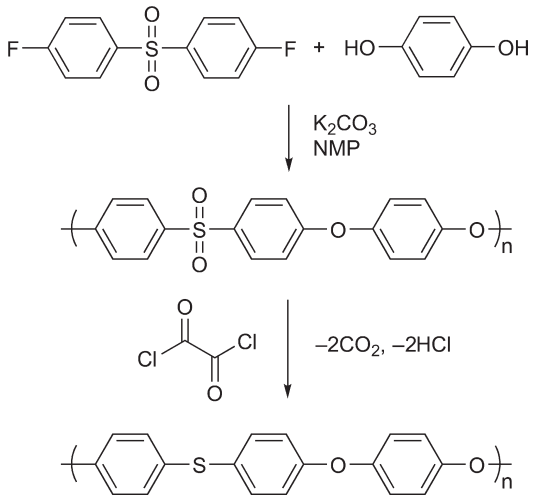

Figure 83 Synthesis of poly(arylene ether ether sulfide) via soluble poly (arylene ether ether sulfone) precursor.

5.17.5.2 Other Functionalized Poly(arylene sulfide)s

Via the S_NAr approach, functionalized poly(arylene sulfide)s and copolymers have been synthesized with broad variations in the chemical structure, which are applicable to many special applications.

5.17.5.2.1 Poly(arylene sulfide) copolymers

Several copolymers containing phenylene sulfide segments or blocks have been prepared to combine or complement the desired properties of all the components present. The synthesis of copolymers such as copoly(phenylene sulfide)s, poly(arylene sulfide sulfone)s, poly(arylene sulfide ketone)s, and poly (arylene sulfide amide) has been reported. Typical repeat unit structures of some of the PPS copolymers are shown in Figure 84.

Copoly(phenylene sulfide)s have been prepared from mixtures of *p*- and *m*-dichlorobenzene and sodium sulfide.[350,351] Incorporation of meta units results in disruption of crystallinity. Copolymers containing 50–100 mol.% meta structure are amorphous. The 50 and 70 mol.% copolymers are quite soluble in tetrahydrofuran. The meta homopolymer is nearly insoluble in refluxing THF, but is soluble in NMP at 100 °C. Copoly(phenylene sulfide)s with phenylene and biphenylene

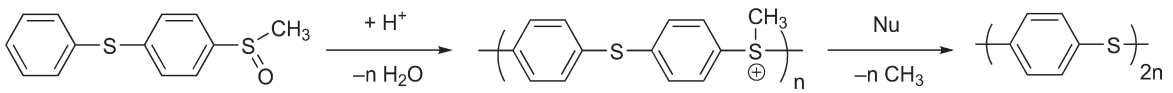

Figure 82 Synthesis of PPS by oxidative polymerization via soluble poly(sulfonium cation).

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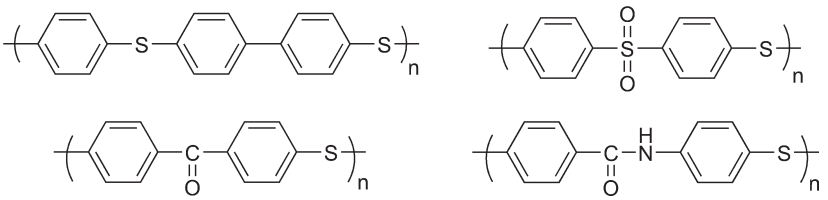

Figure 84 Chemical structures of some poly(phenylene sulfide) copolymers.

units separated by sulfide groups have been prepared in an essentially similar way as in the conventional process.[352] The reaction was conducted in NMP with sodium acetate and sodium hydrogen sulfide as catalysts. Similarly, Park *et al.*[353] reported the synthesis of copoly(*p*-phenylene/biphenylene sulfide)s (PPBSs) from sodium sulfide trihydrade ($Na_2S \cdot 3H_2O$), *p*-dichlorobenzene (DCB), and 4,4′-dibromobiphenyl (DBB) comonomers in NMP solvent using an autoclave. As more rigid biphenylene repeat units were incorporated in the chain, the PPBS copolymers exhibited increasing T_g's and decreasing T_m's. The reactivity of DBB was higher than DCB toward thiolate anion, resulting in DBB rich copolymer at lower reaction temperatures.

Several reports have been published on the synthesis of poly (arylene thioether ketone)s and conceptually their synthesis is similar to that of PAEKs. Researchers at Dow Chemical[354] reported the preparation of poly(phenylene ketone sulfide) (PKS) from ketone-activated aromatic fluoro compounds by reaction with freshly crystallized anhydrous sodium hydrosulfide. The polymerization occurs very rapidly in CHP at 290 °C and in 0.5 h high-molecular-weight PKS was obtained (IV = 0.9 dl g^{-1}) (**Figure 85**). In this polymerization, the purity of the sodium sulfide affects the degree of polymerization. Also, since sodium sulfide is hygroscopic, a slight excess (1%) was found to be necessary to obtain high-molecular-weight PKS.

Ueda *et al.*[355] synthesized a series of poly(thioether ketone)s by the direct polycondensation of aromatic dicarboxylic acids with aryl compounds containing sulfide structures, using phosphorous pentoxide/methanesulfonic acid (PPMA) as the condensing agent and solvent. The polycondensation, in general, proceeded in homogeneous solution and gave quantitative yields of polymers with moderate to high molecular weight. The synthesis of poly(phenylene sulfide ketone) copolymers was also reported by Satake *et al.*[356] A two-step process involving the synthesis of PPS oligomers and coupling reactions was employed, which was claimed to be advantageous in obtaining copolymers with satisfactory uniformity in composition. In the first step, a PPS oligomer of a degree of polymerization of ⊠5 was synthesized. The oligomers were then coupled with aromatic dihalides such as 4,4′-dichlorobenzophenone to give a poly(phenylene sulfide ketone) copolymer bearing both ketone and sulfide linkages in the backbone. The copolymers showed sufficient melt stability to permit the application of conventional melt processing techniques. Wang *et al.*[357] prepared the poly(phenylene sulfide ketone) copolymers via the free radical ROP of macrocyclic ether thioether ketone oligomers. The polymerization of the cyclic oligomers was conducted both in the melt and in solution via a transthioetherification reaction affording high-molecular-weight linear polymers. The ROP could be promoted by a catalytic amount of elemental sulfur or an aromatic disulfide such as 2,2′-dithiobis(benzothiazole) or terminated by 1-iodonaphthalene. Later, Ding and Hay[358] reported the preparation of poly(thioether ketone)s from 4,4′-dimercaptodiphenyl ether and 4,4′-dimercaptodiphenyl thioether, by reaction with a series of ketone-activated aromatic fluoro compounds in DMF in the presence of K_2CO_3. The polymers were amorphous and soluble in normal organic solvents with T_g's between 154 and 237 °C.

The preparation of poly(phenylene sulfide sulfone) (PPSS) copolymers, also addressed as poly(phenylene thioether sulfone), have been synthesized and studied by several groups.[359–362] As a general approach, PPSSs can be prepared by S_NAr polycondensation, utilizing sodium sulfide anhydrate as the nucleophile and 4,4′-dichlorodiphenyl sulfone as the activated aromatic halide. Specifically, PPSS has been prepared through the reaction of 4,4′-dichlorodiphenyl sulfone (DCDPS) with sodium sulfide nonahydrate and sodium acetate in NMP. Another method utilized sodium hydrosulfide, plus either sodium hydroxide or sodium carbonate, along with sodium acetate in NMP, to which distilled water had been intentionally added (**Figure 86**). The polymerization reaction was conducted in a pressure reactor at a temperature of around 200 °C for 3–5 h.

Influences of polymerization conditions such as reaction temperature and time, solvent, and the use of various additives like water and acetate salts on the polymerization and molecular weight of resulting copolymers were examined in detail by Liu *et al.*[359] It was reported that the highest molecular weight polymers were produced from reactions at about 200 °C for 3 h with optimal molar ratios of H_2O-to-NaSH or H_2O-to-NMP in the range from 9.4:1 to 15:1. Longer reaction times and/or higher temperature degraded the molecular weight, probably because of base-catalyzed reactions on the activated backbone. The appearance of a maximum molecular weight was suggested to be a function of the increased solubility of the nucleophile and the growing polymer chains in the reaction medium. These polymeric materials were reported to be amorphous but with some local ordering structures in the presence of organic liquids with T_g values up to 222 °C. Several patents of

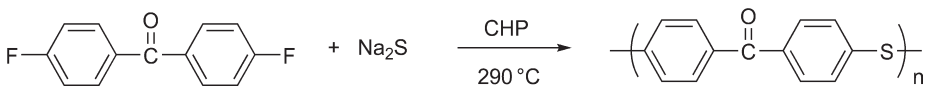

Figure 85 Synthesis of poly(phenylene ketone sulfide) copolymer.

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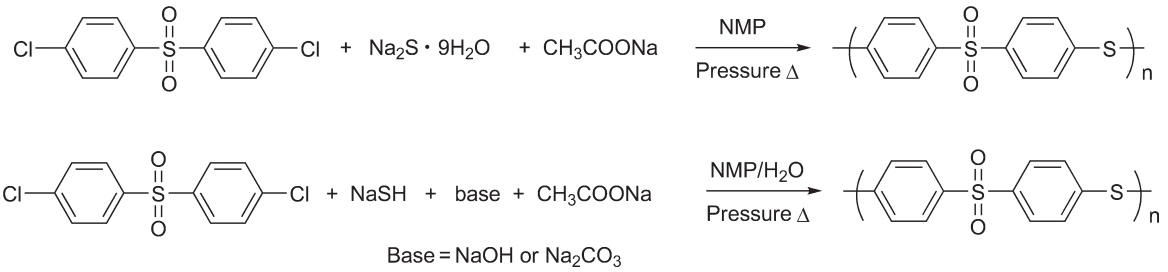

Figure 86 Synthesis of poly(phenylene sulfide sulfone).

Phillips Petroleum[363–365] described the synthesis of poly(arylene sulfide sulfone) polymers containing ether groups via a two-step process. In the first step, a dihalo-terminated polyethersulfone oligomers was prepared by reacting an aromatic diphenol, such as bisphenol A, with a substantial excess of a dihalo aromatic sulfone, such as 4,4′-dichlorodiphenyl sulfone, in the presence of Na_2SO_3 in NMP. In the second step, sodium hydrosulfide, sodium acetate, and water were subsequently added and the excess dihalo aromatic sulfone and the oligomers were copolymerized with sodium hydrosulfide, resulting in a modified poly(arylene sulfide sulfone) polymer containing ether linkages. These polymers exhibit improved softening temperature and T_g and are useful in high-temperature applications.

Aromatic copolymers bearing the sulfide linkage and the amine linkage in the backbone have been synthesized. These types of copolymers are of interest because they can combine the good thermal properties of PPSs with the unique properties of poly(aniline), which is an electric conducting polymer commonly used in organic semiconductor technology. Copolymers of poly(phenylene sulfide amine) (PPSA) alternating in sulfide and amine linkages were reported to be synthesized from either self-polymerization of methyl-(4-anilinophenyl) sulfide with antimony pentachloride followed by demethylation,[366] or from acid-induced self-polymerization of methyl-(4-anilinophenyl) sulfone followed by the same demethylation reaction.[367]

5.17.5.2.2 Sulfonated poly(arylene sulfide sulfone) copolymers

Sulfonated PPSS copolymers have been developed for their applications in ion exchange membranes.[360,368–369] The sulfonated groups were introduced onto polymer chains by either postsulfonation of preformed copolymers using sulfonating reagents or direct copolymerization of sulfonated monomers.

Hwang and co-workers[368] applied the postsulfonation of block copolymers of polysulfone and PPSS to prepare cation exchange membranes. The preparation of the sulfonated block copolymers involved four principal steps: (1) synthesis of poly (arylene sulfone) precursors from bisphenol A (in disodium salt form) and 4,4′-dichlorodiphenylsulfone (DCDPS); (2) synthesis of polysulfone-*co*-PPSS copolymers by polymerizing the sulfone precursor polymers with DCDPS and sodium sulfide; (3) treatment of copolymers obtained in step 2 using $SnCl_4$ and chloromethyl methylether to afford chloromethylated copolymers; and (4) sulfonation of the chloromethylated copolymers using a mixture of triethyl phosphate and sulfuric acid (1:2 in molar ratio). Similar procedures were applied by the same group[369] in the preparation of anion exchange membranes by simply replacing the fourth step of sulfonation with amination by triethylamine.

Wiles *et al.*[360] developed a new synthetic approach of sulfonated polysulfone-*co*-PPSS copolymers from a disulfonated monomer, disodium 3,3′-disulfonated-4,4′-difluorodiphenylsulfone (SDFDPS) and 4,4′-difluorodiphenylsulfone (DFDPS) (or their chlorinated analogs), and 4,4′-thiobisbenzenethiol in the presence of potassium carbonate (**Figure 87**). High-molecular-weight disulfonated copolymers were easily obtained producing tough and ductile membranes. The degrees of disulfonation (20–50%) were precisely controlled by varying the ratio of disulfonated monomer to unsulfonated comonomers, in contrast to no control of sulfonation degree produced via the postsulfonation approach. In addition, the chemical stability of sulfonic acid groups attached to the electron-deficient aromatic rings was improved via the direct copolymerization approach.

Schuster *et al.*[373] synthesized the sulfonated poly(phenylene sulfone)s following the same procedure of synthesizing sulfonated PPSSs copolymers described by McGrath, plus an extra step of oxidizing the sulfide units to sulfone groups in the copolymers using peroxide in acidic solution. This new class of polymers with extremely electron-deficient aromatic rings was reported to possess very high thermooxidative and hydrolytic stabilities, low solubility, and reduced swelling in water at enhanced temperature compared to other sulfonated poly(arylene)s, which made them interesting materials for chemical and electrochemical applications such as PEM fuel cells. However, they were very brittle and water sensitive. More recently, Dang *et al.*[370] reported the synthesis of fully sulfonated homopolymers of poly(phenylene thioether sulfone)s from DFDPS and a in-house synthesized 6F-dithiol monomer, 4,4′-(hexafluororoisopropylidene) bisbenzenethiol, using 4-fluorobenzophenone as the end-capping agent. High-molecular-weight polymers were obtained, from which tough and ductile membranes were prepared for utilization as PEMs. It was reported that the proton conductivity of these types of polymers was as high as 180 ms cm^{-1} when measured at 85 °C and 65% RH, which was approximately 2.5 times higher than that of Nafion® 117 under comparable conditions.

5.17.5.2.3 Crosslinked poly(arylene sulfide)s

Crosslinked poly(arylene sulfide)s were synthesized by either introducing curable functional groups into the monomer before polymerization or end-capping the oligomers with curable moieties. Various curable moieties have been reported, such as nadimide unit and ethynyl group.

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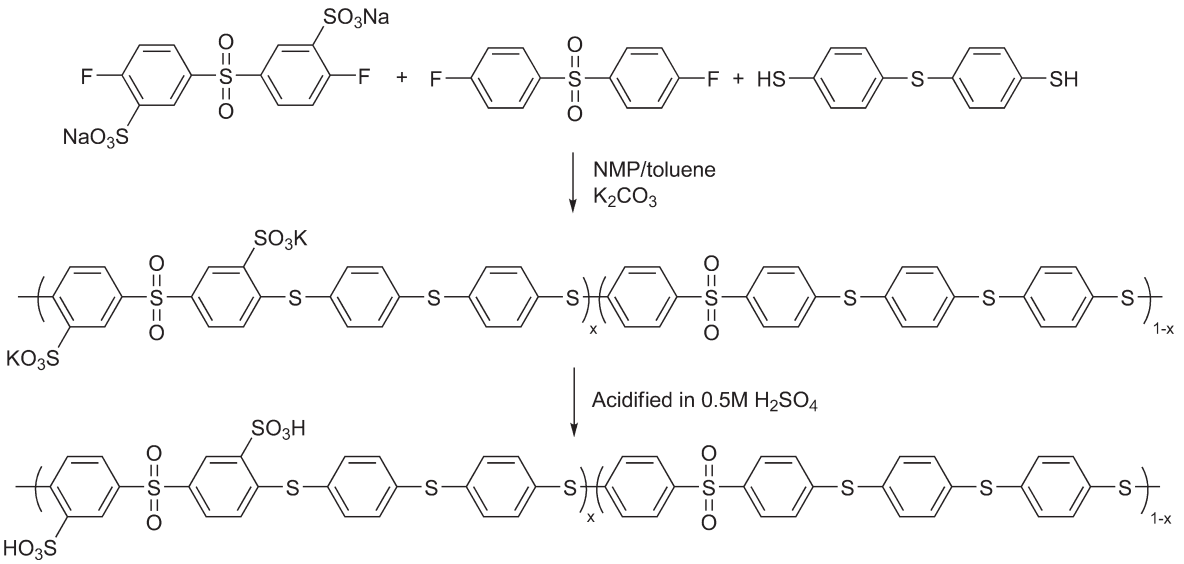

Figure 87 Synthesis of sulfonated poly(phenylene sulfide sulfone) copolymers from disulfonated monomer DFDPS.

Lubowitz *et al.*[371,372] reported in several patents the synthesis of poly(arylene sulfide) oligomers end-capped with a pendant double bond, which served as crosslinking groups upon thermal and/or chemical activation to form a crosslinked poly(arylene sulfide). For example, the curable telechelic poly (arylene sulfide) oligomers were obtained using a monofunctional chloro compound, such as *p*-nadimidochlorobenzene, as the end-capping agent in the reaction mixture of sulfide and aromatic dichloro monomer. In addition, a trifunctional compound, such as trichlorobenzene, was added to compensate the monofunctional compound with respect to molecular weight. The curing of the oligomer solution-impregnated fabrics was conducted under 7 bar at 330 °C for 1–2 h, resulting in the composites with superior solvent resistance, resistance to delamination, shear strength, and thermo-oxidative resistance.

Synthesis of ethynyl-end-capped fluorinated poly(arylene ether sulfide)s were reported by Lee and co-workers[373,374] for their applications in optical waveguide devices. In their work, ethynyl-end-capped poly(arylene ether sulfide)s were prepared from the S_NAr reaction between the fluorinated biphenol monomer and perfluorophenyl sulfide followed by an end-capping reaction using 3-ethynylphenol as the end-capping agent (Figure 88). The polymer films were fabricated by spin-coating and crosslinked by thermal curing at 270 °C for

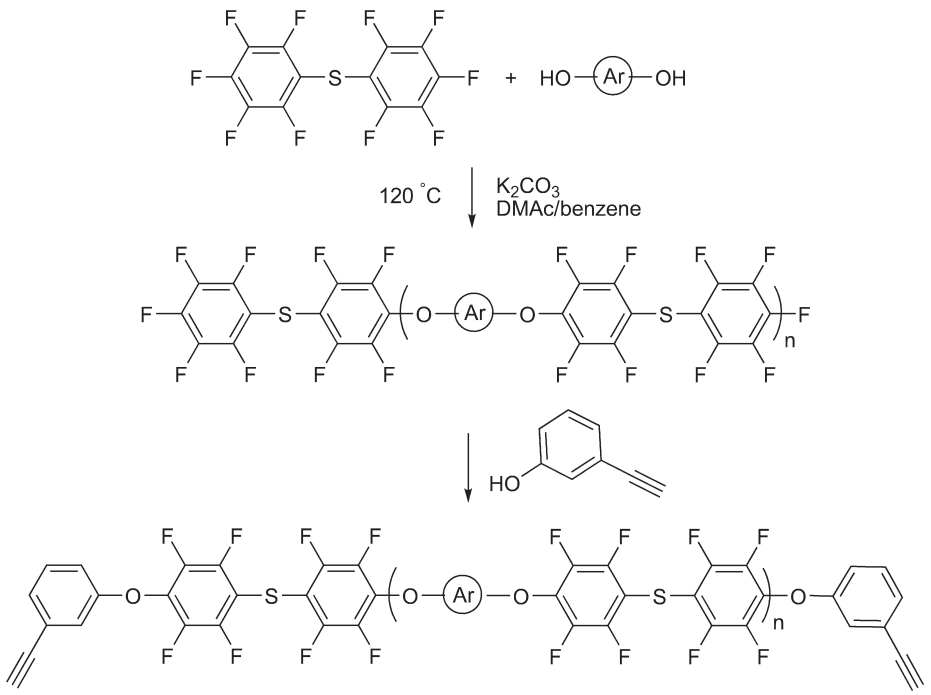

Figure 88 Synthesis of curable ethynyl-end-capped poly(arylene ether sulfide) oligomers.

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2 h. The glass transition temperature of the polymer was increased by about 40 °C after curing and showed high thermal stability up to 489 °C. The resulting polymers possessed high optical clarity at the telecommunication wavelength, sufficient thermal stability, and chemical resistance.

5.17.5.2.4 Hyperbranched poly(arylene sulfide)s

The preparation of hyperbranched poly(arylene sulfide)s has been reported by several groups, though different synthetic methods were used. Jikei *et al.*[375] synthesized the hyperbranched PPSs via a poly(sulfonium cation) precursor starting from an AB_2-type monomer, methyl 3,5-bis(phenylthio) phenyl sulfoxide. The AB_2-type monomer was prepared from 1,3,5-tribromobenzene through nucleophilic substitution. In the polymerization reactions, sodium thiophenoxide was used as both solvent and the reagent for protonation of the sulfoxide, resulting in the poly(sulfonium cation), which was converted into the hyperbranched PPS via demethylation reaction by refluxing in pyridine. The hyperbranched PPS was soluble in many organic solvents, in contrast to the insolubility of linear PPS in any organic solvents.

Mellace *et al.*[376] reported the preparation of hyperbranched PPSs from a commercially available AB_2-type monomer, 3,4-dichlorobenzenethiol. The polymerization was accomplished using anhydrous potassium carbonate as a base in the amide solvents such as *N*,*N*-dimethylformamide (DMF) or NMP to give the hyperbranched structure. In order to reduce the polydispersity of the hyperbranched polymers, a multifunctional core was introduced by using 1,3,5-trichlorobenzene as the comonomer with 3,4-dichlorobenzenethiol.

Hyperbranched PPSs grafted with chemically different linear arms were synthesized by Zhu and Pan[377] In their work, the hyperbranched block copolymers, in which the linear polytetrahydrofuran (PTHF) was linked to the apex of hyperbranched PPS, were synthesized. The synthesis involved three steps: (1) condensation polymerization of 2,4-dichlorobenzenethiol to form hyperbranched PPS; (2) transformation of the resultant thio-ended hyperbranched PPS to hydroxyl end groups; and (3) the cationic ROP of THF on the hydroxyl-ended hyperbranched PPS as a macrotransfer agent using $BF_3 \cdot OEt_2$ as a catalyst. The resultant PTHF-hyperbranched PPS block copolymers showed good thermal stability and could be easily dissolved in organic solvents such as THF and chloroform.

5.17.5.3 Properties and Applications

PPS is a unique semicrystalline resin in many ways. Whereas other polymers can correctly be classified as being either thermoplastic or thermosetting in their behavior, PPS combines the desirable properties of both these types of materials. Under normal handling and processing conditions, PPS behaves as a true thermoplastic in that it can be repeatedly melted and solidified with only minor changes in its flow characteristics. On the other hand, by properly selecting processing conditions, it can be made to undergo the very complicated and incompletely understood 'curing' process, resembling the thermosetting polymers as mentioned before.

Compared with its nearest analogous polymer PPO, PPS has slightly higher glass transition temperature (85–90 °C), while it degrades at a lower temperature due to the susceptibility of the sulfide link to oxidation. The thermal stability of PPS results from the structure of the polymer, involving only carbon–carbon, carbon–hydrogen, and carbon–sulfur bonds, all of which are quite thermodynamically stable. The implication of the thermodynamic stability of the bonds in PPS is that it will take a large input of energy (high temperature) to dissociate any of the bonds (induce thermal degradation). PPS is well suited for use at high temperatures for extended period of time. TGA analysis showed that no appreciable weight loss was observed in PPS up to about 500 °C. In air, degradation of PPS was complete at 700 °C.[378] The effect of structural variables on the thermal stability of PPS has been studied. It was reported that branched polymers seem to be more stable than the linear polymers. In addition, molecular weight does not have obvious effect on the thermal stability of PPS.[379] More recently, fragmentation reactions of PPS have been studied in detail using the combination of matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF)/TOF collision-induced dissociation (CID) fragmentation and pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS).[380,381] It was reported that linear PPS undergoes random main chain fragmentation along the polymer backbone and preferentially fragments at bonds adjacent to dibenzothiophene and phenyl end groups. Cyclic species produce fragment ions similar to linear species. PPS thermal curing in the presence of oxygen, even at trace quantities, leads to oxygen uptake in the form of sulfoxides in the PPS backbone.

PPS is a semicrystalline material and its thermal transitions are appropriate for the melt processing of materials into finished parts. PPS shows a high crystalline melting point ($T_m = 285$ °C). Moreover, the polymer crystallizes rapidly above T_g as indicated by an exothermic crystallization peak located at 120–130 °C. The polymer also crystallizes rapidly when cooled from the melt. PPS also displays a melt crystallization exotherm at approximately 220 °C. Using the appropriate molding and annealing conditions, a crystalline part can be obtained that is dimensionally stable and possesses good mechanical properties. The ability to mold PPS in a crystalline form is critical in achieving solvent resistant and dimensionally stable parts, and to allow those parts to be used at elevated temperatures. According to X-ray diffraction described by Brady,[382] fully crystallized PPS has a crystallinity index of about 65%. The crystallization behavior of PPS has been studied in detail as a function of branching agent and the chemical nature of the end group counteratom.[383,384] It was reported that the bulk crystallization phenomena could be described by the Avrami equation with exponent $n \approx 3$. The effect of branching was more important than that of molecular weight on the linear crystal growth rate. The crystal growth rate decreased in the counteratom order: $Ca^{2+} > H^+ > Zn^{2+} > Na^+$. The order of decreasing crystal growth rates corresponded to a similar increase in melt viscosity, suggesting that the reason for decreasing growth rates could originate from increasing secondary interchain interactions. Researchers at Phillips Petroleum[385] studied the influence of crystallization and polymer end groups on the exposure-induced coloration of PPS. The results suggested that coloration of amorphous PPS films after ultraviolet (UV) irradiation was caused by products different from those that cause coloration in semicrystalline PPS after thermooxidation. In addition, end groups and molecular weights played important roles in the thermooxidative coloration of semicrystalline PPS, but only nominally influenced the

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photooxidative coloration of amorphous PPS. More recently krishnaswamy *et al.*[386] reported the study on the influence of semicrystalline morphology on the physical aging of PPS. The physical aging kinetics was observed to depend on the relative amounts of the mobile-amorphous and rigid-amorphous phases. It was reported that the rigid-amorphous phase was able to accelerate physical aging due to its relative proximity to a state of lower configuration entropy.

Besides high-temperature resistance, PPS also has excellent chemical resistance and there are no known solvents for the polymer below 200 °C. Parts molded from PPS can be utilized in a variety of hostile chemical environments where inertness is required. PPS is affected by high-temperature exposure to only a few organic solvents, strong mineral acids, and strong oxidizing reagents. The reaction of these reagents is due to the expected chemistry for the structure of PPS. Oxidizing reagents can convert sulfides present in PPS to sulfoxides or sulfones. The aromatic ring of PPS can be halogenated, nitrated, or sulfonated under appropriate conditions to yield derivatized polymers. In addition, PPS possesses outstanding fire retardancy, which can be attributed to its aromatic structure and to its tendency to char. When exposed to flame, PPS will burn with a yellow-orange flame until the flame source is removed. It has a high oxygen index of 44, a low heat release rate, a low radiant panel flame spread index (ASTM E 162) and, according to the standard UL 94 laboratory flammability test results, it is classified as V-0/5V (62), that is, self-extinguishing and non-dripping. The autoignition temperature of PPS is 540 °C. Smoke-density measurements indicate that PPS does not produce copious amounts of smoke in either the smoldering or the flaming stage as do some other aromatic polymers.

PPS resins and compounds display properties characteristic of good insulators, including high dielectric strength, low dielectric constant, low dissipation factor, and high volume resistivity. It maintains high volume resistivity and dielectric strength even at high temperatures. However, PPS is not optically stable as it tends to degrade in sunlight, which is caused by the overlap of the absorption spectrum of PPS and the spectrum of the sun in the UV region. Therefore, light stabilizers, such as UV absorbers quenchers, and antioxidants have been added in bulk to PPS to improve its photo stability.

The initial market for PPS was in the area of coatings, in which application the phenomena of curing of PPS under thermal treatment were very important. Application of PPS coatings on metals is quite feasible since PPS is quite fluid and wets the substrates melt well. After thermally cured, the final coating exhibits excellent chemical resistance. Metals with PPS coatings may outperform stainless steel or expensive alloys when used in corrosive environments. In addition, PPS, when properly formulated with relatively small amount of polytetrafluoroethylene (PTFE), can provide a nonstick cookware coating in a one-coat process; while in many other competitive nonstick coatings, a two-step coating operations are generally needed. With the development in understanding of curing and precise control of curing degrees, injection molding began to develop as a market for PPS, which is the major market for Ryton® PPS leading to a large variety of commercial grades of PPS depending on the extent of curing. The largest market fields for PPS injection molding compounds are the electrical/electronic area, such as switches, integrated circuit, capacitor encapsulations, and the mechanical area, such as automotive parts, pumps, heat shield, and oil well valve. A specific application of PPS in automotive parts is an exhaust gas emission control valve on Toyota automobiles. The item, which had been made of 14 separated, machined, stamped, and extruded metal parts (mostly stainless steel), consists of three injection-molded PPS parts that are subsequently ultrasonically welded together. This change considerably saved in materials costs, assembly costs, and weight, which is important to today's fuel-conscious automobile industry.

Although many applications for PPS involve its inherent electrical insulating behavior, it is a member of the family of organic polymers, which can be rendered electrically conductive by doping with appropriate compounds such as arsenic pentafluoride or by incorporating conducting units into the PPS backbone. Copolymers containing alternating sulfide and amine units are semiconducting and can be used in many electronic and electro-optical applications, such as antistatic layers, electromagnetic-shielding layers, and conductor tracks of transistors. An example of this type of copolymer is PPSAs as described in Section 5.17.5.2.1. Layers of this polymer adhere very well to metals, in particular, to gold. By means of oxidation agents, PPSA can be doped to form a p-type material. Doping of a self-supporting layer of PPSA with $SbCl_5$ results in an electric conductivity of $0.18\,s\,cm^{-1}$, while doping with $FeCl_3$ leads to a conductivity of $0.8\,s\,cm^{-1}$.

Sulfonated PPS homopolymers or copolymers have been tested as ion exchange membrane materials for both hydrogen fuel cell and DMFC applications. For example, heterogeneous membranes based on medium-sulfonated PPS were made by dispersing the PPS in a poly(olefin) matrix such as polyethylene.[387] A commercial fuel cell was used for membrane testing. The test showed that membranes with high amounts of sulfonated particles were almost as conductive as Nafion®117. However, these membranes exhibited considerably lower diffusive permeability to methanol. Further, the membranes were less oxidatively stable.

As mentioned before, when PPS is contacted with oxidants, the sulfide units can be oxidized to a sulfoxide. Upon this observation, PPS has been used as ozone filter materials to capture the ozone that is constantly given off into the surrounding air by the apparatuses such as electrophotographic copiers and printers.[388] The removal of ozone from the air-stream released by such apparatuses is based on the oxidation of sulfide to sulfoxide in the PPS by ozone. In this application, PPS can be used as powder, fibers, films, or moldings, which normally have a large surface area to effectively remove the harmful ozone.

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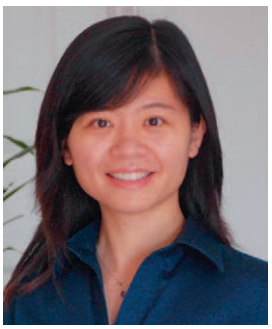
Biographical Sketches



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5.18 Chemistry and Technology of Polyamides

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5.18.1 Introduction

Polyamides (PAs) are defined as polymers in which the monomer residues are connected through amide functionalities (–CONH–). The choice of the monomeric units determines the properties of the PAs. Only a limited number of monomers are used to produce the commercially available PAs. PAs also exist in nature, where they are named polypeptides. Other names that are often used are 'nylon' and 'aramid'.[1] The name 'nylon' was introduced by DuPont with the commercial introduction of the first man-made PA, but is now widely used for fully aliphatic PAs as an alternative for the name PA. Aramids are PAs that consist of aromatic diamines and aromatic dicarboxylic acids. A couple of excellent books and review articles on PA chemistry and technology exist, which formed an important source of information for this chapter.[2–5]

5.18.1.1 Nomenclature and Types of Polyamides

PAs of linear monomers, according to ISO 1874, are to be denoted as PA *XY* or PA *Z*.[6] *X*, *Y*, and *Z* refer to the diamine, dicarboxylic acid, and aminocarboxylic acid monomer residues, respectively. Linear aliphatic monomers are coded by a number indicating the number of carbon atoms in the monomer. Thus, *X* represents diamines $H_2N–(CH_2)_X–NH_2$, *Y* represents dicarboxylic acids $HO_2C(CH_2)_{Y-2}–CO_2H$, and *Z* represents aminocarboxylic acids $H_2N–(CH_2)_{Z-1}–CO_2H$ or their corresponding lactams. For other monomers, letter codes are used, representing an abbreviation of the monomer. As examples we mention here MXD (*m*-xylylenediamine), T (terephthalic acid), and I (isophthalic acid).

The number code for a copolyamide synthesized from a mixture of monomers is indicated by a slash between the codes for the corresponding homopolyamides and the composition is given between brackets. The following may serve as an example: PA *Z*/*XY* (50/50) represents a copolyamide consisting of 50 mol.% amino acid or lactam *Z* residues, 25 mol.% diamine *X* residues, and 25 mol.% dicarboxylic acid *Y* residues.

Mono-, tri-, and higher-functional monomers are optionally added in small amounts and therefore not mentioned in the PA coding. For blends of different PAs, a denotation like PA 6/PA 66 (50/50) is used, which in this example indicates a blend of PA 6 and PA 66 in a 50/50 wt.%/wt.% ratio. Complicated IUPAC names are generally not used. For example, the IUPAC name for PA 46 is poly[imino(1,4-dioxo-1,4-butanediyl)imino-1,6-hexanediyl].

5.18.1.1.1 Types of polyamides

There are several ways to classify PAs:

1. Diamine–dicarboxylic acid or AA/BB-type and aminocarboxylic acid or AB-type PAs
2. Homo- and copolyamides
3. Aliphatic, semiaromatic, and fully aromatic PAs.

The third method is generally the leading classification. In this chapter, we use all three types of classifications in the priority 3-1-2, thereby following most literature on PAs.[2,4]

In case aliphatic PAs contain only small amounts of aromatic comonomer or aromatic monofunctional monomers, they are still classified as aliphatic. According to the US standard ASTM D 5336, the class polyphthalamides (PPAs) is reserved for PA *XY*, where the dicarboxylic acid *Y* consists of at least 55 mol.% T and/or I.[7] In semiaromatic PAs, this limit is not defined and also all other monomers with aromatic moieties are included. For similar reasons, the class of aramids should not be mixed up with the term fully aromatic PAs.

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Further classifications can be made taking into account the properties of PA materials. For example, one can distinguish between amorphous and semicrystalline PAs or between odd- and even-numbered PAs.

5.18.1.2 Natural Polyamides (Polypeptides) and Brief History of Man-Made Polyamides

5.18.1.2.1 Natural polyamides (polypeptides)

PAs based on structures –NH–CHR–CO– occur in nature as polypeptides or proteins, for example, in silk produced by the silk worm *Bombyx mori*. In silk, the proteins are built up from the amino acids glycine (Gly), alanine (Ala), and serine (Ser) in the strict repetitive sequence as shown in Figure 1. These polypeptides crystallize in β-sheets as shown in Figure 2.

Other proteins crystallize in helix forms of repetitive length of 0.51 nm (β-keratin and wool) or 0.86 nm (collagen, gelatin, and triple helix). Proteins are described in more detail in Chapter 9.07.

5.18.1.2.2 History of man-made polyamides

First lab-scale synthesis of PAs such as PA 510 (1934) and later PA 66 (1935) was followed by commercialization of PA 66 in 1938 under the name nylon.[8] The materials were initially used for the production of artificial or man-made fibers as a replacement for silk and were used in stockings and parachutes. In 1938, PA 6 was invented by Dr. Paul Schlack at I.G. Farben and was used by the army and commercialized during World War II under the name Perluran® and later Perlon®.[9] Other PAs that followed soon were PA 610 and PA 11.[10] Today the PAs form one of the most important groups of step-growth polymers for injection molding, extrusion, and film and fiber applications.

5.18.1.3 Chemistry of Amide Bond Formation and Control of Chain Structure and Chain Ends

The most important chemical feature of PAs is the amide link between the condensed monomers and its formation of hydrogen bonds. Besides the dipole moment of 3.7 D, the force of the H bridges with an energy content around 30 kJ mol^{-1} creates strong interchain interactions.[3] This explains, among others, the high strength and stiffness and the excellent wear and friction behavior of PAs compared to other polymers.

The semidouble bond character (see Figure 3) makes the amide link a stiff chain unit with an amide C–N bond length of 0.133 nm, compared to 0.151 nm for the *exo* amide C–N bond length. In cooperation with the earlier mentioned H bonds, this leads to high glass transition temperatures and high melting points for PAs as compared to the corresponding polyesters. Another consequence of the amide bond units in PAs is the water uptake, which makes the T_g and T_m dependent on the relative humidity. This makes most aliphatic PAs are tough materials in humid environments due to the drop of T_g to around or below room temperature.

Besides by reaction of a carboxylic acid group with an amine, amide bonds can also be formed from other carboxylic acid derivates. Table 1 summarizes the different possibilities.

5.18.1.4 Catalysis, Equilibria, and Kinetics of Hydrolytic Polycondensation

Two main equilibria occur that determine the formation of amides by hydrolytic polycondensation involving amine and carboxylic acid groups: the condensation and

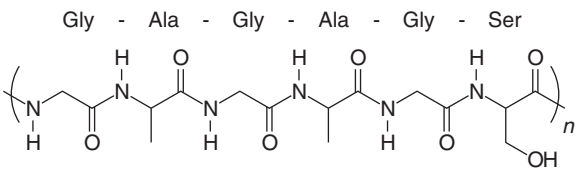

Figure 1 Repeat unit of natural silk consisting of six amino acid residues.

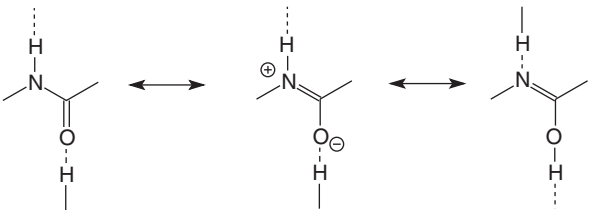

Figure 3 Illustration of the semidouble bond character of the amide bond.

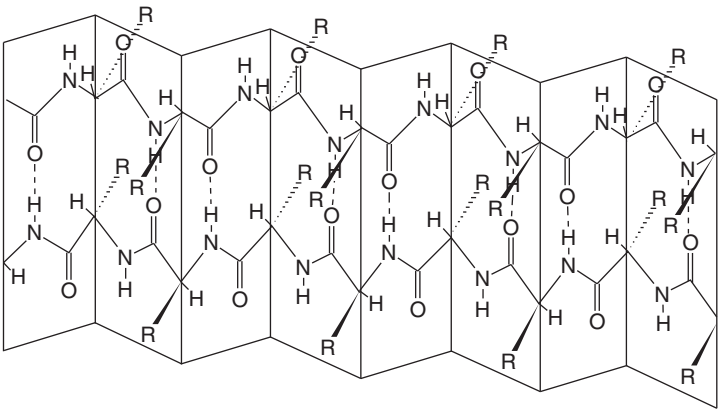

Figure 2 β-Sheet of natural polypeptides.

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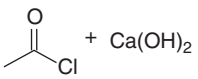
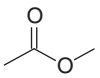
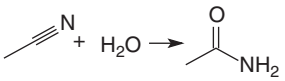
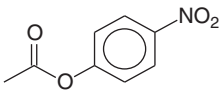
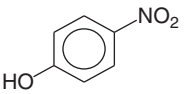
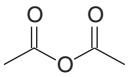
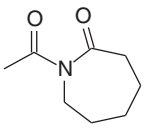
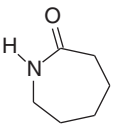
Table 1 Different possibilities for the formation of amide bonds from an amine and other starting materials

Functionality	*Starting material*	*Condensation product*	*Example*
Acid chloride		$CaCl_2+H_2O$	Polyaramids[11]
Ester			Transparent semiaromatic PAs[12]
Nitrile/amide		NH_3	PA 66 from adipodinitrile[13]
p-Nitrophenyl ester			Alternating PA 6/12[14]
Anhydride			Leuchs α-amino acid *N*-carboxyanhydride[15]
Carbamoyl			Chain extender[16]

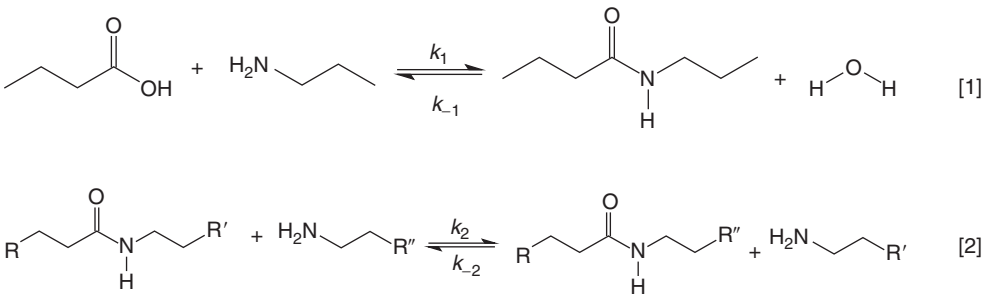


Figure 4 Main equilibria in the amide formation by polycondensation.

hydrolysis (eqn [1]) and the amide interchange (eqn [2]) (see Figure 4).

Both can occur with cyclic lactams and higher oligomers, which leads to ring closure and opening in the case of eqn [1], where k_1 is the amidation rate constant and k_{-1} is the hydrolysis rate constant, and to polyaddition and backbiting in the case of eqn [2]. Both reactions can be catalyzed by carboxylic acid groups and are discussed in the following sections.

In the polycondensation reaction, and also for the addition of (cyclic) aliphatic monomers to PAs, sometimes catalysts such as sodium hypophosphite and phosphoric acid are used to increase reaction rates.

5.18.1.4.1 Ring opening and condensation and hydrolysis reactions

Condensation of an amine and a carboxylic acid functionality is the general way to form an amide link. The reverse reaction, the hydrolysis of amides, limits the maximum achievable molar mass together with unbalance in amines and carboxylic acid groups. In case of an aminocarboxylic acid also, intramolecular condensation can take place leading to a cyclic amide, which, in case of one functional amide group, is a lactam. This reaction is shown for caprolactam (CL) in Figure 5. The reverse reaction is required to start the conversion of CL to PA 6 by polyaddition. Ring-opening reaction typically occurs by hydrolysis of a cyclic amide as shown for CL in Figure 5. Ring opening can also occur by aminolysis by an amine. If this happens by the amine end group of a PA chain, it is called polyaddition (see Figure 9).

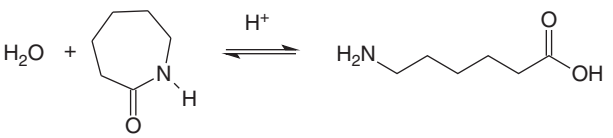


Figure 5 Hydrolysis of CL and the reverse ring closure reaction.

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5.18.1.4.2 Equilibria

For fully aliphatic PAs, *XY* polyamidation kinetics and equilibria are comparable, independent of the values of *X* and *Y*. However, for lactam ring structures, the reaction equilibria with the aminocarboxylic acid depend on the ring size.[17]

The equilibrium constant *K* is denoted in eqn [3], where *B* is the temperature-independent equilibrium constant and ΔH_a is the enthalpy change of the reaction. Reported values of ΔH_a are in the order of 25–29 kJ mol^{-1},[18] indicating that at lower temperatures higher maximum conversions can be reached at constant water concentration.

Besides being temperature dependent, *K* is also water dependent as quantified by Giori and Hayes:[18]

$$K = \frac{k_1}{k_{-1}} = \frac{[H_2O]\cdot[NHCO]}{[NH_2]\cdot[CO_2H]} = B\exp\frac{-\Delta H_a}{RT} \qquad [3]$$

According to Figure 6, water leads to an increase in the equilibrium constant, favoring the amidation in PA 6 up to 2 wt.%, where it reaches a maximum. At water contents > 6 wt.%, *K* is not dependent on the water content anymore.

5.18.1.4.3 Kinetics

The reaction rate constant *k* for the amidation reaction is generally split into a noncatalytic part (k') and a catalytic part (k''), where $k = k' + k''$. The general order of reactivity for the formation of an amide decreases as indicated in Figure 7. The formation of aliphatic PAs easily takes place without a catalyst. Steppan *et al.*[19] have published an excellent polycondensation model applied to PA 66.

The amidation kinetics for forming an amide link between an aromatic carboxylic acid and an aliphatic amide was studied in detail by EMS-Chemie.[20,21] By performing experiments on PA 6T/6I copolyamide in comparison with PA 66, it was found that aromatic dicarboxylic acids have an amidation reaction rate constant k_1 that is about an order of magnitude lower in the reaction with aliphatic diamines compared to adipic acid. For that reason, PAs based on aromatic dicarboxylic acids generally require a catalyst for their formation. Due to the slower reaction kinetics and high melting points, side reactions are generally more pronounced in semiaromatic PAs. Also the amidation equilibrium constant *K* is about a magnitude lower for aromatic carboxylic acids. Because $K = k_1/k_{-1}$, the hydrolysis rate constants k_{-1} of aliphatic and semiaromatic amide links are about the same. Fully aromatic PAs are generally produced from the reactive acid chlorides.

In the production process of PA 6, amine and carboxylic end groups are generated by high-pressure hydrolysis of the CL and/or backmixing of PA oligomers. For high-molecular-mass PA 6 applications such as in film and in industrial yarns, a solid-state postcondensation (SSPC) is carried out, typically during 5–20 h at 160–180 °C, till a relative viscosity η_{rel} of typically 2.3–3.6, as measured in a 1 wt.% aqueous formic acid solvent (90 wt.%) at 25 °C, is reached.

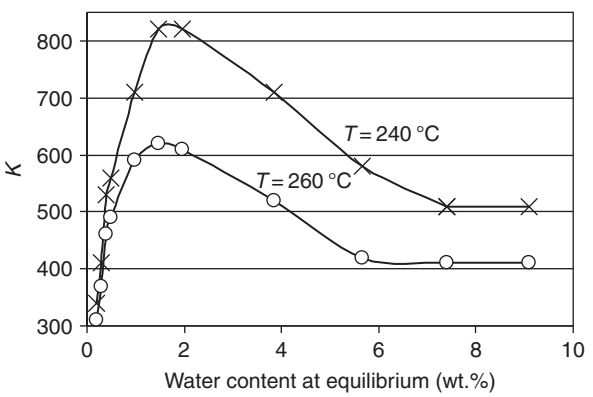

Figure 6 Polycondensation equilibrium constants *K* versus equilibrium water content at 240 °C (X) and 260 °C (O). Reproduced from Giori, C.; Hayes, B. T. *J. Polym. Sci. A-1* **1970**, *8*, 335,[18] with permission of Wiley.

5.18.1.4.4 Catalysts

As mentioned before, the carboxylic acid groups themselves catalyze the amidation and the transamidation reactions. Because they reduce in concentration during polymerization, they are also referred to as 'Einbaukatalysatoren'.[22] The catalytic effect of the carboxylic acid groups is believed to be related to the formation of a dimer complex through hydrogen bonding. The transitions state (#) of the amidation reaction with involvement of the activated dimerized acid complex is schematically shown in Figure 8(a). This increases the polarizability of the reactive site through electron pair delocalization, especially in case of aromatic carboxylic acids. Other chemicals that catalyze the amidation reaction are mainly phosphorous based such as sodium hypophosphite[23] and phosphoric acid. Their catalytic effect, as with the carboxylic acid, is believed to be related to the formation of a dimer complex through hydrogen bonding as shown in Figure 8(b). They are mainly used in the production of semiaromatic PAs due to the lower reaction

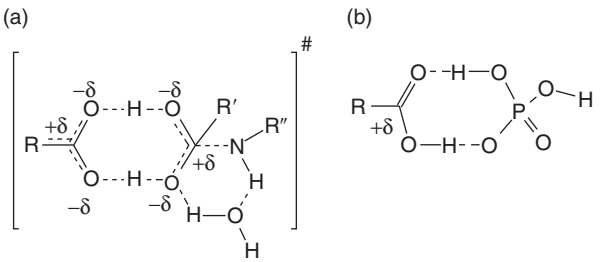

Figure 8 Activated dimer complex of carboxylic acid end groups at its transition state (#) in the amidation process with an amine group (a) and complex of carboxylic acid with phosphoric acid with enhanced polarizability of carbonyl, facilitating the nucleophilic attack of an amine (b).

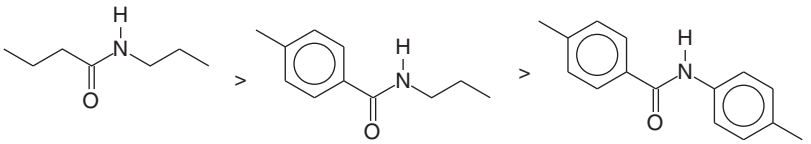

Figure 7 Reactivity of formation of fully aliphatic, semiaromatic, and fully aromatic amide groups.

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rates of terephthalic acid. The dimerization allows a better polarization of the reactive site through electron pair delocalization, especially in case of aromatic carboxylic acids.

5.18.1.4.5 Ring opening and condensation and transamidation reactions

Except for the ring addition reaction described below, transamidation as an intermolecular reaction (see eqn [2]) is usually not noticed, since its reaction does not result in a change in M_n or end-functional group contents. However, the reaction allows re-equilibration of the molar mass distribution and thus shifting of the polydispersity index (PDI, which means M_w/M_n) toward a value of 2 and shifting from blocky toward a statistical distribution in case of a polymer blend or a (multi)block copolymer. A nonequilibrium molar mass distribution can occur for linear PAs in industrial production due to SSPC reactions and due to residence time distribution of the reacting polymer. Upon melt processing, the decrease in the PDI typically results in a drop of solution viscosity, which, however, is often compensated by the condensation reaction.

Blends of PAs can transamidate to multiblock copolymers and ultimately to statistical copolyamides. However, normally this reaction is hindered by demixing of the two PAs in the melt. Also the low end-group content in polymer blends means that transamidation occurs too slow to achieve a statistical distribution of the monomers in acceptable reaction times.[24,25]

5.18.1.4.6 Polyaddition and backbiting

In a polyaddition reaction, transamidation causes a PA chain to grow by coupling of a cyclic amide to an amine end. This is shown for the polyaddition of ε-CL to a PA 6 chain in Figure 9.

In case of lactam polymerization, the rate of lactam conversion is driven by the polyaddition, whereas carboxylic acid groups increase the reaction rate by catalysis. Ring opening and polyaddition can also occur for higher cyclic oligomers and were quantified for the cyclic dimer by Tai and Tagawa.[26] Generally, the equilibrium between the cyclic and linear amide structures is determined by the ring size of the lactam or the cyclic oligomer. Due to their favored ring structure, especially five-membered rings allow only low conversions to the PA. This, together with their high melting points, which further enhances depolymerization, is one of the important reasons why PA 4 and PA 5 have never been developed into commercial products. The effect of lactam content in equilibrium depending on ring size is shown in Figure 10.[27]

In PA 6, the content of the seven-membered CL ring in equilibrium, as shown in Figure 11, has a large dependency on temperature. The high-temperature depolymerization tendency has led to a commercial recycling process of PA 6-based carpet yarns to CL.[28] CL, together with small amounts of low-molecular-mass cyclic oligomers, is removed from the virgin PA 6 in the production process by extraction. When passing the melting point, a strong shift in the equilibrium CL content occurs, relating to the crystallization of PA 6. In the solid state, only the PA 6 part in the amorphous phase contributes to the polyaddition reaction, leading to an increased CL/PA 6 ratio in the amorphous phase due to the exclusion of CL from the crystalline PA 6 phase.

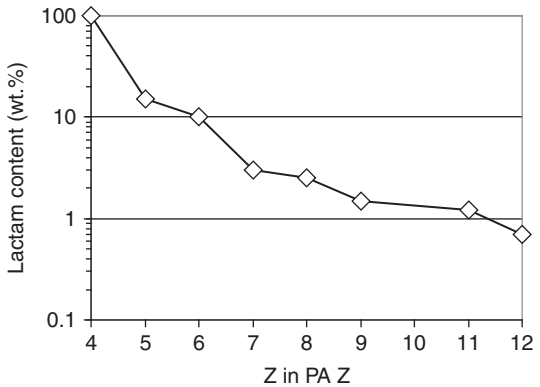

Figure 10 Relation between the number of carbon atoms in the amino acid of PAs such as PA *Z* and the equilibrium lactam content at $T = 280\,°C$ (line drawn to guide the eye). Data taken from Aharoni, S. M. *n-Nylons*; Wiley: Chichester, New York, Weinheim, Brisbane, Singapore, Toronto, 1997; p 357.[27]

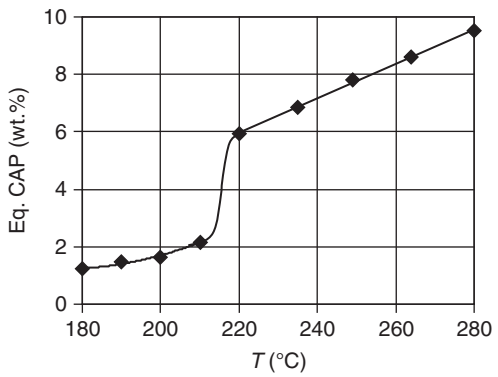

Figure 11 CL equilibrium content in PA 6 as a function of temperature. Data from Kohan, M. I. *Nylon Plastics Handbook*; Hanser Publishers: Munich, Vienna, New York, 1995; p 25.[2]

5.18.1.5 Side Reactions in Polyamide Synthesis

Important in the production and processing of PAs is the minimization of side reactions. Because conversions of typically >99% have to be obtained at high operating temperatures, the selectivity of the amidation reaction has to be very high. Most side reactions depend on the kind of monomers used but occur at higher rate constants if five- or

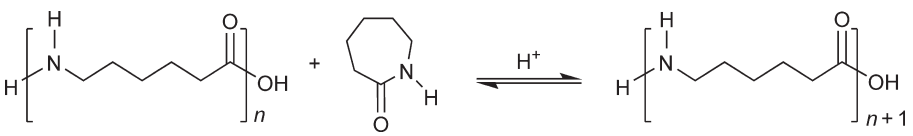

Figure 9 Polyaddition reaction and reverse backbiting reaction.

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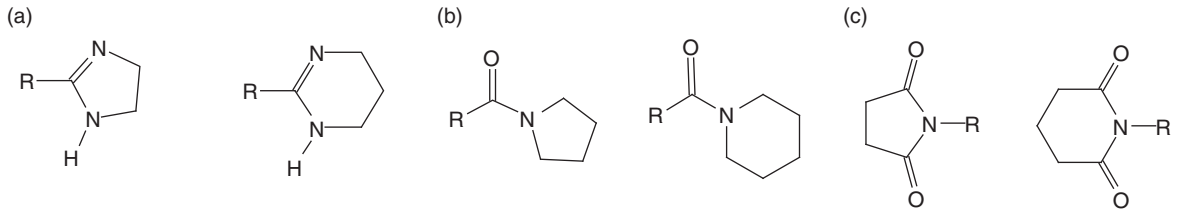

Figure 12 Five- and six-membered monofunctional cycles, formed due to side reactions of short diamines and dicarboxylic acids: (a) enamine or amidines; (b) PRD and piperidine; and (c) cyclic imides.

six-membered cycles can be formed. Thus, in case of short diamines ($X = 2–5$) and dicarboxylic acids ($Y = 4, 5$) monofunctional monomers shown in Figure 12 are formed, which act as a chain stopper. Enamine or amidine rings shown in Figure 12**(a)** are formed in case of very short diamines ($X = 2, 3$).

In case of short diamines ($X = 4, 5$), the cyclic monoamines pyrrolidine (PRD) and piperidine shown in Figure 12**(b)** are formed by cyclic amine condensation. They are reactive with RCO_2H and act as chain stoppers. Nevertheless, the side reaction of 1,4-diaminobutane (DAB) to PRD has not prohibited commercial introduction of polymers such as PA 46 and PA 410. Cyclic imides are formed for short-chain dicarboxylic acids ($Y = 4, 5$) shown in Figure 12**(c)**. Cyclopentanone is formed as a degradation product by an intramolecular Claisen condensation reaction mechanism from adipic acid, adipic acid-derived end groups, and also adipamides (Figure 13).

Cyclopentanone end groups can also form Schiff base structures according to Figure 14. As a follow-up of their polymerization model, Steppan *et al.*[29] reported a quantified model describing the thermal degradation reactions mentioned in Figures 13 and 14, quantified for PA 66, including other side reactions such as nitrile formation and amine condensation. The adipic acid-based degradation reactions explain the increase in NH_2 and decrease in CO_2H end groups at high temperatures. The Schiff bases generally can undergo further coupling reactions on the α-carbon of the CN functionality leading to branched structures. Ultimately, unsaturated heterocycles are formed, causing the thermal degradation-related discoloration. Schaffer *et al.* published an extensive review on the nonoxidative thermal degradation of PA 66[30,31] and later described a more detailed kinetic degradation model.

Of the intermolecular side reactions, amine condensation is the most known. It leads to triamines as shown in Figure 15 for the case of hexamethylenediamine (HMDA), leading to bis-hexamethylenetriamine.[32] The chemistry is similar to the cyclic condensation of DAB to PRD and is an important side reaction in the production and processing of semiaromatic PAs.[33] The condensation of trifunctional amines with the carboxylic acid groups leads to a broader molar mass distribution and implies an unwanted risk of gelation.

Side reactions in PAs can be enhanced by additives such as pigments. Of the unwanted reactions of PAs with other components, the oxidative degradation is the most important one. The principle of oxidation is described in Figure 16.[34,35]

The oxidation is initiated by radical formation $X^{\bullet}$. These radicals can react with oxygen to form hydroperoxides. The hydroperoxides can degrade to imides or hydroxyl amides, which are unstable components in the oxidation process and undergo chain cleavage. Two radicals can also undergo recombination to form an inert nonradical species.

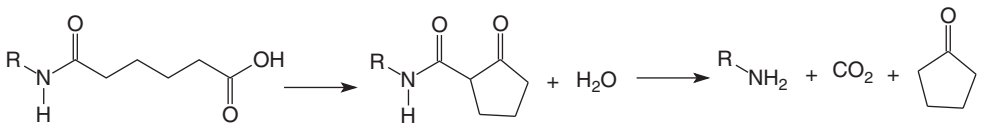

Figure 13 Reaction mechanism for the formation of cyclopentanone.

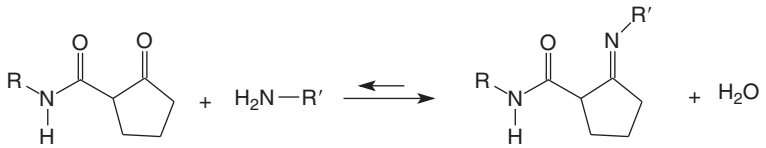

Figure 14 Schiff base formation from a cyclopentanone end groups and an amine.

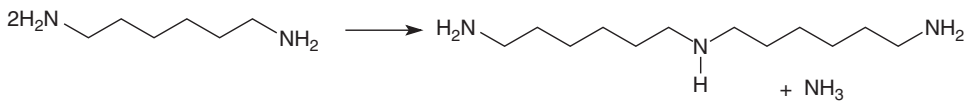

Figure 15 Dimerization of hexamethylene diamine furnishing bis-hexamethylenetriamine.

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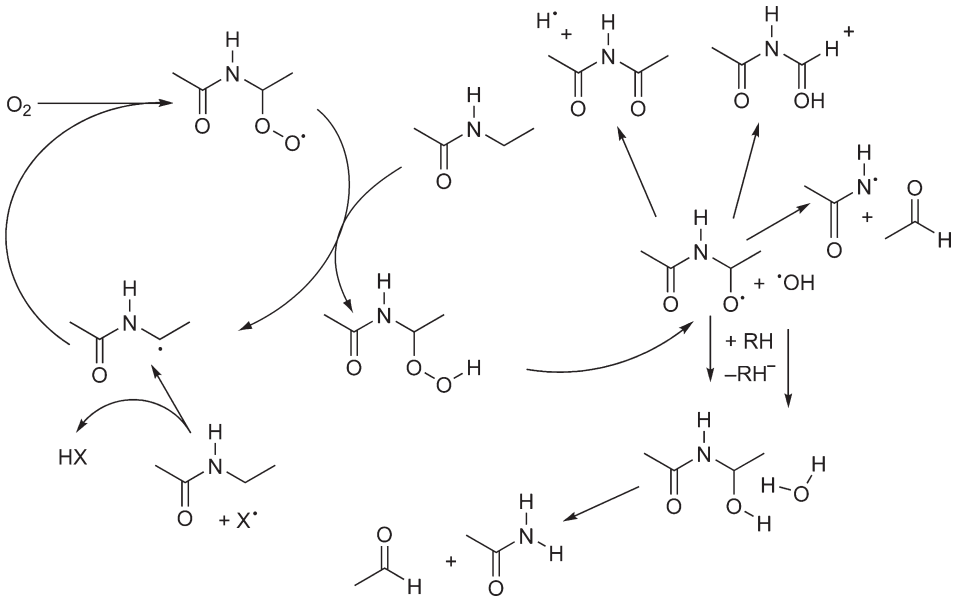

Figure 16 Basic oxidation mechanism for aliphatic PAs. Scheme based on Gijsman, P.; Tummers, D.; Janssen, K. *Polym. Deg. Stab.* **1995**, *49*, 121[34] and Dong, W.; Gijsman, P. *Polym. Deg. Stab.* **2010**, *95*, 1054.[35]

5.18.1.6 Molecular Mass, Molecular Mass Distribution, and Molecular Characterization of Polyamides

Because of the presence of multiple hydrogen bonds per molecule, PAs exhibit strong interchain interactions. This is the reason that the molar mass values of PAs do not need to be very high in order to obtain optimal thermal and mechanical properties. Typical M_n values of commercial PAs range from 12 000 to 40 000 g mol^{-1}, depending on the application. The advantage of the relatively low molar mass values in injection molding applications is that the melt viscosities of PAs are low and processing is relatively easy, even allowing the injection molding of, for example, thin-walled connectors for the electrical and electronics (E&E) industry using limited injection pressure to avoid damaging of the mold. Extrusion grades require higher molar mass values because of the needed shape resistance of the melt after exiting the extruder head. Especially in blow molding, this is important to prevent sagging of the extruded tubes. Often these grades also use PA compositions that show shear thinning behavior, accomplished by introduction of branching units.

For high conversions (degree of conversion of functional groups $p \approx 1$), the theoretical PDI, (PDI = M_w/M_n), for linear polymer having the so-called Flory distribution reaches a theoretical value of 2. If branching occurs during polymerization, the PDI does not follow the Flory distribution and values of higher than 2 are obtained. In case the PA is from an AB type, introducing a 2- or > 2-functional diamine or tricarboxylic acid will generate a star PA. These allow lower polydispersities than calculated according to the Flory distribution.[36]

It was already mentioned before that an SSPC step, during which the part of the PA present within the crystals is not participating in condensation and transamidation reactions, results in a broader distribution than 2, even for linear PA. Usually, the Flory distribution is regenerated after bringing the PA in the melt for a few minutes.

The molecular mass distribution (MMD) of a polymer is one of the most important molecular parameters, since the high-molecular-mass part determines mechanical properties, whereas the low-molecular-mass part assures good processability and flow. So, the determination of the entire MMD, and not just M_n or M_w, is desired for which size-exclusion chromatography (SEC) is the technique. Because of their highly crystalline character and strong interchain interactions, there are only few suitable solvents for PAs. *m*-Cresol is a solvent in which SEC of PAs could be performed at temperatures of 100 °C or higher,[37] and another possibility is the trifluoroacetylation of all amide bonds along the PA chain by reacting them with hexafluoroacetic anhydride, thereby making the modified PAs soluble in well-known SEC solvents such as tetrahydrofuran (THF) and chlorinated hydrocarbons.[38,39] Any contact of the trifluoroacetylated PAs with moisture should be prevented in order to avoid hydrolysis and inevitable precipitation of the polymers. Nowadays, a more popular, although toxic, solvent is 1,1,1,3,3,3-hexafluoroisopropanol (HFIP), in which usually a fluorine-containing lithium, sodium, or potassium salt (e.g., potassium trifluoroacetate, typically 3 g dm^{-3}) has been dissolved for breaking the hydrogen bonds and electrostatic interactions and enhancing the PA solubility. SEC gives not only the MMD of the polymer but also the monomer and higher cyclic oligomer content. Often poly (methyl methacrylate) (PMMA) standards are applied for SEC in HFIP, which generally results in a substantial error of the reported relative molar mass. More reliable values are obtained when using the principle of universal calibration[40,41] in combination with in-line intrinsic viscosity measurements or when coupling with light scattering detection is performed.

Frequently used techniques for the determination of the number-average molecular mass M_n of PAs are the measurement of the end-group concentrations by nuclear magnetic resonance (NMR) spectroscopy or by titration. By quantitative ^{1}H-NMR spectroscopy, the integrals of the $-CH_2-$ protons adjacent to

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the amine and carboxylic acid end groups are compared with the integrals of all the $-CH_2-$ protons present in the spectrum of the PA. In the titration techniques, the carboxylic acid and amine end groups are usually determined by potentiometric detection of the equivalence point of the PA dissolved in *m*- or *o*-cresol or benzyl alcohol. Besides the carboxylic and amino end groups, in case monofunctional monomers S are reacted with an end group, they are also present in the PA chain as end groups. The concentration of these S end groups is typically analyzed by hydrolysis, followed by high-performance liquid chromatography (HPLC). Assuming two end groups per PA chain, M_n is calculated from the reciprocal value of the sum of all end groups present in the PA as

$$M_n = \frac{2}{\sum([NH_2] + [CO_2H] + [S])} \quad [4]$$

Obviously, when M_n is determined by the above equation [4], cyclic oligomers are not taken into account. However, cyclics are taken into account with SEC measurements, which is the reason that M_n values determined by SEC usually differ from those determined by end-group determination.

Probably the most frequently used characterization technique for PAs is solution viscosimetry. Relative solution viscosities are usually determined at 1 wt.% and 25 °C in 90 wt.% formic acid or 96 wt.% sulfuric acid.

5.18.2 Hydrolytically Synthesized Fully Aliphatic Polyamides

5.18.2.1 Polyamide 6

5.18.2.1.1 Introduction

This section will focus on the hydrolytic production of PA 6. For other lactam polymerization techniques, such as the cationic or anionic ring-opening polymerization furnishing PA 6, the reader is referred to the corresponding chapter(s) in this comprehensive work.

Over 90% of the market of all commercially available PAs is covered by PA 6 and PA 66, which gives PA 6 a very prominent place within the engineering plastics and PA fibers. Although poly-ε-caproamide (PA 6) was already investigated by Gabriel and Mass at the University of Berlin in 1899, and although Carothers showed that the polymerization of ε-aminocaproic acid ($H_2N-(CH_2)_5-COOH$) resulted in a high-molecular-mass polymer upon heating, the real breakthrough was accomplished by Paul Schlack and his coworkers at I.G. Farben in Germany when they showed that the heating of CL above 180 °C in the presence of compounds having an active hydrogen, such as water, alcohol, or carboxylic acids, resulted in the formation of PA 6. Already in 1938, I.G. Farben spun PA 6 fibers.[42]

5.18.2.1.2 Commercial monomer production

The monomer CL can be made from cyclohexane, phenol, toluene, or recycled PA 6 feedstock. Six commercially applied routes are known and briefly introduced below, of which routes 1 and 2 mentioned below have significant commercial importance.[43] **Figure 17** shows the reactions of the two most relevant processes:

1. In the industrially most used process to CL, cyclohexane is oxidized to cyclohexanone, which subsequently by reaction with hydroxylamine (H_2NOH) is converted to the corresponding cyclohexane oxime, after which the oxime is transformed into CL in oleum (H_2SO_4, SO_3) by the so-called Beckmann rearrangement.
2. In the phenol-based process, the first step is hydrogenation to cyclohexanol, which is converted to cyclohexanone. Then, as described above, oximation and Beckmann rearrangement are performed.
3. In the second cyclohexane-based process, the photonitrosation process, cyclohexane is reacted directly with nitrosyl chloride (NOCl) and hydrogen chloride under UV irradiation ($\lambda < 600$ nm) with the formation of the cyclohexane oxime, after which again the Beckmann rearrangement is applied furnishing the CL.
4. In the toluene-based route, which has no commercial significance, toluene is first oxidized to benzoic acid (e.g., by oxygen in the presence of a cocatalyst), after which hydrogenation (H_2, Pd catalyst) produces the cyclohexane carboxylic acid. Then nitrosation with $NOHSO_4$ and Beckmann rearrangement are performed.
5. A fifth route, which was developed more recently but gained no commercial importance, can use both phenol and cyclohexane as the feedstock. After the generation of cyclohexanone from either of these starting materials (see routes 1 and 2), this ketone is converted into cyclohexanone oxime by reaction with H_2O_2 and NH_3 in the presence of titanium silicate catalyst. The final step concerns the Beckmann rearrangement to CL.
6. A sixth route to CL is by depolymerization of PA 6, developed and operated by a joint venture of DSM and AlliedSignal under the name ReCap® and now owned by Shaw Industries producing 11–16 kT/a recycle CL.[44] Typically, carpets are used for the recycling process in which shredding precedes the thermal depolymerization process.

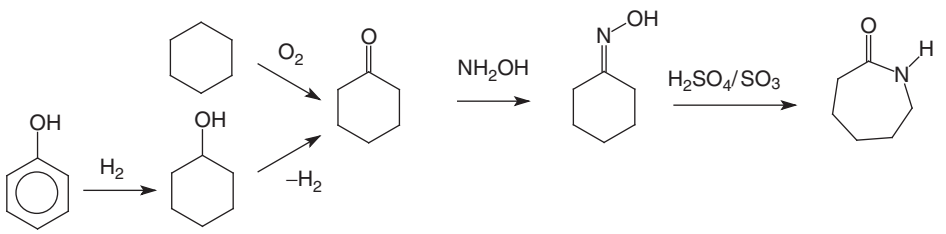

Figure 17 Reaction schemes of the two most relevant processes to produce CL.

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All described routes produce high-purity CL, suitable for the manufacturing of high-molecular-mass PA 6. Alternatives have not reached commercial scale. For example, DSM, working initially with DuPont and later with Shell, developed a process comprising 1,4-butadiene and carbon monoxide to produce CL without ammonium sulfate by-products. Named Altam™, the process employs four steps: carbonylation, hydroformylation, reductive amination, and cyclization. DSM claims cost reductions of 25–30%, simplified plant operations, and lower energy consumption.[45] Another promising alternative was intensively studied by, for example, BASF AG.[46,47] This process uses the HMDA intermediate adiponitrile, which can also be hydrogenated selectively on one of the nitrile functionalities to form 6-aminocapronitrile. This is converted to CL by hydrolyzing the nitrile functionality at temperatures of 300 °C and higher to form aminocaproic acid, which is converted to CL and partially to PA 6 oligomers with elimination of ammonia. Part of the CL is thus also obtained by depolymerization ('backbiting') of some formed PA 6 oligomers.

Basically, the synthesis of PA 6 from (ε)-CL (CL) is performed by a three-step bulk process, in which no organic solvent is involved. Initially, usually either solid or molten CL (of 80–85 °C) is mixed with a few wt.% water (typically 2–4 wt.%), which either at atmospheric or elevated pressure (see further) and at a temperature of up to 250–260 °C causes the hydrolysis or ring opening of part of the CL molecules (see **Figure 5**). This first hydrolysis step is very slow, reversible, and endothermic (reaction heat +7.9 to +18.0 kJ mol^{-1} according to References 48–51). The ring-opening reaction can be catalyzed by acids, typically benzoic acid, the presence of which also limits the molecular mass and melt viscosity and furthermore adjusts the amine/carboxylic acid end-group balance. This acid catalyst is not always added, but can also be provided as a mix of amine and acid end groups by backmixing of the reaction mixture in a continuous reactor. As soon as end groups are formed through hydrolysis, the amine groups react with the nucleophilic carbonyl groups of the CL molecules, which are ring opened and in fact are added to the initiating amine groups of the aminocaproic acid with the formation of dimers, trimers, and so on. This ring-opening polymerization reaction of CL (see **Figure 9**) is also catalyzed by acids, present in the reaction mixture as carboxylic acid end groups. This second polyaddition step in the PA 6 production is fast and exothermic (reaction heat −15.9 to −16.7 kJ mol^{-1} according to References 48–51) and continues at 250–260 °C until the CL concentration reaches its equilibrium concentration of typically about 10 wt.%. The maximum rate of conversion coincides with the maximum concentration of amine and acid end groups. The third reaction is the acid-catalyzed, step-growth condensation of amine and carboxylic acid end groups of different linear PA 6 chains to form high-molecular-mass PA 6 and water until reaching the equilibrium with the hydrolysis back-reaction. This polycondensation reaction, which occurs simultaneously with the ring-opening polymerization reaction of CL as soon as sufficient amine and carboxylic acid end groups are present (see **Figure 18**), is also exothermic and the reported reaction heat is −24.7 to −33.9 kJ mol^{-1}.[48–51] **Figure 18(a)** shows the development of the CL, amine, and carboxylic acid concentration with time for the hydrolytic polymerization of CL in the presence of 0.067 mol water. After ~ 6 h, the CL concentration has significantly decreased. The amine and carboxylic acid group concentrations have reached a maximum concentration, after

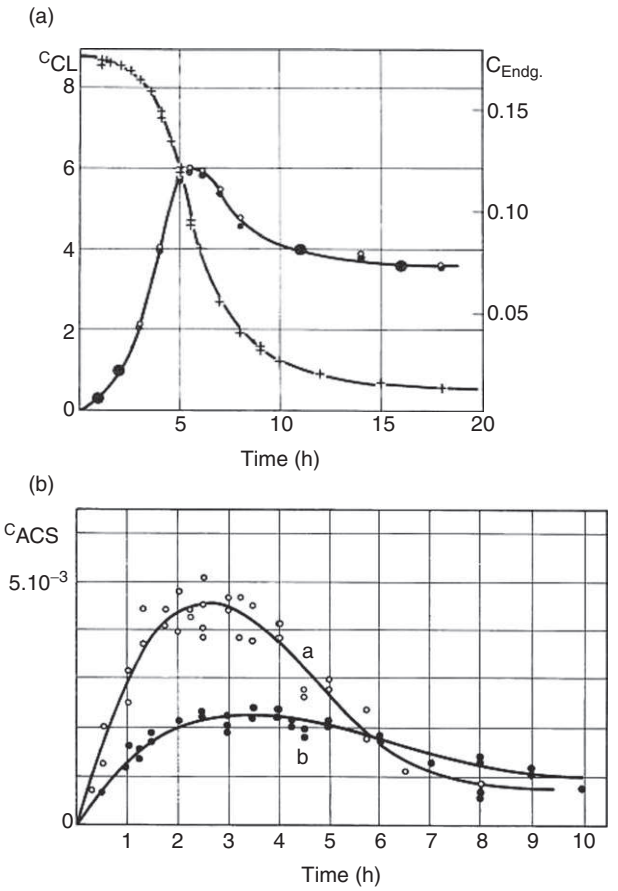

Figure 18 Experimental polymerization data of CL at 0.067 mol water mol^{-1} CL at a reaction temperature of 221.5 °C as a function of time in hours. (a) ○, CO_2H; •, NH_2 in mol kg^{-1} reaction mixture; +, CL content in mol kg^{-1}. (b) ○, aminocaproic acid (or 'aminocapronsaüre', abbreviated as ACS in the Figure) in mol kg^{-1} at H_2O/CL = 0.1 mol mol^{-1}; •, aminocaproic acid at H_2O/CL = 0.067 mol mol^{-1}. Reprinted from Hermans, P. H.; Heikens, D.; Van Velden, P. F. *J. Polym. Sci.* **1958**, *30*, 81,[52] with permission from Wiley.

which they decrease, indicating that the polycondensation reaction between amine and carboxylic acid becomes significant. The CL concentration decreases further by the polyaddition to amine end groups. **Figure 18(b)** shows the concentration of aminocaproic acid versus time in hours for two different water/CL ratios.

For the commercial PA 6 production, typically a 'one-step' VK (Vereinfacht Kontinuierlich) column or tube is frequently used, in which under atmospheric pressure the CL hydrolysis, the ring-opening polymerization, and the step-growth polymerization with water removal are performed, optionally in the presence of chain stoppers for controlling the melt viscosity (see **Figure 19**).[53] The polymer melt, leaving the reactor, is more or less at equilibrium with respect to the PA 6/water/CL/oligomer composition. Sometimes, a 'two-step' VK process is applied, in which the partial CL hydrolysis and the major part of the ring-opening polymerization are performed at elevated pressure (> 1.5 bar) in a first VK tube. This approach enhances the slow CL hydrolysis with respect to atmospheric hydrolysis. At the end of this first step, the PA 6 prepolymer of relatively low viscosity already contains the equilibrium amount of CL monomer. This prepolymer is then postcondensed in a second VK tube under reduced pressure for removal of the condensation water and for achieving the desired end viscosity. Of

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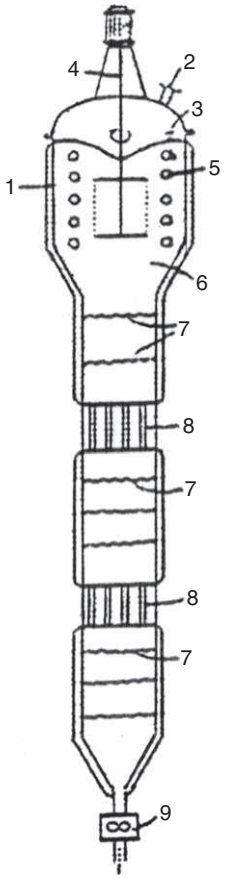

Figure 19 Schematic drawing of a typical 'VK tube' reactor for the commercial PA 6 production. 1, Cylindrical alloyed steel tube; 2, lactam inlet; 3, level control; 4, stirrer; 5, heating tubes; 6, stirring compartment; 7, flow regulation area; 8, heat exchange; 9, discharge of PA 6 melt into water bath. Reprinted with permission of Mr. Harry Rutten, DSM.

course, batch-type reactors are also commercially used,[42,53] but the more recently built polymerization units are usually of the continuous VK type. A batch process, usually found in older plants and suitable for making relatively small quantities of PA 6 specialties (e.g., PA 6 with a specific end-group balance, extremely high viscosity, with special additives or copolyamides), usually starts with the CL hydrolysis step and the CL ring-opening step in an autoclave at elevated pressure (~ 4.5 bar at 250–260 °C), after which the pressure is reduced and polycondensation is promoted by eliminating condensation water.

As in PA 11 and PA 12 (see Section 5.18.2.2), in the case of PA 6 also an equilibrium between high-molecular-mass polymer and low-molecular-mass polymer, mainly cyclic monomeric and cyclic dimeric components, exists at elevated temperatures. The formation of these cyclic compounds occurs by the so-called backbiting reaction explained in Section 5.18.1.4 (see **Figure 9**), implying the attack of amide groups relatively close to the polymer chain ends by the functional amine and/or carboxylic acid end groups. The presence of these low-molar-mass components or 'extractables' requires thorough washing of the PA 6 in order to remove at least 90% of the water-soluble CL together with cyclic oligomers. The CL, if present in end products, would act as a plasticizer and give rise to a sticky surface. So, after the polymerization, a PA strand is extruded from the reactor into a water bath, the polymer crystallizes, and the solidified strand is chopped into granules. These granules are fed to a washing column, in which the water-soluble CL is extracted during 18–24 h at 95–98 °C following the well-known countercurrent procedure and fed back into the production process. The wet granules are dried at 130–185 °C at atmospheric conditions applying a continuous inert gas flow in a moving bed drier or in a vacuum in a batch-operated tumble dryer. The required water content is typically below 0.1 wt.% to avoid hydrolysis and gas bubble formation during melt processing. During the drying procedure, a SSPC can be performed below the melting point of the PA 6 in order to raise the molecular mass further for obtaining high-viscosity grades for, for example, extrusion applications. After cooling and packaging, the granulated product granules are used in injection molding grades after compounding, or in films or fibers by extrusion processing.

It is possible to fully integrate the PA 6 production from CL and the melt-spinning process of PA fibers. An example of a flow scheme of such a fully integrated plant is presented in **Figure 20**. TiO_2 is often added as a matting agent in fiber-grade PA 6.

5.18.2.1.3 Branched PA 6

Several companies have recently commercialized branched PAs for nonfiber applications. A branched PA 6 exhibits better flow properties than do the corresponding fully linear counterparts of similar molecular mass, while the thermal and mechanical properties do not differ a lot. Branching may lead to a slight reduction in melting point and crystallinity, but on the other hand, transparency is enhanced. If the branched PA has a higher M_w than the corresponding linear PA, exhibiting a very similar melt flow, then the melt strength is enhanced, which is favorable for blow molding applications. Branching can be realized by copolymerizing CL or a 'nylon salt' with, for example, a trifunctional amine or carboxylic acid, such as bis-hexamethylenetriamine (the dimerization product of HMDA, see **Figure 15**) or trimellitic acid. The advantage of branched PA *Z* over branched PA *XY* is that in PA *Z* cross-linking is virtually impossible if only trifunctional monomers with one type of functional group are added because all PA molecules carry only one amine and one carboxylic acid end group. Thus, the resulting polymer has a star structure, which can result in a lower MMD. For a nonstar-branched structure based on a PA *Z*, besides a triamine, a dicarboxylic acid also has to be added, resulting in a broader MMD. The synthesis of branched PA *XY* requires the simultaneous presence of carefully dosed amounts of a (minimum trifunctional) branching agent and monofunctional chain stoppers in order to limit the risk of cross-linking.

5.18.2.1.4 Properties, applications, and trade names of PA 6

PA 6 is known for its high stiffness and strength in dry conditions, its high heat distortion temperature (HDT), its toughness, its excellent chemical resistance and electrical properties, its good abrasion resistance, its good processability, its high melting point of about 220 °C, and accordingly its retention of the mechanical and physical properties up to high temperatures. Drawbacks are the relatively high moisture absorption, which limits the dimensional stability, tensile

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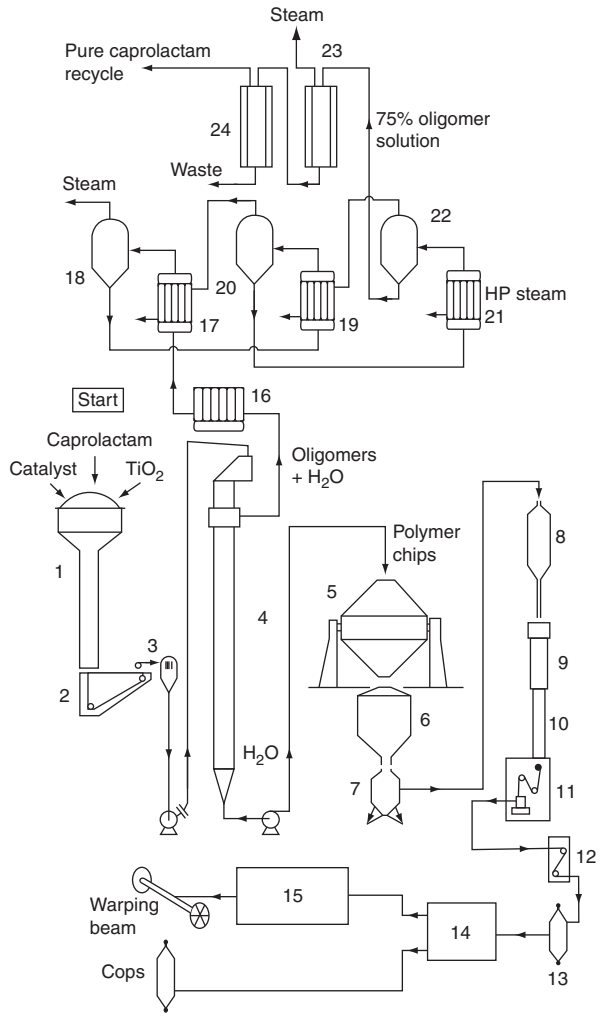

Figure 20 Hydrolytic polymerization of CL to PA 6, fully integrated with recycling of extracted CL and PA 6 melt-spinning process. 1, Polymerization; 2, cooling trough; 3, chips cutter; 4, oligomer extraction column; 5, chips drier; 6, chips storage hopper; 7, chips transport trolley; 8, spinning bunker; 9, melting grid; 10, chimney; 11, winding machine; 12, draw twist area; 13, chops; 14, inspection area; 15, warping area; 16, oligomer solution filter; 17, 19, 21, heat exchangers for triple evaporator system; 18, 20, 22, separators for triple-effect evaporator system; 23, 24, Double-effect failing film evaporator. Reprinted with permission of Mr. Harry Rutten, DSM.

strength, and stiffness in humid environment but, due to the plasticizing effect, enhances impact toughness due to the drop of the glass transition temperature. PA 6 compound and polymer grades are applied in the automotive, electrical, consumer, and other industries.

For fiber and film applications, usually unfilled PA 6 grades are applied, which can be finished with small amounts of additives such as nucleating agents or TiO_2 as matting agent. Melt-spun PA 6 fibers are applied for technical yarns, clothing, and carpet fibers. Extruded films find applications in food packaging. Injection molded products are usually reinforced with glass fibers (GFs) or minerals, and these composites are used for engineering plastics applications in the automotive and E&E industry.

Unfilled injection molding PA 6 applications that can be mentioned are gears, fittings, and bearings. For electrical applications, hinge plugs, on–off switches, bobbins, and rocker switches can be mentioned, all because of the good toughness and wear and heat resistance. Fuel tanks on power tools are made from PA 6 because of the high gasoline resistance. PA 6 monofilaments in, for example, weed trimmers have an excellent performance because of the good abrasion resistance. Blow-molded PA 6-based steering and brake fluid reservoirs are used because of the good chemical resistance and impact strength. Multilayered films containing PA 6 layers have excellent oxygen barrier properties and are very suitable for food packaging. Glass-filled or mineral-filled PA 6 has a dramatically increased stiffness, resistance to creep and fatigue, and a high continuous-use temperature, which makes these composites suitable for consumer applications such as housings for chain saws, drills, and other power tools, and for under-the-hood applications in the automotive sector or connectors in the E&E industry. Also exterior body parts for cars, such as grills, wheel covers, door handles, mirror shells, and even fenders are manufactured from PA 6 or its blends (see Section 5.18.5).

PA 6 is commercially produced by, among others, Honeywell Resins and Chemicals L.L.C. (Capron®), BASF (Ultramid B®), DSM (Akulon® and Novamid®), Toray (Amilan®), Ems (Grilon®), Ube Industries Ltd. (Ube Nylon), DuPont (Zytel®), Rhodia (Technyl®), Lanxess (Durethan®), Aquafil Technopolymers S.p.A. (Aquamid®), and Azoty Tarnów (Tarnamid®). Other producers are China Petrochemical Development Corp., Hua Lon Corporation, Li Peng Enterprise Co. Ltd., Xinhu Nylon, Tai Young Nylon Co. Ltd., Unitika Ltd., Inc., Grodno Khimvolokno, and Kuibyshev Azot.

5.18.2.2 Polyamides 11 and 12

5.18.2.2.1 Polyamide 11

While PA 6 and PA 66 have their roots in Germany and the United States, respectively, the industrial history of PA 11 started in France. After first results obtained by Carothers in 1931,[54] describing the polymerization of 11-aminoundecanoic acid, in 1938 a group of researchers under the leadership of Joseph Zeltner at the French company Société Organico started working on the synthesis of 11-aminoundecanoic acid from castor oil and its subsequent polymerization to PA 11. Nevertheless, commercial production of 11-aminoundecanoic acid and PA 11 started only in 1955.[55] Nowadays, Arkema in France is the only commercial producer of PA 11, which is sold under the trade name Rilsan®. The price is high in comparison with PA 6 and PA 66, which explains the relatively low market share of a few percentage. An important advantage of PA 11, however, is the fact that its monomer is fully based on biomass feedstock, which is moreover not competing with the food chain.

For the monomer production, as shown in **Figure 21**, in a first step, castor oil, which mainly consists of ricinoleic acid (80–95%), is subjected to methanolysis with the formation of methyl ricinoleate. In a second step, heptanal is eliminated from this ricinoleate at 550 °C with the formation of methyl 10-undecenoate, which is then hydrolyzed to the corresponding 10-undecenoic acid. Subsequent bromination leads to 11-bromoundecanoic acid, which in the last step is treated with aqueous ammonia to form 11-aminoundecanoic acid.[56]

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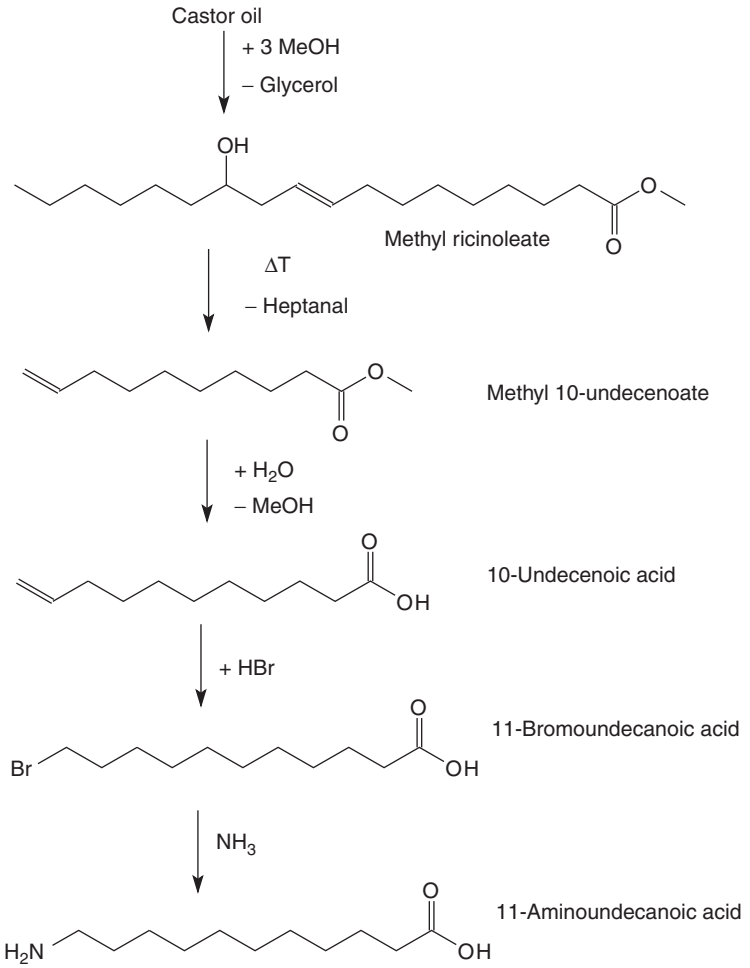

Figure 21 Reaction scheme of 11-aminoundecanoic acid production.

PA 11 is manufactured by the direct step-growth polycondensation of 11-aminoundecanoic acid. The reaction follows second-order reaction kinetics.[57] Notarbartolo[58] described a continuous process for PA 11 production. Usually, an aqueous suspension of 11-aminoundecanoic acid is charged into a continuous polymerization reactor under inert atmosphere, if desired in the presence of stabilizers and phosphoric acid or hypophosphorous acid as catalyst.[10] In Notarbartolo's process, water is removed from this suspension in the upper part of a polymerization column and the monomer is molten, initiating the formation of PA 11 oligomers. In the middle part of the column, in the second step, smaller amounts of condensation water are removed typically at ~20–30 °C above the melting point of PA 11 (T_m being ~188 °C, see Section 5.18.2.7), resulting in low-molecular-mass PA 11. Finally, in the third step, in the bottom part of the column, high-molecular-mass PA 11 is obtained by removing the last traces of condensation water and the polymer material is allowed to obtain a uniform MMD by giving it some residence time in the melt. The polymer can then be extruded into strands or fibers or granulated for injection molding applications. When very high-molecular-mass values are required for certain extrusion applications, SSPC can be performed between 140 and 160 °C, provided that both amine and carboxylic acid end groups are present in the amorphous parts of the granules. In the case of PA 6, ~10 wt.% of CL is formed at the polycondensation equilibrium at 280 °C, whereas in the case of the PA 11, synthesis at this temperature around 1 wt.% lactam is formed by backbiting reactions (see **Figure 10**), which make extraction of the polymer after synthesis superfluous. At lower temperatures, the amount of undecanolactam can even be less than 0.5 wt.%. Care should be taken when phosphorous catalysts are used, since phosphorus oxyacids could initiate branching of PA 11 if the polymer is kept in the melt for longer times.[10] As for other PAs, chain stoppers (mono- or difunctional acids or amines) can be used to control the molecular mass and melt viscosity.

5.18.2.2.2 Polyamide 12

The history of PA 12 started in the 1950s with the first synthesis of its precursor cyclododecatriene,[59] and after pilot plant-scale production in the early 1960s later in the same decade, full-scale industrial production was started.[60] Unlike PA 11, the monomer(s) for this polymer is based on fossil feedstock. PA 12, as expected based on the methylene/amide ratios of the corresponding repeat units, absorbs a slightly lower amount of water in comparison with PA 11, but its melting point is slightly lower than that of PA 11. The lower T_m is due to not only the lower amide density but also the 'odd–even' effect

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(see Section 5.18.2.7.2). Most other properties of PA 11 and PA 12 are quite comparable (see Sections 5.18.2.7 and 5.18.2.8).

For the commercial synthesis of PA 12, unlike for the manufacturing of PA 11, either the monomer ω-aminododecanoic acid or the corresponding lactam, laurolactam or 12-dodecanolactam, is used. The lactam is commercially prepared in at least two different ways. Both routes start with the trimerization of the cheap, petrochemistry-based raw material butadiene using titanium-, chromium-, or nickel-based catalysts. In both routes, the resulting cyclododecatriene is subsequently hydrogenated to cyclododecane. In the Elf Atochem (now Arkema) process, this cyclododecane is then reacted with nitrosyl chloride under light with the formation of cyclododecane oxime,[61] which is then converted into the laurolactam by a Beckmann rearrangement in heated H_2SO_4. In the process of Emser Chemie and Hüls[62] (now Evonik), the cyclododecane is oxidized to cyclododecanone, which is subsequently converted to cyclododecanone oxime by reaction with hydroxylamine sulfate in the presence of NaOH. The oxime is then converted into the laurolactam as described above. The commercial PA 12 production from ω-aminododecanoic acid is performed by Ube Industries in Japan. Here cyclohexanone is the starting chemical and it requires several reaction steps to form the 12-aminododecanoic acid: $H_2N–(CH_2)_{11}–COOH$.[60]

The polymerization of 12-aminododecanoic acid is very similar to the polymerization of ω-aminoundecanoic acid (see earlier). The advantage of using the amino acid instead of the laurolactam, especially for continuous processes, is that the very slow ring opening of laurolactam with water can be omitted.

In a patent assigned to Ube Industries, a large-scale hydrolytic polymerization of laurolactam is described.[63] The recipe in the patent consists of three stages. In the first stage, a preheated mixture of liquid laurolactam and 1–10 wt.% water is continuously fed to the top of a polymerization column, which is set at 300 °C, a temperature required to speed up the slow hydrolytic opening of (part of) the lactam (note: 270–290 °C is sufficient to open the laurolactam hydrolytically).[64] As a consequence, this step is performed under a pressure of 16–20 bar. Further down the column, the temperature is reduced to 250 °C, where laurolactam ring-opening polymerization and some polycondensation are continued under autogenous pressure. The lactam conversion reached in the column is 99.5 wt.% or even higher, which implies that PA 12, unlike PA 6, does not require extraction to remove residual monomer. Even at a slightly higher temperature of 280 °C, the amount of lactam present in the polymerization equilibrium is only 0.7 wt.% (see Figure 10). After the prepolymerization step, the polymer melt is transferred to a second reactor (250–270 °C) in which the pressure is released and condensation water is removed with further molecular mass increase under atmospheric pressure. Here, phosphoric acid can be used as a polymerization catalyst. After being pumped into the third reactor (245–265 °C), containing a heavy rotor with mixing elements causing a quick surface renewal, the polymer melt is stirred under an inert gas stream under atmospheric or even reduced pressure (20 kPa), resulting in the removal of the last traces of reaction water and in final molecular mass buildup. The conditions for the Inventa process are very similar.[65] The hydrolytic polymerization of laurolactam follows the same principle as CL polymerization in Figures 5 and 9, but the lactam hydrolysis and the polyaddition occur much slower due to the absence of ring strain in the laurolactam.[66] Polymerization times of at least 20 h are mentioned in literature.[67] For the acidolytic and aminolytic polymerization of laurolactam at 260–280 °C, Elias and Fritz used 1 mol.% lauric acid as catalyst.[68] Kralicek *et al.*[69] used 2 mol.% 12-aminododecanoic acid as catalyst and reported polymerization times of up to 200 h at 270 °C or 100 h at 310 °C in nitrogen-purged and subsequently evacuated vessels. In this way, number-average molecular mass values (M_n) of ~18 000 g mol^{-1} (310 °C)–36 000 g mol^{-1} (270 °C) were obtained. The required long-melt polymerization times for manufacturing high-molecular-mass PA 12 may cause degradation and discoloration, and also result in high costs. Therefore, sometimes the last step in molecular mass buildup is performed by SSPC of intermediate-molecular-mass PA 12 granules in vacuum or in a stream of inert gas just below T_m (140–160 °C). After this SSPC, the polymer does not exhibit a Flory distribution, but after a quick melting step, the MMD already approaches such a distribution.[70]

5.18.2.2.3 Applications and trade names of PA 11 and PA 12

Both PA 11 and PA 12 are suitable for extrusion and injection molding applications. The lower moisture absorption of PA 11 and PA 12 compared to PA 6 and PA 66 results in a better dimensional stability. Also the low-temperature toughness of PA 11 and PA 12 is superb with respect to that of PA 6 and PA 66. Furthermore, PA 11 and PA 12 exhibit an excellent chemical (e.g., metal salt and hydrocarbons) and tear resistance, a low density, good thermal and weathering stability, and an excellent processing behavior. These properties are responsible for their commercial success in spite of the fact that the price is significantly higher than that of PA 6 and PA 66. Nevertheless, the market volumes of PA 11 and PA 12 are small.

Applications that can be mentioned are air brake tubings for heavy trucks, hoses, automotive fuel systems, pipes for the offshore petroleum production industry, natural gas distribution networks, food packaging, precision moldings for engineering uses and pump parts, fuel-resistant quick connectors, bearings for windshield wiper arms and other car parts, medical articles and monofilaments for screen fabrics and bristles, sports articles (e.g., ski boots), and (after mixing with carbon black or carbon fibers) antistatic housings for electrical switches, lamps, or mining equipment.

For PA 11, the only manufacturer is Arkema (Rilsan B®). For PA 12, four manufacturers exist, namely Evonik (Vestamid®), Ems-Chemie (Grilamid®), Ube Industries Ltd. (Ube Nylon 12®), and Arkema (Rilsan® A).

5.18.2.3 Polyamide 66

5.18.2.3.1 Introduction

PA 66 is the first commercial man-made PA and was developed and patented by DuPont in 1937.[71] PA 66 and PA 6 account for about 90% of the market of all PAs, although the volume share of PA 66 is larger in the United States than in the rest of the world.[72] The synthesis of PA 66 has been studied extensively and several good overviews have appeared describing its currently applied industrial production processes.[73,74]

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5.18.2.3.2 Monomer production

PA 66 consists of the residues of the monomers HMDA and adipic acid. HMDA is currently produced as shown in Figure 22 by Michael addition of HCN to butadiene to form adiponitrile. The adiponitrile is hydrogenated using Co catalysts at a H_2 pressure of 280–410 bar and a temperature of 100–200 °C in the presence of NH_3.[75–77]

Originally, adiponitrile was produced by DuPont by reacting adipic acid with NH_3 in the gas or the liquid phase as shown in Figure 23. The diamide was converted to dinitrile by dehydration.

Adipic acid is produced by oxidation of cyclohexanol and/or cyclohexanone using HNO_3 catalyst together with homogeneous Cu- or V-based catalysts to avoid further oxidation of the adipic acid.[78] As an intermediate, α-nitronitrosocyclohexanone is formed, which is split into adiponitrolic acid and hydrolyzed to adipic acid. Due to the high generated amounts of the greenhouse gas N_2O as by-product, the carbon footprint of adipic acid is high. The option is to isolate the N_2O and use it for further chemical production processes or react it with N_2.[79] Adipic acid (A) and HMDA (H) are mixed to form an aqueous solution of 66 or AH salt with a concentration of 50–62 wt.%.

5.18.2.3.3 Polymerization

PA 66 is introduced as nylon by DuPont in unfilled molded products in 1943 (nylon resins)[80] and in fibers in 1938.[81] In a typical technical PA 66 grade, 2 wt.% of cyclic oligomers of up to three repeat units is contained.[82] Especially, the cyclic diamide can potentially cause problems by unwanted sublimation during processing in, for example, film extrusion. In some cases, the product is extracted for this reason.[83]

Figure 24 shows a generalized phase diagram of the production process of PA 66. In the beginning, when the salt is concentrated, the 66 salt crystallization line (C) determines the minimum pressure at which the solution should be evaporated. The process entirely takes place below the steam pressure line (leftmost line in Figure 24) due to the boiling point elevation of the 66 salt. With increasing salt concentration, the boiling temperature of the salt increases at equal pressure due to the increasing boiling point elevation. This is

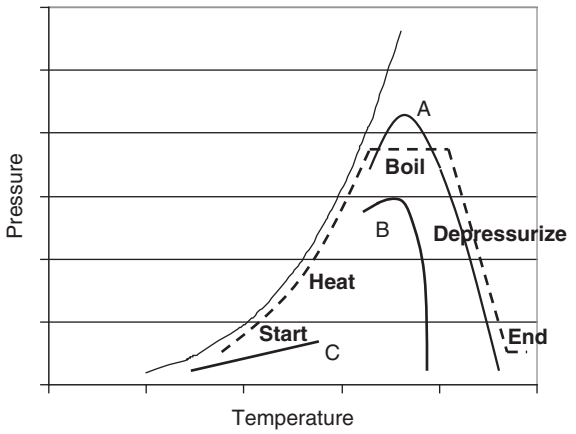

Figure 24 Generalized phase diagram of a PA 66 process with the PA 66 crystallization line (B), the PA 66 melt line (A), and the 66 salt crystallization line (C). The thin line indicates the steam line. Taken from Augstkalns, V. A. In *Nylon Plastics Handbook*; Kohan M. I., Ed.; Hanser Publishers: Munich, Vienna, New York, 1995; Section 5.18.2.3.1, pp 17–23,[84] with slight adaptations.

represented by the horizontal part in Figure 24. When the salt starts to convert to oligomers, the 66 salt crystallization line (C) will shift downward and then at sufficiently high conversion, the melting line (A) of PA 66 becomes relevant. At higher steam pressures, the melting point is lowered by the water content, acting as a plasticizer. At lower conversion, the melting point is also lowered due to the large amount of end groups present. Thus, the process can be safely operated even slightly below the melting line of the polymer due to the low conversion. However, generally the crystallization line of PA 66 (B) should not be crossed.

A typical batch melt polymerization cycle is shown in Figure 25. Typically, the initial salt concentration in water is about 55 wt.%. The water is evaporated off at higher pressures. When the majority of the water has been removed, the pressure is slowly dropped, while the temperature of the melt is slowly increased and kept about 20 °C above the melting point, ending at 280 °C at atmospheric conditions. Six hours after starting

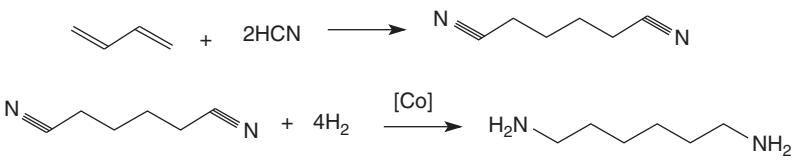

Figure 22 Reaction scheme of HMDA production from butadiene and HCN.

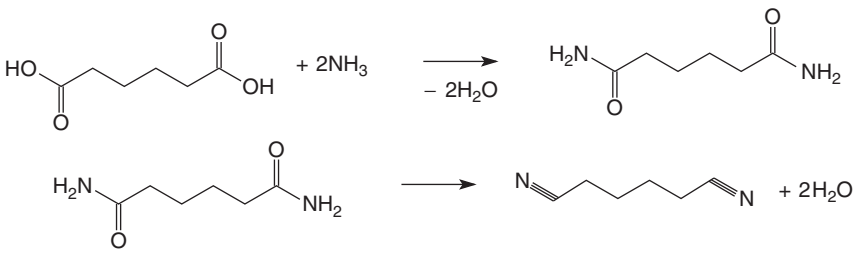

Figure 23 Reaction scheme of HMDA production from adipic acid.

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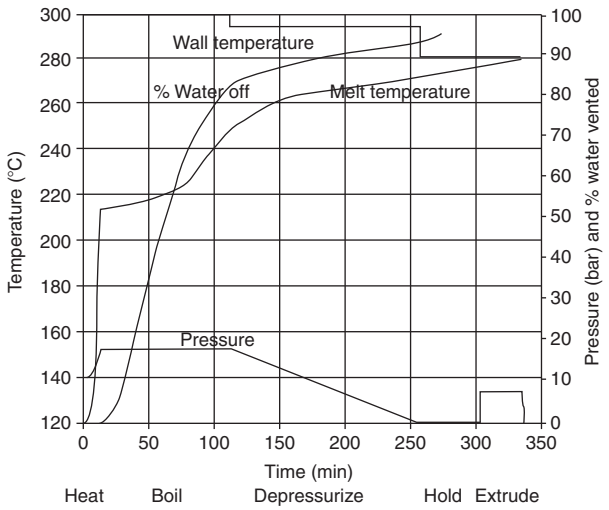

Figure 25 Typical PA 66 batch melt polymerization cycle. Reproduced from Augstkalns, V. A. In *Nylon Plastics Handbook*; Kohan M. I., Ed.; Hanser Publishers: Munich, Vienna, New York, 1995; Section 5.18.2.3.1, pp 17–23,[84] with permission from Hanser Publishers.

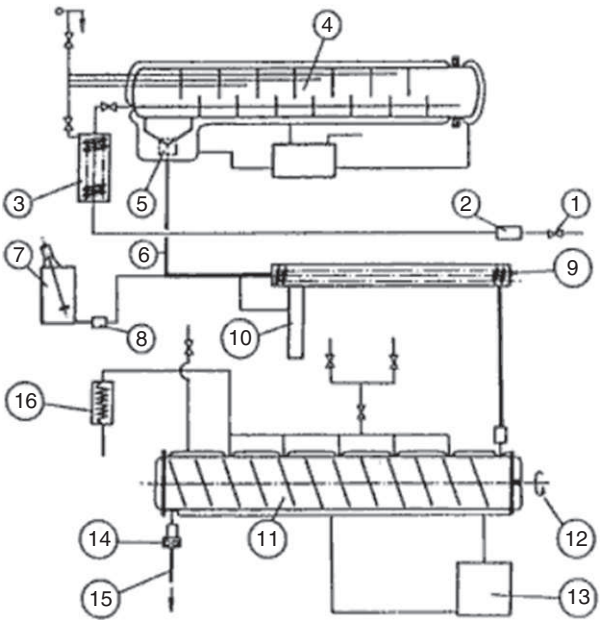

Figure 26 Flow diagram of a continuous PA 66 polycondensation process. 1, Entrance of 66 salt; 2, pump; 3, preheater (106–>208 °C); 4, reactor (235 °C); 5, extrusion pump; 7, TiO_2 tank; 8, mixer for TiO_2; 9, flasher (290 °C, atmospheric); 10, Dow condensate; 11, finisher (275 °C, atmospheric); 12, finisher screw drive; 13, Dow condensate; 14, extrusion pump (275 °C); 15, to extrusion or spinning. Adapted from Fourné, F. *Synthetic Fibers Handbook*; Hanser Publishers: Munich, Vienna, New York, 1999; p 61,[85] with permission from Hanser Publishers.

the heating of the salt solution, the polymerization is completed. The polymer is pressed out of the reactor by 5–8 bar N_2 pressure. The strands exiting the reactor are cooled and granulated. The polymerization temperature should be kept at a minimal level to minimize side reactions described in Section 5.18.1.5, such as bis-hexamethylenetriamine (**Figure 15**) and cyclopentanone (**Figure 13**) formation. These side reactions result in branching and even gelation.

In a continuous melt polymerization process, the batch process is essentially duplicated. A process flow diagram is shown in **Figure 26**. As for the batch polymerization, it is crucial to limit the loss of the volatile diamine and to minimize side reactions. The process is described in more detail in the *Nylon Plastics Handbook*.[84]

5.18.2.3.4 Applications and trade names of PA 66

PA 66 is valued for its combination of high thermal and mechanical properties. It has a melting point of 265 °C, which makes it the highest melting aliphatic PA after PA 46 (see Section 5.18.2.4). The melting point is ~40 °C above the highest melting PA 6 grades. The water uptake when saturated in water at room temperature until reaching equilibrium according to ISO 1110 is relatively high, that is, 8–9 wt.%, but it is still lower than that of PA 6 (10 wt.%) and PA 46 (13 wt.%).[86] The water uptake can be reduced by mixing the PA 66 or the PA 6 with hydrophobic additives. These are typically bisphenols,[87] trisphenols,[88] and polyphenols,[89] which allow a 30% reduction in the water uptake. The phenol groups block the accessibility of the amide for water by forming a stronger hydrogen bond (33 kJ mol^{-1}).

The high-temperature stability makes PA 66 suitable for industrial yarns, for example, air bags and in radial tires and for under-the-hood automotive applications. Specific applications are intake manifolds, engine covers, gears, and so on. Also mirror houses and door handles are made from PA 66.

The most important PA 66 manufacturers are DuPont (Zytel®), Invista, BASF AG (Ultramid® A), DSM (Akulon® S), Rhodia (Technyl®), and Ascent Performance Materials (Vydyne®).

5.18.2.4 Polyamide 46

PA 46 was first synthesized by Carothers[90] but was commercialized only in 1990 by DSM under the name Stanyl® after the implementation of several significant improvements in the initially developed preparation method suggested by Gaymans *et al.*[91] Melt polymerization from its PA salt results only in low-molecular-mass and discolored polymers.[91,92] This is due to the cyclization of DAB to PRD (**Figure 27**), which is a chain stopper in PA synthesis.

The cyclization of DAB is a first-order process starting from its protonated form, the $-NH_3^+$ group being a good leaving group. The formed PRD can react with a carboxylic group to form a terminal amide.

High-molecular-mass polymers could be obtained by preparing a prepolymer from its PA salt in the presence of some water at 210 °C and 1.5×10^6 Pa and postcondensing this semicrystalline prepolymer with an M_n of ~1000 g mol^{-1} in the solid state.[93] In this process, free PRD is removed together with PRD formed by release of part of the terminal PRD groups,

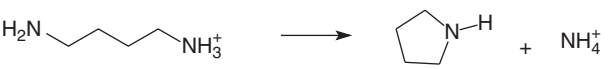

Figure 27 Acid-catalyzed PRD formation from DAB.

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which is generated through an aminolysis reaction. In the preparation of PA 46, an excess of DAB compensates the loss of diamine due to PRD formation. In the commercial production process, the intermediate aqueous prepolymer solution is released from the pressure vessel by flashing to atmospheric conditions, resulting in a fine powder with a water content between 2 and 15 wt.%. The powder is compacted into pellets below 100 °C to increase the density and avoid fluidization in the subsequent SSPC process.[94] The SSPC is performed in a moving bed reactor at temperatures up to 40 °C below the melting point in an atmosphere containing 20–50 wt.% water vapor.[93]

The DAB needed in the production of Stanyl is produced by DSM from acrylonitrile and HCN by Michael addition, followed by a catalytic hydrogenation of the formed succinonitrile.[95]

PA 46 is the highest melting commercially available aliphatic PA with a melting point of 295 °C. In fact, PA 46 can show a wide variety of melting points, that is, from 283 to 319 °C.[91] As shown in Figure 28, according to the Hoffman–Weeks relationship, T_m relates with the lamellar thickness (l) of the crystalline phase ranging from 3.6 to 5.9 nm.[96]

Compared to other commercial PAs, PA 46 has unique morphological properties, such as the possibility to crystallize in an oblique and normal form besides the usual α and β structures, as known for other PAs such as PA 66, and the presence of amide bonds in the chain folds of the lamellae.[97,98] Another special property of PA 46 is its very fast crystallization from the melt, as shown in Figure 29, where the peak temperature of the cooling exotherm is plotted against the crystallization rate for different cooling rates. The crystallization rate was determined from the width at half height of the crystallization curve.

The high crystallization rate originates from the highly symmetric chain structure together with the high number of nuclei that remain during melt processing. The fast crystallization allows extremely short injection molding cycle times.

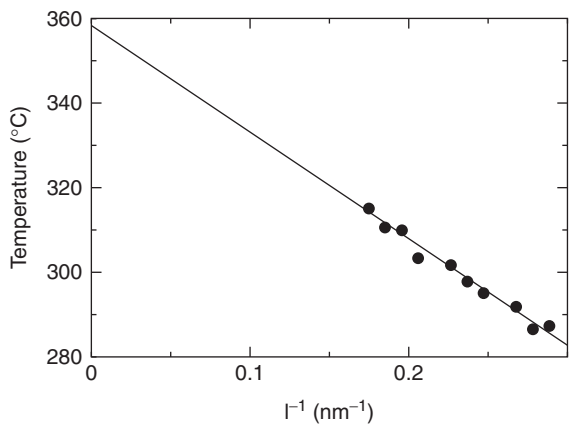

Figure 28 Variation of the melting point of PA 46 in relation to the reciprocal crystal thickness l^{-1} according to the Hoffman–Weeks relationship. Samples produced by variation of crystallization time at 270 °C. Reprinted from Yamanobe, T.; Kurihara, Y.; Uehara, H.; Komoto, T. *J. Mol. Struct.* **2007**, *829*, 80,[96] with permission from Elsevier.

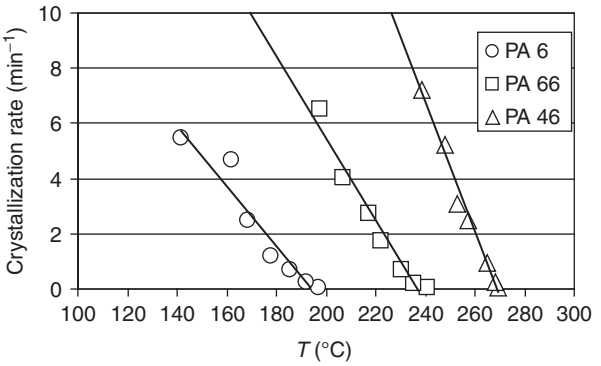

Figure 29 Rate of crystallization as a function of the crystallization temperature for PA 46 in comparison with PA 66 and PA 6. Data taken from Eltink, S. In *Kunststoff Handbuch 3/4 Polyamide*; Becker, G. W., Braun, D., Eds.; Hanser: München/Wien, 1998; p 576.[99]

5.18.2.4.1 Applications and trade names of PA 46

The basic advantages of PA 46 versus PA 6 and PA 66 (higher melting temperature, higher crystallinity, and higher crystallization speed) proved themselves in a multitude of successful applications, such as the following:

- E&E, for example, so-called surface-mounted device (SMD) components, where PA 46 resists the high soldering temperatures, contrary to PA 6 and PA 66
- Automotive applications, for example, chain tensioners in which the high crystallinity results in excellent wear and fatigue behavior
- Technical uses, such as gear wheels and bearings in which the combination of temperature, oil, and chemical resistance, low friction, and wear of PA 46 corresponds to the customer requirements.

In its applications, PA 46, with DSM as the single worldwide manufacturer (Stanyl®), competes with other high heat-resistant resins such as polyphenylenesulfide (PPS), polyetherimide (PEI), polyethersulfone (PES), liquid crystalline polyesters (LCPs), and semiaromatic PAs (PPAs). The water uptake of PA 46 is higher than that of other PAs (see Section 5.18.2.8) because of the high amide density. Since this affects the dimensional stability, in critical applications already during the design of end products, this should be taken into account. The favorable processing characteristics (good melt flow, no tool corrosion, and very short cycle times) contribute to the growing market acceptance of PA 46.

5.18.2.5 Polyamides 69, 410, 610, and 612

Besides PA 6 and PA 66, there is also a demand for more hydrophobic PAs *XY*, which are discussed in this chapter. The reason why they received more interest is that all of these PAs, except for PA 612, are based on nonedible biorenewable feedstock. The increasing demand in society and industry for enhanced sustainability is a strong driver for the development of new polymers from renewable feedstock, preferably not in competition with the food chain. Castor oil is a nonedible oil and the castor oil plant (*Ricinus communis*) grows on poor soil with minimal use of fertilizers and herbicides and insecticides.

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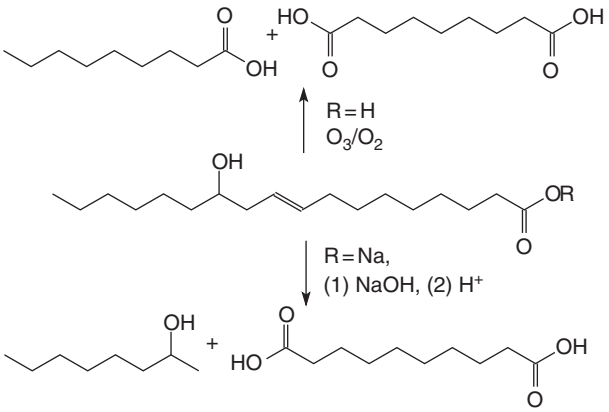

Figure 30 Overall reaction for the synthesis of azelaic acid (top) and sebacic acid (bottom) from ricinoleic acid.

Of the castor oil-derived monomers, especially sebacic acid ($Y = 10$) is a very promising monomer for the development of new polyesters and PAs (see **Figure 30**).

Thanks to the commercialization of PA 66, larger quantities of HMDA were available on the market. This enabled the development of other HMDA-based PAs and, although PA 69 has been commercially available, the two most important HMDA-based PAs in addition to PA 66 are PA 610 and PA 612. The synthesis of HMDA has been described in Section 5.18.2.3.

The condensation product of HMDA and azelaic acid, derived from the natural oleic acid by ozonolysis (**Figure 30**), is PA 69.[100] For the manufacturing of azelaic acid (containing seven methylenes) and sebacic acid (eight methylenes), the ricinoleic fatty acid component of the castor oil is cleaved in aqueous sodium hydroxide at 240–300 °C at elevated steam pressure according to the overall reaction given in **Figure 30**.[101,102]

So, for both PA 69 and PA 610, the dicarboxylic monomer residue is derived from renewable resources, which gives these polymers a green image. Recently, three other PAs that are based on sebacic acid and the sebacic acid-derived 1,10-decanediamine have been commercially introduced. PA 410 was developed by DSM (see further) and this company launched this 'bio-based' engineering plastic as EcoPaXX®, opening opportunities to utilize renewable resources.[103]

The nonbio-based hydrophobic PA *XY*, PA 612, is based on 1,12-dodecanedioic acid. It is derived from the petrochemistry-based cyclododecatriene, the trimerization product of butadiene. In Section 5.18.2.2, where the synthesis of PA 11 is discussed, it was stated that this cyclododecatriene is oxidized to cyclododecanone. In fact, this oxidation step results in a mixture of cyclododecanone and cyclododecanol, which is directly transformed into the desired dodecanedioic acid by ring-opening oxidation with concentrated HNO_3 (60%).[104]

The synthesis of PAs 69, 610, and 612 is performed in a way very similar to that of PA 66. Since the solubilities of the 'nylon salts' 69, 610, and 612 are lower than those of the 66 salt, the starting and handling nylon salt concentrations are somewhat lower, but the PA synthesis is typically performed in a batch operation in very similar equipment as described for the industrial production of PA 66 (see Section 5.18.2.3). The concentrated salt solution is prepolymerized in a closed reactor at 220–230 °C for 1–3 h.[105] This step is necessary in order to keep the stoichiometry and to prevent the loss of the relatively volatile diamine during the later melt condensation with removal of water. Subsequently, the water is removed by evaporation, and at the end an inert gas is led over the reacting polymer melt at 230–250 °C to remove water continuously. SSPC can be performed typically above 150 °C for high-molecular-mass grades used for extrusion applications.

Already in 1999, DSM reported the synthesis and thermal and mechanical properties of PA 410.[106] The PA 410 was synthesized following the 'Stanyl recipe' (see Section 5.18.2.4), implying a prepolymerization of the 410 'nylon salt' in water to a prepolymer with a M_n of 1000–1500 g mol^{-1}, followed by flashing of water and by a SSPC step at ~35 °C below the T_m, furnishing PA 410 with an M_n of 17 000–18 000 g mol^{-1}. Interestingly, DAB is also found in nature as putrescine, just like the 1,5-diaminopentane (cadaverine). So, basically PA 410 and PA 510 could be 100% renewable PAs, PA 410 having a higher melting point than PA 510, not only because of the lower CH_2/amide ratio but also because of the 'odd–even' effect observed for the series of linear aliphatic PAs (see Section 5.18.2.7.2).

As thermal, physical, and mechanical properties of PAs are directly related to the amide bond density along the PA chain, it is not surprising that melting points and mechanical properties of PAs 69, 410, 610, and 612 are located in between those of PA 6 and PA 66 on the one hand and PA 11 and PA 12 on the other hand. Main properties are summarized in Sections 5.18.2.7 and 5.18.2.8. This implies relatively low moisture absorption, good dimensional stability, good tensile properties, and high toughness. For example, PA 69 has a melting point of ~210 °C, a moderate crystallinity, and mechanical properties in between the properties of PA 66 on the one hand and PA 610 and 612 on the other hand. PA 410 exhibits a high melting point of 249 °C, a high crystallization rate from the melt enabling high productivity with respect to PA 6 and PA 66, a moisture uptake significantly lower than that of PA 6 and PA 66, excellent tensile properties, even after conditioning at 23 °C and 50% RH, and an excellent resistance against chemicals and hydrolysis as well as against aqueous zinc chloride and calcium chloride ('road salt'). For other properties, see Sections 5.18.2.7 and 5.18.2.8.

5.18.2.5.1 Applications and trade names of PAs 69, 410, 610, and 612

The typical applications of PAs 69, 610, and 612 are bushings, cams, electrical connectors, industrial parts, bristles, tubings, rods, profiles, sheet applications, and extruded monofilaments for bristles for, for example, toothbrushes. For this application, especially PA 610 and 612 outperform PA 6 and PA 66, and even PA 11 and PA 12, with respect to improved bend recovery and higher resistance against deformation under load in wet environment. The combination of stiffness, abrasion resistance, low moisture absorption, good dimensional stability, and good chemical resistance enables the manufacturing of precision injection molding parts for the automotive and E&E industries. The aqueous $ZnCl_2$ and $CaCl_2$ resistance regarding environmental stress cracking, important in winter time due to salt spray on roads, is much better than that of PA 6 and PA 66. Pipes made from PA 612 are stiffer and accordingly have a higher resistance against burst compared to pipes made from

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PA 11 and PA 12, which on the other hand outperform pipes made from PA 612 with respect to cold impact strength. PA 612 exhibits a somewhat better chemical resistance against fuel and lower oxygen permeability in comparison with PA 11 and PA 12. PA 410 is highly suitable for various demanding applications, for instance, in the automotive and electrical markets.

Until recently, Solutia manufactured PA 69 with the trade name Vydyne®. The main producers of commercial PA 610 are BASF AG (Ultramid S®), Rhodia (Special Technyl® grades), and the Toray Resin Company (Amilan®). PA 612 is commercially produced by DuPont (Zytel® 150 series) and by Evonik (Vestamid® D series). DSM recently launched PA 410 as EcoPaXX®.

5.18.2.6 Other Aliphatic Polyamides and Copolyamides

5.18.2.6.1 Introduction

In view of the commercial availability of numerous aliphatic diamines (from 1,2-ethylene diamine through 1,12-dodecanediamine up to C36 dimer fatty acid-based diamines) and dicarboxylic acids (from oxalic acid through 1,12-dodecanedioic acid up to dimer fatty acid-based dicarboxylic acids), the list of possible commercial fully aliphatic PAs is huge. The most important aliphatic PAs *Z* (PA 6, 11, and 12) and PAs *XY* (46, 66, 69, 610, and 612) have already been discussed earlier in this chapter. In this section, we will not give an overview of all fully aliphatic PAs that have ever been synthesized in industry and in the academic world, but we will rather restrict ourselves to the commercial aliphatic (co)polyamides PAs 1010, 1212, 66/6, 46/6, and 236.

5.18.2.6.2 Polyamide 1010

Evonik introduced a hydrophobic bio-based PA based on decanediamine and sebacic acid, called Vestamid® Terra DS. It can be used for cable jacketing, for example, in optical fibers, in tooth brush bristles, and in dish washers as a thermoplastic powder coating material due to its low moisture uptake and excellent resistance against hydrolysis.[107]

5.18.2.6.3 Polyamide 1212

Until 1991, PA 1212 was commercially manufactured by DuPont, that is, by step-growth polymerization of 1,12-dodecanediamine and 1,12-dodecanedioic acid. Properties, processing characteristics, and also applications of PA 1212 are very similar to those of PA 11 and PA 12. The T_m is ~ 185 °C. The low water solubility of the 1212 salt requires handling at high pressure and temperature for the first prepolymerization step. For the polycondensation step, both batch and continuous reactors can be applied.

5.18.2.6.4 Polyamide-based hot-melt adhesives (PA 236)

PA-based thermoplastic or hot-melt adhesives are often based on dimer fatty acid and ethylenediamine.[108] Normally, other comonomers such as HMDA, dimer fatty diamine, polyetherdiamines, and/or piperazine are added. The piperazine forms good bonds with polyvinylchloride, resulting in good adhesion. The secondary amide can act only as proton acceptor and does not form hydrogen bonds within the PA but forms H bridges with the hydrogen atom adjacent to the chlorine.[109] The homopolymer has a melting point of 103 °C.[110]

5.18.2.6.5 PA 66-based copolyamides (PA 66/6 and others)

For distinct applications, PA 66 is copolymerized. Reasons are increasing the processing window by lowering the melting point and reducing the crystallization speed and crystallinity, which leads to increased gloss and surface quality of GF-reinforced compounds. For the manufacturing of random copolyamides, usually hydrolytic polymerization of lactams with amino acids, diamines, dicarboxylic acids, or nylon salts is performed. The monomers are mixed with water and homogenized under pressure. The remaining procedure is very similar as described for PA 66, and initially added water and condensation water are removed, first with pressure retention and later optionally under reduced pressure to achieve the desired viscosity.

The copolymerization of 66 salt with CL results in PA 66/6 (excess 66 salt) or PA 6/66 (excess CL) copolyamides with higher solubility, a lower stiffness, and a lower melting point compared to pure PA 66. The copolyamides have a better stretchability, lower processing temperatures, higher transparency, higher elongation at break, more flexibility, a higher toughness, and a better surface quality. Applications of PA 66/6 are injection molded articles, films, fibers, and melt adhesives.[111] Several PA-manufacturing companies such as Rhodia (Technyl® B series) and BASF (Ultramid® C series) sell copolyamides PA 6/66 or PA 66/6, containing different ratios of CL and 66 salt. The formulation of the PA 6/66 copolyamide is claimed to provide enhanced flowability in injection molding and higher clarity in film extrusion applications. To mention one example, Ultramid® C33 01 is an intermediate-viscosity PA 66/6 grade. Its lower melting point than that of standard PA 66 (243 vs. 265 °C) is advantageous for coextrusion with temperature-sensitive polymers such as ethylene vinyl alcohol (EVOH). Typical applications include multilayer film, monofilaments, and nonsymmetric blown film with reduced curl.[112]

Figure 31 shows the melting point of PA 6/66 copolyamides. Melting points of copolymers can be calculated according to the Flory theory of polymer dilution (eqn [5]):

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{\Delta H_m} \ln N_A \qquad [5]$$

In eqn [5], T_m is the melting point of the copolyamide, T_m^0 is the melting point of the homopolyamide, R is the gas constant, ΔH_m is the heat of fusion, and N_A is the mole fraction of the major constituent. Calculated melting points are indicated in Figure 31 by the solid lines.

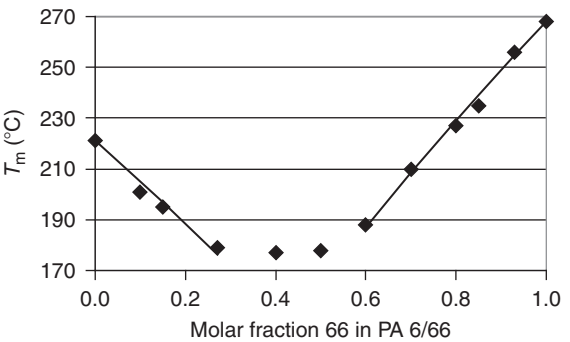

Figure 31 Melting point of PA 6/66 copolyamides. Melting points from Harvey, E. D.; Hybart, F. J. *J. Appl. Polym. Sci.* **1970**, *14*, 2133.[113] The lines indicate calculated melting points according to Flory's principle of polymer dilution.

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Invista markets 2-methylpentamethylenediamine (MPMD), a side product in the HMDA production, under the name DYTEK® A. It can be used for the production of PA 66/MPMD 6 copolyamides for fiber applications.[114] Recently, the development of a PA 66/6T copolyamide with about 25 mol.% 6T units was mentioned in patents with the claimed advantage of increased thermo-oxidative stability for automotive applications.[115]

5.18.2.6.6 PA 46-based copolyamides (PA 46/6)

Another aliphatic copolyamide that is commercially available is PA 46/6 (95/5), a special Stanyl® fiber grade (KS411) produced on small scale by DSM. The homopolyamide PA 46 with its very high melting point (295 °C) and very rapid crystallization from the melt is less suitable for fiber spinning. For every mass percentage CL incorporated into PA 46, the T_m is reduced by ~1.5 °C. The reduction of the melting point increases the processing window for fiber spinning and the random incorporation of CL disturbs the chain regularity, thereby retarding the crystallization from the melt, which is also favorable for melt spinning. Moreover, the incorporation of CL improves the stretching of the fibers. The copolyamide is suitable for industrial fiber applications such as yarns for timing belts, sewing threads for air bags, and wear-resistant textiles.

Table 2 Fully aliphatic PAs, their respective monomers, and their second heating (dry as molded) melting points

Aliphatic PA	*Monomer(s)*	T_m (°C)
6	CL	223
11	11-Aminoundecanoic acid	188
12	Laurolactam	179
66	Hexamethylene diamine/adipic acid	265
69	Hexamethylene diamine/azelaic acid	210
610	Hexamethylene diamine/sebacic acid	223
612	Hexamethylene diamine/1,12-dodecanedioic acid	212
46	Tetramethylenediamine/adipic acid	295
48	Tetramethylenediamine/suberic acid	262
49	Tetramethylenediamine/azelaic acid	244
410	Tetramethylenediamine/sebacic acid	249
412	Tetramethylenediamine/1,12-dodecanedioic acid	238
1212	1,12-Dodecanediamine/1,12-dodecanedioic acid	185

Data for PA 6/PA 46 and for PA 1212 from Rapra review reports, Report 121, *Polyamides as Engineering Thermoplastic Materials*, by I.B. Page, I. B., Vol. 11, 1, 2000 (ISSN: 0889–3144).[116] Data for PA 48/PA 412 from Koning, C.; Teuwen, L.; De Jong, R.; et al. *High Perf. Polym.* **1999**, *11*, 387.[117]

5.18.2.7 Thermal Properties of Fully Aliphatic Homopolyamides

5.18.2.7.1 General rules for the relation between chain structure and melting point

Almost all PAs with a sufficiently regular chain structure render semicrystalline materials. The melting points of PAs are much higher than those of the corresponding semicrystalline, aliphatic polyesters. For comparison, the aliphatic polyester polycaprolactone (PCL) exhibits a T_m of ~60 °C, whereas the T_m of the corresponding polycaprolactam, or PA 6, is ~223 °C. The only difference in the repeat units is the presence of either an ester or an amide group between two $[-(CH_2)_5-]$ sequences. The amide moiety contains both a hydrogen bond donor (the NH) and a hydrogen bond acceptor (the C=O), which enhance the interchain interaction and, more importantly, reduce the gain in entropy upon melting of the PA, since the hydrogen bonds are still existing in the melt, which limits the gain in chain mobility and entropy upon melting (note: $T_m = \Delta H_m/\Delta S_m$). In addition, the PA 6 chains are stiffer due to the semi-double bond character of the amide bond (see Figure 3), which reduces ΔS_m even more. This explains the very significant difference in the T_m values of PCL and PA 6. If all-aliphatic PAs are compared mutually, then one has to realize that all polymers of both the PA *Z* or the PA *XY* type exhibit a low ΔS_m value, and differences in melting points are directly related to differences in interchain interactions, which are stronger for PAs with a higher amide bond density along the chain and accordingly a higher chain polarity. For aliphatic PAs, the chain polarity is sometimes indicated by the ratio of the number of methylene units per repeat unit to the number of amide bonds per repeat unit. So, PA 6 has a methylene/amide ratio of 5/1 = 5, PA 6/12 has a ratio of (6+10)/2 = 8, and PA 12 has a ratio of 11/1 = 11. The general rule is the higher the methylene/amide ratio, the lower the melting point, but this is just a rule of thumb and fine-tuning of this general statement is necessary (see further). Nevertheless, as shown in Table 2, within the series PA 6, PA 11, and PA 12, the melting point decreases with increasing methylene/amide ratio. The same is true for the series for which the number of carbons in the dicarboxylic acid *Y* is increased from 6 to 12 in PA 4*Y* and PA 6*Y*. Currently, PA 46 is the commercially available all-aliphatic PA with the lowest methylene/amide ratio and accordingly the highest melting point, that is, 295 °C. The (once commercially available) PA *XY* with the lowest amide bond density and the lowest melting point is most probably PA 1212 (T_m = 185 °C). PA 12, commercially available and with a methylene/amide ratio equal to that of PA 1212, has an even lower melting point (T_m = 179 °C).

5.18.2.7.2 Fine-tuning of the rule of thumb for the relation between chain structure and T_m

5.18.2.7.2(i) The 'odd–even' effect in the melting points of aliphatic polyamides

Upon a closer examination of the melting points listed in Table 2, some exceptions to the general rule of thumb can be noticed. In spite of their lower amide bond density, PA 610 and PA 612 exhibit a higher melting point than do the more polar PA 69. The same is observed when PA 49 and PA 410 are compared, with the PA 410 having a higher methylene/amide ratio but also a higher T_m. Also for amino acid-based PAs such as PA *Z*, this phenomenon is observed, and was reported by Aharoni.[118] Aharoni shows that, for example, PA 7 has a higher T_m than does PA 6, that PA 9 has a higher T_m than does PA 8, and that PA 11 has a higher T_m than does PA 10. One should keep in mind that in the series PA *Z*, the odd-numbered PAs have an even number of methylene groups in their repeat unit (e.g., PA 6 has five methylene groups in the repeat unit, whereas PA 7 has six). So, PAs such as PA *Z* and PA *XY* with an even, respectively even–even, number of methylenes have a higher melting point compared to PAs with an odd, respectively even–odd, number of methylenes in the diamine or in the dicarboxylic acid residue, a phenomenon that is illustrated in Figure 32 for PAs from diamines and dicarboxylic acids PA *XY*.[119]

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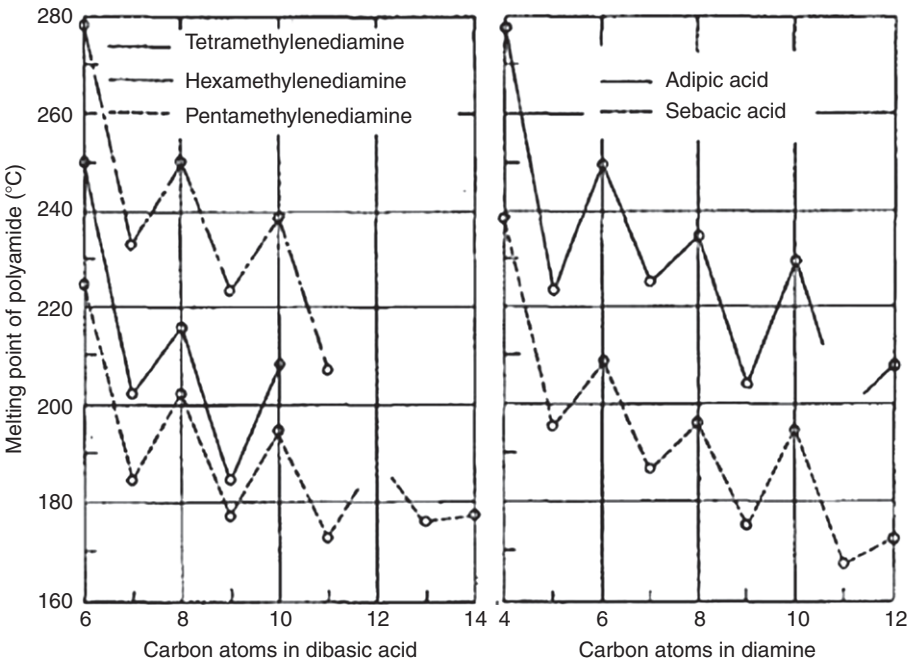

Figure 32 Illustration of the odd–even effect in the melting points of aliphatic PAs. Left: Even number of carbon atoms in diamines, odd or even number of carbon atoms in dicarboxylic acid. Right: Even number of carbon atoms in dicarboxylic acid, odd or even number of carbon atoms in diamine. Reprinted from Coffman, D. D.; Berchet, G. J.; Peterson, W. R.; Spanagel, E. W. *J. Polym. Sci.* **1947, *2***, 306,[119] with permission from Wiley.

The explanation for this phenomenon is not entirely the same for PA *Z* and PA *XY*. For PA *Z*, the macromolecules are nonsymmetric and the chains have a directional orientation. The amide is always oriented in the same direction along the backbone and following the main chain in one direction, all amide bonds in the chain have, for example, their nitrogen on the left and their carbonyl on the right side of the amide bond (e.g., in (…$(CH_2)_{z-1}$–NH–CO–$(CH_2)_{z-1}$–NH–CO for PA *Z*)). If all chains are oriented in the same way, all with the NH on the left side of all amide bonds and the CO on the right side, then the orientation is called 'parallel'. If on the other hand, two neighboring chains have a different orientation, one like (…$(CH_2)_{x-1}$–NH–CO–$(CH_2)_{x-1}$–NH–CO… for PA *Z*) and the other one like (…$(CH_2)_{x-1}$–CO–NH–$(CH_2)_{x-1}$–CO–NH…), then the orientation is defined as 'antiparallel'. The antiparallel orientation is naturally occurring during adjacent reentry folding of PA chains during crystallization into lamellae, and the parallel orientation is frequently found in chain-extended crystals formed during melt spinning. These different orientations are illustrated in Figure 33 for PA 6 and PA 7. For PA 7, with an even number of methylene groups in the repeat unit, irrespective of the orientation of two neighboring chains, all possible hydrogen bonds can be formed without any problem. On the other hand, for PA 6, only when the two neighboring chains have an antiparallel orientation, all H bonds can be formed and only then the most stable α-form crystals can be formed. In the parallel orientation, complete H-bond formation is possible only if the chains are severely distorted, which is the case if the chains crystallize in the so-called γ-form. The lack of complete hydrogen bonding in the case of the PAs with an odd number of methylenes in the repeat unit is responsible for the observed lower melting point, in spite of a higher amide bond density.

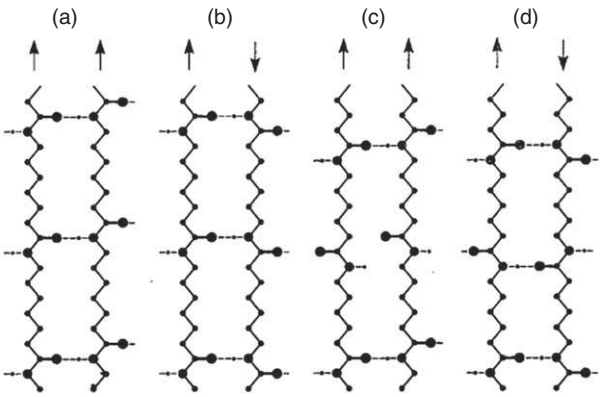

Figure 33 In the case of PA 7 (a and b), both the parallel (a) and the antiparallel (b) orientations result in complete hydrogen bonding. In the case of PA 6, only the antiparallel orientation (d) gives complete H bonding, whereas the parallel orientation gives incomplete H bonding (c). The latter causes a lowering of the melting point. Figure taken from Aharoni, S. M. *n-Nylons*; Wiley: Chichester, New York, Weinheim, Brisbane, Singapore, Toronto, 1997; Chapter 1.3,[118] and reprinted with permission from Wiley.

In the case of PA *XY*, one cannot define a parallel or an antiparallel orientation of the chains, since the chains are symmetric and there is no fixed direction of the NH–CO unit. If in every pair of amide neighbors within one chain, one amide has the NH on the right side, then the neighbor has the NH on the left side, and vice versa (see, e.g., (…$(CH_2)_y$–CO–NH–$(CH_2)_x$–NH–CO…) and (…$(CH_2)_x$–NH–CO–$(CH_2)_y$–CO–NH…)). The explanation for the lower melting points of PA *XY* with an odd number of methylenes either in the diamine or in the

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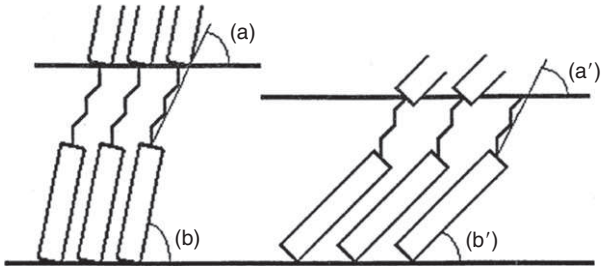

Figure 34 Schematic illustration of odd–even effect in PA *XY*. Left: Even number of methylenes results in more efficient packing and higher T_m. Right: Odd number of methylenes gives less efficient packing and lower T_m.

dicarboxylic acid residue is a less efficient packing of these PA molecules and accordingly a lower crystal perfection with respect to the more straight even–even PA *XY*. This results in lower melting points and is illustrated in Figure 34.

5.18.2.7.2(ii) The influence of the way of chain folding during crystallization on melting points

Now, let us compare PA 412 with PA 610. In spite of the same methylene/amide ratio in the repeat unit ((4+10)/2 = 7 for PA 412 and (6+8)/2 = 7 for PA 610), and in spite of the fact that both PAs are even–even PAs such as PA *XY*, a significant difference in melting points of 15 °C is observed (see also Reference 117). Although this phenomenon has not been entirely understood yet, it is believed that it is related to the different ways a PA chain folds during crystallization into lamellae. Atkins *et al.*[98] showed that PA 46 folds with an amide bond in the fold. The four methylenes in both the diamine and the dicarboxylic acid residue do not allow a fold in these aliphatic chain parts and at the same time allow the formation of the first hydrogen bond closest to the fold. There is just too much strain in such a fold. On the other hand, Koenig *et al.*[120] showed that in order to obtain complete hydrogen bonding, PA 66 folds only in the diamine residue, exhibiting six methylene groups. The dicarboxylic acid residues with four methylenes are not participating in the chain-folding process for the aforementioned reasons, whereas a sequence of minimum six methylenes allows the formation of a fold with hydrogen bonding at the end of the fold without too much strain. Translating these results to PA 412 and PA 610, PA 412 can make large folds only in the dicarboxylic acid residue, whereas PA 610 will make smaller folds in both the diamine and the dicarboxylic acid residues. This difference, most probably related to different entropy values of the crystals,[117,121] could be responsible for the observed difference.

5.18.2.7.3 The Brill transition

Upon cooling them down from the melt or from solution without too much shear, PAs crystallize by chain folding in the form of chain-folded, hydrogen-bonded sheets with a single molecular layer thickness, the so-called β-sheets, which are stacked together by van der Waals forces with formation of crystalline lamellae. This stacking can occur in a progressive way, implying an incremental displacement of the β-sheets with the formation of the α-crystal structure, or in an alternating way, implying a staggered displacement of the β-sheets with the formation of the so-called β-phase. The distance between the chains within the H-bonded β-sheets is called the interchain distance, and the distance between the stacked sheets is called the intersheet distance. So, hydrogen bonds exist only within the sheets and not between the sheets. This is illustrated in Figure 35.

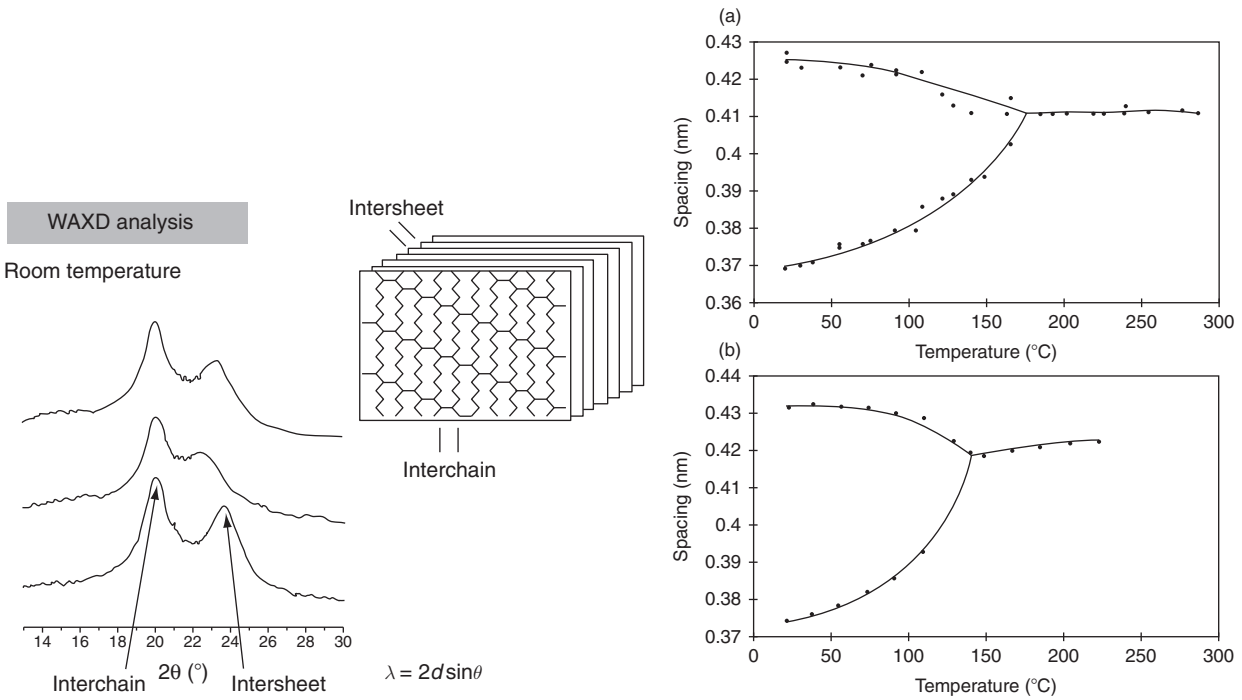

Figure 35 Part of powder diffractogram of a fully aliphatic PA *XY*, showing the interchain and the intersheet reflections (a) and plots of intersheet and interchain spacings versus temperature for PA 44 (upper plot in b) and PA 124 (lower plot in b), showing the Brill transition temperatures at which both spacings merge. Figure b is reproduced from Jones, N. A.; Atkins, E. D. T.; Hill, M. J.; *et al. Macromolecules* **1996**, *29*, 6011,[122] with permission from ACS Publications.

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The interchain and intersheet distances give rise to two pronounced reflections in a wide-angle X-ray diffractogram. The interchain distance is the larger one (typically 0.428–0.436 nm for PAs 44, 64, 84, 104, 124, and 66),[122] since the hydrogen bonds push the chains away from each other, and therefore this reflection is usually found as the peak at the lowest 2θ value, whereas the shorter intersheet distance (typically 0.367–0.375 nm for PAs 44, 64, 84, 104, 124, and 66) gives rise to the reflection at the higher 2θ value.[122] When aliphatic PAs are slightly heated up from room temperature, already at 50 °C, the interchain and intersheet reflections significantly shift toward each other, and from the so-called 'Brill' temperature, the interchain distance within a hydrogen-bonded β-sheet and intersheet distance between the β-sheets become equal to result in one single 'Brill' spacing with one reflection. This is illustrated in Figure 35(b). For PAs 44, 64, 84, 104, 124, and 66, this Brill spacing is ~0.420 nm.[122]At the Brill transition, a solid-state crystalline transition, the triclinic crystal structure of the PAs is converted to a 'pseudo-hexagonal' crystal structure.[123] According to some researchers, and in agreement with Brill's ideas, the formation of the 'pseudo-hexagonal' phase causes a partial rearrangement of hydrogen bonds from intrasheet to intersheet H bonds, and it was even proposed that amide groups flip out of the β-sheets by 60° or even 120° in order to be able to form these intersheet H bonds.[124] Other groups, however, are convinced that the hydrogen bonds do not show any rearrangement below, at and even above the Brill transition,[125] sometimes not even up to the melting point.[126] More recently, it was proposed that the origin of the Brill transition is conformational disorder in the main PA chain. During the transition, the hydrogen bonds between the amide groups are maintained but the methylene sequences are disordered and start rotating, thereby pushing the nonhydrogen-bonded sheets further away from each other until the inter- and intrasheet distances have become the same.[127] The value of the Brill transition temperature depends on the molecular structure of the PA and on the crystallization conditions.[128]

5.18.2.7.4 Glass transition temperatures and thermal stability of fully aliphatic polyamides

Since T_g values are directly determined by chain stiffness and polarity, it will be no surprise that the T_g values of linear aliphatic PAs decrease with an increasing methylene/amide ratio in the repeat unit. In dry conditions, the T_g values vary from ~78 °C for PA 46 to ~50 °C for PA 12. Upon conditioning in a humid atmosphere, because of the high moisture absorption, the T_g of PA 46 may drop to below room temperature, whereas for PA 12, still ~45 °C is measured. The nonpolar PA 12 absorbs only low amounts of the plasticizing water.

Above temperatures around 330–340 °C, the aliphatic PAs usually start showing thermal degradation. Usually, melt processing of PAs takes place at ~30–50 °C above the melting point, and so most fully aliphatic PAs can be melt processed below 300 °C. PA 46 is the exception with a T_m of 295 °C. This polymer requires processing temperatures of ~320–330 °C, but for relatively short residence times in the melt (< 10–15 min), this is no problem.

5.18.2.8 Other Properties of Fully Aliphatic Polyamides

5.18.2.8.1 Mechanical properties

For the most frequently used and studied PAs, the most important mechanical properties are listed in Table 3. Like the melting point and glass transition temperature, mechanical properties are also directly related to the methylene/amide ratio of the repeat unit. A lower (CH_2)/NHCO ratio renders a higher polarity, a higher amide group density, and stronger interchain interactions, which is, for example, reflected in higher density, strength, and stiffness. With some exceptions, a higher (CH_2)/NHCO ratio renders less strong interchain interactions, lower stiffness but a higher toughness. Mechanical properties are directly determined by the molecular mass, which makes a fair comparison not always easy.

For injection molding applications, PAs are usually reinforced with GFs. This raises the tensile properties enormously. The addition of 30 wt.% GF to neat PA 46 raises the tensile strength at 23 °C from 100 to 210 MPa, the tensile modulus increases from 3.3 to 10.5 GPa, and the HDT at 1.8 MPa load is enhanced from 160 to 290 °C. On the other hand, the elongation at break is reduced from 40% to 4%. For PA 66 filled with 30 wt.% GF, the corresponding data are 180 MPa, 10.0 GPa, 250 °C, and 3%, respectively. For PA 46 filled with 50 wt.% GF, the tensile strength is even 230 MPa, the tensile modulus is 16.8 GPa, and the elongation at break is 2%. This latter

Table 3 Mechanical properties, density, and moisture absorption of fully aliphatic, unfilled PAs. Measured dry as molded at 23 °C and 50% RH

Polyamide	*Density ($g\,cm^{-3}$) ASTM D792*	*Tensile strength (MPa) ASTM D638*	*Tensile modulus (GPa) ASTM D638*	*Flexural modulus (GPa) ASTM D790*	*Elongation at break (%) ASTM D 638*	*Izod impact strength ($kJ\,m^{-2}$) ASTM D256*	*Moisture absorption (wt.%) ISO 1110*
6	1.13	70–78*	2.8–3.0*	2.2	15–80*	45–65	10
11	1.03	38	1.4	1.2	250	100	1.9
12	1.02	45	1.4		200	50–200	1.5
66	1.14	85–88*	3.0–3.4*	2.8	5–40*	40–60	8.5
69	1.08	70			50	35	4.5
610	1.07	55–66*	2.1–2.5*		37*70	50	3.3
612	1.06	61–63*	2.1–2.6*	2.3	7*–10	50	2.7
46	1.18	100	3.3	3.0	40**	10	13
410	1.10*	82*	3.2*		10*		
412	1.08*	67*	2.7*		31*		

Data taken from Rapra review reports, Report 121, *Polyamides as Engineering Thermoplastic Materials*, by I.B. Page, I. B., Vol. 11, 1, 2000 (ISSN: 0889–3144).[116] Data labeled with * have been taken from Koning, C.; Teuwen, L.; De Jong, R.; et al. *High Perf. Polym.* **1999**, *11*, 387.[106] Data labeled with ** have been taken from a Stanyl® brochure (DSM, 2010).

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compound has an Izod impact strength of 16 kJ m^{-2}, compared to 10 kJ m^{-2} for the unfilled PA 46.[129]

5.18.2.8.2 Moisture absorption

The moisture absorption of PAs is directly determined by the (CH_2)/NHCO ratio. The most polar commercially available PA, PA 46, absorbs ~13 wt.% water after being immersed in water at 23 °C until full saturation (ISO 1110). Under the same conditions, the most nonpolar PA, PA 12, absorbs ~1.5 wt.% water. For the other fully aliphatic PAs, the water absorptions fall between these extremes (see Table 3). Semiaromatic PAs such as PA MXD6 and PA 6T/66 absorb less water than do their fully aliphatic counterparts (see Tables 4 and 5). Since water is absorbed only by the amorphous phase, the water absorption is determined by not only the molecular structure (methylene/amide ratio) but also the degree of crystallinity. The water absorption changes the dimensions of a PA-based end product, and designers have to take this dimensional growth into account. The plasticizing water reduces strength and stiffness but significantly enhances the toughness (impact strength and elongation at break) of PAs, which can be regarded as an advantage.

5.18.3 Semiaromatic Polyamides

Semiaromatic PAs are PAs in which part of the monomer residues contain an aromatic structural unit. Another definition, introduced in the United States, is PPA and as explained in Section 5.18.1.1 it holds only for part of the semiaromatic PAs. Generally, the aromatic monomer content in the PA is > 55 mol.%, resulting in specific properties to be different from fully aliphatic PAs. The most frequently used monomer in semiaromatic PAs is terephthalic acid (T). In combination with linear diamines, high-melting (co)polyamides with low moisture uptake can be formed.

5.18.3.1 Preparation and Processing of Semiaromatic Polyamides

In general, the preparation is a batch operation similar to the synthesis of PA 66 and starts with a salt preparation, followed by water evaporation and melt polymerization to a linear-chain PA with a molar mass M_n of > 15 000 g mol^{-1}. The low solubility of the salts is often a problem, limiting the productivity of a batch plant, since the salt preparation step assures the stoichiometric check by titration of pH only when a homogeneous mix is formed. In case of Trogamid® T (see Table 5), the problem is overcome by using dimethyl terephthalate that can be dosed as a melt. In a first step, the methyl ester is saponified to form the salt, before proceeding with the polycondensation.

For semicrystalline, semiaromatic PAs, the preparation in the melt is often limited to low molar mass followed by reactive extrusion and/or SSPC to avoid thermal degradation.

Semiaromatic PAs typically have high melt viscosities that relate to the introduction of stiff monomers to obtain higher glass transition values. This makes injection molding into small thin-walled articles of these polymers difficult but makes them suitable for extrusion and blow molding. The maximum injection molding temperature of about 320 °C is similar to that of semicrystalline, semiaromatic PAs. For amorphous semiaromatic PAs, the processing window is wider due to the absence of crystallinity.

5.18.3.2 Semiaromatic Semicrystalline Polyamides

Most semiaromatic PAs are semicrystalline materials. Certainly, when the main dicarboxylic acid used is terephthalic acid, this is the case. In general, mostly linear monomers are used to keep the crystallinity as high as possible.

5.18.3.2.1 PA 6T and PA 6T-based copolyamides

The largest class of semiaromatic PAs are copolyamides based on PA 6T, for which the melting point is lowered with respect to pure 6T for acceptable melt processability. The advantage of the monomers is their low market price and wide availability. The most commonly introduced monomer is adipic acid (see further for the reason). Practically, every comonomer introduced into PA 6T will lower the melting point and crystallinity. Main reasons for selecting comonomers other than adipic acid are to raise the glass transition temperature with respect to 6T and at the same time to lower T_m. High T_g values are obtained by introducing the monomers isophthalic acid (I) leading to PA 6T/6I and MPMD leading to PA 6T/MPMDT. Replacing HMDA by DAB also results in a high T_g material PA 6T/4T, where the crystallinity is less disturbed by avoiding stiff-kinked comonomers.[134]

In case the moisture uptake is to be minimized in PA 6T-based copolyamides, long aliphatic comonomers such as decanediamine and dodecanediamine can be introduced into PA 6T. These copolyamides have recently been described in detail.[135,136] Figure 36 shows the melting data for a number of PA 6T-based copolyamides taken from these references.

Another monomer introduced to reduce the melting point of PA 6T is CL. PA 6T/6, marketed by BASF as Ultramid T, has a lower stiffness at high temperature compared to PA 6T/66 due to the nonisomorphous replacement of the comonomer and requires higher GF loadings to compensate for this.[137]

5.18.3.2.2 Other semiaromatic semicrystalline polyamides

5.18.3.2.2(i) PA 9T- and PA 10T-based copolyamides

The commercially used codes suggest these materials to be homopolyamides. However, in all cases, comonomers are added.

A PA based on 1,9-nonanediamine was commercialized by Kuraray in the 1990s of the previous century under the name Genestar®.[138] Brochures refer to PA 9T as a homopolyamide, although most grades are copolymers with 2-methyl-1,8-octamethylenediamine. The diamine is produced following a multistep procedure from butadiene. The hydrophobic nature of the material together with its high melting point makes it very suitable for E&E connector applications, although it is also applied in light-emitting diode (LED) lights as a highly TiO_2-filled reflectant.

Recently, several PA 10 T-based copolyamides have been commercialized. The advantage of the 1,10-decanediamine is its bio-based origin and the slightly higher melting point (due to the odd–even effect described in Section 5.18.2.7.2(i)) and hydrophobicity compared to PA 9T homopolymer.[139,140] The first commercial PA 10T is EMS' Grivory® HT3, which seems to contain HMDA as a comonomer.[136]

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Table 4 Properties of the main commercial semiaromatic PAs[137]

			Unreinforced				*Reinforced*					
Property	*Norm*	*Unit*	*Ultramid® T KR 4351 (BASF)*	*Amodel® AD1000 (Solvay)*	*Arlen® AE4200 (Mitsui)*	*Reny® 6002 (Mitsubishi)*	*Ultramid® T KR4355 (BASF)*	*Amodel® A1133 HS (Solvay)*	*Arlen® A330 (Mitsui)*	*Arlen® C230 (Mitsui)*	*Zytel® HTN 51G35 (DuPont)*	*Ixef® 1002 (Solvay)*
PA		wt.%	6T/6	6T/6I/66	6T/6I	MXD6	6T/6	6T/6I/66	6T/6I	6T/66	6T/M5T	MXD6
GF content		wt.%	–	–	–	–	35	33	30	30	35	30
Density		g cm^{-3}	1.18	1.17	1.10	1.21	1.44	1.43	1.42	1.42	1.47	–
Water uptake	ISO 1110	wt.%	7.0	5.8	6.5	6.5	4.8	4.6	4.5	5.0	3.5	5.0
E modulus, 23 °C	ISO 527	MPa	3200	3200	2800	3600	12 000	11 500	11 500	10 400	11 800	
T_m	ISO 4364	°C	295	310	320	243	295	310	320	310	300	243
HDT 1.8 MPa	ISO 75	°C	100	120	110	96	260	270	270	273	260	228
CUT (5000 h)	IEC 216	°C	135	–	–	–	165	170	165	165	–	160

HDT, heat deflection temperature; CUT, continuous-use temperature.

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Table 5 Amorphous partially aromatic PAs and their monomers, T_g, and water uptake

Diamine	*Dicarboxylic acid*	*Lactam*	*T_g (°C)*	*[H_2O] (wt.%)*	*PA*	*Common name (company)*	*Reference*
1,6-Diamino-2,2,4-trimethylhexane (ND) 1,6-Diamino-2,4,4-trimethylhexane (IND)	Terephthalic acid (T)	–	155	5.1	PA NDT/INDT	Trogamid® T (Evonik)	130
3,3′-Dimethyl-4,4′-diamino-dicyclohexylmethane (MACM)	Isophthalic acid (I)	Laurolactam (12)	159	3.5	PA MACMI/12 (65/35)	Grilamid® TR55 (EMS-Chemie)	131
HMDA (6)	Isophthalic acid (I)	–	127	6.0	PA 6I	Durethan® T40 (Bayer)	132
HMDA (6) Bis-(*p*-aminocyclohexyl)-methane (PACM)	Isophthalic acid (I) Terephthalic acid (T)	–	135	–	PA 6I/6T/PACMT (70/26/4)	Zytel® 330 (DuPont)	133

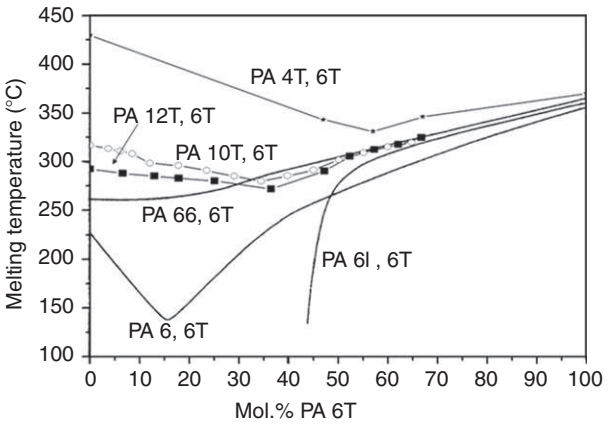

Figure 36 Melting points of copolyamides PA 6T/10T, PA 6T/12T, PA 6T/66, PA 6T/4T, PA 6T/6I, and PA 6T/6 versus PA-6T content in the copolyamide. Reprinted from Novitsky, T. F.; Lange, C. A.; Mathias, L. J.; *et al. Polymer* **2010**, *51*, 2417,[135] with permission from Elsevier.

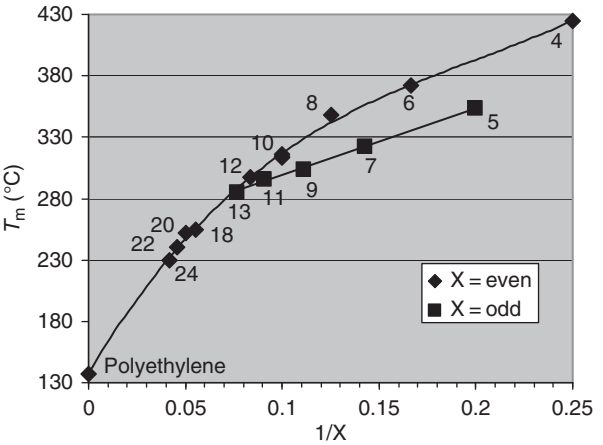

Figure 37 Melting points of PA *X*T homopolyamides with data taken from Morgan, P. W.; Kwolek, S. L. *Macromolecules* **1975**, *8*, 104;[141] Hewel, M. In *Nylon Plastics Handbook*; Kohan M. I., Ed.; Hanser: New York, 1995; pp 372–373;[145] Götz, W.; Roerdink, E. In *Kunststoff Handbuch 3/4 Polyamide*; Becker, G. W., Braun, D., Eds.; Hanser Verlag: München/Wien, 1998; p 804;[146] and Mao, J.; Durchholz, M.; Biermann, M. Cognis IP Management GmbH, WO Patent 2,009,068,242, 2009.[147] The numbers indicate the number of CH_2 groups (X) in the diamine.

PAs based on aromatic diamines and aliphatic dicarboxylic acids have been studied but never obtained interest for commercialization, although they showed very good resistance to yellowing and degradation by ultraviolet light.[141]

5.18.3.2.2(ii) PA MXDY- and PA PXDY-based copolyamides

m-Xylylenediamine (MXD) is produced by Mitsubishi by aminoxidation of *m*-xylene and hydrogenation for production of PA MXD6 with the commercial name Reny®. This semiaromatic PA has a relatively low melting point of 243 °C. It has outstanding oxygen barrier properties compared to other PAs.

p-Xylylenediamine (PXD) is currently not produced on a large scale, but potentially interesting PAs are made when combining PXD with aliphatic dicarboxylic acids. Melting points of PA PXD*Y* are slightly lower than those of their isomers PA *X*T.[142] It seems that recently a PA resin based on PA PXD10 has been commercialized by Mitsubishi and Solvay.[143,144]

5.18.3.2.3 Thermal, physical, and mechanical properties of semiaromatic semicrystalline polyamides

Figure 37 shows an overview of the melting points of PA *X*T homopolyamides with data taken from literature.[141, 145–147] The numbers in the figure indicate the number of methylene (CH_2) groups in the linear diamine (*X*). It shows that odd-numbered diamines result in lower melting points up to tridecanediamine (*X* = 13). Due to the different sources of information, trends might look different from reality. Of the PA *X*T materials, PA 4T, PA 6T, PA 9T, and PA 10T have become commercially available melt-processable materials used for engineering plastics applications (the very-high-melting PA 4T and PA 6T certainly require comonomer incorporation to reduce T_m). In some cases, for example, in PA 10T and PA 11T, PA *X*T homopolyamides have a double melting peak.[148] The reported melting point generally refers to the highest value, indicating that high-temperature material properties especially in these cases might deviate from expectations in view of the melting point.

The isomorphous replacement of terephthalic acid by adipic acid is well known, which has resulted in special attention for the semiaromatic copolyamides PA *X*T/*X*6. Melting points are shown in Figure 38. It shows that the melting points of the copolyamides lie close to a straight line between the

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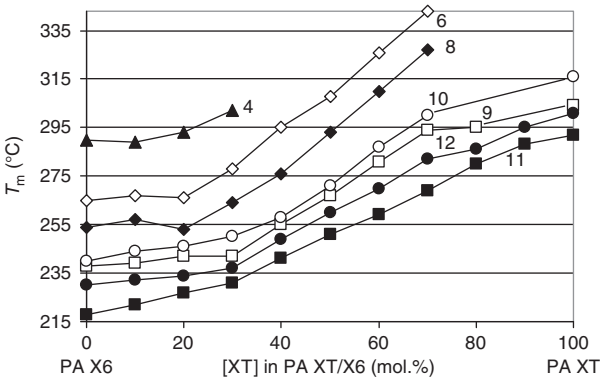

Figure 38 Melting points of PA *XT*/*X*6 copolyamides. The numbers indicate the number of CH_2 groups (X) in the diamine. Data from Harveym, E. D.; Hybart, F. J. *Polymer* **1971**, *12*, 711;[149] Gaymans, R. J.; Aalto, S.; Maurer, F. H. J. *J. Polym. Sci.* **1989**, *27*, 423;[150] and Yamamoto, S., Mitsui Petrochemical Industries LTD, EP 0449466, 1991.[151]

corresponding melting points of the two homopolyamides PA *X*6 and PA *X*T, which would represent perfect cocrystallinity. Thus, exchanging terephthalic acid by adipic acid offers a possibility of lowering the melting point with a limited loss of crystallinity due to the fit of the adipic acid unit in the PA *X*T crystal lattice leading to cocrystalline behavior.[149–153]

Other structures that are used to produce commercially available semiaromatic PAs are MXD in PA MXD6 and isophthalic acid (I), which is used as a comonomer to lower T_m while maintaining a high T_g or to render amorphous, high T_g, transparent semiaromatic PAs.

Table 4 shows the properties and the manufacturers of the main commercial semiaromatic PAs.[137] Other commercial semiaromatic PAs are Genestar® (PA 9T; Kuraray), Grivory® HT3 (PA 10T; EMS), Stanyl® ForTii™ (PA 4T/6T; DSM), and Vicnyl® (PA 10T, Kingfa).

5.18.3.2.3(i) Applications

The strength of semicrystalline semiaromatic PAs is the combination of a high melting point and low moisture absorption. Thus, the most important applications of semiaromatic PAs are in high-temperature automotive and E&E connector fields.

For amorphous partially aromatic PAs (see Section 5.18.3.3), special properties such as high heat deflection temperature (HDT) and high mechanical stiffness together with high impact resistance, even down to temperatures of below 0 °C, and excellent chemical resistance lead to their specific applications. Typical applications are pressurized air systems, lubricating systems in automotive applications, and hollow fibers as semipermeable membranes in medical applications such as dialysis. They are also often used in spectacles and sunglasses, where specifically their blends with aliphatic PAs are used to make them resistant to alcohol-based cleaning agents.

5.18.3.3 Amorphous Partially Aromatic Polyamides

5.18.3.3.1 General characteristics

Amorphous partially aromatic PAs combine the characteristic of being transparent with an excellent chemical resistance and resistance against environmental stress cracking (ESC) as compared to other transparent plastics such as PMMA or polycarbonate. Optionally, the PA is blended with semicrystalline PAs such as PAs 6, 11, or 12, keeping the transparency but improving the chemical resistance and ESC even further.[154] The most important physical property is the glass transition temperature, which is known to lower when PAs pick up moisture. Therefore, the commercially introduced amorphous partially aromatic PAs all use hydrophobic monomers to limit the amide density and polarity of the material. Especially when articles have to withstand steam sterilization, a limited amide density and a high T_g are important selection criteria. Examples of hydrophobic monomers are the diamines 1,6-diamino-2,2,4-trimethylhexane (ND), 1,6-diamino-2,4,4-trimethylhexane (IND), 3,3′-dimethyl-4,4′-diamino-dicyclohexylmethane (MACM), and bis-(*p*-aminocyclohexyl)-methane (PACM), mentioned in Table 5 shows different monomers used and commercialized transparent PAs based thereon.

5.18.3.4 Fully Aromatic Polyamides or Polyaramids

Fully aromatic PAs, in case of polyaramids, are defined as homo- or copolyamides consisting of at least 80 mol.% aromatic monomer units. They are typically intrinsically flame retardant, have very high melting points, and show nematic liquid crystalline behavior. Therefore, these materials are processed from solutions, in which the *para*-linked aramids exhibit lyotropic behavior, making them suitable for high-strength fiber production. Typical examples are polyaramids based on *p*-phenylenediamine and terephthalic acid (Kevlar®, Twaron®) and based on *m*-phenylenediamine and isophthalic acid (Nomex®). The all-*para* polyaramid fibers are, for example, used for bulletproof vests and other armor plating applications, whereas the all-*meta* polyaramid-based fibers have a higher wearing comfort and are used for overalls, for example, for fire fighters. They are discussed in Chapter 5.19 in more detail.

5.18.4 Segmented Block Copolymers of Polyamides and Elastomeric Polyethers

In thermoplastic elastomers (TPEs), the processing characteristics typical for thermoplastic polymers and the elastomeric or elastic properties typical for chemically cross-linked rubbery materials are united over a broad temperature range, which renders unique materials. Usually, PA-based TPEs consist of segmented block copolymers of PA blocks and polyether blocks[155–158] and they are normally called polyether block amides (PEBAs), which contrary to tough PA/EP(R)(DM) blends (see Section 5.18.5 on PA blends) consist of one type of phase-separated macromolecules with a multiblock copolymer structure. In the TPE, the usually amorphous, soft, low-T_g polyether blocks provide the low-temperature toughness and the elastomeric properties, whereas the semicrystalline, hard PA blocks provide chemical resistance and strength and form a kind of reversible, physically cross-linked network that can be molten and processed at $T > T_m$. The polyether blocks could in fact be regarded as internal plasticizers for the PA. The polyether blocks, usually polytetrahydrofuran (PTHF), polyethylene oxide (PEO), or polypropylene oxide (PPO), and the PA blocks, mostly of the PAs 6, 11, or 12 type and also of PA 66 and PA 612 type, are chemically connected by either ester or amide bonds,

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furnishing poly(ether ester amide)s and poly(ether amide)s, respectively.

In this section, the chemistry, the morphology, the most important physical properties, and some applications of PEBAs are discussed.

5.18.4.1 Chemistry and Chemical Structure of PEBAs

For the manufacturing of PEBAs, difunctional carboxylic acid end-capped oligoamides with typical M_n values of 500–2000 g mol^{-1} are prepared in a first step.[155–157] Baumann *et al.*[159] describe a general recipe for the manufacture of a PA 12-based poly(ether ester amide). In a first step, a dicarboxylic acid such as 1,12-decanedicarboxylic acid and laurolactam are reacted at 250–290 °C at 1–20 bar, furnishing a difunctional carboxylic acid end-capped PA or oligoamide PA 12 of the structure $HO[OC(CH_2)_{11}NH]_x–CO(CH_2)_{10}CO–[NH(CH_2)_{11}CO]_y–OH$. This COOH-terminated prepolymer, with molecular mass values as mentioned above and determined by the amount of dicarboxylic acid added, can then in a second step be further reacted in the melt (200–270 °C under vacuum) with difunctional polyether diols, such as PTHF with very similar number-average molecular mass values as the PA prepolymers (see also, e.g., Reference 160). For this multiblock copolymer formation, with the structure $H–\{[O(CH_2)_4–]_zO–[OC(CH_2)_{11}NH]_x–CO(CH_2)_{10}CO–[NH(CH_2)_{11}CO]_y\}_n–OH$, the presence of a suitable esterification catalyst is required, and the connection between the PA and the polyether blocks is an ester bond. In literature, several catalysts for this esterification coupling reaction are mentioned, such as dialkyl tin(IV) compounds,[158] phosphoric acid,[161] tetraalkyl titanates,[162] tetraalkyl zirconates,[163] tin(II) salts,[164] antimonium trioxide,[165] and combinations of antimonium trioxide and tin and phosphorous compounds.[166] Especially when the preformed PA and polyether segments have a relatively high molecular mass, and when the oligoamide segments are relatively polar, the described route can be problematic because of phase separation during synthesis, causing a limitation of the molecular mass buildup. However, for the system oligoamide 11 or 12 with PTHF, phase separation is less pronounced.[157,167,168] The compatibility between the oligoamide and the polyether phase can be somewhat enhanced by the introduction of water vapor.[169] An interesting option is to mix the oligoamide-forming monomers directly with the dicarboxylic acid and the polyether diol, and perform a one-pot reaction. This is certainly an attractive option when reactive lactams such as laurolactam are applied, which can be ring opened at relatively low temperature, which is beneficial for the polyether diols, which would have difficulties to withstand higher temperatures for a longer time. In this case, at elevated water vapor pressure, the laurolactam ring-opening polymerization is initiated, after which under reduced pressure, esterification conditions are established.[161] Similar recipes have also been suggested for poly(ether ester amide)s based on CL,[170] aminocarboxylic acids,[171] and equimolar 'nylon salts' from aliphatic diamines and dicarboxylic acids.[172] As an alternative for polyether diols, α,ω-diaminopolyethers can be applied for the synthesis of polyetheramides, yielding hydrolytically more stable amide bonds between the oligoamide and the polyether segments.[173–175] These α,ω-diaminopolyethers, such as poly(propylene oxide)diamine, can, for example, be mixed with CL and a dicarboxylic acid, after which the corresponding PEBA is formed in a one-pot synthesis, during which phase separation is not a major problem. No esterification catalyst is required, and the amine end groups of the polyether initiate the ring-opening polymerization of the CL.

5.18.4.2 Morphology of PEBAs

Depending on the PA and polyether content, the phase-separated structure can either be co-continuous or have a dispersed phase-in-matrix character. If the PA forms the continuous phase, the material should rather be regarded as an impact-modified PA, but materials exhibiting a continuous or co-continuous polyether phase can be considered as TPEs. In PA-rich, PA 12-based PEBAs, the usually semicrystalline PA phase clearly shows the spherulitic superstructure of PA 12 lamellae, which forms the 'physical network structure' in a continuous, phase-separated mixture of amorphous PA 12 and polyether. For higher polyether contents, the spherulitic superstructure is lost, and for very high polyether contents, a weak, ribbon-like crystalline PA 12 structure supports the soft continuous amorphous polyether/noncrystalline PA 12 mixture, which in itself exhibits two T_g transitions.[159]

5.18.4.3 Physical Properties and Processing of PEBAs

As mentioned before, the PA blocks of the commercial PEBAs may consist of PA 6, 66, 612, 11, or 12, but in academia, even high-melting PA 46 blocks have been used for the manufacturing of PEBAs.[174,175] This PA block type determines the melting point of the physical network structure formed by the semicrystalline PA, the water absorption, the chemical and salt resistance (stress cracking resistance), and the density. The length of the PA blocks, on the other hand, determines melting point, crystallinity, and transparency. The polyether type, being either PTHF, polyethylene glycol (PEG), or polypropylene glycol (PPG), determines water absorption, antistatic behavior, chemical and thermal resistance, and low temperature T_g. Finally, the mass ratio semicrystalline PA/amorphous polyether determines the rigidity, hardness, and flexibility. It is obvious that with increasing polyether content, the rigidity and the hardness decrease, whereas the flexibility and the elasticity increase. With the large variability in the PA type and block length, the polyether type and block length, and the mass ratio PA/polyether, a very broad range of physical properties is within reach. Here, we just mention a few examples, which are limited to the most basic properties.

PEO-based PEBAs have a higher water absorption, a higher water permeability, and a better antistatic behavior compared to the corresponding PTHF-based TPEs; PA 12–PTHF TPEs exhibit the lowest possible density (1.01–1.03 g cm^{-3}) and moisture absorption (1.2 wt.% after 24 h in pure water, as compared to 120 wt.% for a PA 6–PEO TPE[176]), PA 6-based TPEs have higher melting points and a higher moisture absorption than the corresponding PA 11- and PA 12-based TPEs with polyether blocks of the same type and molecular mass, and polyether diols are generally cheaper than the corresponding polyether diamines.

With respect to hardness, any shore hardness between 60 A and 75 D can be realized.[176] For a PEBA based on PA 12 and PTHF (1000 g mol), the yield stress varies from ~45 N mm^{-2}

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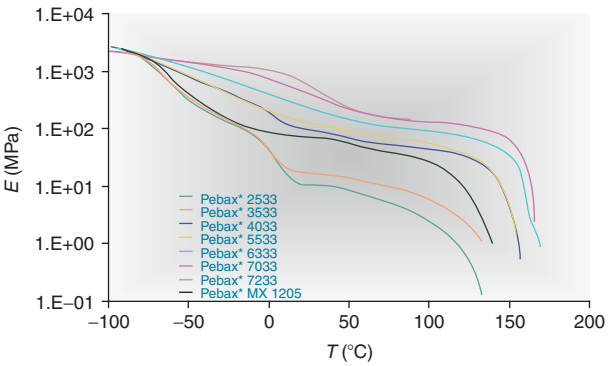

Figure 39 DMTA curves for commercially available PEBAX® grades, measured at 1.6 Hz ramp at 2 °C min^{-1} after preconditioning for 15 days at 50% RH and 23 °C, showing the wide range of stiffness and flow temperatures of the commercial products. Reprinted from http://www.pebax.com/sites/pebax/en/properties/mechanical _properties1,[177] with permission from Pebax.

for 100 wt.% PA 12 to ~ 4 N mm^{-2} for 28 wt.% PA 12, while the strain at break for all samples is over 180%. For PA 12-based TPEs, the bending modulus varies from 500 N mm^{-2} for the hardest types to ~ 20 N mm^{-2} for the softest types.[159] The cold impact strength of PA 12–PTHF TPEs is extraordinary. In notched Izod impact tests at −30 °C, the softer types show no break at all.

With respect to thermal properties, depending on the molecular structure, the DSC-determined melting points of the physical network can vary between 122 °C for the softer TPEs and 205 °C for the harder TPEs. In Figure 39 some typical Dynamic Mechanical Thermal Analyzer (DMTA) curves and in Figure 40 some stress–strain curves for several commercial PEBAX® grades are shown. The data have been taken from Arkema's PEBAX® website.[177]

Injection molding of PEBAs should be performed at a moisture content of below 0.1 wt.% at melt temperatures of 170 °C (soft TPEs) to 210 °C (hard TPEs). The low melt viscosity and the fast crystallization allow short injection molding times. By extrusion, thin foils, prophiles, tubes, plates, and monofilaments can be manufactured at 180–230 °C.

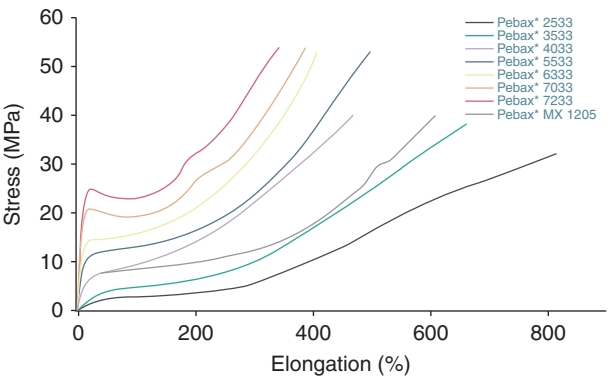

Figure 40 Stress–strain curves for commercially available PEBAX® grades, showing the wide range of tensile strength and elongation at break of the commercial products. Reprinted from http://www.pebax.com/sites/pebax/en/properties/mechanical _properties1,[177] with permission from Pebax.

5.18.4.4 Applications and Trade Names of PEBAs

The building blocks of PEBAs are relatively expensive, which positions these TPEs in the high-end TPE market. An important application area is sports goods, such as ski shoes and ski connections (low-temperature dependency of bending modulus), (parts of) diving equipment and flippers (low water absorption and good dimensional stability), roller skates (toughness and constant mechanical properties at different moisture contents), and parts of sports shoes (soccer shoes, spikes, and cycling shoes). Other applications are bracelets for watches (flexibility and low irritation level of the skin), frames for sunglasses (low irritation level of the skin and good paintability), small gears for video recorders, and so on. (good flow and processability), housings for car mirrors, antenna parts, seals and sealing prophiles in cars, membranes for clothes for surgeons (PEO-based TPEs allow penetration of water vapor), blend components for materials with antistatic properties (for water-absorbing PEO-based TPEs), tubes for catheters (good rigidity prevents buckling), and adhesives (for metal, glass, leather, and plastics).

Trade names of some important commercial PEBAs are PEBAX® (Arkema), Vestamid® (Evonik), Grilamid® (EMS-Chemie), Dynyl® (Rhône-Poulenc), and PAE® (Ube).

5.18.5 Polyamide Blends

5.18.5.1 Introduction

Although PAs can be considered as engineering plastics with superior properties, like other polymers they have some shortcomings. The main limitations are (1) the brittleness at low temperature, especially at low humidity and when PA-based products have sharp notches, (2) the moisture absorption due to the presence of amide groups, resulting in (3) a limited dimensional stability in humid environment, (4) the relatively low glass transition temperature, especially after conditioning, which causes a relatively low HDT, and (5) the lack of flame retardancy. If these drawbacks are attempted to be overcome by changing the molecular structure of the PA main chain, for example, by incorporating comonomers, some beneficial properties such as crystallinity, high melting point, and high strength and stiffness may be reduced, which is undesirable. However, by blending a PA with other polymers, 'best-of-both-worlds' materials are generated, in which the PA blend component provides high strength and stiffness up to high temperature (because of the high melting point), excellent chemical resistance, good flow properties and melt processability, and good paintability, whereas the other blend components enhance (low temperature) notched impact strength, raise the HDT of unfilled products, reduce the moisture absorption, enhance the dimensional stability, and improve the flame retardancy. Although PAs have been blended with numerous polymers, in this section we will focus on the most important commercial PA-containing polymer blends.

Most commercial PA blends belong to the group of fully incompatible, heterogeneous blends and they therefore require a compatibilizer, usually a block- or a graft-type copolymer that not only reduces the interfacial tension, thereby refining the blend morphology, but also enhances the interfacial adhesion and stabilizes the generated morphology against subsequent

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processing.[178] PA-containing blends are usually compatibilized by reactive processing, which generates the required block or graft copolymer at the blend interface making use of the amine and/or carboxylic acid end groups. The other blend component is predominantly modified with anhydride groups, which are known to react instantaneously with primary amine groups of the PA. The next section presents some examples of important commercial PA-containing blends.

5.18.5.2 Polyamide/Elastomer Blends

Mixtures of PAs and elastomers such as ethylene–propylene–rubber (EPR) or ethylene–propylene–diene monomer (EPDM) are commercially very important. Although strictly speaking these are heterogeneous PA blends, they are usually called 'impact-modified PAs', since by far the most important reason for adding EPR or EPDM is for providing the PA with low-temperature impact and for reducing its notch sensitivity at room temperature. Since PAs and EP(R)(DM) are incompatible polymers, compatibilization is required in order to reduce the particle size of the dispersed elastomer particles to the submicrometer level, which results in the highest impact. Usually, maleic anhydride-grafted EPR or EPDM (EPR–MA and EPDM–MA, respectively) is applied, and during melt blending, the amine end groups of the PA react with the anhydride groups present along the elastomeric main chain with the formation of the desired graft copolymers. The elastomer segments and the PA segments are chemically connected by stable imide bonds (see Figure 41).

The impact modification of PAs has been studied by many researchers and has been described extensively in both scientific and patent literature. As an illustration, we here mention part of the work of Borggreve[179] on PA 6/EPDM–MA blends. Figure 42 shows the notched Izod impact strength of PA 6/EPDM–MA blends with an MA content on the EPDM of 0.4 wt.%. In these reactively compatibilized blends, the rubber particle size is virtually constant, that is, between 0.29 and 0.38 μm, and the rubber content varies between 0 vol.% (pure PA 6) and 26.1 vol.%. Please note that in noncompatibilized PA/EPDM blends (without grafted MA), the rubber particle size can be several micrometers, and the blends remain brittle. Figure 42 clearly illustrates that the tough–brittle transition is shifted to lower temperature for increasing rubber content and that the toughness keeps increasing with increasing amount of elastomer. For 10.5 vol.% rubber and higher, the PA 6/EPDM blends are tough at room temperature.

A drawback of the introduction of relatively high rubber contents is the lowering of the stiffness, the tensile properties (yield stress and stress at break), and the HDT, but for some applications, toughness is a key property and a corresponding lower modulus has to be taken for granted. A clear additional advantage of introducing the nonpolar EPR- or EPDM-based impact modifier is a reduced moisture absorption and a correspondingly enhanced dimensional stability in humid conditions.

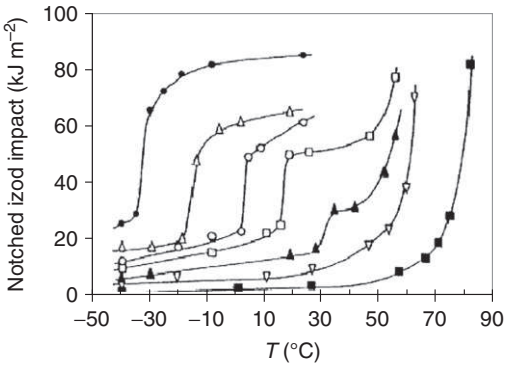

Figure 42 Notched Izod impact strength versus temperature of blends of PA 6 and EPDM–MA containing 0.4 wt.% MA. Rubber particle size for all blends is 0.33 ± 0.04 μm. Constant interfacial adhesion. Rubber content (vol.%) for curves from right to left: 0 (■); 2.6 (▽); 6.4 (▲); 10.5 (□); 13.0 (O); 19.6 (△); 26.1 (●). Reproduced from Borggreve, R. J. M. *Toughening of Polyamide 6*; Thesis University of Twente, 1988,[179] with permission from the author R. J. M. Borggreve.

The results described above can be expected for blends of maleic anhydride-modified elastomers, which will react with imide moieties with an amine end group of the PA. AB-type PAs carry one reactive amine end group and one other end group (e.g., a carboxylic acid end group for hydrolytically produced PAs and a lactamate end group for anionically synthesized PAs) and thus result in comb-like structures. One should be careful with raising the amount of EPR–MA or EPDM–MA in PAs of the AABB type, synthesized from diamines and dicarboxylic acids, such as PA 66 or PA 612. In these PAs, some chains will carry either one NH_2 and one COOH end group (as in the case of PAs of the *Z* type), or two NH_2 or two COOH end groups. Chains carrying two amines can cause cross-linking reactions in the MA-grafted EPR/EPDM phase if too much MA-grafted elastomer is present, preventing sufficient reduction of the rubber particle size to the required submicrometer level. Therefore, in the case of, for example, PA 66, the impact in the first instance increases with increasing amount of EPDM–MA, as in the case of PA 6/EPDM–MA, but starts to decrease upon addition of too large amounts of the MA-grafted elastomer. Impact-modified PAs usually carry the trade name of the PA, which once again illustrates that these materials are considered as a special (impact-modified) PA grade rather than a real polymer blend.

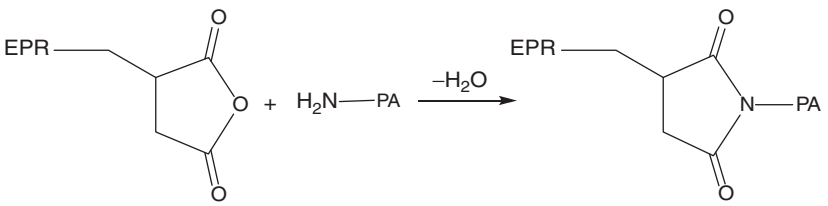

Figure 41 Compatibilization reaction at the interface between the amine end groups of PA and the anhydride groups grafted onto an EPR elastomer.

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5.18.5.3 Polyamide/Polypropylene Blends

Also the semicrystalline polyolefin polypropylene (PP) is blended with PA. Also here the reactive compatibilization is based on the reaction between MA groups, grafted onto the PP chains, and the amine end groups of the PA. In these blends, the PA is responsible for good tensile properties and high stiffness up to the (relatively high) melting point, the good processability, and the paintability, whereas the cheaper PP provides low moisture absorption and a better dimensional stability. Examples of trade names of commercial PA/PP blends are Akuloy® and Orgalloy®.

5.18.5.4 Polyamide/ABS Blends

In these blends, the PA gives once again good paintability, good flow properties, good chemical resistance, and high stiffness and strength up to high temperature. The acrylonitrile-*co*-butadiene-*co*-styrene (ABS) in fact is a blend in itself of lightly cross-linked polybutadiene (B) rubber particles, partly grafted with a styrene (S)/acrylonitrile (A) copolymer, dispersed in a continuous phase of styrene-*co*-acrylonitrile (SAN). This ABS provides the PA/ABS blend with low moisture absorption and good dimensional stability in humid environments and high impact strength up to low temperature. Moreover, the T_g of the amorphous SAN phase is ~60 °C higher than the (dry) T_g of the PA phase, which somewhat enhances the HDT of unfilled, nonreinforced polymer grades. In the commercial PA 6/ABS blends such as Terblend® N and Triax®, the compatibilizer is a tercopolymer of styrene, acrylonitrile, and maleic anhydride, the latter being randomly distributed along the styrene-*co*-acrylonitrile-*co*-maleic anhydride main chain. The terpolymer is miscible with the continuous SAN phase of the ABS, and the MA units in the terpolymer react with the amine end groups of the PA, forming the compatibilizing SAN-*graft*-PA 6 copolymer at the PA/SAN interface of the phase-separated PA 6/ABS blend. The MA content of the styrene-*co*-acrylonitrile-*co*-maleic anhydride (SANMA) terpolymer is important. For too low weight percentages, there is insufficient formation of graft copolymer, resulting in a suboptimum impact strength (see **Figure 43(a)**), whereas for too large amounts of MA, too many PA 6 chains become grafted onto the SANMA terpolymer, the balance is lost, and the heavily grafted copolymer is removed from the interface and forms micelle-like structures in the PA phase. This was described by Majumdar *et al.*[180] and the phenomenon is illustrated in **Figure 43(b)**. PA/ABS blends can either be co-continuous or have dispersed ABS particles in a PA matrix.

5.18.5.5 Polyamide/Polyphenylene Ether or Polyphenylene Oxide Blends

Polyphenylene ether (PPE) or polyphenylene oxide is an intractable amorphous polymer with a T_g of 215–220 °C, which cross-links at the required melt processing temperature of 320 °C or higher. It is a very tough material because of its high entanglement density, it exhibits a low moisture absorption and good dimensional stability, the high T_g gives it a high HDT and it is intrinsically flame retardant. On the other hand, the amorphous character is responsible for its poor solvent resistance and its vulnerability to environmental stress cracking. When the intractable PPE is dispersed in a continuous PA phase, for which usually PA 66 is used, the continuous PA phase provides not only first of all processability but also chemical resistance, paintability, strength, and stiffness. This makes PA 66/PPE an almost ideal heterogeneous polymer blend, which obviously needs to be compatibilized. Also, here the anhydride/amine reaction has been chosen for the reactive compatibilization. One of the routes to compatible blends is the end capping of part of the phenolic end groups

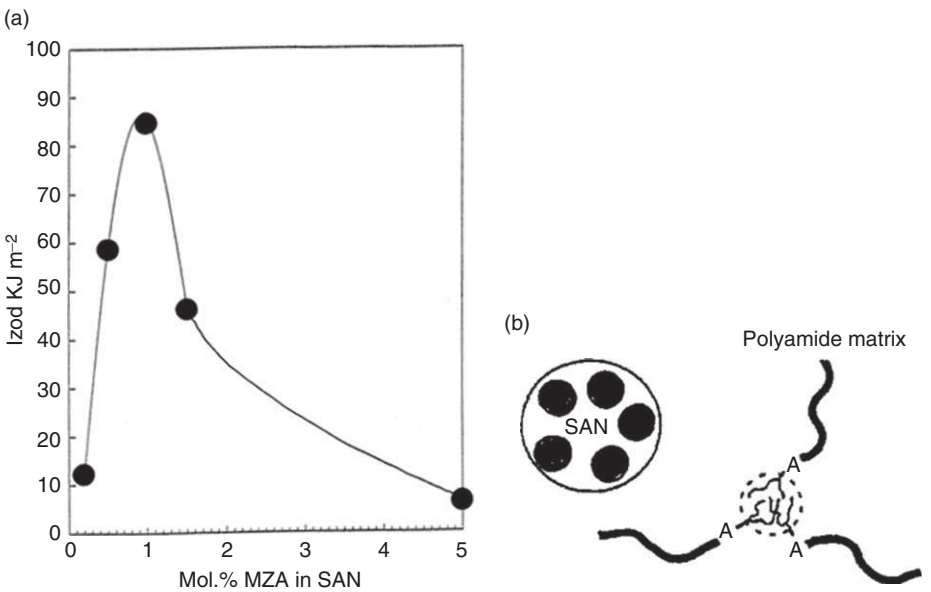

Figure 43 (a) Izod notched impact strength of ABS/nylon 6/Styrene-co-Acrylonitrile-co-Maleic Anhydride (SANMA) 50/44/6 (wt/wt/wt) blends versus mol.% MA in the SANMA compatibilizer. Data taken from Internal data collected at DSM Research.[181] (b) Cartoon explaining the decrease in compatibilizer efficiency for too high mol.% MA in the SANMA (dark spheres in SAN particles stand for polybutadiene rubber particles in ABS). Inspired by Majumdar, B.; Keskkula, H.; Paul, D. R.; Harvey, N. G. *Polymer* **1994**, *35*, 4263.[180]

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of PPE with the acid chloride of trimellitic anhydride. At the interface, the resulting anhydride-terminated PPE molecules form block copolymers with amine-terminated PA molecules.[178] The patent literature also describes the addition of minor amounts of citric acid to the PA/PPE blend. At the high processing temperature, the citric acid is most probably dehydrated with the formation of a citric anhydride moiety and a double carbon–carbon bond.[178] These functionalities can react with amines and phenol groups, respectively. Usually, the PA 66/PPE blends contain a PPE-compatible polystyrene-*block*-hydrogenated polybutadiene-*block*-polystyrene (or polystyrene-*block*-ethylene-*co*-butylene-*block*-polystyrene, SEBS) impact modifier in the dispersed PPE phase.

5.18.5.6 Polyamide/Brominated Polystyrene Blends

Polybromostyrene is blended with PAs to enhance the flame retardancy, especially for compounds for the E&E industry. No compatibilizer is added, since the mechanical properties such as stiffness, toughness, and elongation at break are predominantly determined by the simultaneous presence of 20–40 wt.% glass fiber. An additional advantage of the addition of polybromostyrene, typically polydibromostyrene (PDBS), is that the dimensional stability is also improved. The PDBS provides a gas-phase-active mechanism and is the most efficient flame retardant known to provide UL V0 ratings in GF-reinforced PA compounds for E&E connector applications. Besides the PDBS, a synergist such as Sb_2O_3 has to be added to provide the desired level of flame retardancy.

5.18.5.7 PA 6/PA 66 Blends

Blends of PA 6 and PA 66 are known to be compatible, and the addition of an external compatibilizer to the blend is not necessary in order to obtain good mechanical properties. The amorphous parts of PA 6 and PA 66 are most probably homogeneously miscible,[182–186] or during melt blending, transamidation reactions compatibilize these two polymers with a very similar overall chemical structure[187] (the methylene/amide ratio in the repeat unit is 5 for both PAs). It has to be noted, however, that both PAs crystallize separately in their own crystal lattice, and therefore PA 6/PA 66 blends are heterogeneous. The reason for blending these two aliphatic PAs is that the somewhat higher toughness and the better fiber dyeability of PA 6 is combined with the somewhat lower moisture absorption and the faster crystallization of PA 66. In PA 6/PA 66 blends containing up to ca. 30 wt.% of the more symmetric PA 66, the PA 66 crystals are formed first upon cooling from the melt, and these PA 66 crystals are nucleating agents for the crystallization of the asymmetric PA 6 chains, thereby enhancing the crystallization temperature, the crystallization speed, and the crystallinity of the PA 6 phase.[186,188] The enhanced crystallinity of PA 6 results in enhanced physical properties.

5.18.6 Applications of Polyamides

5.18.6.1 General Remarks on Properties

PAs have found their way in various applications in many industries, such as automotive, electrical & electronics, general industries, and packaging and (film, fiber, and sheet) extrusion. This is merely a result of their excellent performance balance as related to temperature resistance (excellent peak temperature resistance in combination with great oxidative heat ageing resistance, even up to 230 °C), mechanical properties (high stiffness levels at elevated temperatures above 100 °C, high toughness levels at low temperatures, and excellent fatigue resistance), chemical resistance (high retention level of various properties when exposed to various chemicals, and less sensitive to hydrolysis than polyesters), and processability (easy to process, by injection molding, extrusion, or blow molding, good flowability, short cycle times, and excellent weldability).

Also secondary operations such as gluing, welding, lacquering, snap fitting, riveting, laser marking, and painting are in general quite easy to do with PAs, which is mainly due to their polar character. The only point of attention with PAs is the limited dimensional stability in case of exposure to (high) humidity levels. For most applications, the dimensional stability is however sufficient, as can be seen from the many application examples described below.

5.18.6.2 Automotive Applications

PAs are used in many different applications in the automotive industry:

- air/fuel/oil (air inlet manifolds (PA 6), air ducts and charge air cooler caps (PA 6, PA 46, and PPA), exhaust gas recirculation (EGR) valve components (PA 46), fuel lines (PA 11 and PA 12), oil filters, and oil sumps (PA 6 and PA 66))
- cooling (radiator components (PA 66))
- power train (timing system and front-end accessory drive components (PA 46 and PA 66), alternator and transmission bearing cages (PA 66 and PA 46), and mechanical torsion dampener parts (PA 46))
- engine (aesthetic under-the-hood covers and pulley covers (PA 6))
- Auto E&E (connectors, sensors, switches, electromotor components, gears (PA 66, PA 46, and PPA), and fuse boxes (PA 6))
- safety restraint (air bag containers (PA 6))
- interior/exterior (pedal and pedal boxes (PA 6 and PA 66), seat components (PA 6), mirror brackets, and door handles (PA 6))
- body/chassis/structure (structural reinforcements and insets (PA 6), body plugs (PA 6), front-end modules (PA 6), transmission beams and lower bumper stiffeners (PA 6 and PA 66), engine mounts, and torque rods (PA 6 and PA 66)).

The main reasons to choose for a PA lay in the area of high temperature and chemical resistance for power train and under-the-hood parts, excellent wear and friction behavior for gears and bearing cages and chain tensioners, good toughness levels for safety-related parts, good weldability for air inlet manifolds, and improved surface appearance for under-the-hood covers and interior or exterior parts. PA 6 is mainly selected for its good heat aging resistance, surface appearance, and toughness; PA 66 is the material of choice for applications exposed to water/glycol and PPA in case a very high chemical resistance is needed. PA 46 outperforms the other PAs especially on abrasion, friction, and fatigue behavior, which makes it ideally

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suitable for applications such as gears, bearing cages, and chain tensioners.

5.18.6.3 Electrical and Electronics Applications

PAs are used in many different applications in the E&E industry:

- Printed circuit board (PCB) connectors; PA 46 and semiaromatic PAs are preferred. PA 46, for example, because of its high melt flow and the semiaromatic PAs because of their good dimensional stability. High heat resistance in combination with low moisture uptake is needed to withstand the reflow soldering process (which implies that PA 46 parts require drying before soldering).
- Industrial connectors; PA 6 and PA 66 are the materials of choice because of high toughness, lower price, and processability.
- Power distribution; PA 6 is used for circuit breaker housings because of the halogen-free flame retardancy of the compound and relatively low price.
- Internal components of miniature circuit breakers (MCBs); PA 46 because of high melt flow and high temperature resistance during reflow soldering.
- E-motor parts, bobbins, switches, and sensors; PA 66 is the main material of choice. PA 46 and PPA are used here in case higher temperature resistance is required.

The main reasons to use PAs here originate from their excellent temperature resistance, good toughness levels, good insulation properties, and easy processability.

5.18.6.4 General Industry Applications

There are many applications outside automotive and E&E based on PAs processed via injection molding. The most important ones are sports and leisure (ski fixations and in-line skate frames), lawn and garden (chain saw components and gardening tools), furniture (chair bases and other chair components, and kitchen drawer guides), domestic (power tool components and water kettle switches), and transportation (railway pads and bearing cages).

In a lot of cases, PA 6 is used because of its excellent surface appearance and colorability. PA 66 and PA 46 are used for those components where wear and friction are important criteria. PA 46 and PPA are used in the neighborhood of hot spots.

5.18.6.5 Packaging and Film, Fiber, and Sheet Extrusion Applications

A very big application area, especially for PA 6, is that of packaging, especially food packaging. PA 6 films, often combined with polyolefin and ethylene vinyl acetate (EVA) films in a multilayered structure, are used here mainly for their excellent oxygen barrier and puncture resistance properties. Other extrusion applications are tubes and hoses (convoluted tubes from PA 6), and rods, plates, and disks. From the latter, all kinds of small-series parts such as gears can be machined. More and more, these films are biaxially stretched to enhance barrier properties further. These bis-oriented PA films (bopa) require materials with a small variance in viscosity for good stretchability. Here besides the wider processing window, PA 6 has the advantage over PA 66 of being more uniform in viscosity due to a lower amount of branched molecules in PA 6, which can be formed due to side reactions.

Last but not least, we mention the huge and traditional application of PAs as fiber materials, as a basis for technical yarns and yarns for clothing and carpets. The PA fiber market is almost exclusively covered by PA 6 and PA 66 fibers. Historically, in view of the development of PA 6 in Western Europe and that of PA 66 in the United States, 'nylon' carpets in Europe are predominantly based on PA 6, whereas those in the United States are mainly PA 66 based. The fibers are produced by melt spinning, which results in a strong orientation of the PA molecules in the fiber direction. Stretching or drawing of the spun fiber results in a further alignment of the PA molecules and of the chain axis of the crystals parallel to the fiber axis, resulting in a strong increase of strength and stiffness in the fiber direction. Upon drawing and during the alignment process, part of the folded chain crystals are 'unfolded' and part of them remain folded. These remaining crystals are connected by so-called tie chains, which are crucial for the mechanical properties of the fibers. As an illustration of the effect of chain alignment on strength, the following may serve: injection molded PA 66 has a strength of 80–90 MPa (see **Table 3**), whereas drawn PA 66 fibers have a strength of at least 700 MPa.

5.18.7 Summary, Main Conclusions, and Future Perspectives

PAs are a very important class of materials that find their applications as such or in combination with other polymers in the field of engineering plastics, fibers, and films. The manufacturing of hydrolytically produced, fully aliphatic, and semiaromatic PAs started just before World War II after the pioneering activities of Wallace Carothers and has since then developed into a very mature business. Nevertheless, PA-manufacturing companies are still developing new types of PAs or 'nylons' in order to further improve properties or sustainability. By far, the two most important representatives of this subgroup of PAs are PA 6 and PA 66, both of which have superior properties for many applications but which also have their shortcomings. The beauty of PAs is that their properties can be tailored by choosing the proper monomer building blocks. As an example, we mention the complete replacement of adipic acid residues in PA 66 by sebacic acid residues, furnishing PA 610, which reduces the moisture absorption and enhances the dimensional stability at the cost of a lowering of the melting point and tensile properties. By choosing the stiff terephthalic acid monomer, semiaromatic, semicrystalline PAs with very high melting points and glass transition temperatures are obtained. On the other hand, the less favorable properties of PAs can be improved by blending with other polymers. Indeed, in most commercially available PA blends, the added non-PA blend component compensates for the shortcomings of PA, whereas the PA compensates for the drawbacks of the other blend component. The incompatible blends such as PA/ABS and PA/EPDM are usually compatibilized by reactive processing, during which block or graft copolymers are generated at the blend interface by the highly efficient amine/anhydride reaction. Commercial PA 6/PA 66 blends are compatible as

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such, and compatibilization is not required for obtaining useful products. A third way to improve certain properties of PAs is the formation of multiblock copolymers of PAs and polyethers. Depending on their composition, these so-called PEBAs have properties ranging from those typical for impact-modified PAs to thermoplastic elastomers with superior properties.

What can we expect in the future from the PA manufacturers? As mentioned before, the chemistry furnishing PAs is very mature, and as far as the PA synthesis is concerned, we do not expect great breakthroughs in this field: also in the future, PAs will predominantly be made from diamines and dicarboxylic acids or from aminocarboxylic acids (or the corresponding lactams). If the monomer costs become very high, then the alternative, not yet commercialized monomer synthesis routes, for example, developed for CL (BASF's adiponitrile-based route and DSM's 'butadiene/CO-based Altam' process, see Section 5.18.2.1), may be picked up again, but essentially the polymerization of these alternative CLs will be the same as that of CL produced via the nowadays commercial processes. As for developments in the manufacturing technology, we expect that batch-type polymerizations will become increasingly replaced by large-scale, cheaper continuous processes, and we also expect that, especially for PAs exhibiting high melting points, the trend will be to realize most of the molecular weight buildup by solid-state polycondensation after a short prepolymerization step in the melt in order to limit degradation and undesired side reactions as much as possible. Another trend is a direct result of the general driving force toward more sustainable polymers. The use of renewable monomers offers an excellent opportunity for step-growth polymers in general and for PAs in particular. Several biomass-based dicarboxylic acids (e.g., succinic acid, azelaic acid, and sebacic acid) and diamines (e.g., putrescine, cadaverine, and the dimer fatty acid-derived diamine) and at least one bio-based aminocarboxylic acid (11-aminoundecanoic acid) are commercially available and form the basis for excellent (partially) renewable PAs such as PA 610, 410, 69, and 11. Relevant for the market acceptance will be the absence of competition with the food chain. Monomers derived from nonedible biomass such as sebacic acid, azelaic acid, and 11-aminoundecanoic acid are the expected winners. So, even if the fossil feedstock has been completely used, the indispensible PAs are expected to remain available materials in our daily life.

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5.19 Lyotropic Polycondensation including Fibers

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5.19.1 Introduction

5.19.1.1 Invention of Lyotropic Liquid Crystals

A linear flexible polymer chain in solution configurates a random coil as shown in **Figure 1(a)**.[1] Rigid polymer chains, however, are made from stiff units, show a rodlike shape, and are arrayed randomly as shown in **Figure 1(b)**.[1] As the concentration of rigid molecular chain polymers increases, the molecular chains are packed tightly as shown in **Figure 1(c)**.[1] As predicted by Flory's equation [1], an isotropic solution transforms to an anisotropic phase above the critical concentration ψ^*, where ψ^* will decrease with increasing axial ratio (x) or molecular rigidity.[2]

$$\psi* = \frac{1}{8}\left(1-\frac{2}{x}\right) \qquad [1]$$

Thus, a polymer with a high axial ratio (rigid or stiff) is preferred for the formation of anisotropic solutions. An anisotropic solution forms liquid crystals consisting of domains in which molecules align in the same direction (director). The directors of domains easily orient in the flow direction and form an extended molecular chain structure as shown in **Figure 1(d)**.[1] In general, the viscosity of the solution increases dramatically with the increase of polymer concentration below the critical concentration as shown in **Figure 2**.[3] However, Kwolek[4] found that above the critical concentration a solution of *p*-aramid shows opaque appearance and the viscosity of the solution dramatically decreases as shown in **Figure 2**. This was a great breakthrough for the production of high-modulus and high-strength fibers (super fibers). The first commercialized superstrong fiber named Kevlar® (Fiber B) in 1971 had 2 times higher tensile strength and 3 times higher tensile modulus than a previous strong fiber such as a polyester tire yarn.

Before DuPont Company developed *p*-aramid, Monsanto Company had developed a polyamide-hydrazide named X-500.[5] After Kevlar's marvelous success, many researchers had developed many types of aramids. Many polyarylates having liquid crystalline nature without solvents were also

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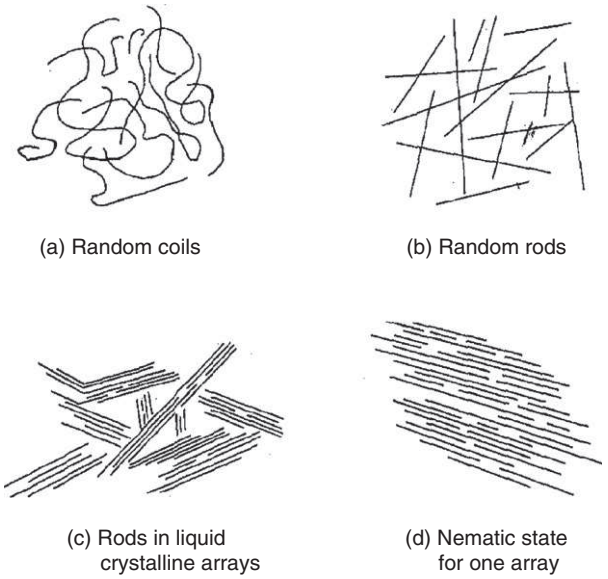


Figure 1 Schematic representation of polymer state in solution.[1] (a) Random coils, (b) random rods, (c) rods in liquid crystalline arrays, and (d) nematic state for one array.

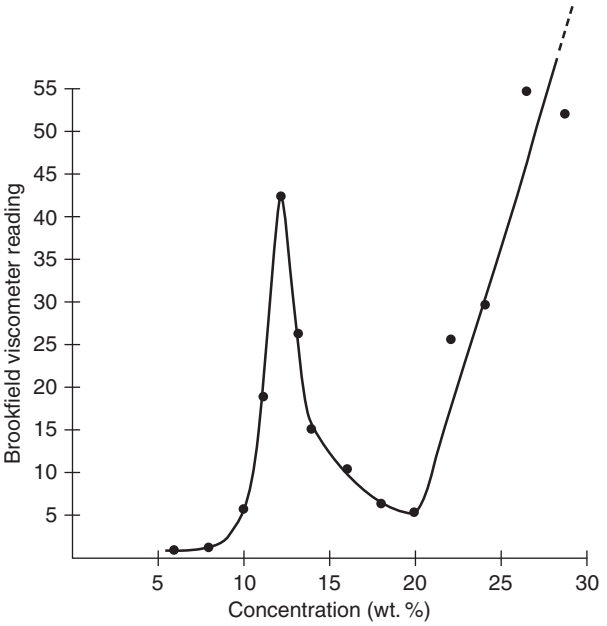
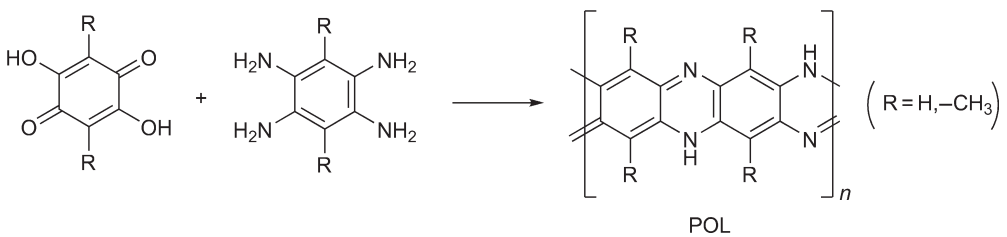


Figure 2 Relationship between viscosity and concentration of poly(*p*-phenylene terephthalamide) (PPTA) in H_2SO_4 solution. Reproduced from Close, L. G.; Fornes, R. E.; Gilbert, R. D. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 1825, [3] with permission of John Wiley & Sons, Inc.

developed in order to eliminate solution processing that is essential but costly for the aramids. These newly developed stiff polymers mostly have a linear backbone.

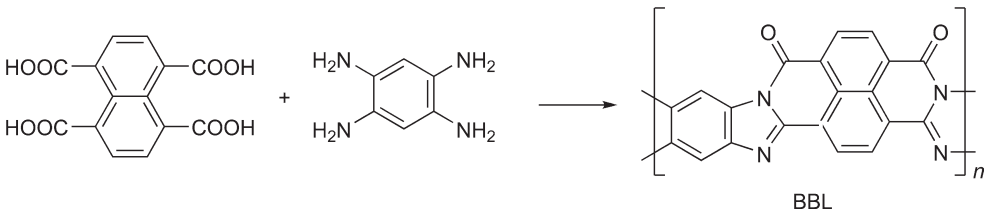
5.19.1.2 Ladder Polymers

The properties of the newborn fiber, Kevlar®, from a liquid crystalline polymer were marvelous. However, United States Air Force (USAF) researchers were not satisfied with its properties. Ladder polymers are designed to increase rigidity of the molecular chains, and to have high thermal stability and high mechanical properties, using the polyphosphoric acid (PPA) condensation method developed by Imai and Iwakura.[6,7] POL (poly(1,6-dihydropyrazino[2,3-*g*]quinoxaline-2,3,8-triyl-7-(2H)-ylidene-7,8-dimethylidene)) was prepared from 2,5-dihydroxy-*p*-benzoquinone and 1,2,4,5-tetraaminobenzene in hexamethylphosphoramide (HMPA) at 180 °C or from 116% PPA at 140 °C as shown in eqn [2].[8]



[2]

BBL (poly[(7-oxo-7H,10H-benz[*de*]-imidazo[4′,5′:5,6]-benzimidazo[2,1-*a*]isoquinoline-3,4:10,11-tetrayl)-10-carbonyl]) was prepared from a reaction of tetraaminobenzene and 1,4,5,8-tetracarboxylnaphthalene in PPA at 180 °C (eqn [3]).[9]



[3]

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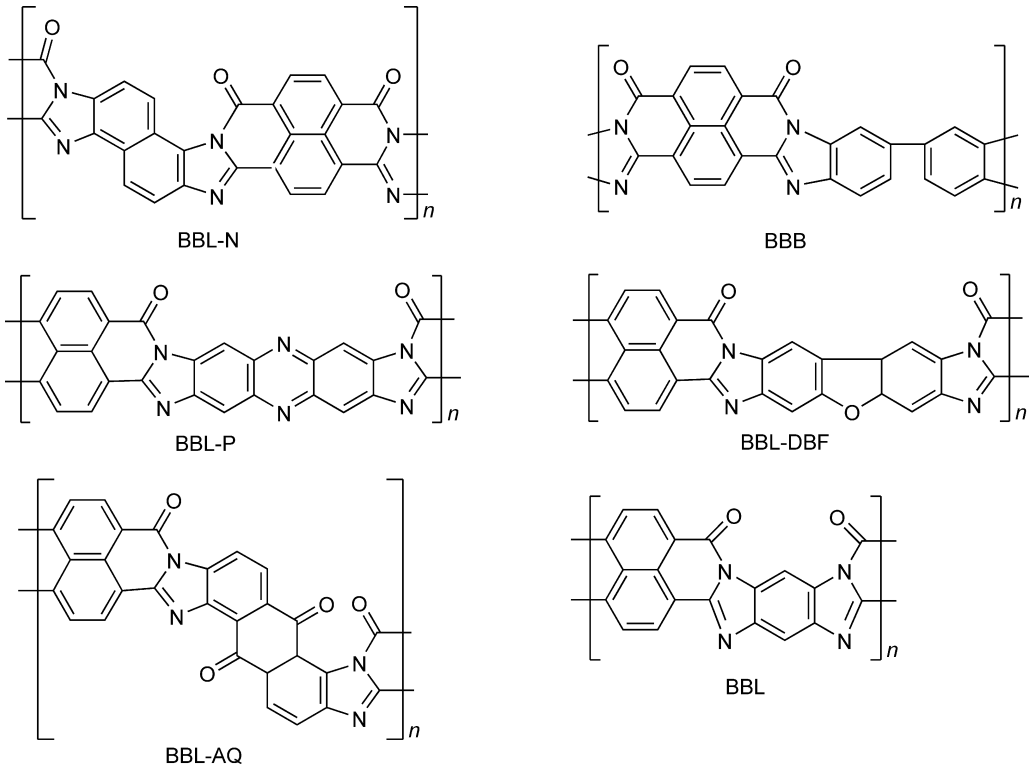

Figure 3 Ladder polymers.[10,11]

Other ladder polymers are shown in Figure 3. These ladder polymers show very good thermal stability up to 550 °C in air.[10,11]

Although these ladder polymers showed excellent heat resistance, polymerized materials were not easy to handle for forming articles because of their insolubility and non-melt-processability. Applying these PPA condensation methods to linear polymers is expected to achieve high modulus and excellent heat-resistant properties and processability. USAF sponsored the consortium to develop polybenzazoles (PBZs). Dow Company developed the polymerization method for synthesis of poly(*p*-phenylene benzobisoxazole) or polybenzoxazole (PBO) and found its excellent properties as a fiber. Dow and Toyobo Companies developed fiber production technologies. Finally, Toyobo Company succeeded to commercialize a PBO fiber named Zylon®. The tenacity and modulus of Zylon® are, respectively, 2 and 3 times as high as those of Kevlar® 29.[12]

5.19.1.3 Achieved Properties of Super Fibers from Lyotropic Polycondensates

The above-mentioned scheme of developments targeted to achieve the extended chain crystal (ECC) morphology through a liquid crystalline state of solution (lyotropic state). Generally, fibers having tenacity (strength of a fiber) and modulus more than 2 and 50 GPa, respectively, are called 'super fibers'. In sum, the properties currently achieved of super fibers manufactured from lyotropic polymers are shown in Table 1.

Table 1 Mechanical and thermal properties of super fibers

Polymer	*Product name*	*Tenacity (GPa)*	*Modulus (GPa)*	*Density (g cm^{-3})*	*Decomposition temperature (°C)*	*Elongation at break (%)*	*LOI*
PPTA	Kevlar® 49[13]	3.0	112	1.45	500	2.4	29
	Kevlar® 29[13]	2.9	71	1.44	500	3.6	29
	Technora®[14]	3.4	72	1.39	500	4.6	25
PBO	Zylon® AS[15]	5.8	180	1.54	650	3.5	68
	Zylon® HM[15]	5.8	280	1.56	650	2.5	68
PBZT	Experimental AS[16]	2.2	159–186	1.50			
	Experimental HT[17]	4.2	330	1.57			
PIPD	M5[18]	2.5	291	1.7	530	1.5	50

AS, as spun; HM, high modulus; HT, heat-treated fiber; LOI, limiting oxygen index; PBO, poly(*p*-phenylene benzobisoxazole); PBZT, poly(*p*-phenylene benzobisthiazole); PIPD, poly (bisimidazopyridinylene dihydroxyphenylene); PPTA, poly(*p*-phenylene terephthalamide).

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5.19.2 Aramids

'Aramid fiber' is defined as

> a manufactured fiber in which the fiber-forming substance is a long chain made of synthetic polyamides in which at least 85% of the amide (-CO-NH-) linkages are attached directly to the two aromatic rings.[19]

Aramids are prepared by the reaction of amino and carboxylic groups. First commercial aramid was the *m*-aramid fiber named Nomex® launched in the early 1960s by DuPont Company. In spite of wholly aromatic polyamide, Nomex® is not liquid crystalline because of the *meta*-linked backbone. It has high heat resistance but does not show excellent mechanical properties as classified super fiber. It has been widely used in the field of thermal and electrical insulation. As a completely stiff *para*-version of aramid, Kwolek[4] prepared poly(*p*-benzamide) (PBA) and poly (*p*-phenylene terephthalamide) (PPTA) that can form liquid crystalline solutions. Thus, *p*-aramid fiber Kevlar® was developed and commercialized in 1971 also by DuPont Company.

5.19.2.1 AB-Aramids

AB-aramid polymers are synthesized as in eqn [4]:

$$n\ H_2N{-}Ar{-}COCl \longrightarrow \left(HN{-}Ar{-}CO\right)_n + n\ HCl \qquad [4]$$

PBA is the first semicommercialized all-*para* homopolymer having the simplest chemical structure among the *p*-aramids prepared by Kwolek *et al.*[20] PBA is seemingly obtained from the self-condensation reaction of *p*-aminobenzoic acid. But *p*-aminobenzoic acid is unstable on prolonged exposure to light and air. So, this synthetic route is somewhat complex to protect the amino group compared to the AABB polymer condensation as shown in Scheme 1. PBA is polymerized from *p*-aminobenzoic acid with three- or two-step reactions. *p*-Aminobenzoic acid is converted to sulfinyl aminobenzoyl chloride with thionyl chloride, which is then treated with dry hydrogen chloride in ether to yield *p*-aminobenzoyl chloride hydrochloride. This salt is then dissolved in an amide solvent such as *N,N*-dimethylacetamide (DMAc) and hydrogen chloride is released, so that the polymerization reaction can proceed and generate PBA.

Also, PBA can be obtained directly by dissolving sulfinyl aminobenzoyl chloride in an amide solvent such as tetramethylurea with equivalent water.

The polymerization degree of PBA is influenced by many factors such as purities of the monomers and the solvents, reaction temperature, and stirring rates.[20]

PBA can form liquid crystalline solution in amide solvents. Figure 4 shows the relationship between viscosity and

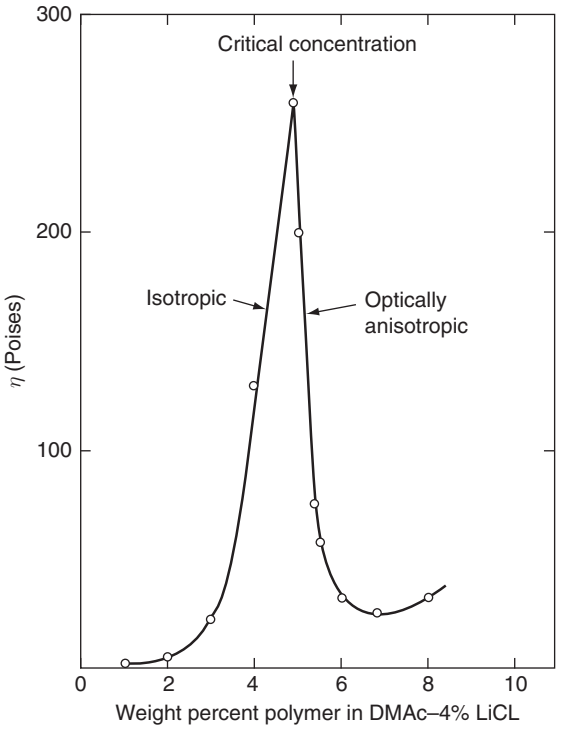
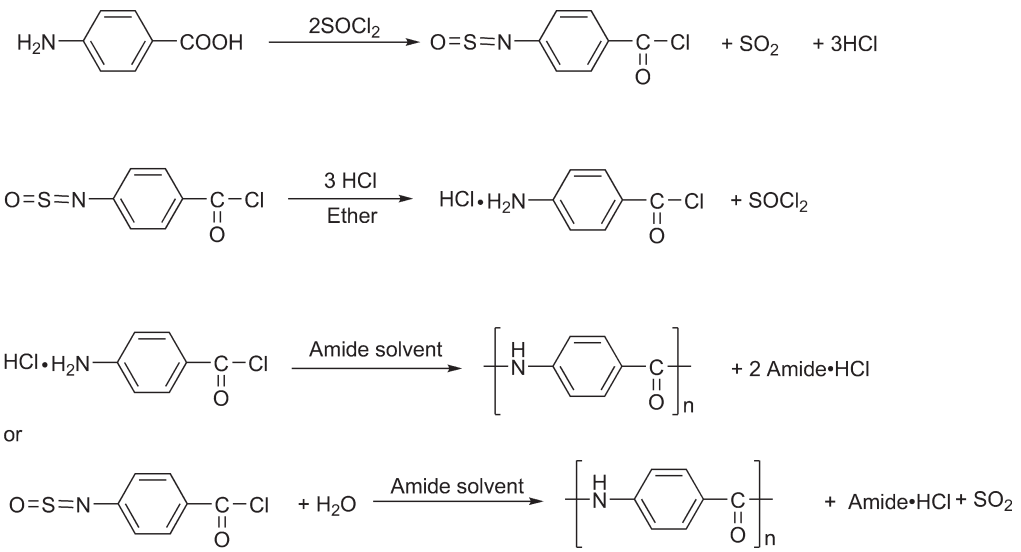


Figure 4 Relationship between concentration of polymer and solution viscosity for PBA ($\eta_{inh} = 2.41$).[20]



Scheme 1 Synthetic route of poly(*p*-benzamide) (PBA).[20]

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concentration for a solution of PBA in DMAc with 4 wt.% lithium chloride (LiCl). Viscosity of this solution increases steeply with increasing concentration of PBA. Above the critical concentration, viscosity of the solution decreases dramatically. PBA fiber could be made of this anisotropic solution with a dry or wet spun. The tenacity of the fiber was 9.7 g denier^{-1} (1.3 GPa) at its maximum.[20]

5.19.2.2 AABB-Aramids

AABB aromatic polyamides are prepared from aromatic diamines and diacids including diacid chlorides. The first representative for the polymer of this classification is *m*-aramid fiber named Nomex®.[21] It is polymerized from *m*-phenylenediamine and isophthaloyl dichloride in an amide solvent such as DMAc by solution polymerization. On the other hand, Conex® commercialized by Teijin Company is prepared by interfacial polymerization (eqn [5]).[22]

PPTA is prepared from *p*-phenylenediamine and terephthaloyl dichloride in the amide solvent at −15 °C (eqn [6]).[4,23–27] PPTA is insoluble in general organic solvents. Only two solvent systems have been found to dissolve for PPTA polymerization. One of the systems is mixture solvent of HMPA and small amount of polar solvents such as *N*-methylpyrrolidone (NMP), DMAc, and tetrahydrofuran (THF). Another system is the polar solvents with LiCl or calcium chloride ($CaCl_2$).[28] It was found that the mixture solvent system of HMPA and NMP in the volume ratio 2:1 produced PPTA with the highest inherent viscosity (η_{inh}) as shown in **Figure 5**.[29]

However, the use of HMPA is not permitted in the commercial production due to its carcinogenic nature for rats.[30] The NMP/$CaCl_2$ system has become more important now.

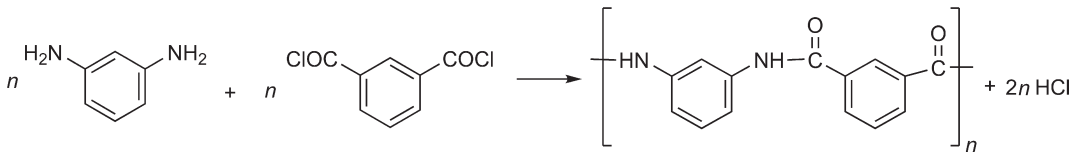
5.19.2.3 Other Preparation Methods of PPTA

Some studies have been performed to find different ways to synthesize PPTA.

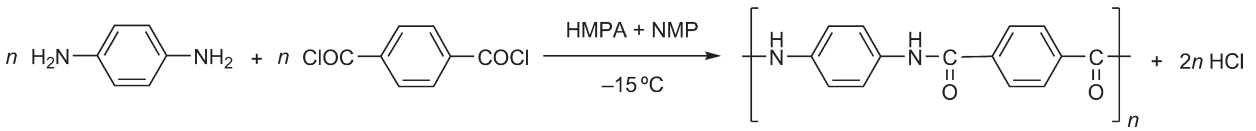
The direct polycondensation of aromatic dicarboxylic acids and diamines was studied using diphenyl and triaryl phosphates in the mixture solvent of NMP and pyridine containing LiCl (**Scheme 2**).[31]

Another direct polymerization was reported as shown in eqn [7], in which terephthalic acid (TA) and *p*-phenylenediamine were dissolved in NMP containing $CaCl_2$ and LiCl in the presence of pyridine.[32]

Furthermore, the direct polymerization method was developed, in which the process was catalyzed by 3,4,5-trifluorophenylboronic acid. This reaction proceeds in the presence of 1–10 mol.% of the catalyst at 27 °C in the mixed solvent of *m*-terphenyl and *N*-butyl-2-pyrrolidinone (NBP) (eqn [8]).[33]



[5]



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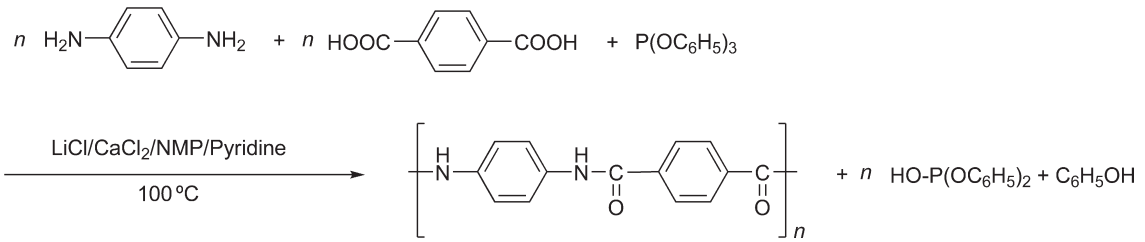
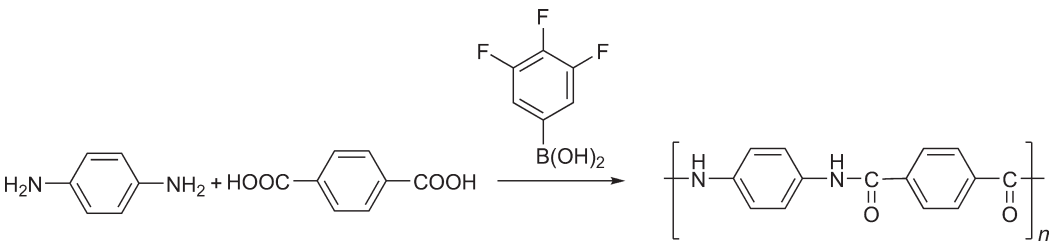


[7]



[8]

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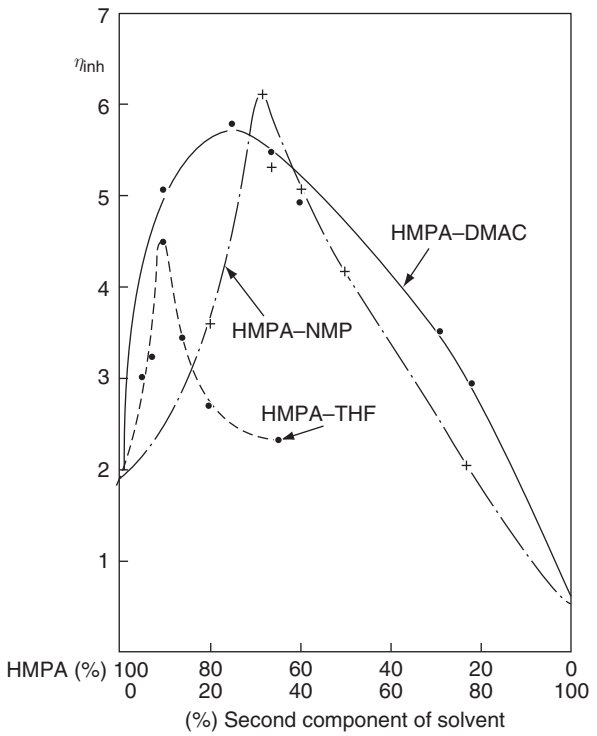


Figure 5 Relationship between volume ratio of mixed solvents and η_{inh} of PPTA polymer.[29]

The advantage of these synthetic methods is no generation of hydrogen chloride.

5.19.2.4 Fiber Spinning

5.19.2.4.1 PPTA solution

Polymerized PPTA is dissolved in concentrated sulfuric acid (H_2SO_4) to prepare a dope for fiber spinning. The H_2SO_4 solution of PPTA shows a typical lyotropic solution feature. The relationship between viscosity and concentration of PPTA is shown in Figure 2. Oriented domains are formed at the concentration more than 12 wt.%. The viscosity of the solution reaches its minimum point at around 20 wt.%, and then increases again in the region of much higher concentration beyond the minimum point. Phase diagram of the anisotropic solution of PPTA ($\eta_{inh} = 4.9$) in concentrated H_2SO_4 is shown in Figure 5.[29]

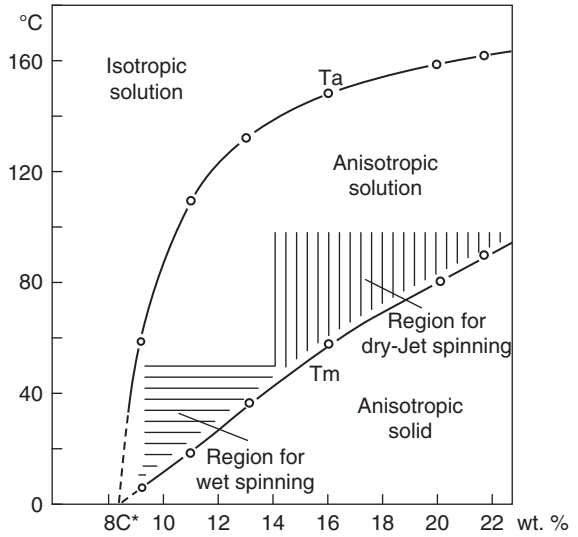
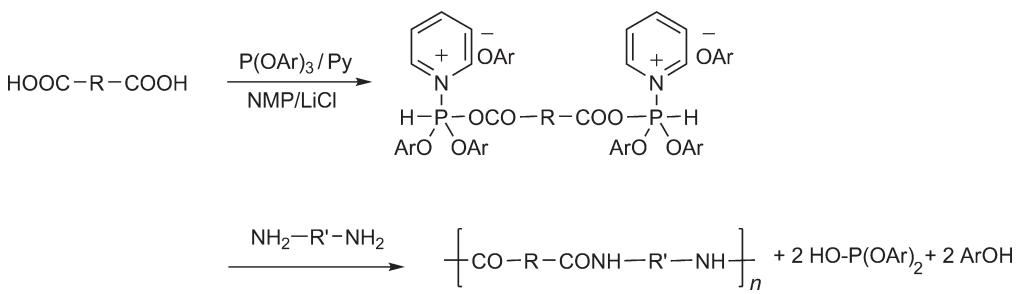


Figure 6 Phase diagram of the H_2SO_4 solution of PPTA ($\eta_{inh} = 4.9$).[29]

From the viewpoint of commercial production, the higher polymer concentration and the lower solution viscosity are better for spinning solution. The higher spinning temperature shows the lower viscosity. However, higher temperature causes the decomposition of a polymer. Therefore, the spinning specification for solution is chosen in the region of vertical striped area of Figure 6.

5.19.2.4.2 Fiber preparation

It was found that the high-strength and high-modulus fiber was made by the dry-jet wet spinning with an anisotropic solution of PPTA by Blades.[25] The process is schematically shown in Figure 7.[25] According to the explanation of Yang,[34] the mechanism of the polymer chain orientation is as follows. The anisotropic solution of PPTA is extruded from spinneret through an air gap into a coagulation bath. The liquid crystalline domains align along the flow direction and form highly ordered regions of molecular chains during the process by extrusion from spinneret to the coagulation bath. Although some deorientation of the director of liquid crystalline domain occurs at the exit of the spinneret by the relaxation nature of a polymer chain, the dope is oriented by being stretched again in the air gap as shown in Figure 8.[35] The fibers are washed with water and neutralized with a basic reagent such as sodium hydroxide (NaOH) and finally dried. As-spun (AS) fiber can be treated under high temperature (250–550 °C) with high



Scheme 2 Direct polycondensation of aromatic dicarboxylic acids and diamines.[31]

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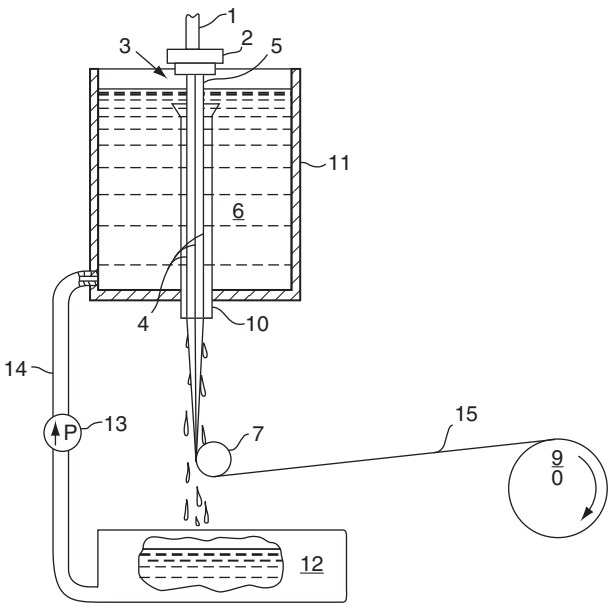

Figure 7 Dry-jet wet spinning process of PPTA.[25] 1, a transfer line; 2, a spinning block; 3, a spinneret; 4, extruded filaments; 5, a layer of gas; 6, a coagulating liquid; 7 guides; 9, a rotating bobbin; 10, a spin tube; 11 and 12, containers; 13, a pump; 14, a tube; and 15, an as-spun yarn.

tension to increase the modulus of fibers because of the increase in orientation and crystallinity of molecules.[25]

5.19.2.5 Fiber Structure

The crystal structures of PPTA fibers were first reported by Northolt and van Aartsen.[36] Also, Hasegawa *et al.*[37] and Yabuki *et al.*[38] independently proposed the X-ray crystal structure analysis. By assuming the monoclininc unit cell, the crystal structure of well-oriented PPTA fibers was proposed with the dimensions of $a = 7.87$, $b = 5.18$, c (fiber axis) = 12.9 Å, $\gamma \approx 90°$. The crystal structure is shown in Figures 9 and 10. Figure 10 shows hydrogen-bonded molecular chains of PPTA fiber.[36] Hydrogen bonds between amino and carbonyl groups of the adjacent molecular chains are represented by broken lines. Thus, the compressive strength of PPTA fibers is slightly higher among super fibers.

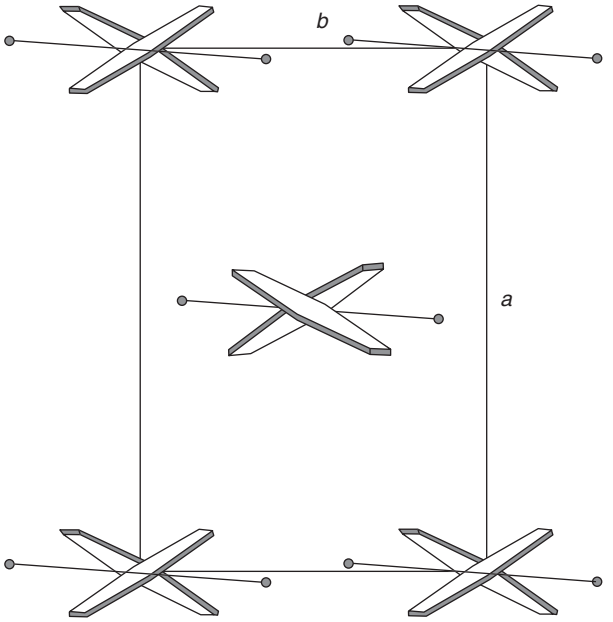

Figure 9 Crystal structure of PPTA fiber parallel to the *c*-axis. Reproduced from Northolt, M. G.; van Aartsen, J. J. *Polym. Lett. Ed.* **1973**, *11*, 333, [36] with permission of John Wiley & Sons, Inc.

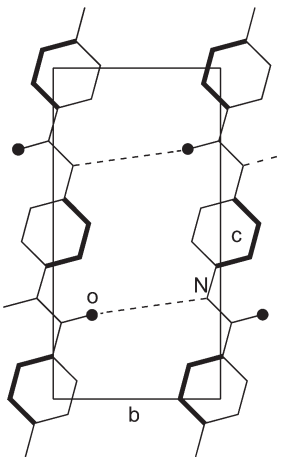

Figure 10 Hydrogen-bonded molecular chains of PPTA fiber. Reproduced from Northolt, M. G.; van Aartsen, J. J. *Polym. Lett. Ed.* **1973**, *11*, 333, [36] with permission of John Wiley & Sons, Inc.

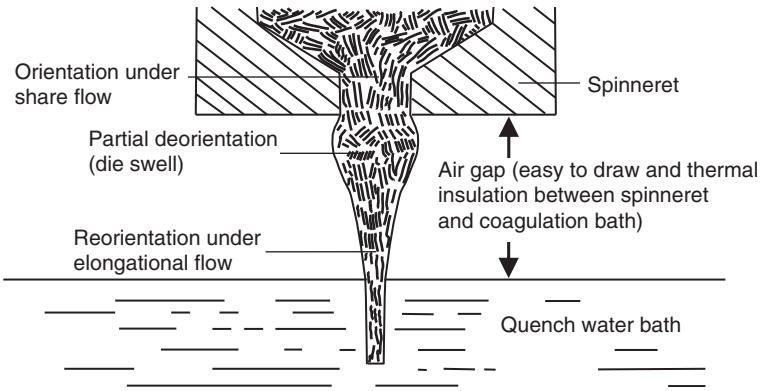

Figure 8 Molecular orientation during dry-jet wet spinning after the original figure.[35]

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The supramolecular structure of PPTA fiber has also been studied using a combination of electron diffraction and dark-field image techniques by Dobb *et al.*[39] A schematic model of the PPTA fiber of Kevlar® 49, named as a radial pleated-sheet model, is proposed as shown in **Figure 11**. The sheets composed of wavy extended chain structure show the preferential orientation of *b*-axis of crystal toward radial direction. In addition to this model, PPTA fibers have a skin-core structure, which is caused by the different achievement of coagulation between inside and outside of a filament.[39]

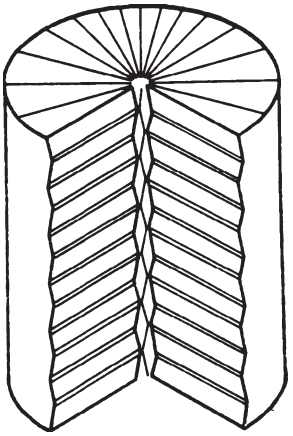
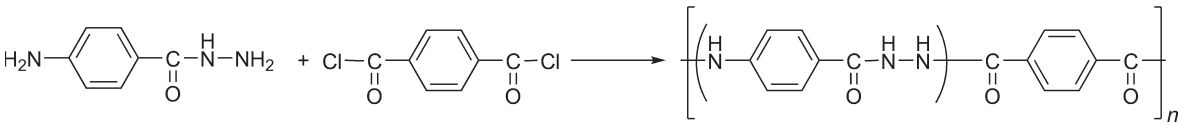


Figure 11 Schematic diagram of Kevlar® 49 fibers showing the radially arranged pleated sheets.[39] Reproduced from Dobb, M. G.; Johnson, D. J.; Saville, B. P. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 2201, with permission of John Wiley & Sons, Inc.

5.19.2.6 Copolymers

5.19.2.6.1 Aromatic polyamide-hydrazide: X-500

In order to overcome the insolubility of rigid polymers to a general organic solvent, a lot of investigations have been performed and it is understood that the development of a semirigid molecule is one of such solutions. For example, aromatic polyamide-hydrazides were developed by Monsanto Company in the early 1970s. X-500 is one of such representatives, which is derived from *p*-aminobenzohydrazide and terephthaloyl dichloride at low temperature (eqn [9]). X-500 is soluble in organic solvents such as dimethylformamide (DMF) and dimethyl sulfoxide (DMSO).[5]

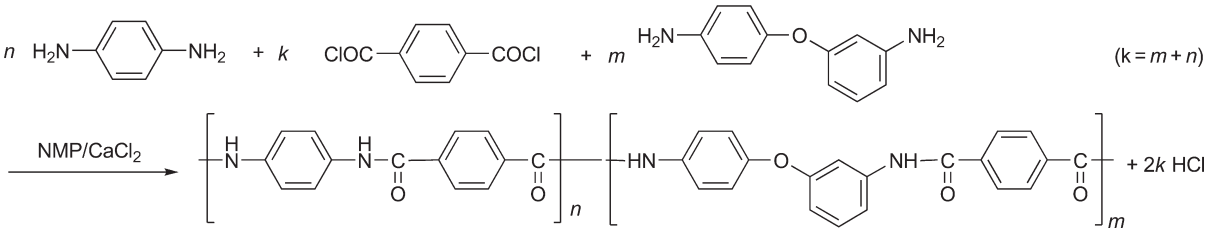


[9]

The solution of these polymers does not show anisotropy, but it has been speculated that a transient mesophase is formed when the solution is subjected to an elongational flow. Fibers of X-500 are produced with a normal wet spinning and drawing. Thus, high molecular chain orientation is achieved, and the fiber exhibits high tenacity of 2.0–2.2 GPa and high modulus of 80–100 GPa.[5,40–43]

5.19.2.6.2 Technora®

Teijin Company succeeded in development of an aramid copolymer fiber named Technora® and commercialized it in 1985. Technora® exhibits high mechanical properties and resistance to chemicals. It is prepared from *p*-phenylenediamine, 3,4′-diaminodiphenylether, and terephthaloyl dichloride in an amide solvent with a small amount of alkali salt at 0–80 °C (eqn [10]).[44]



[10]

where $m = 0.25$, $n = 0.25$, and $k = 0.5$. The amide solvents used in this polymerization are HMPA, NMP, DMF, DMAc, and so on. The alkali salts used are $CaCl_2$ and LiCl.

The reaction mixture is neutralized with calcium hydroxide ($Ca(OH)_2$), and then it is spun through a spinneret into an aqueous coagulation bath containing $CaCl_2$ using the dry-jet wet spinning technique. The washed filaments are superdrawn and dried at 500 °C.[44]

5.19.2.6.3 Hoechst aramids

The major drawback of the above-mentioned process of PPTA fiber is to redissolve isolated PPTA in concentrated H_2SO_4. Hoechst Company developed some aramid fibers to perform direct spinning from the polymerized dope. A balance of stiff and flexible monomer units in a polymer chain is a key factor to design soluble aramid polymers. The stiff moieties have a function to develop high tenacity and high modulus. The flexible or kinked units have a function to raise the solubility of polymers in organic solvents such as NMP. The

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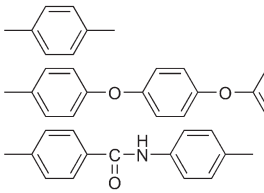
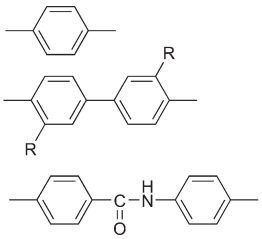
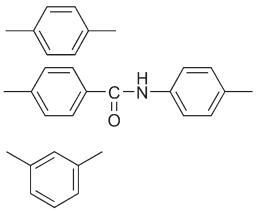
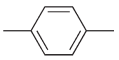
Table 2 Mechanical properties of Hoechst aramid fibers[45]

Polymer type	*1*	*2*	*3*	*PPTA*
TPC + diamines				
Tenacity (GPa)	2.5	2.6	1.5	2.6
Modulus (GPa)	54	126	38	69
Elongation (%)	4.1	2.2	6.0	3.3

The unit of tenacity and modulus is converted from cN tex^{-1} in the original article to GPa.
TPC, terephthalic acid dichloride.

mechanical properties of the Hoechst aramid fibers are shown in Table 2.[45]

5.19.2.6.4 Russian aromatic fibers

Manufacturing methods and properties of aromatic fibers in Russia are well summarized by Perepelkin.[46] The research for high-performance polymers began in Russia in the 1970s. Polymers related to PPTA, poly-*p*-amidebenzimidazole, and their copolymers have been studied. Now three fibers named Terlon®, SVM®, and Armos® are commercially produced as high-strength fibers.[46,47]

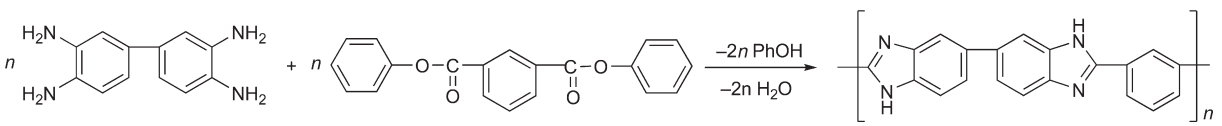
Terlon® is an aramid copolymer fiber based on PPTA containing 10–15% of comonomer units. The chemical structures of SVM® and Armos® are shown in Figure 12.[46,47]

5.19.3 Polybenzazole

The research of high heat-resistant polymer in 1960s was focused on the ladder polymers such as semiladder poly(benzobisimidazobenzophenanthroline) (BBB) and ladder poly (benzobisimidazobenzophenanthroline) (BBL) as stated in Section 5.19.1.2. Although due to difficulties in processing of the ladder polymers, the target of the research is shifted to aromatic heterocyclic polymers, above all, *para*-ordered structure polymers. PBZs are found to have good mechanical and thermal properties compared with aramids. Among others, PBO exhibits excellent mechanical and thermal properties because of the linearity of the molecular chains.

5.19.3.1 Polybenzimidazole

Polybenzimidazole (PBI) fiber manufactured by Celanese Company is a high-performance fiber having high thermal stability and chemical resistance. It is polymerized from the free amine of 3,3′-diaminobenzidine and diphenyl isophthalate as starting materials as shown in eqn [11], although the polymerization proceeds in a two-stage reaction process. First, the reaction begins when both the monomers melt above 260 °C, removing water and phenol as by-products in vacuum. Second, the generated polymer is smashed into powder, and heated for 9 h at 400 °C to complete the polymerization reaction. The obtained polymer is dissolved in DMAc with LiCl. The PBI fiber is made from the condensed solution with dry spinning. A semisolid fiber is stretched in a chamber of high temperature.[48,49]



[11]

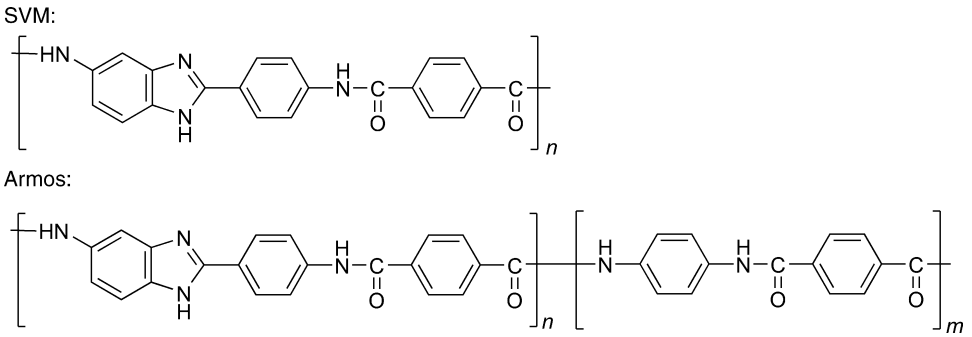


Figure 12 Chemical structures of SVM® and Armos® fibers.[46,47]

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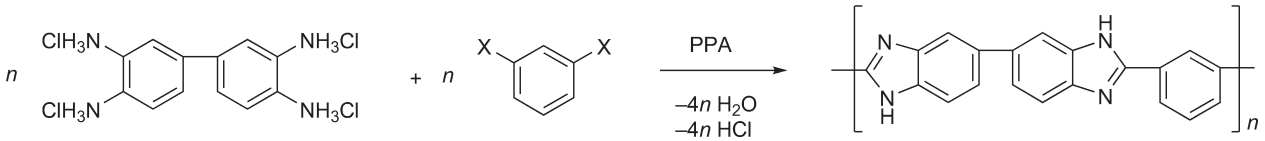
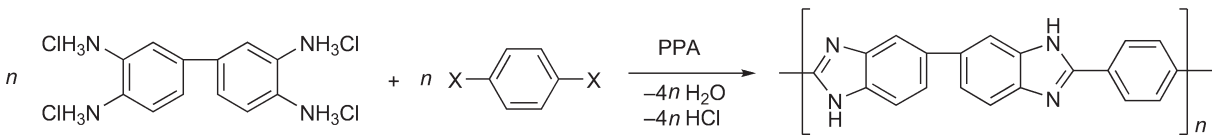
On the other hand, the polymerization method using 3,3′-diaminobenzidine tetrahydrochloride dihydrate was developed by Iwakura *et al.*[7] The use of the tetrahydrochloride dihydrate increases stability of the reaction sites, and PPA increases uniformity of the reaction solution. The polymerizations were performed at 140–200 °C for 30 h (eqns [12] and [13]).[7] Jung *et al.*[50] performed this polymerization using 3,3′-diaminobenzidine tetrahydrochloride dehydrate instead of the dihydrate.



[12]

where X = –COOH, –$COOCH_3$, –$CONH_2$, or –CN.

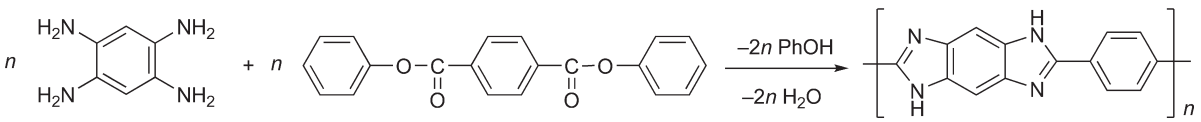


[13]

where X = –COOH, –$COOCH_3$, or –$CONH_2$.

Poly(*p*-phenylene benzobisimidazole) (PPBI) has a linear and planar molecular structure because of two five-membered rings on both sides of the benzene ring. It is synthesized from tetraaminobenzene tetrahydrochloride and diphenyl terephthalate in dibenzyltoluene for 6 h at 350 °C under nitrogen flow (eqn [14]). η_{inh} is 0.58 dl g^{-1} in 97% H_2SO_4.[51]

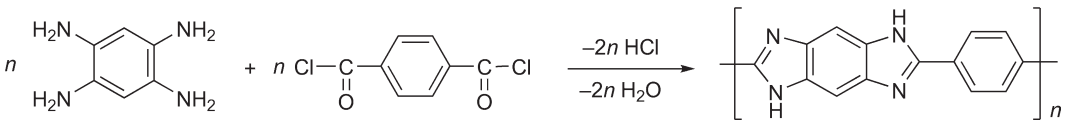
In order to circumvent the problem of instability of tetraaminobenzene and inexact stoichiometry of the AA and BB monomers, the use of the AB-type monomer was investigated as shown in Scheme 3.[52] 2-(4′-Methoxycarbonylphenyl)-4,5-dinitrobenzimidazole was obtained from 1,2-diamino-4,5-dinitrobenzene and *p*-(methoxycarbonyl)benzoyl chloride in dichlorobenzene under reflux for 2 h. The generated compound was hydrolyzed in aqueous KOH solution at 90 °C for 8 h. 2-(4′-Carboxyphenyl)-4,5-diaminobenzimidazole was obtained as hydrochloride by reduction of 2-(4′-carboxyphenyl)-4,5-dinitrobenzimidazole with 55 psi of H_2 and Pd-C in concentrated hydrochloric acid at room temperature for 8 h. Finally, the polymerization of PPBI was performed in PPA at 90 °C to decompose the hydrochloride, and then heated at 200 °C for 8 h. The intrinsic viscosity (η_{sp}) was 1.3 in methanesulfonic acid (MSA).[52]



[14]

Interfacial polymerization was studied with tetraaminobenzene tetrahydrochloride and sodium carbonate in a water phase and terephthaloyl dichloride in chloroform (eqn [15]). η_{inh} is 0.08 dl g^{-1} in concentrated H_2SO_4.[49] The degree of polymerization is not so high.

PPBI was prepared successfully by another method shown in Scheme 4. 1,3-Diamino-4,6-(*p*-toluenesulfamido)benzene was prepared from the nitration of 1,3-toluenesulfamidobenzene and subsequent reduction with catalyst. 1,3-Diamino-4,6-(*p*-toluenesulfamido)benzene and



[15]

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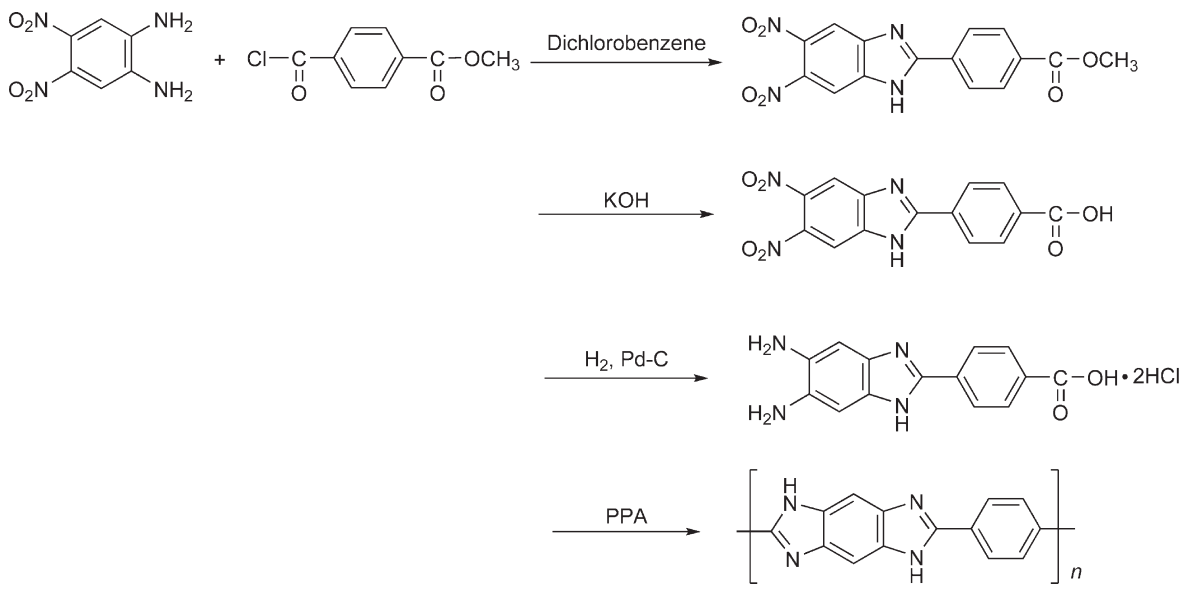
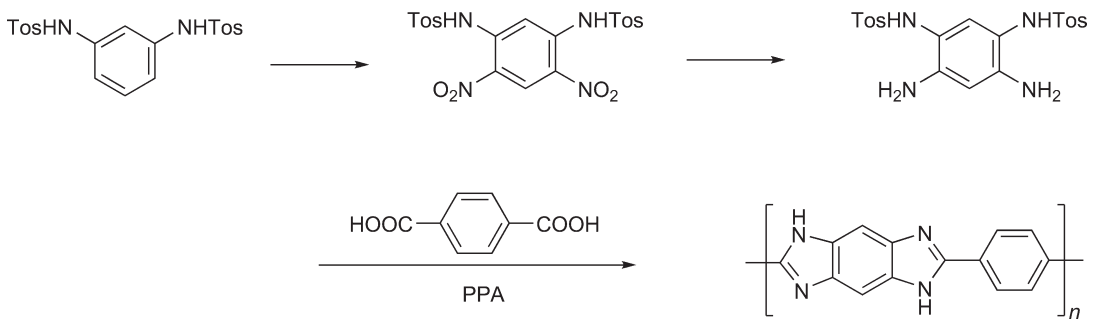


Scheme 3 Synthetic route of PPBI from AB type monomer.[52]



Scheme 4 Synthetic route of PPBI from *m*-phenylenediamine.[52]

terephthalic acid were heated to 95 °C in PPA to obtain the free amine. High-molecular-weight PPBI was obtained by heating it up to 195 °C for 6 h. η_{inh} is 5.0 dl g^{-1}.[52]

5.19.3.2 PBO and Poly(*p*-phenylene benzobisthiazole)

PBO and poly(*p*-phenylene benzobisthiazole) (PBZT) have highly ordered and rigid structures in their molecular backbones. ABPBO and ABPBZT are semirigid polymers because of the presence of kinks in the molecular chains. These polymer unit structures are shown in Figure 13.

PBO fiber is manufactured commercially under the trade name of Zylon® by Toyobo Company since 1998. PBO is prepared from 1,3-dihydroxy-4,6-diaminobenzene (DHDAB) and TA in PPA.[53] Aromatic diamines are easily oxidized in air. Therefore, reduction reagents such as stannous chloride ($SnCl_2$)

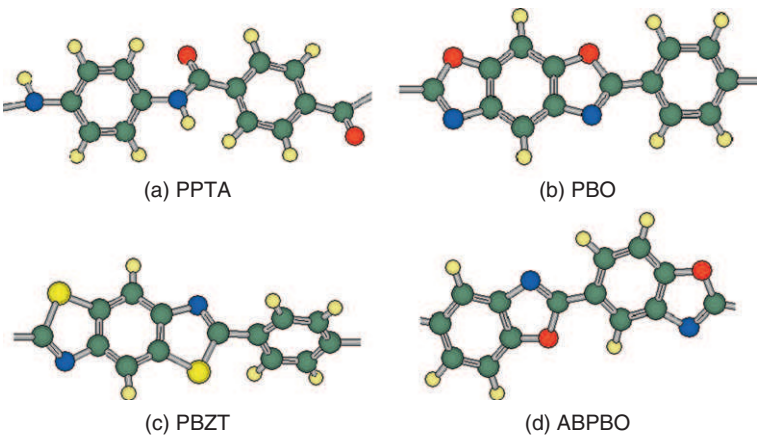


Figure 13 Polymer unit structures of (a) PPTA, (b) PBO, (c) PBZT, and (d) ABPBO calculated the using Molecular Orbital Package-Parameter Method 3 (MOPAC PM3 method).

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are often added in the polymerization reaction system in order to prevent the amino groups of the monomer and the oligomer chain ends from oxidation.

PBZT is prepared from 1,4-diamino-2,5-benzenedithiol (DABT) and TA in PPA.[53]

PBO and PBZT are polymerized from the corresponding BB monomers (which have two basic functional groups, such as DHDAB or DABT, respectively) and TA in PPA.[54] The polymerization mechanism of PBO was revealed in detail based on the study of NMR data by So *et al.*[55] Based on their studies, the mechanism proposed is shown in **Figure 14**.[55] The carbonyl group in TA is activated through the formation of a carboxylic-phosphoric anhydride. The hydroxyl group attacks the anhydride and forms an ester, then an acyl migration undergoes to form the amide, and yields an oxazole ring as a result. Because of the very low solubility of TA in PPA, PBO oligomers are end-capped with DHDAB. In this manner, a PBO molecular chain grows up gradually in PPA (eqns [16] and [17]).[55]

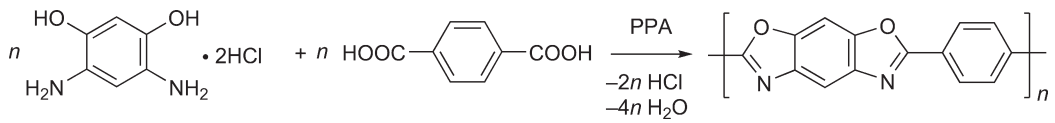
The functions of PPA in the polymerization are solubilization of the monomers and release of the hydrogen chloride, protecting amino groups of the aromatic diamines. PPA with around 60% P_2O_5 content was found to perform the two functions well. During the dehydrochlorination step, P_2O_5 content in PPA is kept more than 60%. PPA with P_2O_5 content above 82% promotes the condensation reaction at sufficient rate. After the release of hydrogen chloride completes, P_2O_5 is added to become above 82% at the end of polymerization reaction. A typical P_2O_5 content for the dehydrochlorination and the polymerization steps of a 15 wt.% PBT polymerization is shown in **Figure 15**.[54]

5.19.3.2.1 Monomer synthesis of PBO and PBZT

One of the big challenges in PBO manufacturing is to develop synthetic routes of DHDAB.

The most orthodox synthetic method starts with a nitration of 1,2,3-trichlorobenzene as shown in eqn [18]. It is a highly selective process and the overall yield of DHDAB is very good.[56]

The synthesis of DHDAB from resorcinol with sodium phenyldiazonium salt in water is followed by hydrogenation as shown in eqn [19].[57]



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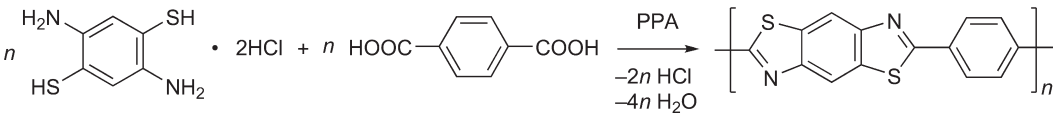

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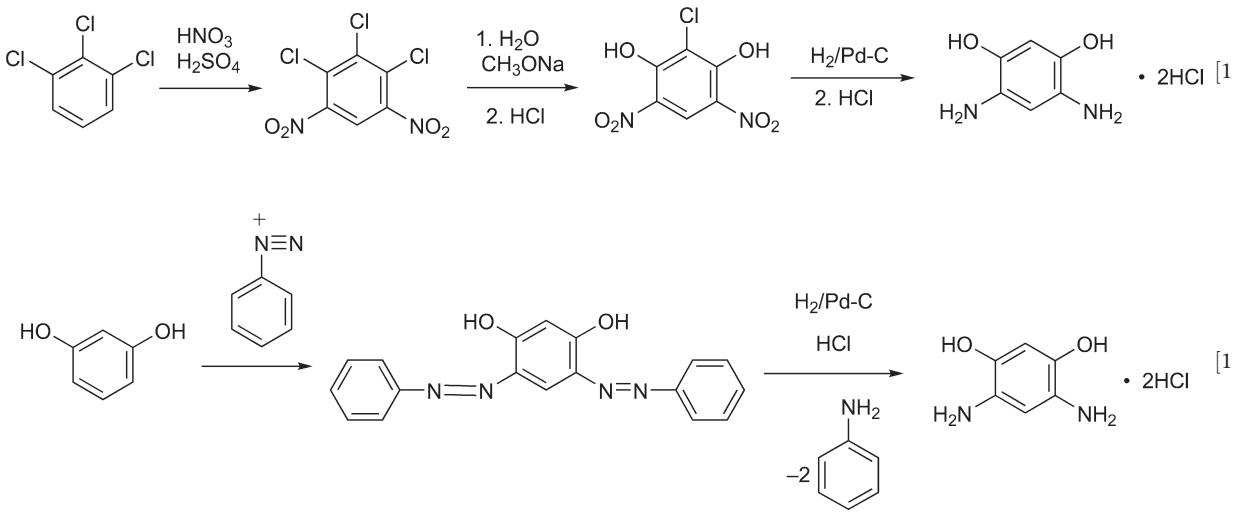

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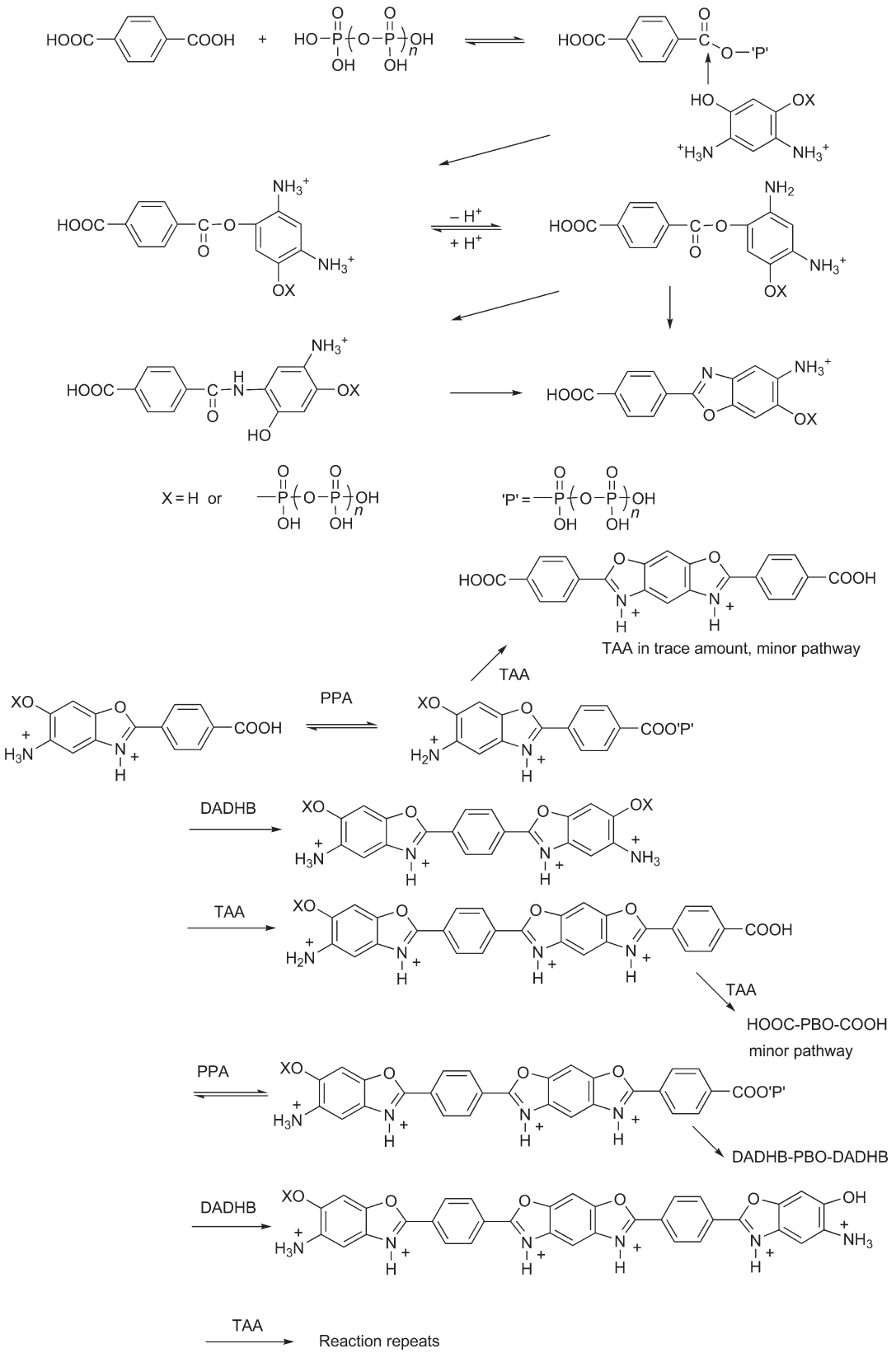

Figure 14 The polymerization mechanism of PBO.[55]

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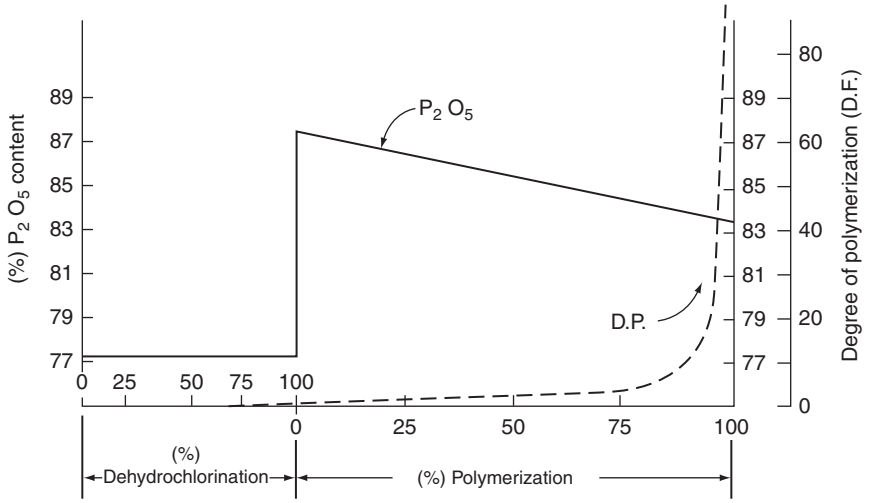
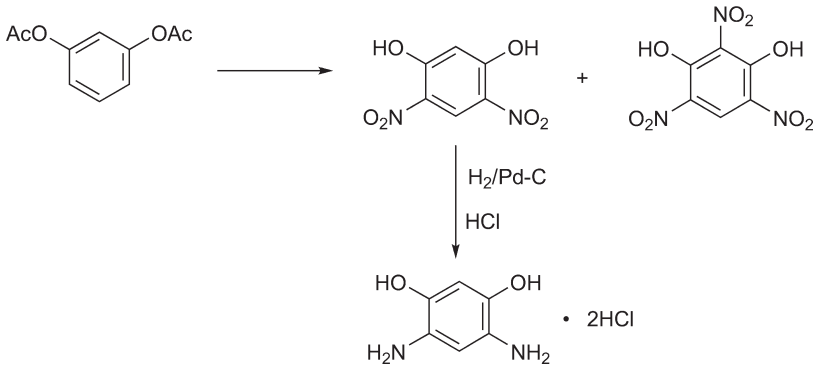


Figure 15 Calculated P_2O_5 content for a 15 wt.% PBT polymerization.[54]



Scheme 5 Preparation of DHDAB from 1,3-diacetoxybenzene.[58,59]

DHDAB was also prepared from 1,3-diacetoxybenzene as a starting material through two steps, nitration and reduction, as shown in Scheme 5.[58,59]

The use of the AB-type monomer was investigated by Jin *et al.*[60] as shown in Scheme 6. This synthetic route is similar to that shown in Scheme 3. It is noteworthy that 4,6-dinitroresorcinol was synthesized with high purity and high yield of 75%. The overall yield was 38%. It is slightly lower, although 2-(4′-methoxycarbonylphenyl)-5-amino-6-hydroxybenzoxazole (MAB) is stable in air. Thus, MAB can be used for PBO polymerization without converting the hydrochloride.[60] An advantage of using MAB is the ability to omit the exchange reaction stage of dehydrogen chloride in PPA, that is, no generation of hydrogen chloride. So, polymerization time can be shortened.

On the other hand, DABT was prepared from *p*-phenylenediamine as a starting material. *p*-Phenylenediamine was converted to *p*-phenylenebisthiourea with an excessive ammonium thiocyanate. The reaction yield for the cyclization step from *p*-phenylenebisthiourea to diaminobenzobisthiazole is about 55%. Because of this low efficiency in the reaction, the scale-up of PBZT polymerization has been given up. The synthetic scheme of DABT is shown in Scheme 7.[61]

5.19.3.2.2 ABPBO and ABPBZT

The synthetic routes of ABPBO and ABPBZT are shown in Scheme 8.[62] 3-Amino-4-hydroxybenzoic acid hydrochloride (AHBAH), a monomer for ABPBO, was prepared in two steps by nitration of *p*-hydroxybenzoic acid with nitric acid (HNO_3) in concentrated H_2SO_4, followed by reduction of the nitration product with $SnCl_2$ in hydrochloric acid.

The monomer for ABPBZT, 3-mercapto-4-aminobenzoic acid hydrochloride (MABAH), was prepared in two steps by a cyclization reaction of *p*-aminobenzoic acid with sodium thiocyanate and bromine in methanol at −5 to −10 °C and up to 5 °C, followed by a ring-opening reaction by hydrolysis in aqueous potassium hydroxide (KOH) under reflux.[62]

ABPBO and ABPBZT were polymerized from AHBAH and MABAH, respectively, in PPA at high temperature.[62] The tenacity of ABPBO fiber is equal to that of PPTA fiber and the heat resistance is equal to that of PBO fiber.

5.19.3.2.3 Fiber spinning of PBO

An anisotropic spinning solution (dope) of PBO was prepared by dissolving approximately 10% of polymer in an acidic solvent such as concentrated H_2SO_4, MSA, and PPA. The relationship between viscosity and concentration of PBO in concentrated H_2SO_4 at 70 °C is shown in Figure 16.[63]

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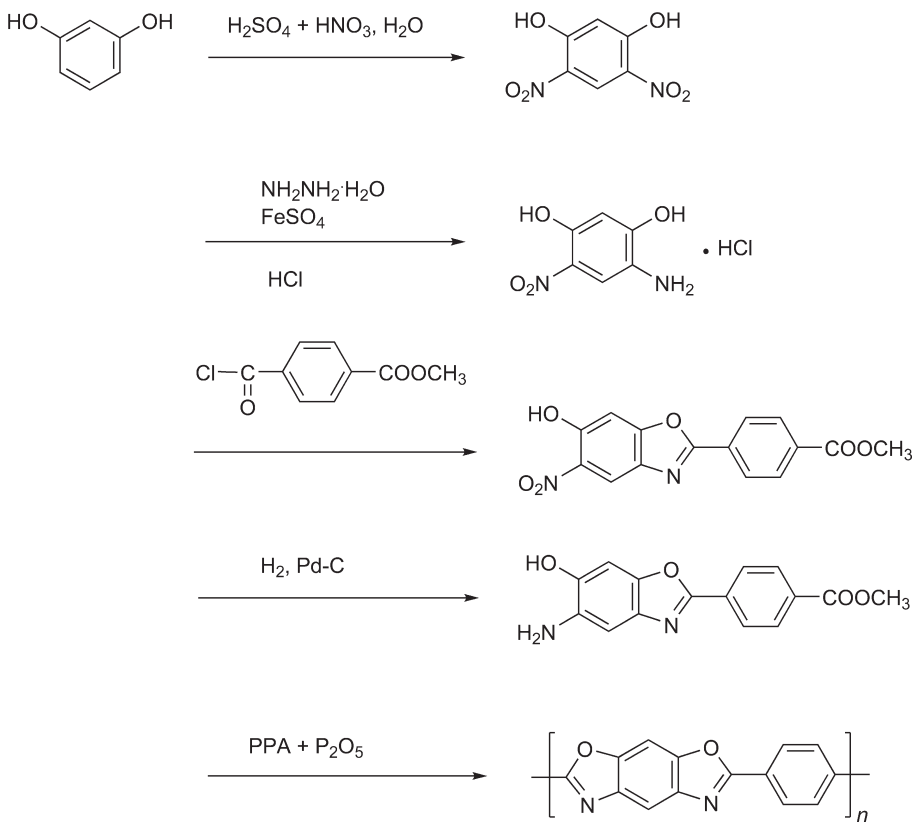
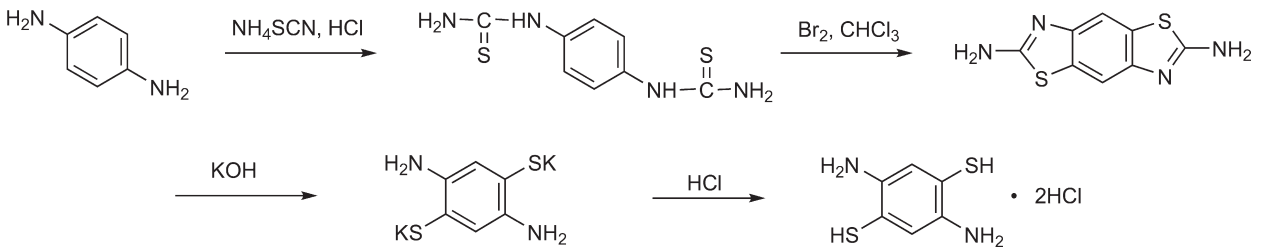
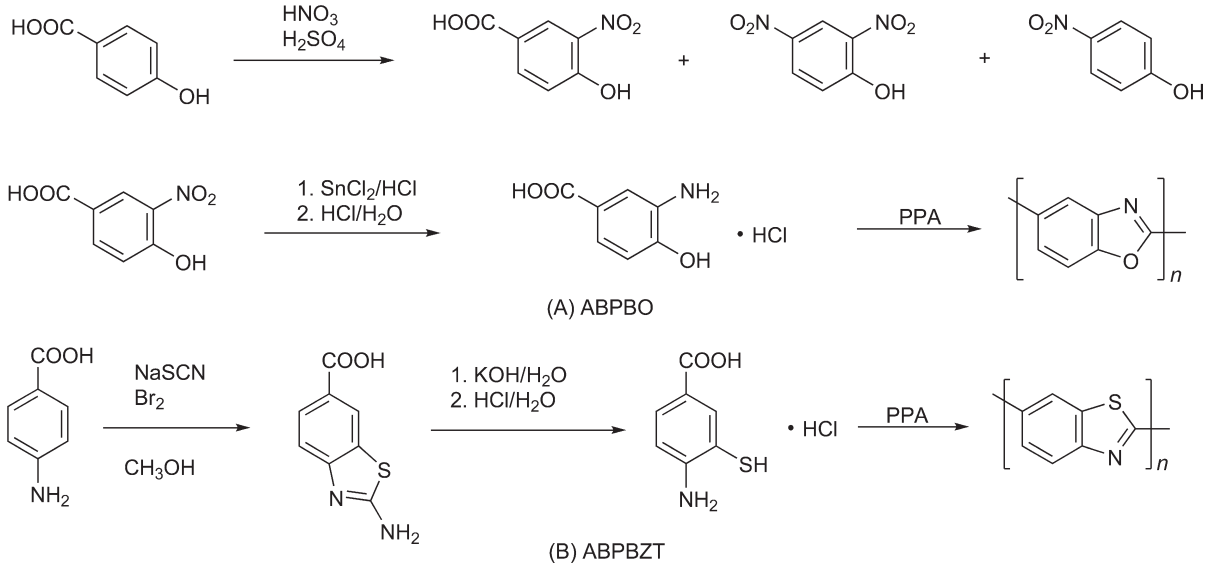


Scheme 6 New synthetic route of PBO.[60]



Scheme 7 Synthetic route of DABT.[61]



Scheme 8 Preparation routes of ABPBO and ABPBZT.[62]

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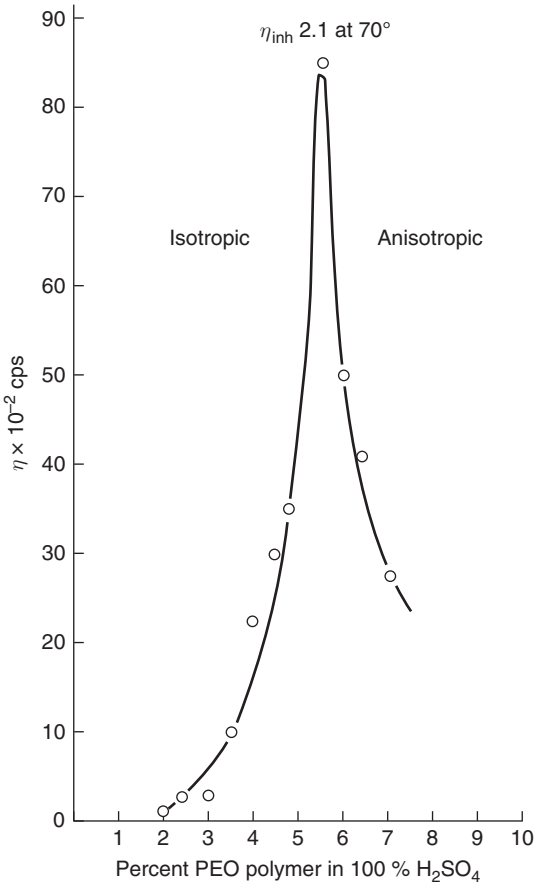

Figure 16 Relationship between concentration of polymer and solution viscosity of PBO.[63]

Oriented domains are formed at concentration more than 6 wt.%. The PBO dope is semisolid at concentration more than 8 wt.% and at ambient temperature.

The PBO spinning is performed by the dry-jet wet spinning technique using the spinning machine as shown in Figure 17.[63] The PBO dope is extruded into air, and PBO molecular chains are oriented by being stretched with high draw ratio as stated in the session of PPTA spinning. Then, the stretched dope goes into the coagulating liquid. In order to obtain the fiber having high mechanical properties, the spin draw ratio is very important.[62]

For the commercial production of PBO fiber, PBO is synthesized with controlled molecular weight using the polymerization system as shown in Figure 18.[64] As a first step, dehydrochlorination of DHDAB is performed in PPA with TA and P_2O_5 at up to 120 °C. The P_2O_5 is added at the beginning of the dehydrochlorination stage to keep its content in PPA above 82% at the end of polymerization. After the dehydrochlorination stage, PBO oligomer is prepared by heating at 120–150 °C for 3 h. Next, additional TA in PPA is poured into the oligomer dope at the entrance of an extruder to produce PBO with high molecular weight. The polymerization reaction is completed by vigorous stirring at 200–220 °C. The molecular weight is adjusted to be suitable for fiber spinning by controlling the quantity of adding TA to the oligomer dope.

The spinning of PBO is performed by the dry-jet wet spinning technique as mentioned above. After the coagulation of the PBO dope, PPA in the PBO fibers is removed by being washed with water and neutralized with a dilute NaOH aqueous solution, and washed with water again. Subsequently, the fiber is dried at high temperature. This fiber manufacturing process of PBO is basically similar to the PPTA fiber process.

5.19.3.2.4 Fiber structure

The fiber structure model for PBO fiber (Zylon® AS) was proposed by Kitagawa *et al.*[65] as shown in Figure 19. According to their explanation, the fiber is formed by microfibrils with diameter of 10–50 nm and contains many capillary-like microvoids. The microvoids exist between microfibrils, and are connected to each other through openings between microfibrils. There is void-free region in the outermost layer of a fiber. The microfibril is made up of extended PBO molecules, highly oriented to the fiber axis. The preferential orientation exists and the *a*-axis of the PBO crystal is aligned radially in the cross-section of the fiber.[65]

The tensile strength of Zylon® AS is 5.8 GPa, tensile modulus 180 GPa, and elongation at break 3.5%. The modulus increases substantially by heat treatment at 580 °C up to 280 GPa, while elongation at break decreases to 2.5%.[16]

5.19.3.3 PBZ Fiber with Enhanced Lateral Interaction

Fibers made from PBO and PBZT show outstanding mechanical and thermal properties. However, their compressive

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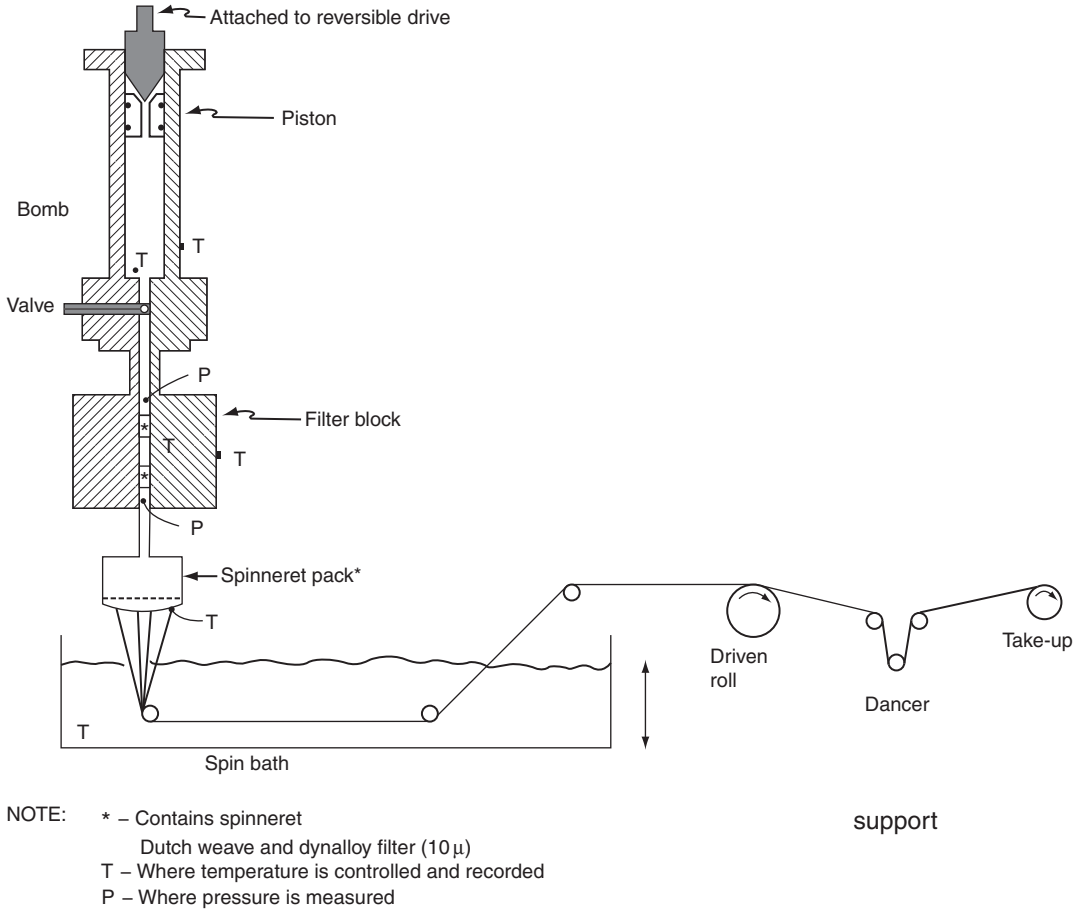

Figure 17 Schematic diagram of PBO spinning machine.[63]

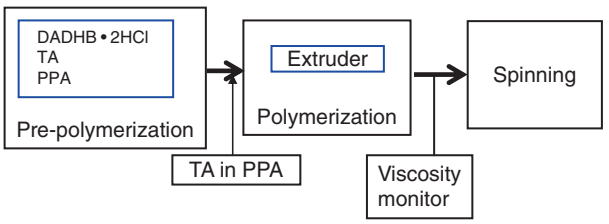

Figure 18 Diagram for staged PBO polymerization with controlled molecular weight.[64]

characteristics are not enough for certain applications that need high compressive strength. It was thought that the compressive failure occurred by the lack of appropriate interaction between molecules. Many approaches were performed in order to improve the compressive strength of PBZ fibers by increasing interactions such as van der Waals interactions, hydrogen bonds, and cross-links between adjacent molecular chains.[64,66–72]

The cross-linked PBT fiber was made by a heat treatment at 700 °C and the compressive strength was measured as a composite made of fiber with epoxy matrix, and it was found that its compressive strength has improved. The compressive strength increased from 0.16 GPa to 0.25–0.28 GPa, which is higher than that of Kevlar® as reference. The heat-treated AS PBO fiber at 740 °C became insoluble in MSA, and the compressive strength measured by the mini-composite method was improved from 0.31 to 0.39 GPa.[64]

Sweeny[66] introduced cross-links to PBZT molecular chains by heating aryl halide-substituted PBZT fibers at 450 °C. Similarly, in order to form cross-links, methyl groups[67–70] and dimethylphenoxy groups[71] were introduced to PBO and PBZT. For example, the possible chemical structures generated from methyl-substituted PBZT by heat treatment are shown in Scheme 9. Furthermore, PBO was treated with polyphenylene sulfide pendant groups on phenylene groups in molecular chains at 600 °C.[72] These treatments succeeded to increase the compressive strength up to 20%. Heterocyclic pendant groups were introduced to increase the interaction force of lateral direction, and the compressive strength was improved by 10% and then no further.

Another approach is to introduce hydrogen bonds between molecular chains. Although hydroxyl groups were introduced to PBO and PBZT with expectation to form hydrogen bonds between intermolecular chains, it was found that intramolecular hydrogen bonds were formed in a molecular chain as shown in eqn [20]. It should be noted that they are not interchains. The compressive strengths of the fibers were the same or lower than normal PBO and PBZT fibers.[73–75]

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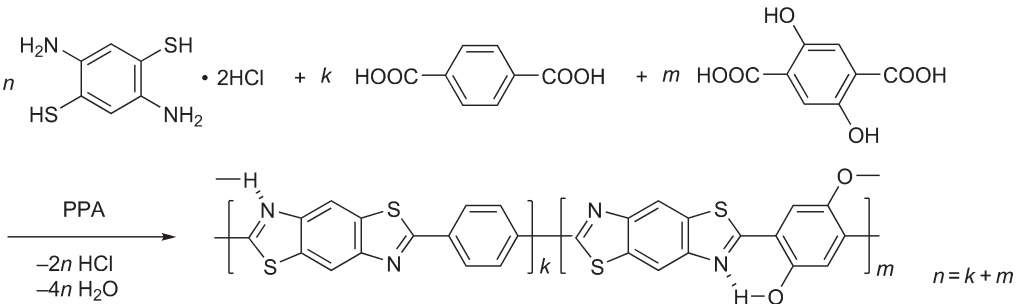

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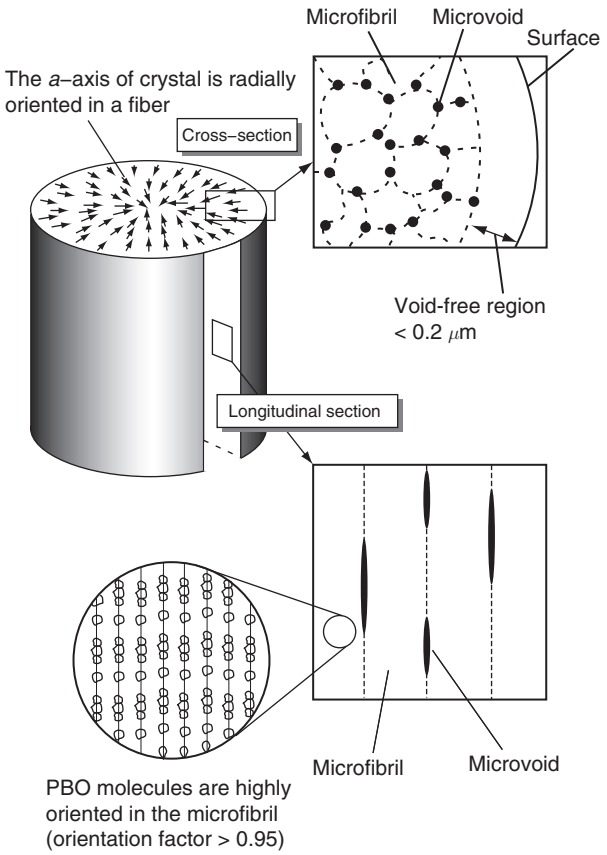

Figure 19 PBO structure model for AS fiber.[65]

On the other hand, Me-PPBI (chemical structure shown in Figure 20) was found to form hydrogen bonds between only adjacent paired molecules when the fiber was heat treated at 250 °C as shown in Figure 21. Nevertheless, such a polymer did not afford the improved compressive strength as expected for Reference 76.

5.19.3.4 Poly(diimidazopyridinylene dihydroxyphenylene)

Poly{2,6-diimidazo[4,5-*b*:4′,5′-*e*]pyridinylene-1,4-(2,5-dihydroxy) phenylene} (PIPD, or M5) fiber shows higher compressive strength among super fibers. PIPD was polymerized from 2,3,5,6-tetraaminopyridinum 2,5-dihydroxyterephthalate (TD salt) in PPA in the presence of a trace of tin under nitrogen flow as shown in Scheme 10. The 18 wt.% solution of the polymer forms anisotropic phase.[18] TD salt was synthesized from tetraaminopyridine and 2,5-dihydroxyterephthalic acid (DHTA). Tetraaminopyridine was derived with the two-step reaction, nitration of 2,6-diaminopiridine in mixed acid and reduction of the nitro compound in H_3PO_4. DHTA was synthesized by a convenient aromatization of diethyl succinoylsuccinate in acetic acid with aqueous hydrogen peroxide and a sodium iodide (NaI).[18]

The spinning of PIPD was performed by the dry-jet wet spinning of the dope prepared by the above-mentioned polymerization. The fiber manufacturing process is similar to the PBO fiber process. In order to produce the high-modulus fiber, the AS fiber is heat treated at high temperature above 400 °C under constant stress.[77]

The process of the crystal structural formations at each stage of the fiber manufacturing process was depicted in detail by Lammer *et al.*[77] as shown in Figure 22. According to their explanation, the polymer dope is oriented by being stretched and forms a crystal solvate phase at positions 2 and 3. After the fiber washing process, PPA is extracted from the fiber and a crystal hydrate is formed at position 4. During the drying process, water molecules in the crystal hydrate are removed and then the water-free PIPD structure is formed at position 5.[77]

The crystal structure of heat-treated PIPD fiber is shown in Figure 23.[78] Hydrogen bonds, revealed by broken lines, are formed between hydroxyl groups and imidazole rings of not only the intramolecular chain but also the intermolecular chain. Thus, the strong interactions between polymer chains are formed. This is the reason for a high compressive strength of PIPD (1.7 GPa).[78]

5.19.3.5 Other Synthesis Methods of PBZ

Aromatic PBOs can be prepared by the following routes besides above-mentioned methods.

The first is a two-step route that involves the polymerization of bis(*o*-aminophenole)s from aromatic dicarboxylic acid chlorides and thermal cyclization in the solid state or solution. Recently, the two-step method using trimethylsilyl-substituted bis(*o*-aminophenol) monomers has been applied to the synthesis of various PBOs as shown in Scheme 11.[79–83] While isolated PBOs are insoluble in general organic solvents, the intermediate poly (*o*-hydroxyamide)s are soluble in general organic solvents. Thus, various aromatic PBOs films can be prepared using these intermediates.

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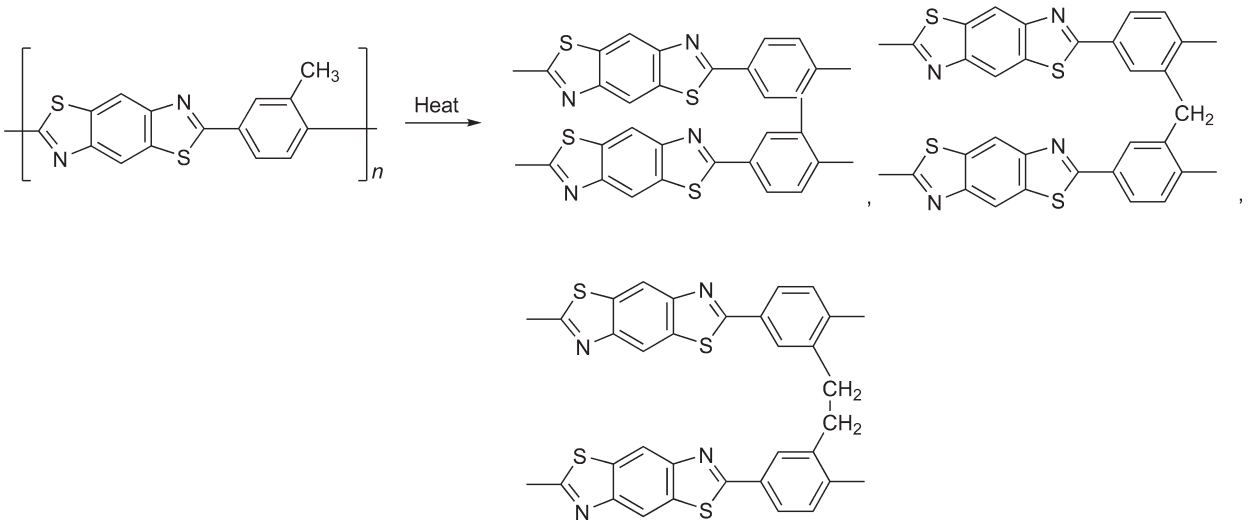


Scheme 9 Possible structures from heat-treated PBZT with methyl pendant groups.[69,70]

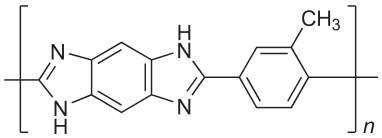


Figure 20 Me-PPBI.[76]

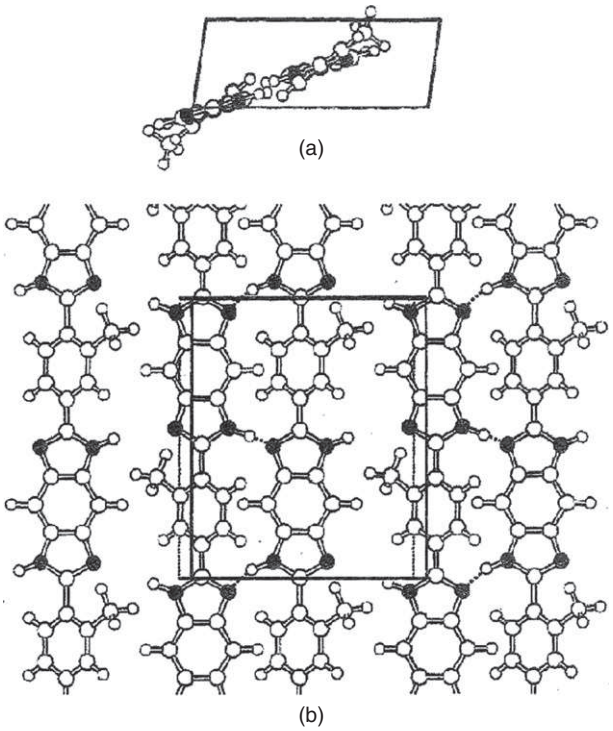


Figure 21 (a) *a–b* plane and (b) *a–c* plane of proposed monoclinic crystal structure of Me-PPBI.[76]

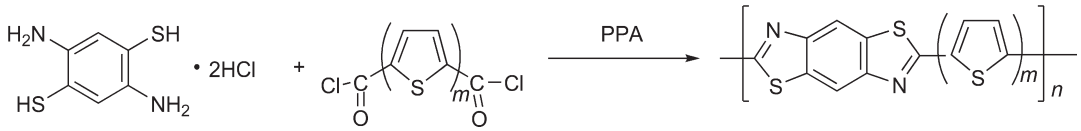
PBO was synthesized by the trimethylsilyl-substituted DHDAB and terephthaloyl dichloride as shown in Scheme 12.[84]

The second is a method involving the polycondensation of bis(*o*-aminophenol)s with aromatic dialdehydes. The generated poly(*o*-hydroxyazomethine)s were cyclized in the solid state or solution at high temperature as shown in Scheme 13.[85]

The third is a method using soluble poly(*o*-hydroxyimide)s derived from bis(*o*-aminophenol)s and bis(acid anhydride)s. Poly(*o*-hydroxyimide) was found to rearrange to a PBO at a temperature above 400 °C as shown in Scheme 14.[86]

5.19.3.6 Other Structures

PBZTs containing thiophene moieties instead of phenylene group were polymerized in PPA (eqn [21]).[87,88] These polymers are expected to possess high electric conductivity.



[21]

where $m = 1–3$.

PBO and PBZT develop the deep original colors. Colorless PBX was synthesized by introducing cage-like hydrocarbon moieties such as bicyclo[2.2.2]octane to a monomer unit.[87] This polymer was obtained from DABT and bicycle[2.2.2] octane-1,4-dicarboxylic acid chloride in PPA (eqn [22]). The

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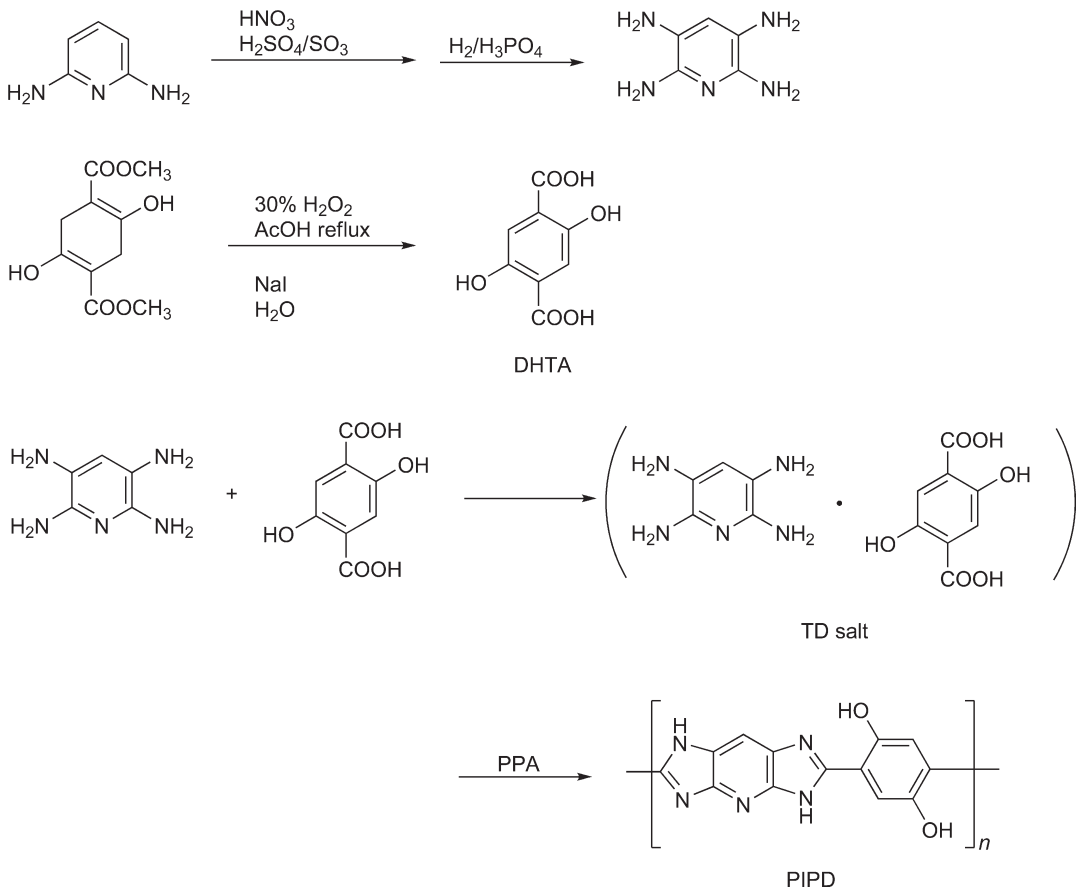

Scheme 10 The synthetic route of PIPD.[18]

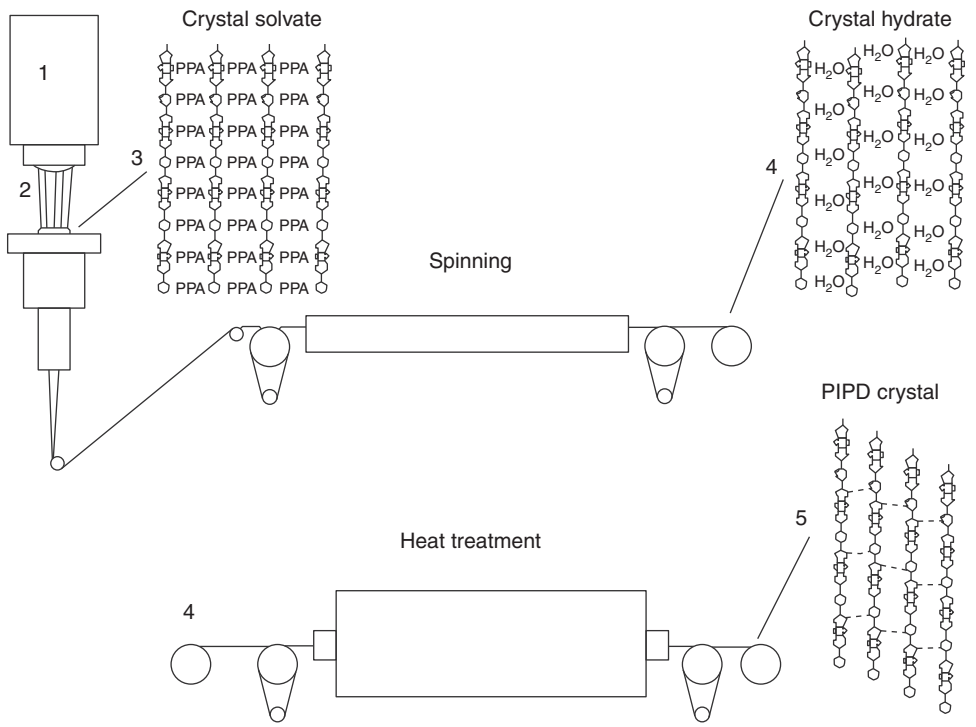

Figure 22 Formation process of crystal structure of PIPD fiber: 1, nematic phase; 2, oriented nematic phase; 3, crystal solvate; 4, crystal hydrate; and 5, water-free structure.[77]

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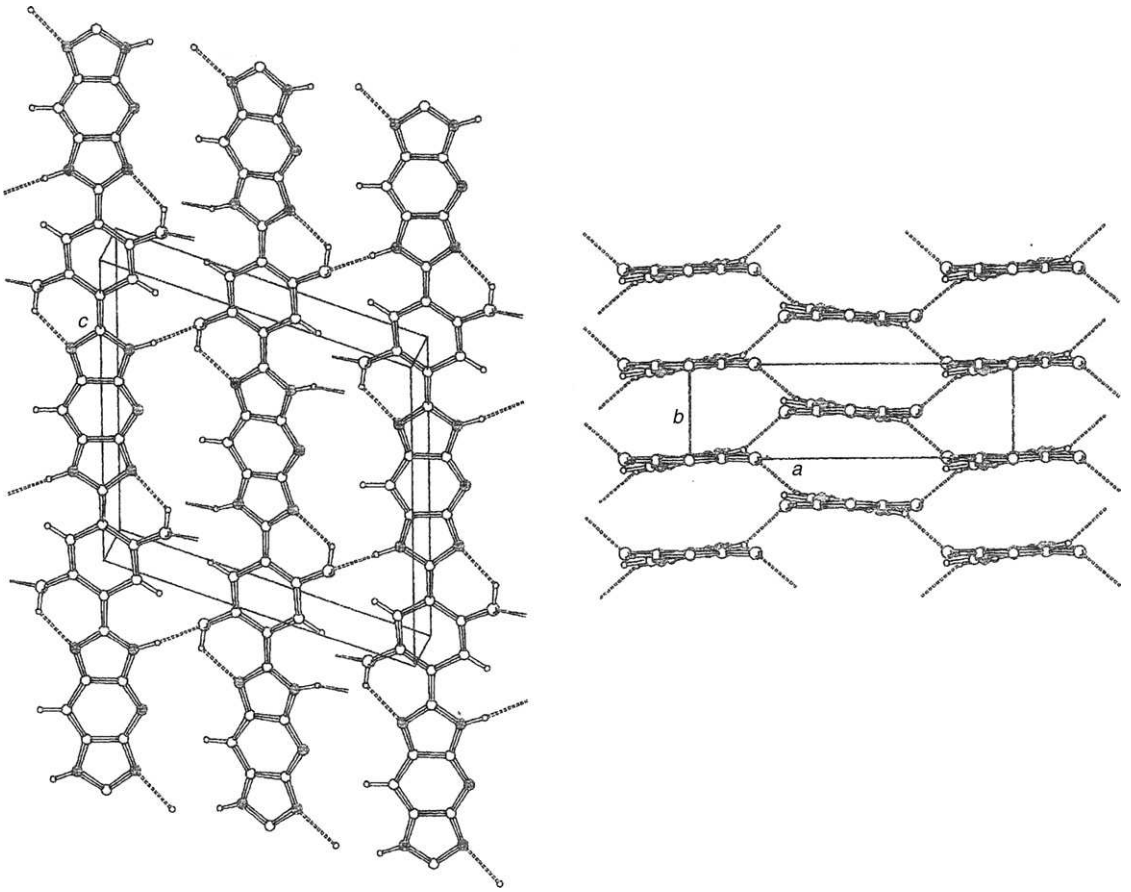
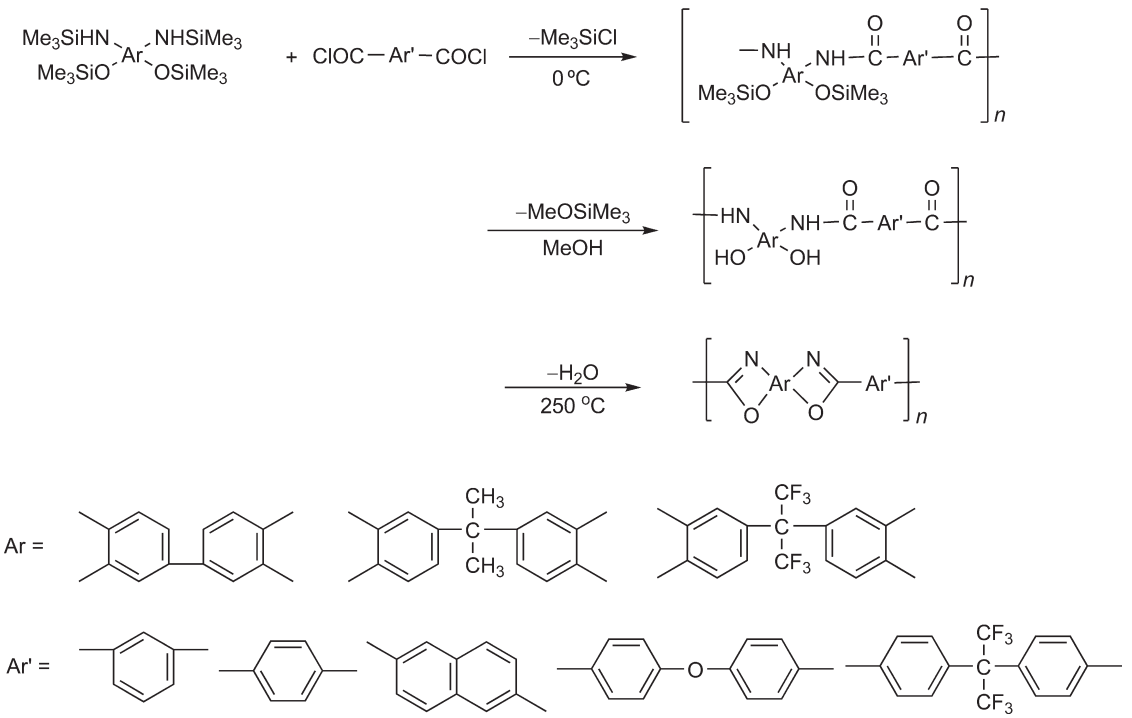


Figure 23 Crystal structure of heat-treated PIPD with hydrogen bond network.[78]



Scheme 11 Synthetic scheme for polybenzoxazoles.[79]

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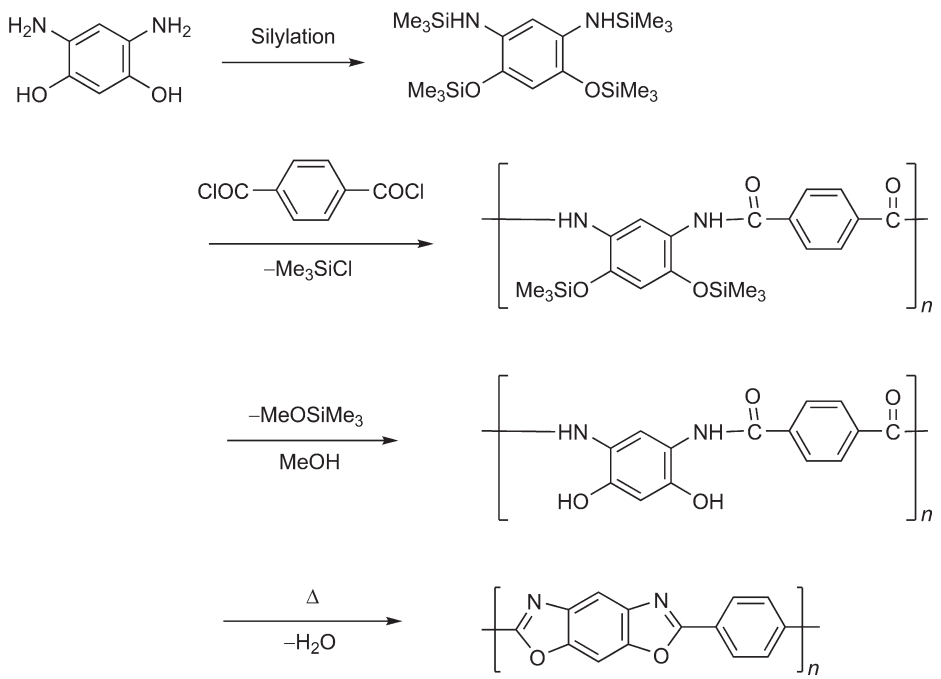
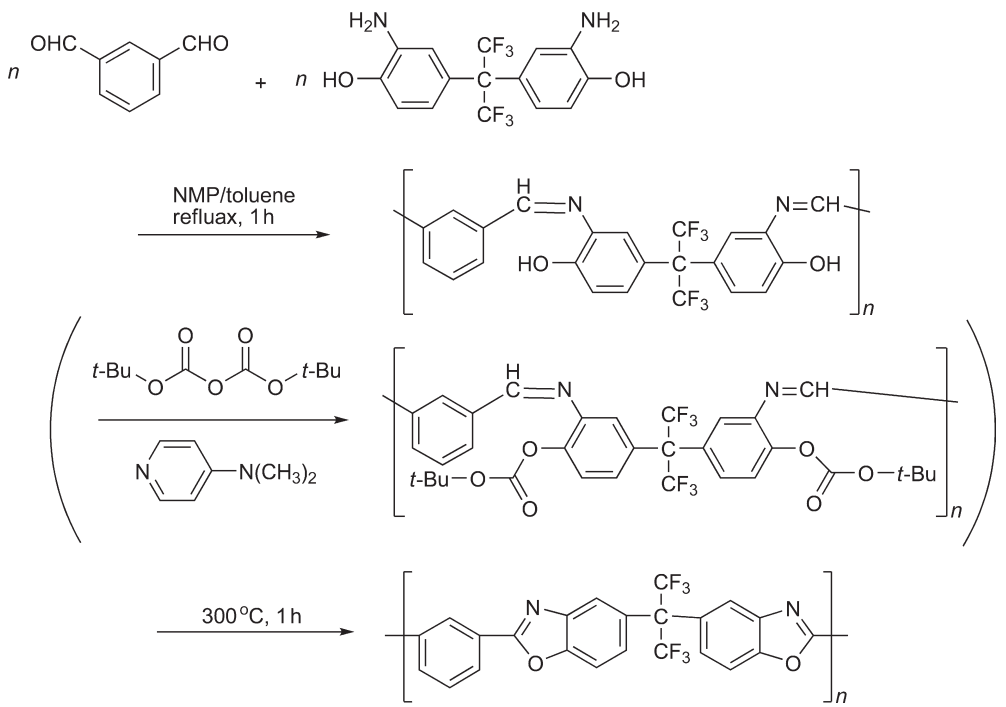
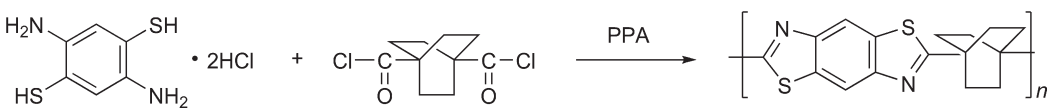


Scheme 12 Synthetic scheme for poly(*p*-phenylene benzobisoxazole).[84]



Scheme 13 Synthetic scheme for polybenzoxazoles.[85]

obtained polymer was colorless and showed high thermal stability, with the decomposition temperature being 423 °C in air. The structure calculated using MOPAC PM3 is shown in **Figure 24**. Although bicyclo[2.2.2]octane moiety cuts π-electron conjugate system, it keeps the linear and rigid molecular structure as shown in **Figure 24**.



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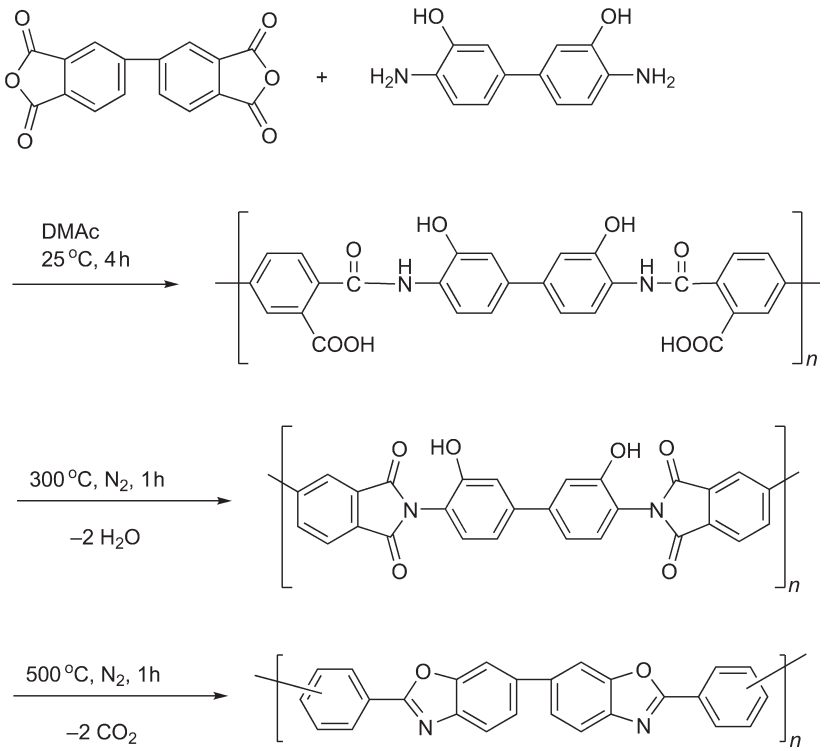

Scheme 14 Synthesis of polyamic acid and thermal conversion to hydroxy-containing polyimide and polybenzoxazole.[86]

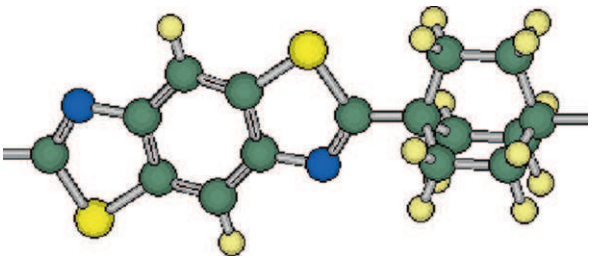

Figure 24 Molecular structure of the propeller-type PBZT calculated using MOPAC PM3.

5.19.4 Beyond PBZ

5.19.4.1 3D Polymers

There is an idea to realize the higher elastic modulus in the lateral direction in fibers. It is to introduce cross-links with covalent bonds such as single and double bonds between the adjacent molecular chains. The cross-links can be introduced to all types of polymers. Actually, Tashiro *et al.*[89] calculated moduli of cross-linked structures of PBO, poly-*p*-phenylene (PPP), and polyacetylene (PA) as shown in Figures 25 and 26 using the molecular mechanics technique. The calculated values are close to or exceed the value of diamond crystal as shown in

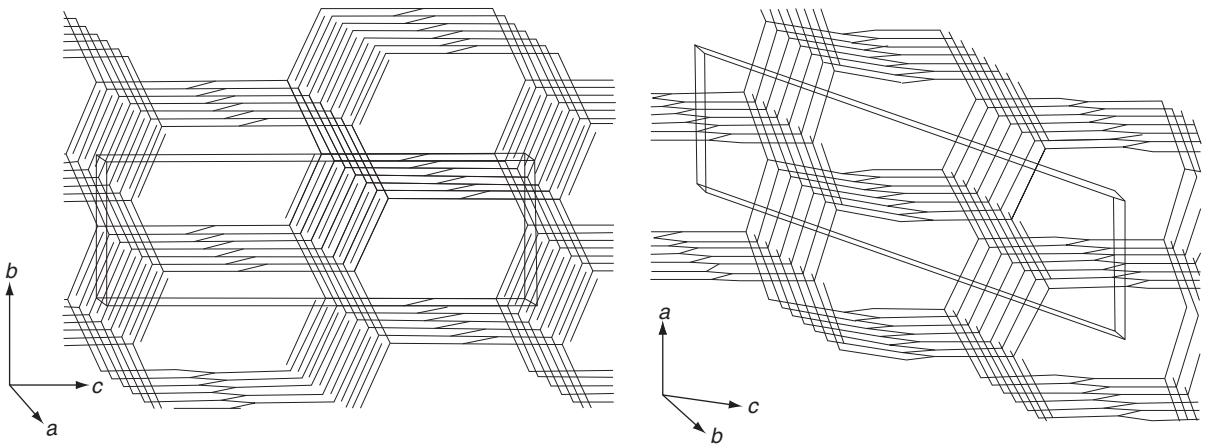

Figure 25 Crystal structure of the three-dimensionally cross-linked PA.[89]

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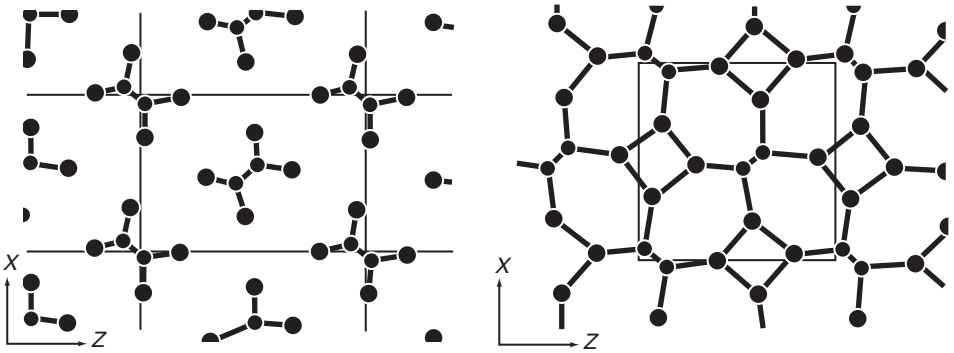


Figure 26 Crystal structure of the three-dimensionally cross-linked PPP.[89]

Table 3 The elastic moduli calculated for cross-linked polymers[89]

	Cross-linked PBO (GPa)	*Cross-linked PPP (GPa)*	*Cross-linked PA (GPa)*
Chain axis	873	1768	1699
Lateral directions	665–712	724–739	998–1796

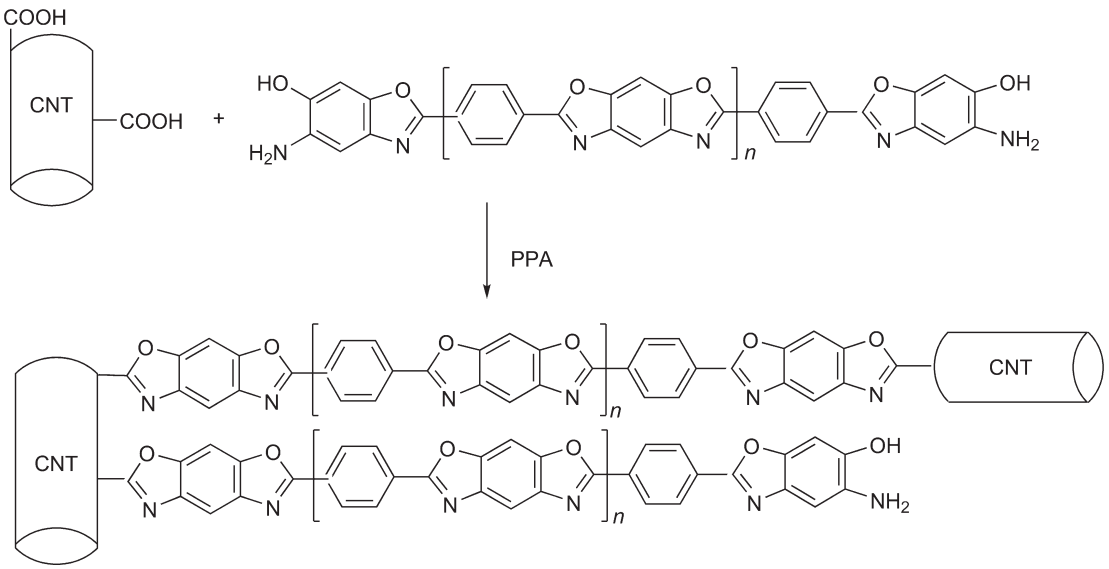
Table 3. The synthetic routes and the processing method will be developed in the future.

5.19.4.2 Carbon Nanotube–PBO Nanocomposite

In order to develop a fiber possessing high compressive strength, carbon nanotube (CNT)–PBO nanocomposite has been investigated. According to the study by Li *et al.*,[90] CNTs are used as not only reinforcements but also cross-linkers of PBO molecular chains as shown in Scheme 15. Multiwall carbon nanotubes (MWCNTs) were treated with mixing acid to introduce carboxyl groups on their surface. PBO was polymerized from 4,6-diamino-1,3-dihydroxybenzene (DADHB) and TA and the carboxylated MWCNT in PPA. The PBO fiber made from this reaction dope showed higher tensile strength and the knot strength by 33% than the PBO fiber not containing MWCNTs. This shows the possibility of improvement of the compressive strength of PBO fiber by introduction of cross-links.

5.19.4.3 Polyindigo

As a candidate for an environment-conscious super fiber, a brand-new recyclable polyindigo has been developed by two synthetic routes. One of the synthetic routes is shown in Scheme 13 as an example. It is expected to show high tensile strength and tensile modulus, which are twice as high as those



Scheme 15 Reaction of CNT-COOH and PBO.[90]

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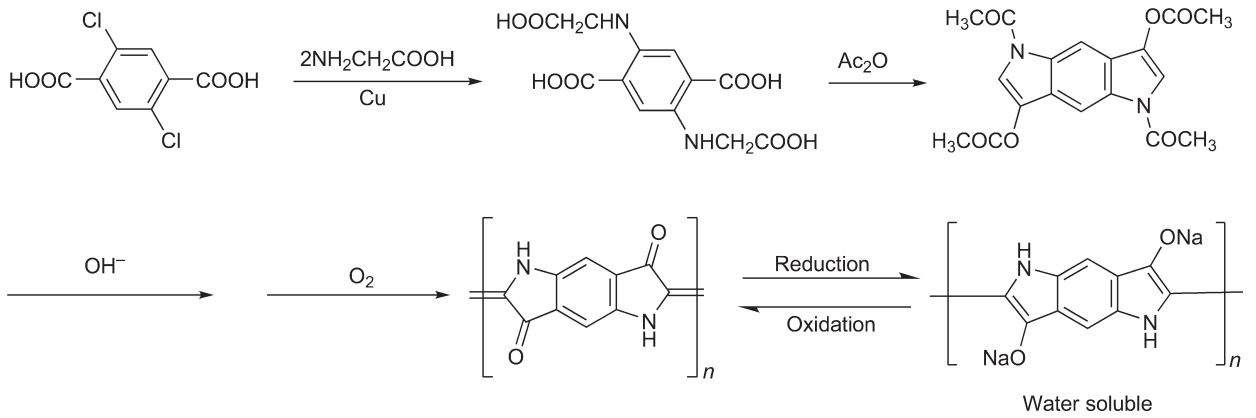

Scheme 16 Synthetic route of polyindigo.[91]

of *p*-aramid fibers on the prediction of the molecular orbital method (MOPAC PM3). Furthermore, it takes a leuco form to dissolve into water by reduction with sodium dithionite ($Na_2S_2O_4$), and returns to a keto form by oxidation in air.[91] Thus, we will be able to reuse the polyindigo fiber by collection separately as shown in Scheme 16.

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5.20 Polyimides

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5.20.1 Introduction

Aromatic polyimides (PIs) have been well known as one of the most important classes of high-performance polymers with a combination of exceptional mechanical, thermal, electrical, and optical properties along with chemical and solvent resistance.[1–11] The excellent combination of properties makes them suitable for a wide range of applications, from engineering plastics in aerospace industries to membranes for fuel-cell applications and gas or solvent separation. PIs exhibit high solubility, high optical transparency, low dielectric constant, low refractive index, low water absorption, and low coefficient of thermal expansion (CTE), which are being explored considerably for use as materials for interlayer dielectrics in electronic devices such as integrated circuits and in such optical devices as lenses, optical waveguides, antireflective coatings, and membranes for gas separation.[12–31] The first commercial PI was Kapton® (DuPont), made from pyromellitic dianhydride (PMDA) and 4,4′-oxydianiline possessing a high T_g (390 °C) and excellent mechanical properties, and it is still widely used in a variety of applications such as electrical insulating materials and as interlayer/intermetal dielectrics. The annual production in 1984 was about 1600 tons and the growth rate is estimated at 20% per year. There are many papers devoted to the syntheses and applications of PIs. This chapter focuses mainly on the synthesis and development of linear PIs and their extended functions.

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5.20.1.1 Polymerization of Tetracarboxylic Dianhydrides and Diamines

5.20.1.1.1 Formation of poly(amic acid)s

As illustrated in Scheme 1, the polycondensation of PMDA (1) with an aromatic diamine (2) is a two-stage reaction leading to poly(amic acid) (PAA; 3) and then to PI (4).[32,33]

5.20.1.1.1(i) PAA formation in aprotic polar solvents

Various solvents can be used to perform the first step of the reaction. Dimethylformamide (DMF), dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), and *N*-methylpyrrolidone (NMP) are the most commonly used. At first, the complexation between the tetracarboxylic dianhydride and the solvent occurs, as was observed in the case of PMDA.[34] Then, the nucleophilic attack of anhydride takes place, leading to PAA.

As would be expected, water has very deleterious effects. First, water can hydrolyze the tetracarboxylic dianhydride function of either the starting monomer or the growing chain. Indeed, it was observed that higher-molecular-weight PAA was obtained when PMDA was added in a solid form to the solution of diamine[35] because solid anhydrides are less sensitive to moisture than dissolved ones. Another effect of water is the hydrolysis of PAA. As a matter of fact, an ortho amide acid such as 2-[(phenylamino)carbonyl]benzoic acid (5) is hydrolyzed 10^5 times faster than the corresponding unsubstituted *N*-phenylbenzamide (6), by a cooperative effect[36] (Scheme 2).

The reaction temperature is generally room temperature or lower; higher temperatures induce imidization with evolution of water[37] and precipitation of low-molecular-weight PI, thus stopping the chain growth.[38]

When tetracarboxylic dianhydrides react with diamines, the viscosity for the same extent of reaction depends on the nature of the solvent in the following order: in DMSO > in DMAc > in DMF.[39] This observation is in agreement with a complexation of the PAA by the solvent.

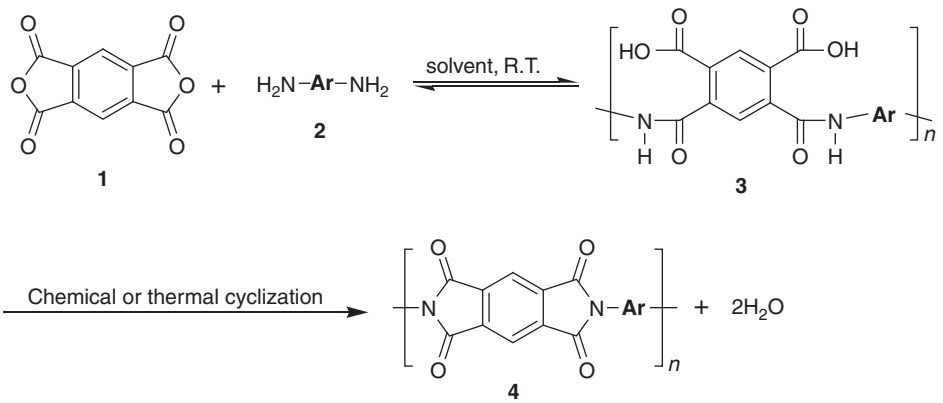
5.20.1.1.1(ii) Synthesis of PAAs in other solvents

The adhesion properties of the PAA prepared from benzophenonetetracarboxylic dianhydride (BTDA) (7) and 3,3′-carbonyldianiline (8) are improved if a diglyme solution is used[40] (Scheme 3). In the case of a diamine with a low reactivity, such as 4,4′-sulfonyldianiline (9), the solvent enhances the basicity of the amine by complexation (10), and the obtained polymer exhibits a higher inherent viscosity than the same one prepared in NMP, DMAc, or DMF.[41]

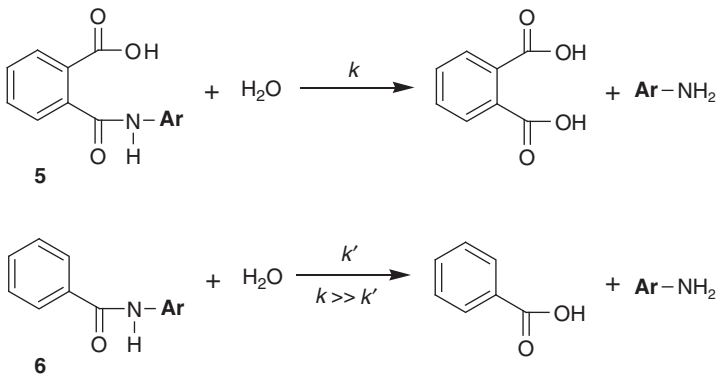
5.20.1.1.2 Cyclization of PAAs

5.20.1.1.2(i) Thermal cyclization of PAAs

This reaction is generally performed by heating a PAA film cast from a low solid content of PAA solution (15–25% solid) *in vacuo* or in an inert atmosphere. Different thermal cycles have been studied as a function of the nature of the main chain (flexibility) and of the application required. Generally,



Scheme 1



Scheme 2

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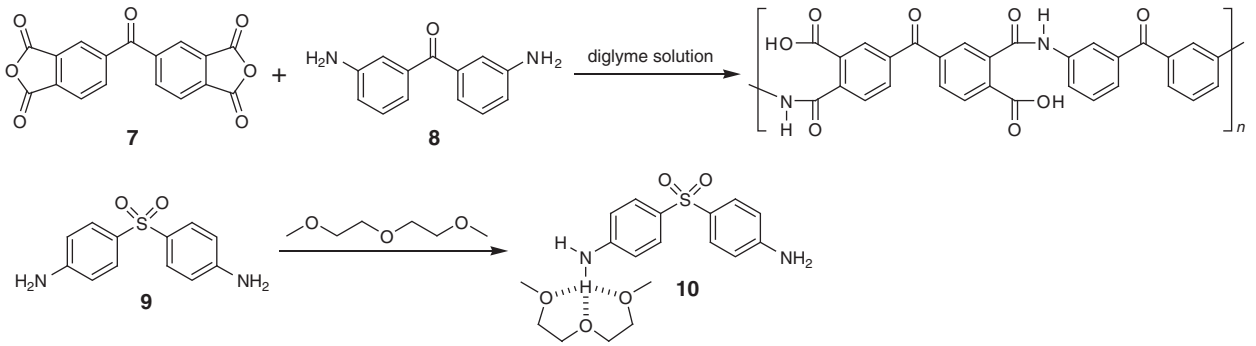
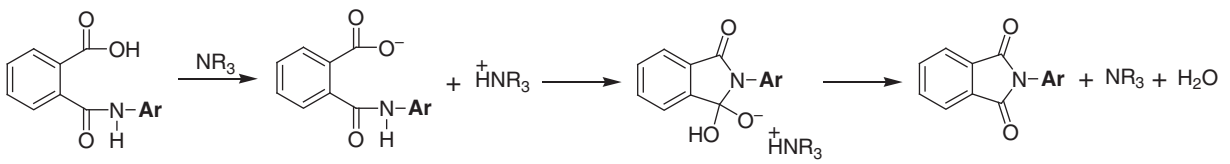


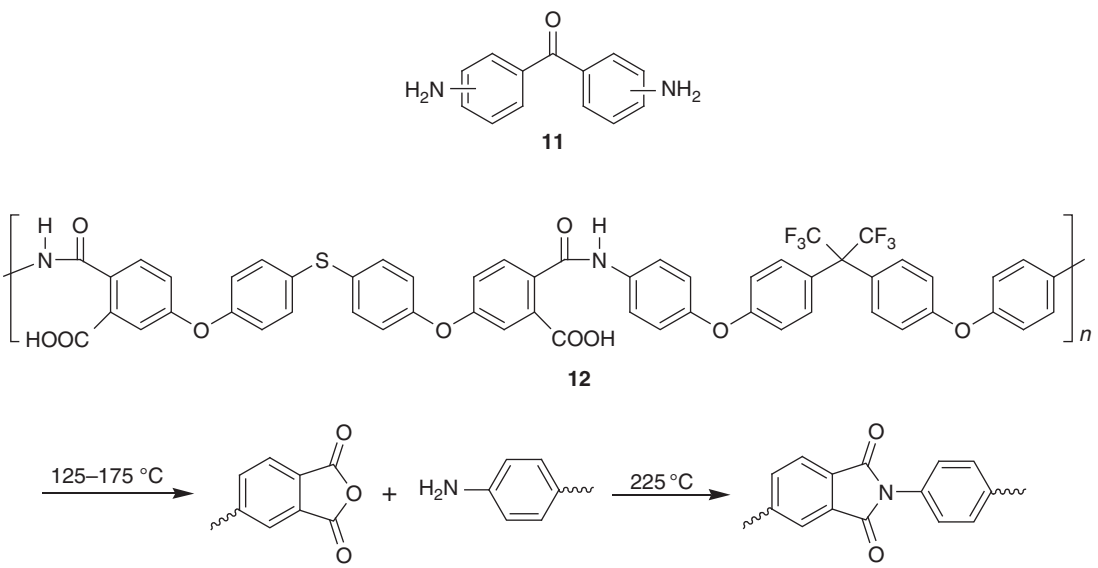
Scheme 3



Scheme 4

the solvent is removed at a temperature between 100 and 150 °C, and then the temperature is increased to 300 or 350 °C.[39] The loss of weight observed with PAA by thermogravimetric methods at 170, 185, and 200 °C was interpreted as a two-stage imidization via a complex between PAA and the solvent (DMAc).[42] A process of complexation/decomplexation between amic acid and NMP was also demonstrated by Russian researchers.[43] In the case of PAA derived from PMDA and ODA, the rate of thermal cyclization at 161 °C was increased by adding a tertiary amine,[42] according to Scheme 4. Correlation between the basicity of the starting diamine and the rate of cyclization has been mentioned by Soviet workers;[44] the higher the pK_a of the diamine, the higher the rate constant of ring closure.

Competition between cyclization and depolymerization was observed in the case of polymers obtained from condensation of PMDA with 4,4′-, 3,4′-, and 3,3′-carbonyldianilines (11). These polymers provide brittle films between 175 and 225 °C, but the films become flexible at 300 °C.[45] Using Fourier transform infrared (FTIR) spectroscopy, Young and Chang[46] observed the changes in the anhydride C=O stretching band at 1850 cm^{-1}, which reached a maximum intensity between 150 and 200 °C and diminished in intensity at higher temperatures during the cyclization of PMDA-ODA PAA. This phenomenon was also observed for the soluble polymer (12) carrying flexible linkages (Scheme 5). The anhydride band appeared when the film was heated to 152 °C and showed a maximum intensity at 175 °C and then was not detectable



Scheme 5

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at 225 °C. The good solubility of these polymers made size-exclusion chromatography and inherent viscosity characterization possible, which agreed with an initial reduction in molecular weight before final solid-state polycondensation.

5.20.1.1.2(ii) Chemical cyclization of PAAs

PAA can be dehydrated by chemical processes. By using dicyclohexylcarbodiimide (DCC), polyisoimide (13) could be obtained[47] as shown in Scheme 6, and then rearranged into imides by heating or chemical treatment with acetate ions.

Another chemical dehydration extensively studied involves the use of an anhydride in the presence of organic bases such as pyridine or trialkylamine,[48] the mechanism of which was studied on a model compound.[49] When dehydration was performed with acetic anhydride using triethylamine, only imide was obtained, but pyridine gave a mixture of predominantly imide and isoimide; tertiary amine plays a catalytic role. The suggested mechanism is given in Scheme 7. The first step is the formation of a mixed anhydride, and then two independent routes can give imide or isoimide. Isoimide formation is kinetically favored via intramolecular O-acylation through an ion pair in equilibrium with the mixed anhydride. The imide form is thermodynamically favored. In the case of PAA cyclization, viscosity measurements show that no degradation and no cross-linking occur during cyclization. However, chemical cyclization with trifluoroacetic anhydride gives only the isoimide product.

5.20.1.1.3 Polymerization of a tetracarboxylic dianhydride with a diamine without solvent

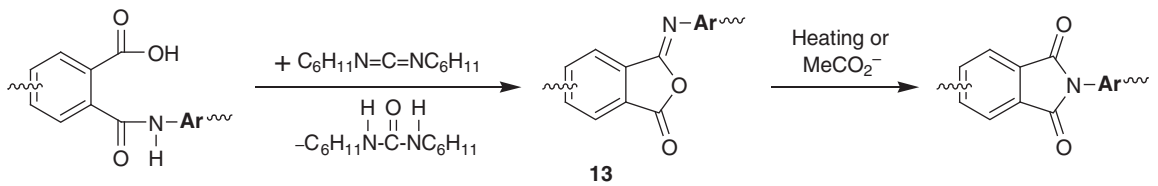
In microelectronics, PIs are used as dielectric coatings by the process of spin coating of the PAA solutions, solvent removal, and thermal imidization. To avoid problems due to solvent evaporation, PMDA and ODA are coevaporated at 200 °C under a vacuum on a substrate. The diffusion rate of each reactant could be controlled in order to keep the stoichiometric balance. The substrate is kept at 25–50 °C, and the resulting deposited film contains 30–50% of unreacted product and PAA. Final polymerization could be accomplished by heating at 175 and 300 °C for 30 min in nitrogen, respectively, but only lower-molecular-weight PIs could be obtained (M_w = 13 000). Thermal properties of the PI obtained by the vapor deposition method are very similar to the corresponding PI by conventional two-step methods, but the dielectric properties are better (ε = 2.9, tan δ = 0.008 for the former vs. ε = 3.2, tan δ = 0.01 for the latter).[50]

5.20.1.1.4 Polymerization of a tetracarboxylic dianhydride with a diamine in phenolic solvents: Poly(ether imide)s

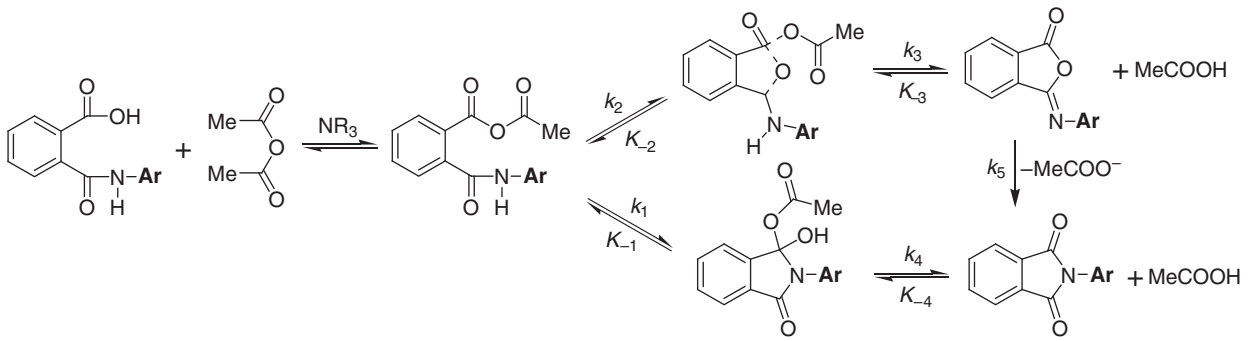
Tetracarboxylic dianhydrides containing diaromatic ethers were prepared by the aromatic nucleophilic substitution of nitroimide (14) by phenoxide dianions (15),[51] followed by alkaline hydrolysis and cyclodehydration to tetracarboxylic dianhydrides (16) (Scheme 8). The reaction between the tetracarboxylic dianhydride and the diamines was conducted in phenol, cresol, or chlorinated solvents, in combination with inert diluents such as toluene or chlorobenzene. The reaction mixture was heated to 160–180 °C and the water was removed azeotropically; the polymer was recovered by precipitation in methanol. The scope of the reaction for formation of aromatic polymers via nitro group displacement has been reviewed by Takekoshi.[52]

5.20.1.2 Polymerization of Tetracarboxylic Dianhydrides with Diisocyanates

In 1967, it was observed that aromatic and aliphatic diisocyanates react with PMDA to yield PIs.[53] Moldable PIs were obtained by the reaction of a mixture of diisocyanates with a tetracarboxylic dianhydride.[54] The reaction could be activated by water,[55] metallic alkoxides,[56] and alkali-metal lactamates.[57] The catalytic effect of water is interpreted as arising from a



Scheme 6



Scheme 7

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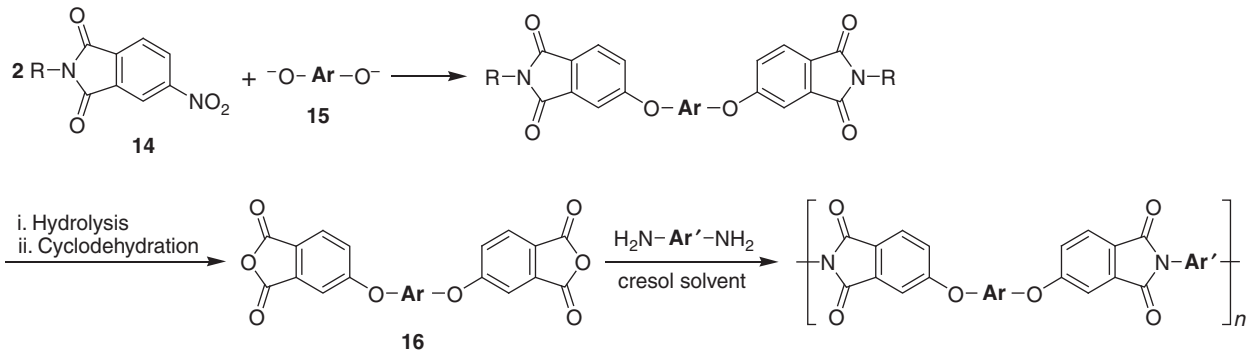
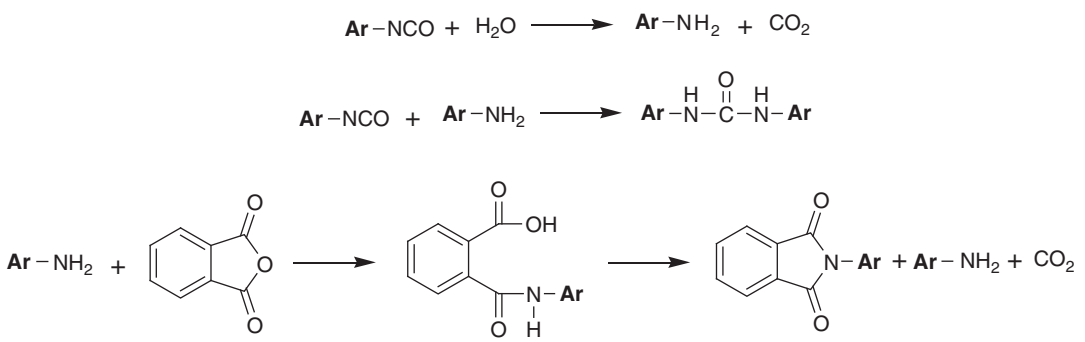


Scheme 8



Scheme 9

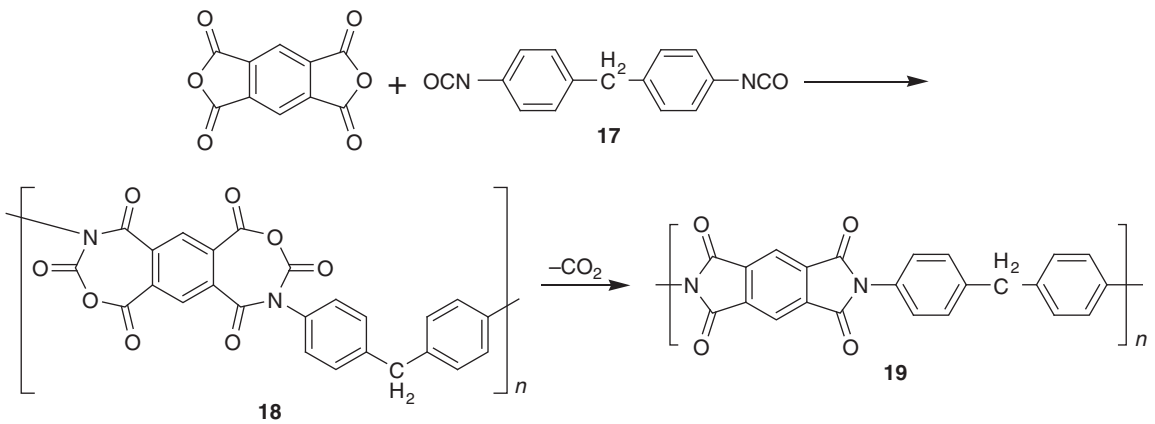
partial hydrolysis of the isocyanate,[58] followed by reaction of the aromatic amine with the anhydride (Scheme 9).

Meyers[59] isolated a soluble seven-membered ring intermediate (18) from PI (19) in the reaction of PMDA with diisocyanate monomer (17) in DMF at 130 °C (Scheme 10), and then the intermediate could release carbon dioxide by further heating. This mechanism was supported by IR spectra and increasing yield of the seven-membered intermediates when the reaction was carried out in CO_2 pressure.

Although the synthesis from isocyanates could afford PIs with only lower molecular weight, the reaction is used industrially to produce PI-2080 (Upjohn). The polycondensation of trimellitic anhydrides with diisocyanates was an early patent[60] and has been said to give soluble poly(amide imide)s (PAIs) with high molecular weight in *N*-methyl-2-pyrrolidinone (NMP).[61] The PAI prepared by this process is used for wire insulation.

5.20.1.3 Polymerization of Tetracarboxylic Dianhydrides with Silylated Diamines

Silylated diamines (20) were obtained by reaction of trimethylchlorosilane with diamines. The resulting silylated diamines could be used to react with the tetracarboxylic dianhydride in solvents such as tetrahydrofuran at room temperature, giving a poly(amide trimethylsilylester) (21) by a transfer of the silyl



Scheme 10

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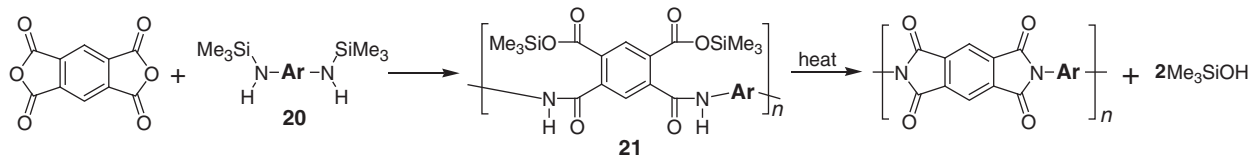


Scheme 11

protective group to the carboxylic group which was subsequently cyclized to PIs with elimination of trimethylsilanol by heating at 150 °C for 30 min (Scheme 11). It was also reported that the diamines fully substituted by trimethylsilyl groups could react with anhydrides to form an imide ring by giving disiloxane as a by-product.[62]

5.20.1.4 Polymerization of Diester Diacids with Diamines

Many applications, such as adhesives or matrices for composites and coatings in electronics, need high solid content solutions. The reactivity of diester diacids is lower than that of the corresponding tetracarboxylic dianhydrides, so it is possible to obtain soluble low-molecular-weight chain-extendable PIs by reaction with diamines.

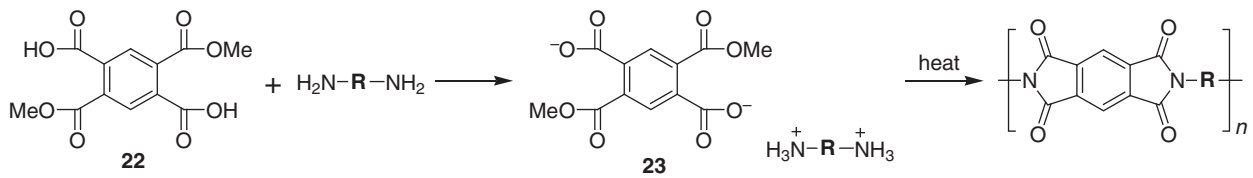
Aliphatic PIs were prepared in 1955 from dialkyl tetracarboxylates (22) and aliphatic diamines by a two-stage melt condensation of the resulting organic salts (23) at 110–140 °C, then at 250–300 °C (Scheme 12).[63]

In the case of aromatic diamines, formation of the diesters of PAA by heating the reactants at 150 °C has been claimed.[64] The formation of an intermediate salt between the diester diacid and the aromatic diamine was observed before polycondensation.[65]

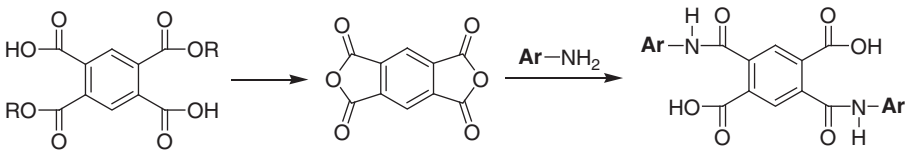
Reactions of more acidic alcohols, such as chloro- or fluoropropanols or ethyl glycolate with anhydrides, give ester acids with better leaving groups than the case of alkyl ester acids.[66] Reactivity with aromatic amines could be greatly enhanced due to the fast elimination of alcohol followed by reaction of the amine with anhydride (Scheme 13).

5.20.1.5 Formation of PIs via Nucleophilic Nitro Group Displacement Reactions

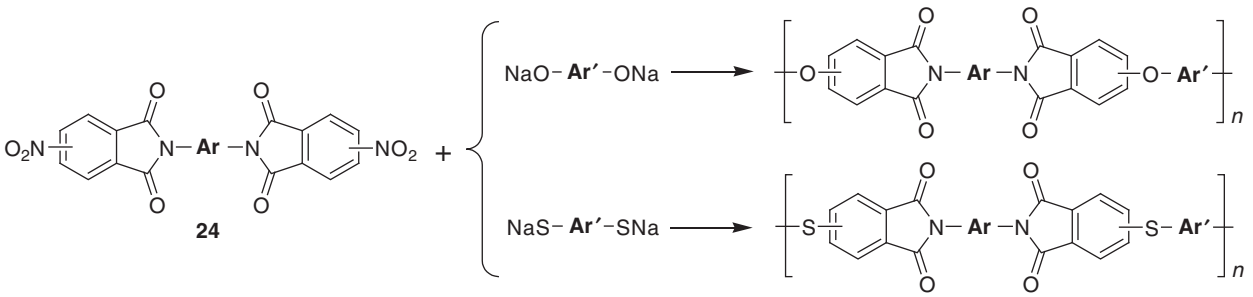
The application of aromatic nucleophilic substitution reaction to polymer synthesis has been well documented. Industrial polymers such as polysulfone, poly(phenylene sulfide), and poly(ether ketone) are produced by this synthetic route.[67] As mentioned, nitro groups activated by the imide function react very smoothly with phenolate anions. This reaction has been extended to prepare poly(ether imide)s and poly(sulfide imide)s from arylenebis(nitroisoindoledione) (24) with bisphenol and bisphenylthiol salts, respectively (Scheme 14).[68,69]



Scheme 12



Scheme 13



Scheme 14

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5.20.1.6 Linear Polymerization of Bismaleimides by Michael Addition

The maleimide carbon–carbon double bond is strongly electrophilic and can react with nucleophilic reagents such as amines and thiols as shown in Scheme 15.[70] The addition with thiols has to be carried out in protic solvents in order to avoid the side reactions of intermediate anionic maleimido species with maleimide, resulting in cross-linking.

Polymerization of maleimide with aromatic diamines took place in *m*-cresol solution and polymers with high molecular weights could be obtained. However, in the case of aliphatic diamines such as 1,2-ethanediamine and 1,3-propanediamine (26), could react with 1,3-bismaleimidobenzene (25) by a ring-opening reaction to yield the corresponding polymaleamide (27) (Scheme 16).

5.20.1.7 Palladium-Catalyzed Carbonylation Polymerization for the Formation of PIs

A synthetic method for the formation of PI from the reactions of bis(*o*-diiodobenzene)[71] or bis(*o*-iodoesterbenzene)[72] compounds with diamines was carried out in the presence of CO, a palladium catalyst and a base in a dipolar aprotic solvent. A goal of isolating the intermediate amide esters from the *o*-iodo esterbenzene was not realized. Even though all the examined conditions indicated that the intermediate amide esters were not observed, this reaction for preparing PIs was found in model compound approach to be an efficient route to cyclic imides (Scheme 17).[71–73]

5.20.2 Conventional PI

5.20.2.1 Poly(ether imide)s

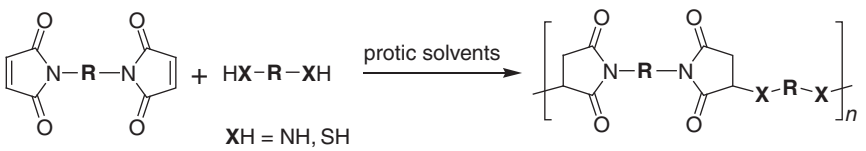
Aromatic PIs are well-known high-performance polymers that have excellent thermal, mechanical, and electrical properties. However, the problems for most aromatic PIs are their poor processability caused by limited solubility in organic solvents and high melting and softening temperatures. Therefore, much effort has been spent on preparing tractable aromatic PIs by changing the chemical nature of the molecular structures to some degree while maintaining their desired properties. One of the strategies to increasing solubility and lowering melting/softening temperature is the introduction of flexible bonds in the polymer backbone. The ether group is the most popularly flexible linkage introduced into the polymer backbone. It has been generally recognized that aryl-ether linkage imparts properties such as better solubility and melt-processing characteristics. On the other hand, introduction of bulky substituents, noncoplanar structures, and spiro skeletons into the polymer backbone could also increase the solubility due to the decreased packing and crystallinity. Recent studies demonstrated the PIs derived from ether-bridged diamines with trifluoromethyl (CF_3) groups are thermally stable and organosoluble polymeric materials with low moisture uptake, low dielectric constant, and high optical transparency.[74] Therefore, we summarize the recently reported poly(ether imide)s and divide them into two parts which are as follows.

5.20.2.1.1 Organosoluble poly(ether imide)s

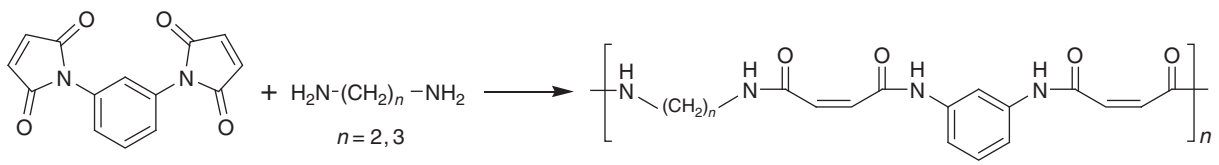
Many efforts on the modification of the backbone structure of PIs to obtain soluble and/or thermoplastic PIs without sacrificing their excellent thermal and mechanical properties have been devoted to extend the utility of PIs by incorporation of bulky groups such as pyridine with pendant phenyl (28), fluorenyl (29), and triphenylamine (TPA) (30) groups (Scheme 18).[75–77]

Chern *et al.*[78–80] synthesized new PIs derived from asymmetric diamines and aromatic tetracarboxylic dianhydrides (Scheme 19). Due to the introduction of the asymmetric di-*tert*-butyl groups into diamine monomer, the resulting PIs exhibit excellent solubility and retain other desirable properties such as low dielectric constant and high thermal stability.

Yang and Hsiao[81–86] reported several types of poly(ether imide)s with light color and good physical properties from the bis(ether–anhydride)s and various aromatic diamines via a conventional two-stage procedure that included a ring-opening polyaddition to yield PAAs, followed by chemical or thermal imidization to the poly(ether imide)s (Scheme 20). These poly(ether imide)s could be cast into light-colored and tough films with low dielectric constants. They also exhibited moderately high T_g and good thermal stability. Thus, these poly(ether imide)s demonstrated a good combination of properties and



Scheme 15



25 26 27

Scheme 16

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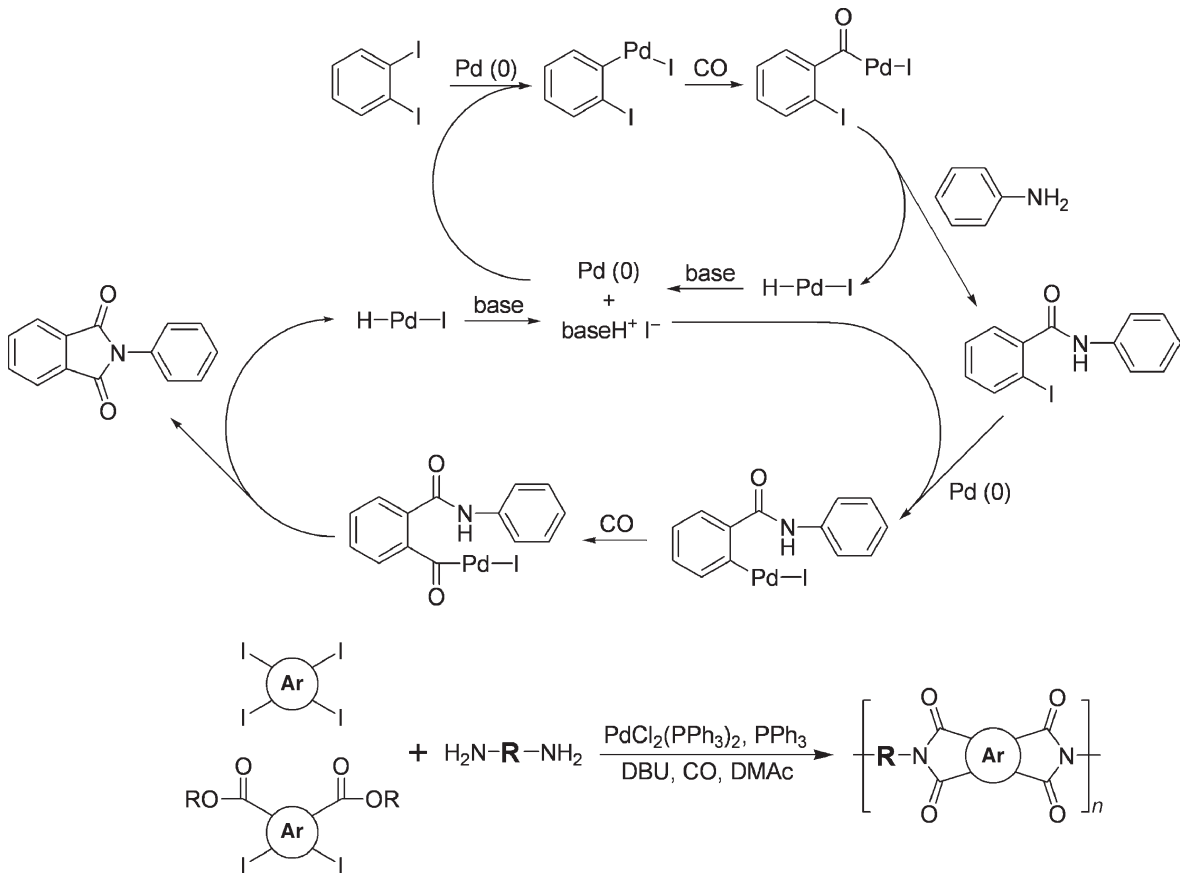
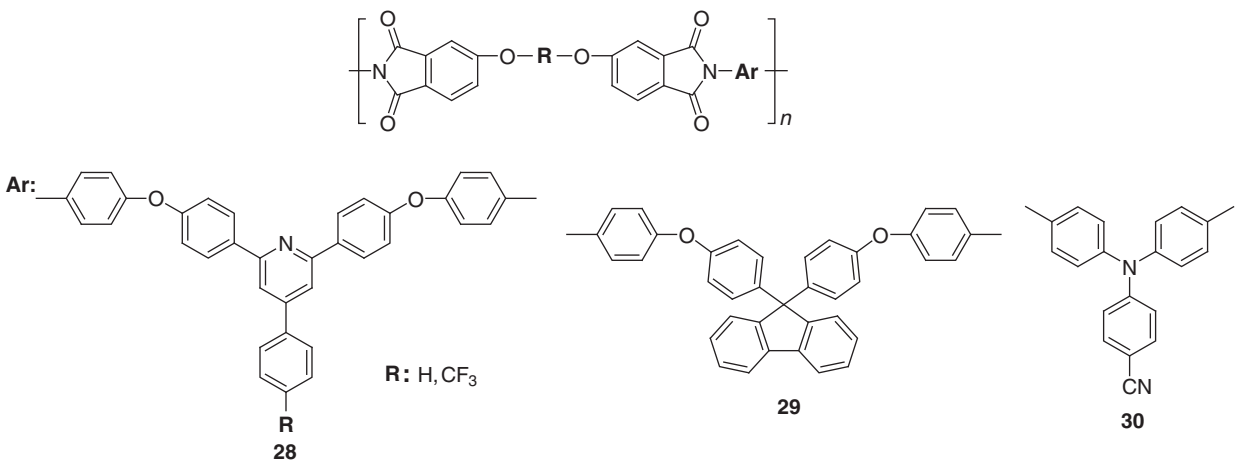


Scheme 17



Scheme 18

may be of interest for microelectronic and optoelectronic applications.

5.20.2.1.2 Fluorinated poly(ether imide)s

Banerjee *et al.*[87–89] took a different strategy to impart solubility while retaining good thermal properties in the PIs (Scheme 21). They reported the synthesis of semifluorinated PIs based on rigid monomers containing indane (31), phthalimide (32), and anthracene (33) moieties. All the obtained polymers exhibited excellent solubility in various solvents including dichloromethane with a very low boiling point. The resulting poly(ether imide)s were amorphous and revealed good thermal stability with good mechanical strength. Besides, these poly(ether imide)s could be solution cast into light-colored films with good optical transparency and low moisture uptake. Hence they are promising materials for optoelectronic applications and as gas separation membranes.

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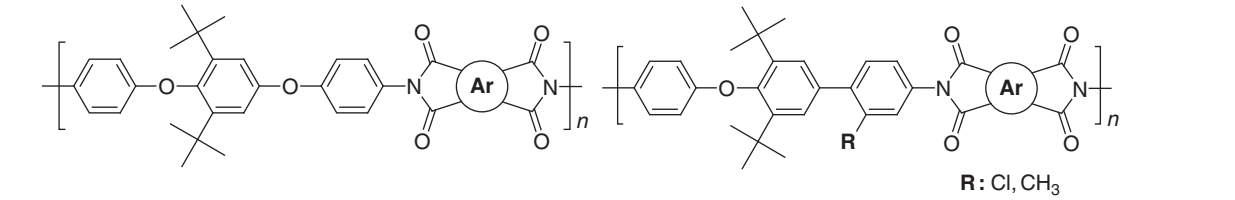
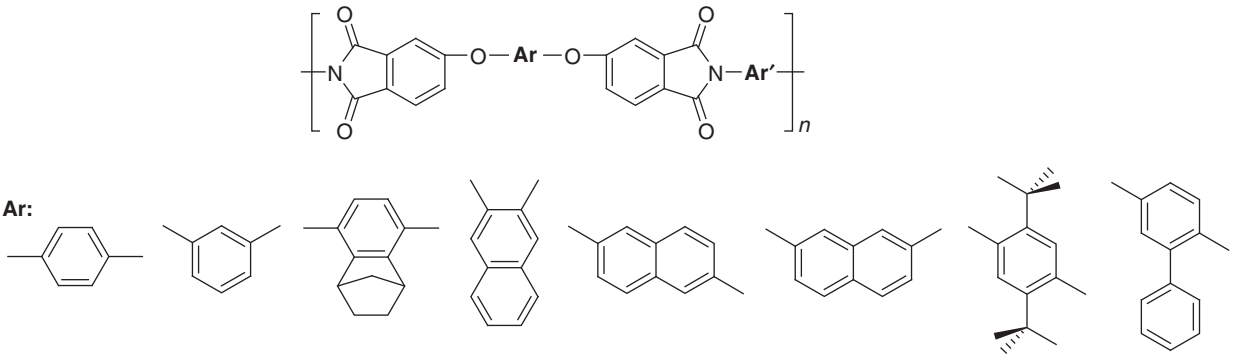
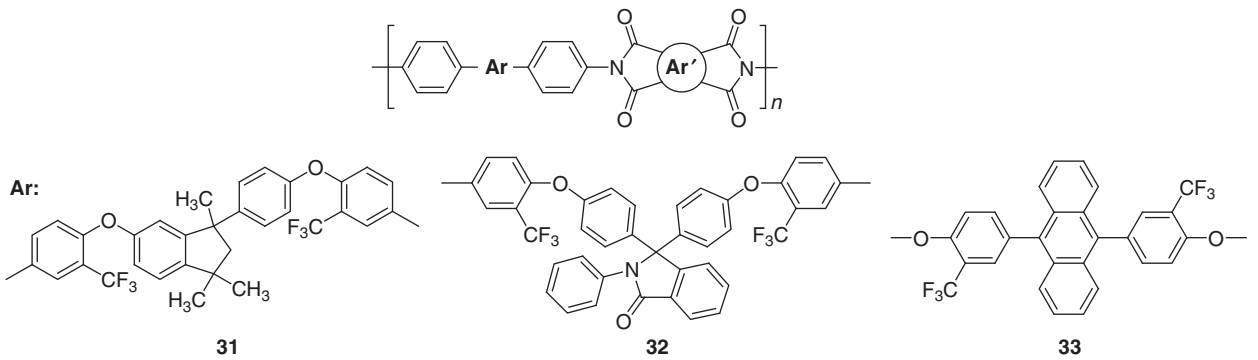


Scheme 19



Scheme 20



Scheme 21

Yang and Hsiao[82–85,90–92] reported the synthesis of soluble and light-colored fluorinated poly(ether imide)s using bis (ether–anhydride)s and various fluorinated aromatic diamines by a conventional chemical imidization (Scheme 22). All polymers made from fluorinated diamines showed light color, high optical transparency, good solubility, low dielectric constant, and low water absorption.

New family of fluorinated PIs with moderate to high molecular weights have been synthesized from the newly synthesized bis(ether-amine), 1,5-bis(4-amino-2-trifluoromethylphenoxy)naphthalene (34), 1,7-bis(4-amino-2-trifluoromethylphenoxy)naphthalene (35), and various aromatic tetracarboxylic dianhydrides by two-step thermal or chemical imidization method (Scheme 23).[93,94] Because of the presence of CF_3 and aryl ether groups along the polymer backbone together with the asymmetric structure of the repeat unit, the obtained PIs exhibited good solubility in many organic solvents and could be solution cast into transparent, flexible, and tough films. The PIs also showed high thermal stability, high optical transparency, and low dielectric constants.

In 2009, fluorinated polynaphthalimides were successfully synthesized from 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA) and trifluoromethyl-substituted aromatic bis (ether–amine)s by high-temperature solution polycondensation in *m*-cresol (Scheme 24).[95] The obtained polynaphthalimides exhibited good solubility in many organic solvents and could afford flexible and ductile films with

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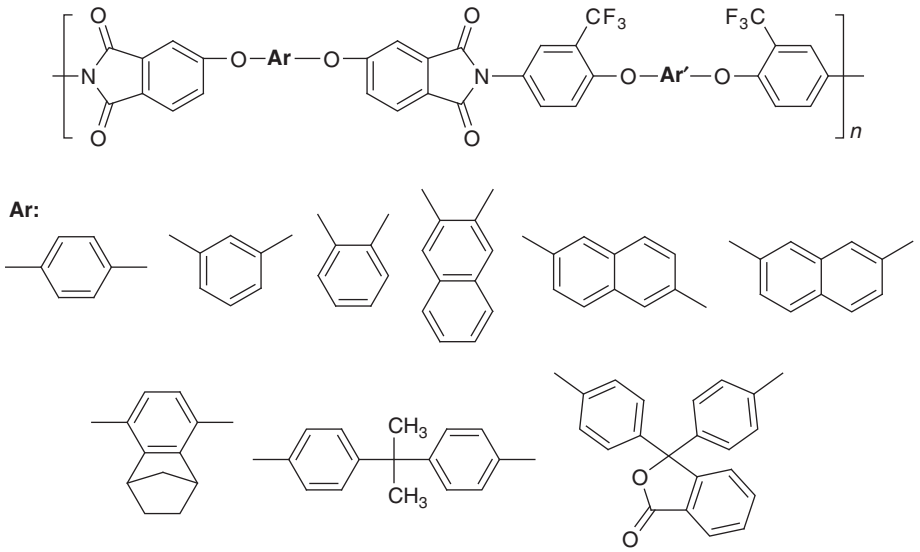
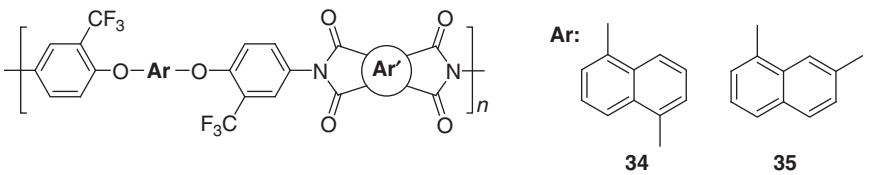
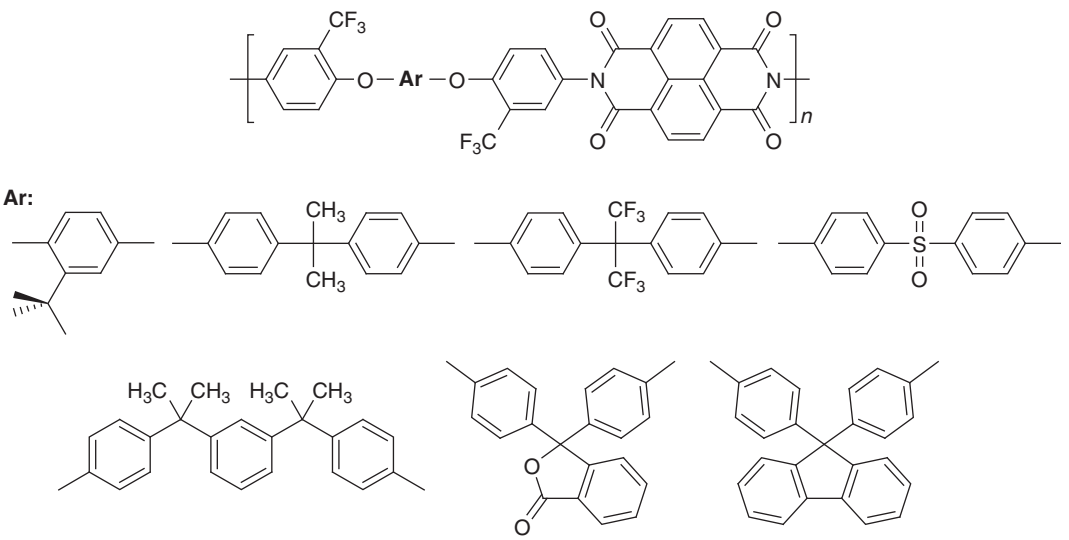


Scheme 22



Scheme 23



Scheme 24

excellent mechanical properties and high thermal stability. These properties suggest the potential usefulness of these novel polynaphthalimides in high-tech applications.

5.20.2.2 Poly(amine imide)s

Poly(amine imide)s were first prepared in 1992 from 4,4′-diaminotriphenylamine (36) and various tetracarboxylic dianhydrides by Imai *et al.*[96] (Scheme 25). In the past, new arylamines, such as *p*-anisidine (37), hydroxy-aniline (38), naphthylamine (39), 1,4-phenylenediamine (40), and benzidine (41), were used to prepare poly(amine imide)s (Scheme 26).[97–102]

Recently, Liou *et al.*[103–105] reported the synthesis of high-performance poly(amine imide)s carrying the TPA (42), *N*-phenylcarbazole (43), and methoxy-substituted TPA (44, 45) as

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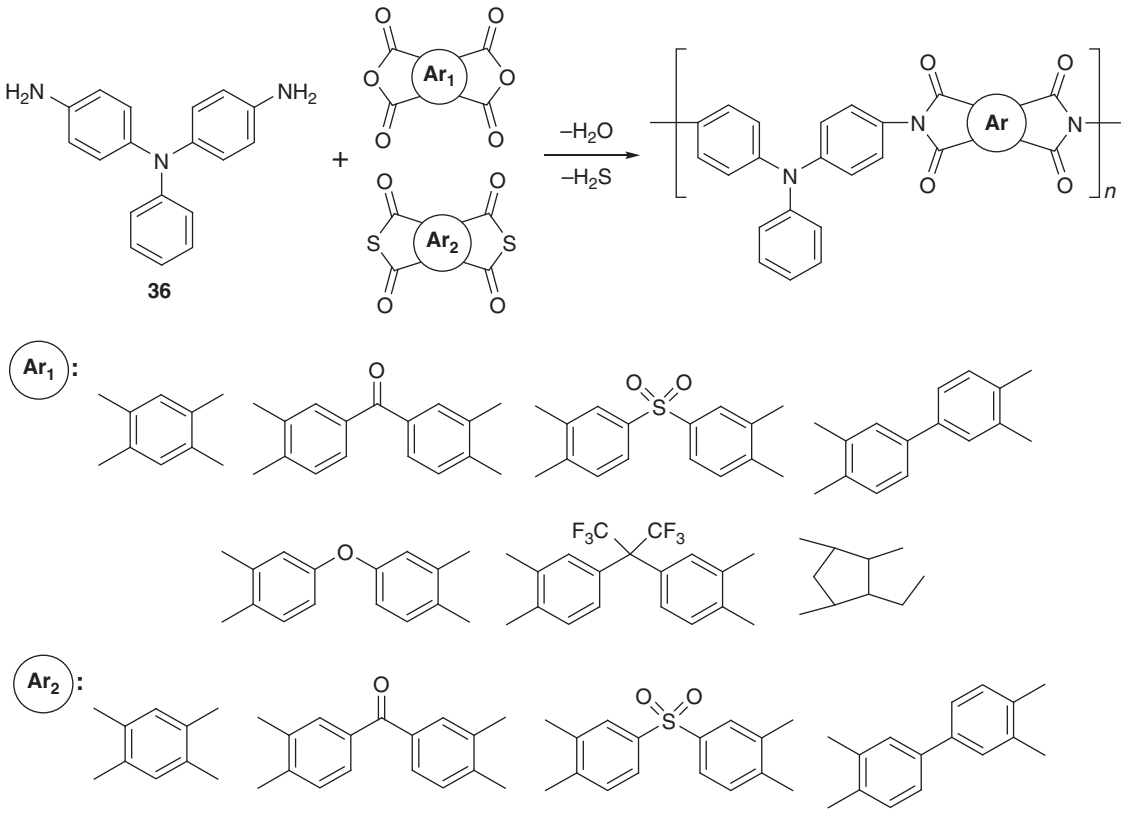
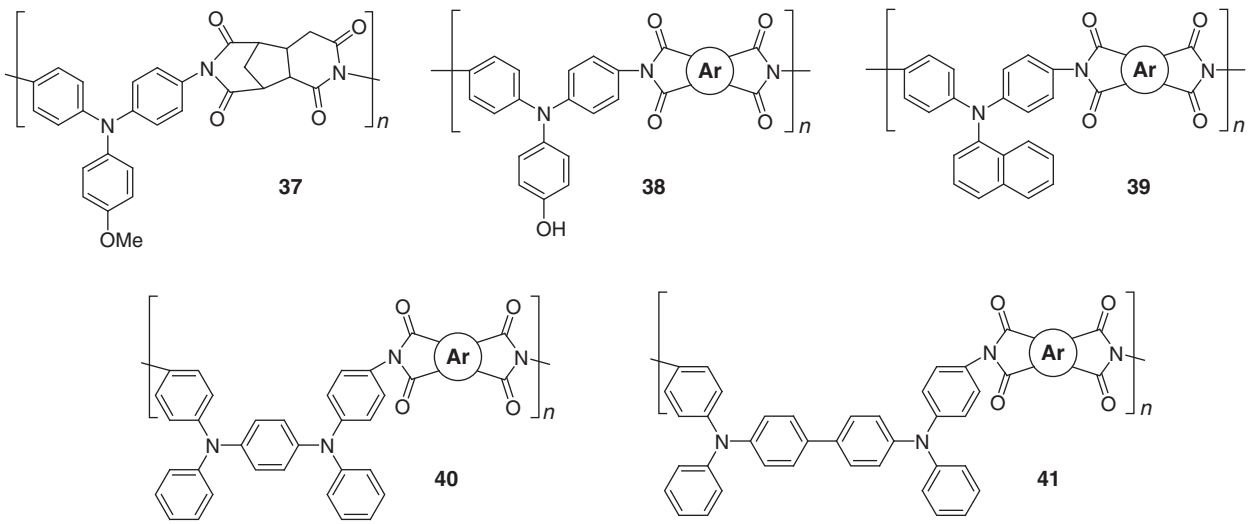


Scheme 25



Scheme 26

electroactive functional moieties (Scheme 27). All the nitrogen-containing PIs revealed high thermal stability, organosolubility, good film-forming ability, high electrochemical reversibility, and good electrochromic behavior.

5.20.2.3 Poly(sulfide imide)s

Conventional sulfur-containing polymers afford high transparency, high refractive indices, and good adhesion, although the thermal stability of the polymers was often limited owing to their intrinsic thermally less stable structures. Recently, high refractive index PI coatings with high thermal stability have been proposed for optoelectronic applications, such as charge-coupled device (CCD) image sensors and complementary metal oxide semiconductor (CMOS) image sensors. Ueda *et al.*[106–117] reported new poly(sulfide imide)s prepared from sulfur-containing diamine or tetracarboxylic dianhydrides by a two-step polycondensation procedure to develop optical

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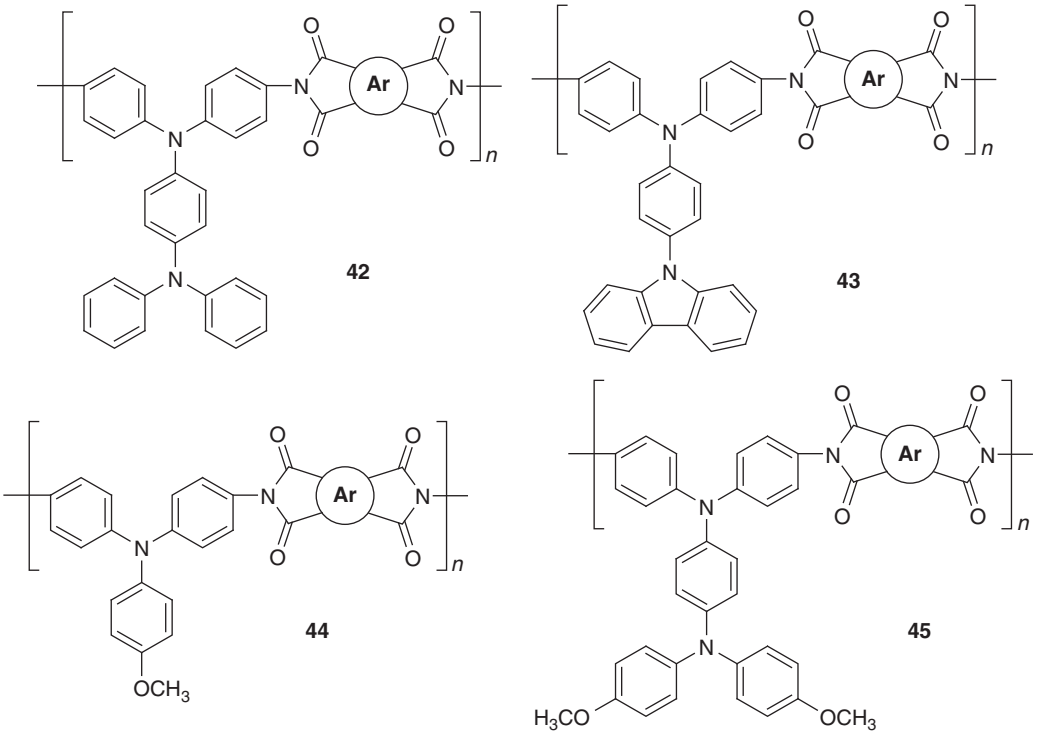


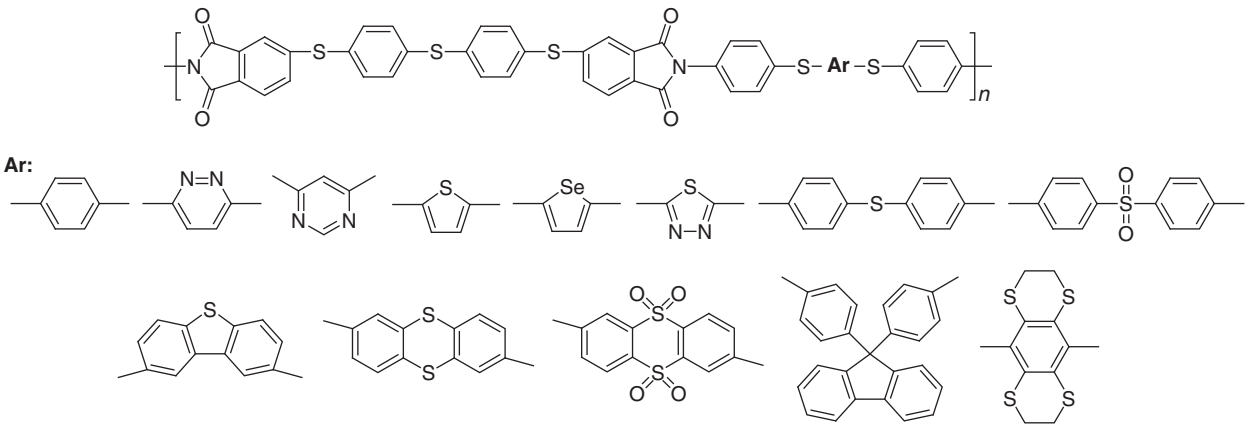
Scheme 27

polymers exhibiting high refractive indices, combined with low birefringence, high thermal stability, and high optical transparency. The diamines or tetracarboxylic dianhydrides with sulfur atoms were used to prepare PIs containing *p*-phenylenedisulfanyl, *p*/*m*-sulfonylbis(phenylenesulfanyl), dibenzothiophene, fluorene, thianthrene, tetrathiaanthracene, thiophene, selenophene, pyridazine, and pyrimidine moieties (Scheme 28). These PIs exhibited good transparency in the visible region with a transmittance >80% at 500 nm, high refractive indices higher than 1.7200, and low birefringence lower than 0.0200. All these properties are desired for advanced optical materials.

5.20.2.4 Phosphorus-Containing PIs

Phosphorus (P)-containing polymers have been known for many years to exhibit the primary advantage of flame retardancy, and they are increasingly gaining popularity over their halogen counterparts because they generally generate less toxic combustion products. The incorporation of organophosphorus functionality either within the main chain or as groups appended to it has led to the production of inherently fire-retardant polymers.

In 2001, Liou and Hsiao[118] prepared two series of phosphorus-containing aromatic poly(ester amide imide)s via low-temperature solution polycondensation from phosphorus-containing aromatic di(ester-amine)s (46) with three imide ring-preformed diacid chlorides (47) (Scheme 29). All the polymers had good solubility in many polar aprotic solvents and could be cast into transparent, tough, and flexible films. Good solubility, moderate T_g or T_s values suitable for molding, reasonable thermal stability, and good flame-retardant properties make these phosphorus-containing poly(ester amide imide)s as promising high-performance polymeric materials.



Scheme 28

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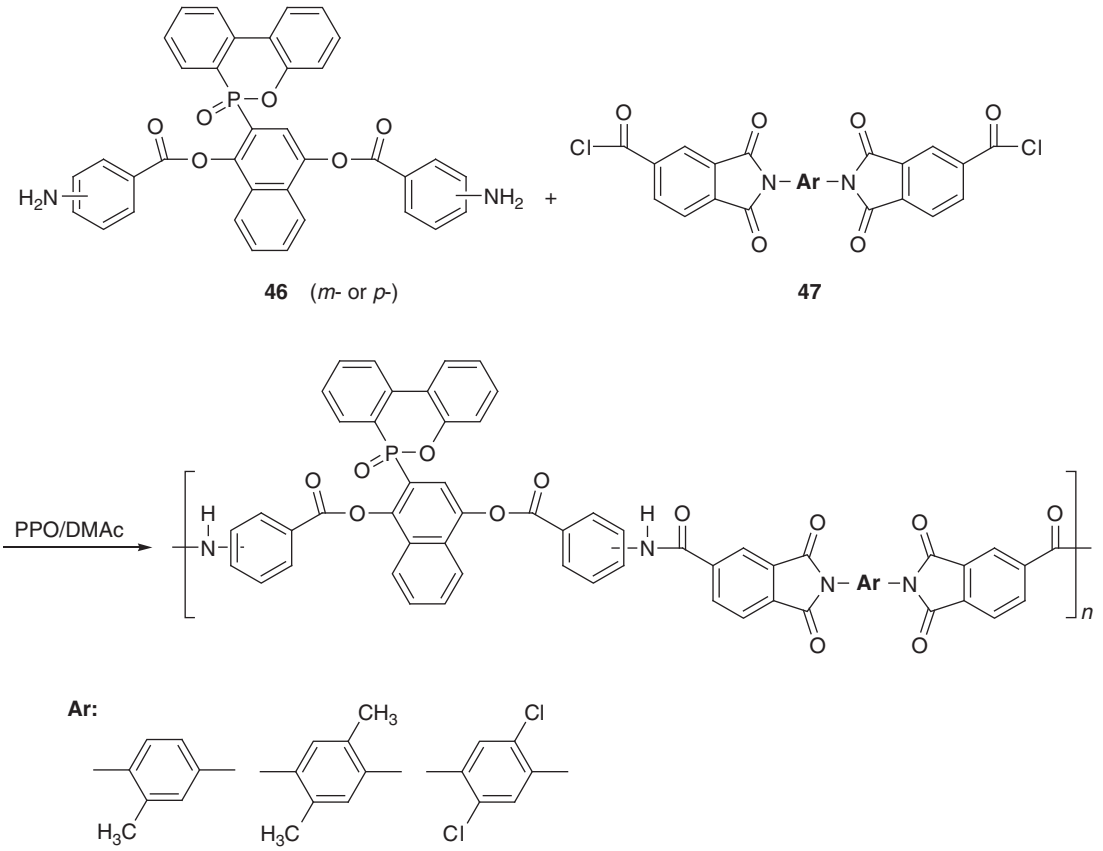
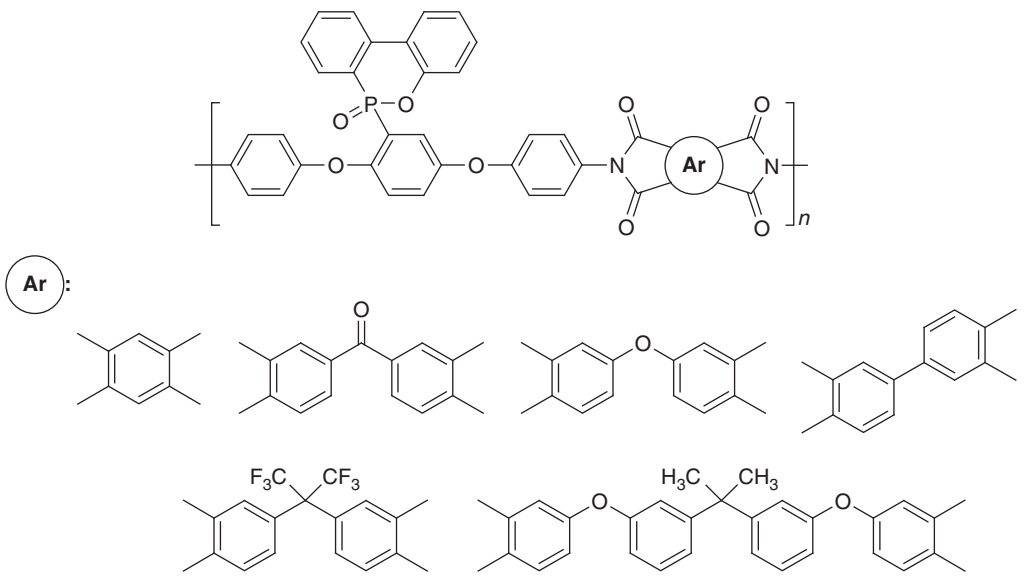


Scheme 29

Since 2007, Lin *et al.*[119,120] reported phosphorus-containing aromatic diamines and its derived PIs ((Schemes 30 and 31). The bulky biphenylene phosphinate pendant is responsible not only for the improved solubility but also for the suppressed coloration. The combination of flexibility, high glass transition temperature, high antioxidative stability, excellent flame retardancy, and improved organosolubility makes the phosphorus-containing PIs as promising polymers for electronic applications, especially in the field of halogen-free flexible printed circuit (FPC) boards, in which flame retardancy and high T_g are essential.

The phosphorus-containing PI/SiO_2 nanocomposites were prepared from the imidization of PAA of PMDA/ODA/triethoxysilane (Scheme 32).[121] In addition to the microstructure and



Scheme 30

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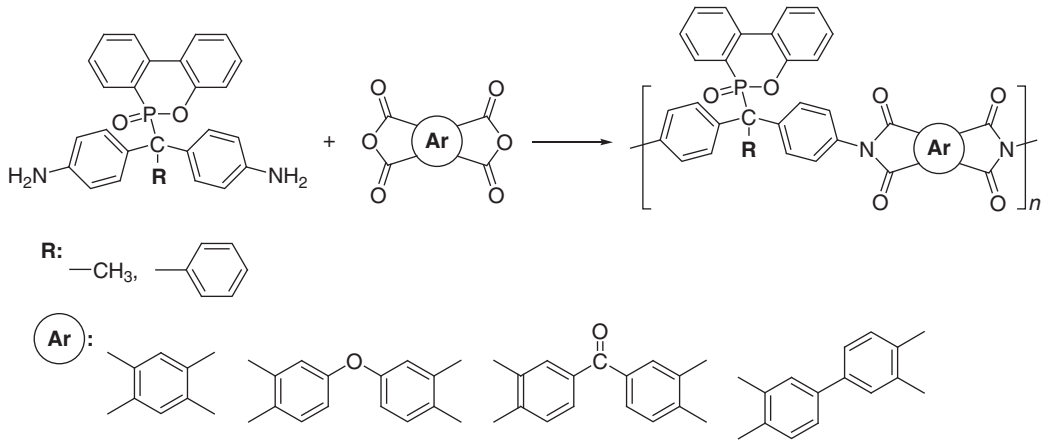
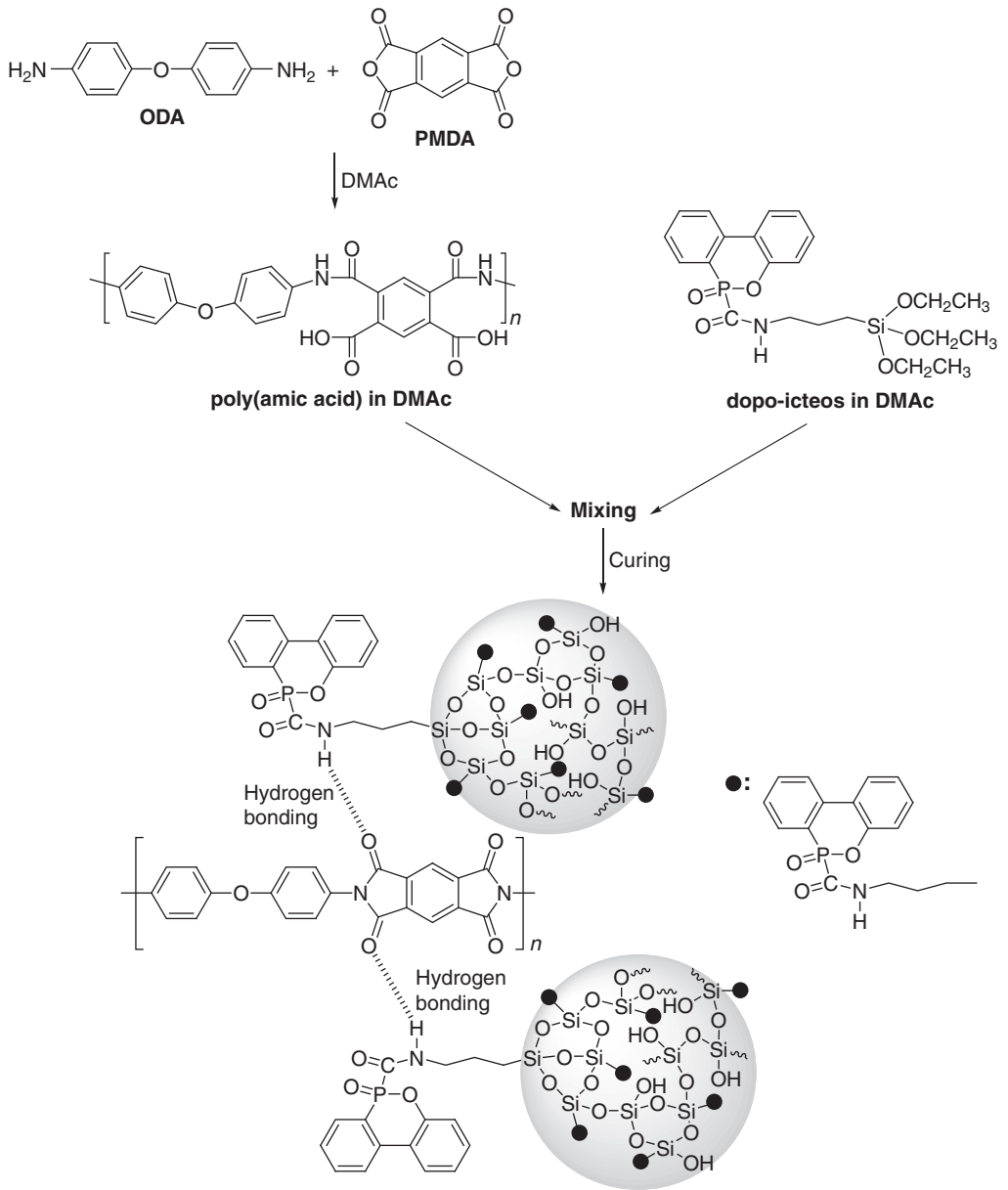


Scheme 31



Scheme 32

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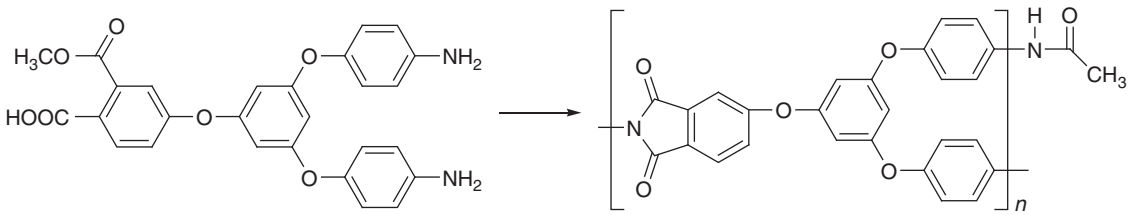
morphology, dielectric, flame retardant, and thermal properties of the organic–inorganic hybrids were investigated. The results of scanning electron microscopy (SEM) and atomic force microscopy (AFM) surface analysis indicated that the particle size of silica domain in the PI/SiO_2 system was nano-scale. The possible hydrogen bonding site of the four carbonyl groups in the repeating unit of PI made the distribution of silica network more homogeneous and the silica domain size in PI/SiO_2 hybrids smaller.

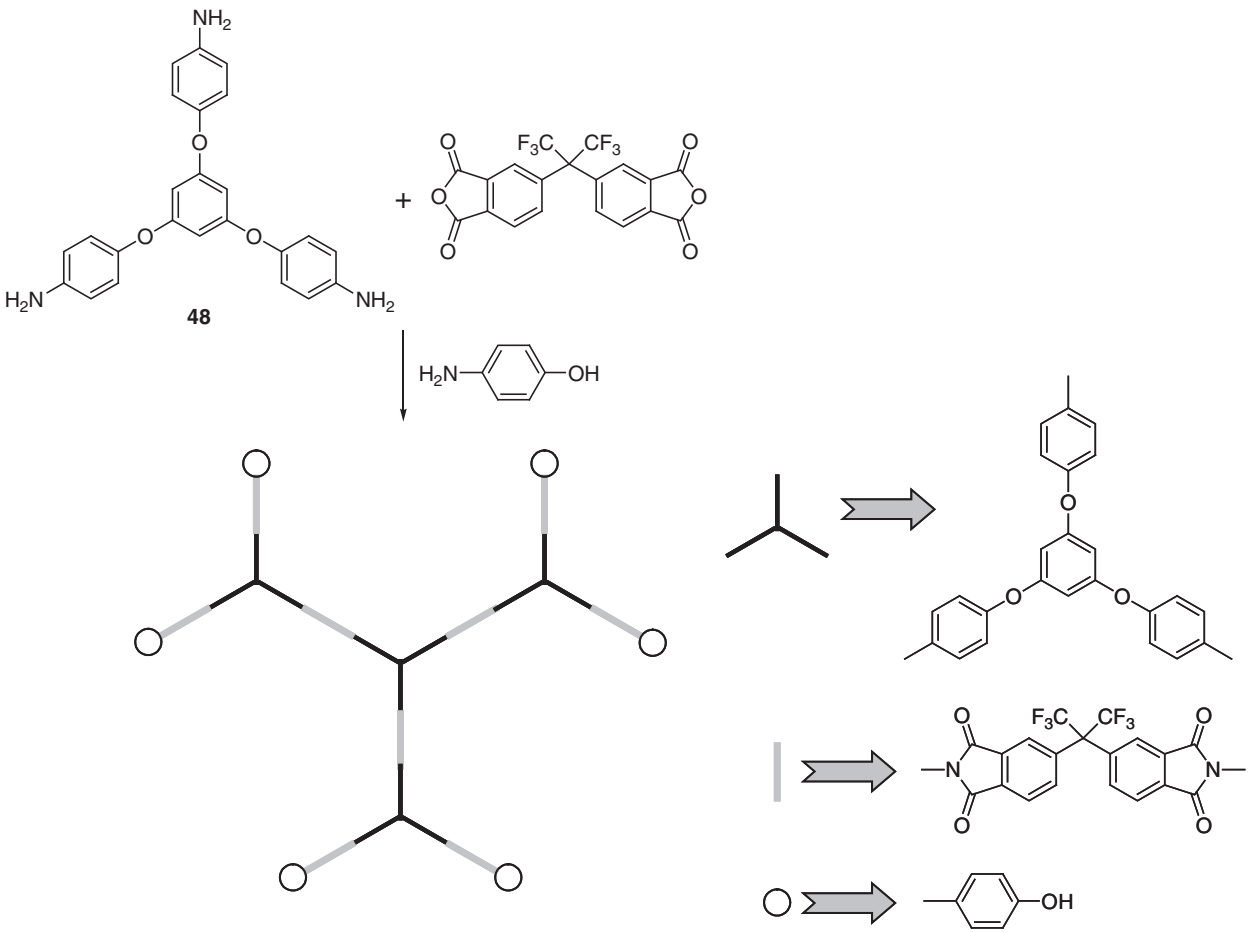
5.20.2.5 Hyperbranched PIs

Hyperbranched polymers have received much attention due to their unique chemical and physical properties as well as their potential applications in various fields from coatings, additives, drug and gene delivery, macromolecular building blocks, nanotechnology, and supramolecular science (Scheme 33).[122–127] This chapter deals with hyperbranched PIs mainly from a synthetic point of view.

Chen and Yin[128–130] reported a negative-type hyperbranched photosensitive PI based on a triamine, 1,3,5-tris (4-aminophenoxy)benzene (48), and 4,4′-(hexafluoroisopropylidene)diphthalic anhydride. The photosensitive cinnamate groups were incorporated at the periphery of the polymer by the reaction of cinnamoyl chloride with the terminal phenol groups of the fully imidized hyperbranched PI, which was obtained via the end group modification of the anhydride-terminated hyperbranched PAA (Scheme 34). The polymer showed good thermal stability and excellent solubility even in acetone and 1,1,2-trichloroethane. Photolithographic property



Scheme 33



Scheme 34

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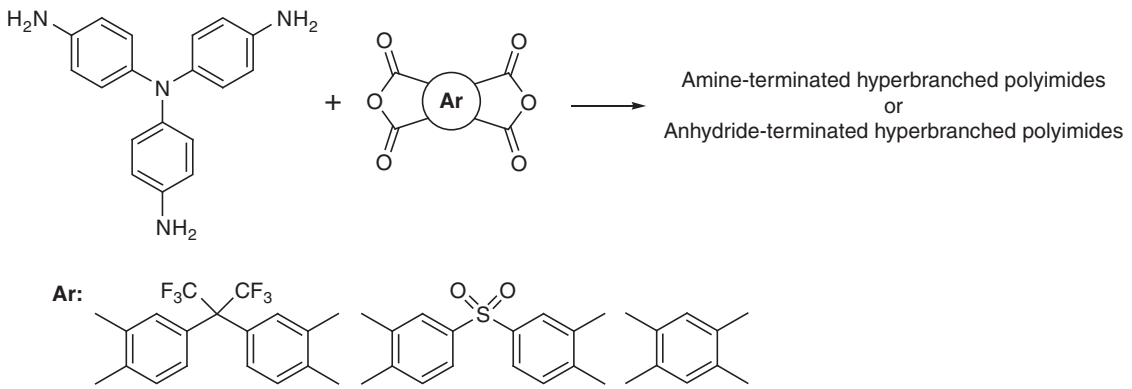
of the polymer was examined by UV exposure. SEM analysis revealed that highly resolved patterns with a line width of 10 μm were obtained, and a well-defined line as thin as 3 μm in width could be patterned, demonstrating its good photolithographic property.

Okamoto et al.[131,132] prepared two types of hyperbranched PIs (amine terminated and anhydride terminated) by controlling the manner of monomer addition and the monomer molar ratio. The resultant hyperbranched PI membranes were tough enough for gas permeation measurements based on the chemical reaction between the terminal functional groups of the hyperbranched PIs and the cross-linking agents leading to the combination of globular hyperbranched macromolecules. The amine-terminated hyperbranched PI membranes generally displayed higher gas permeability coefficients than the anhydride-terminated ones. The prepared TPA-cross-linked hyperbranched PI membranes displayed better separation performance than that of the linear analogues and many other linear polymeric membranes (Scheme 35).

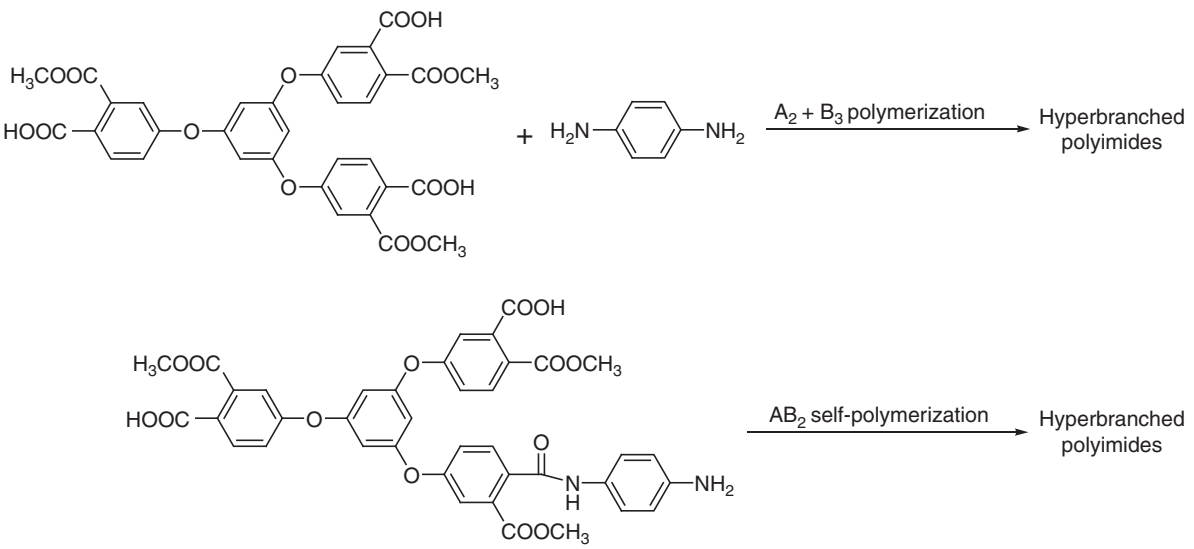
Kakimoto *et al.*[133,134] designed a AB_2 monomer from a template of the repeating unit of the hyperbranched PIs by nonideal $A_2 + B_3$ polymerization via a multistep synthesis (Scheme 36). Hyperbranched PIs having the same repeating unit as that by nonideal $A_2 + B_3$ polymerization were prepared from this new AB_2 monomer by direct self-polycondensation in the presence of diphenyl (2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate. The results revealed that hyperbranched PIs by nonideal $A_2 + B_3$ polymerization have a certain extent of chain entanglement and intermolecular interaction. A comprehensive analysis finally suggested that hyperbranched PIs by AB_2 self-polymerization have a compact highly branching structure, whereas those by nonideal $A_2 + B_3$ polymerization have a low-branching density topology.

5.20.2.6 Bismaleimide-Type PIs

It is also well known that thermosetting PIs derived from bismaleimides (BMIs) exhibit excellent thermal and mechanical properties, thus making them extremely popular for advanced composites and electronics. BMIs can be self-polymerized through their reactive maleic double bonds to give highly cross-linked, rigid, and brittle PIs. On the other hand, nucleophilic difunctional reagents such as diamines and dithiols could react with the strongly electrophilic maleic double bonds to afford linear and high-molecular-weight PIs. In



Scheme 35



Scheme 36

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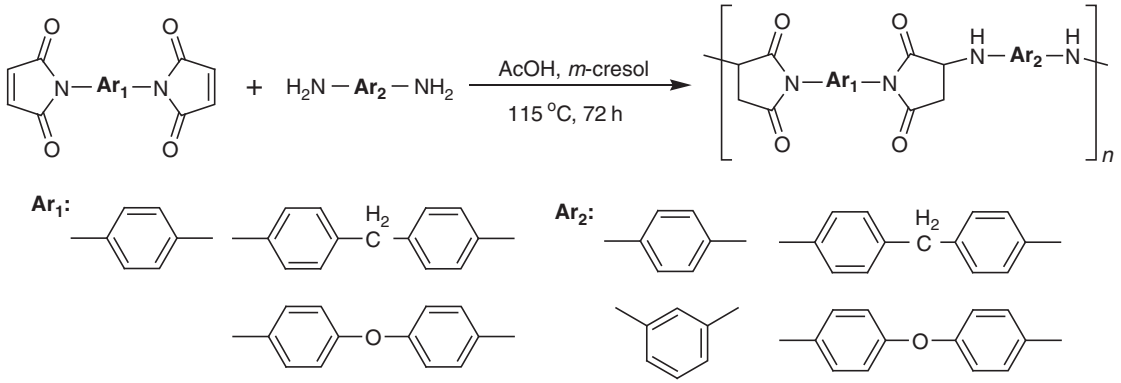


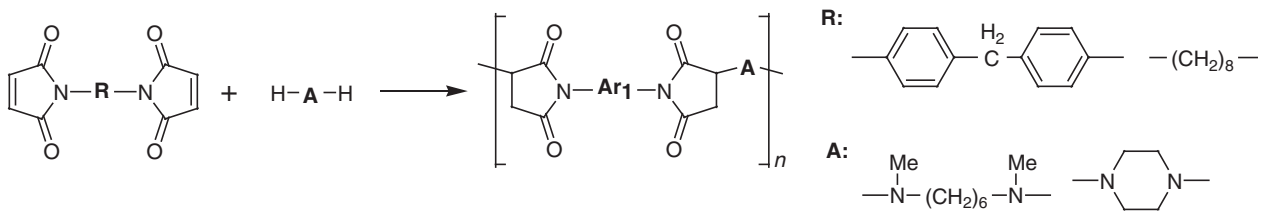
Scheme 37

particular, diamines have been used to extend BMIs, resulting in polyaspartimides and polyimidothioethers (PITEs).

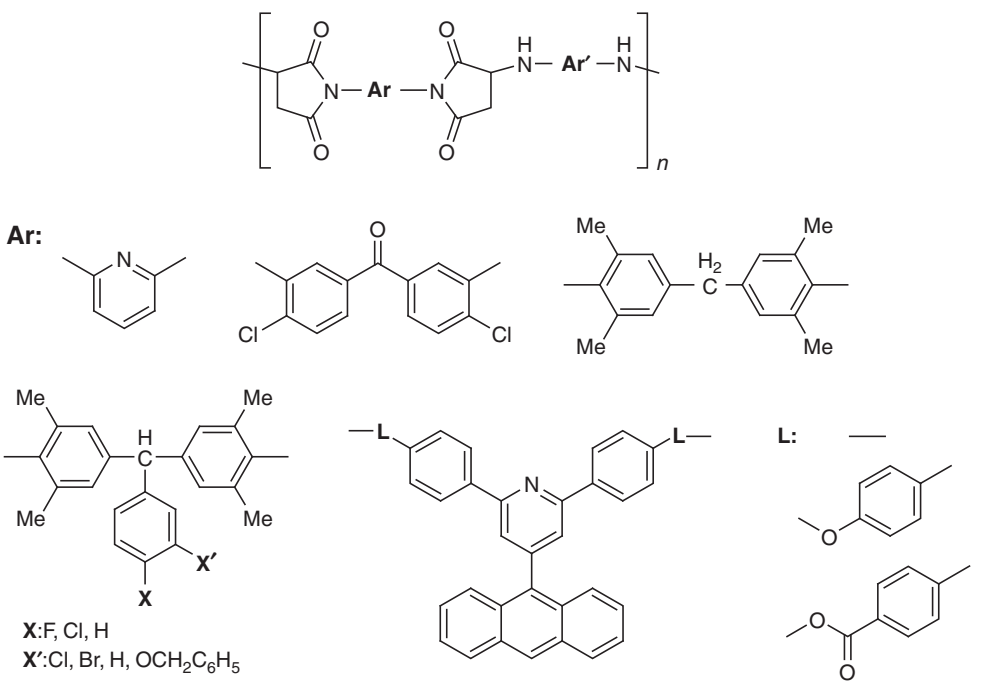
Crivello[135] reported a detailed investigation of the condensation of aromatic amines and maleimide in 1973 (Scheme 37). White and Snider[136] then prepared and compared the reactions of the secondary diamines with BMIs via Michael polyaddition (Scheme 38).

Recently, new linear polyaspartimides were obtained via Michael addition from several functional diamine-based BMIs with various aromatic diamines in *m*-cresol (Scheme 39).[137–141] These polymers exhibited an amorphous morphology with good solubility, high T_g values, and good thermal stability, which could be considered to be new processable polymeric materials.

Through the Michael addition, thermally stable nonlinear optical (NLO) hyperbranched systems consisting of azobenzene dyes have been successfully synthesized (Scheme 40).[142] All of the obtained polymers were soluble in DMF, DMAc, and



Scheme 38



Scheme 39

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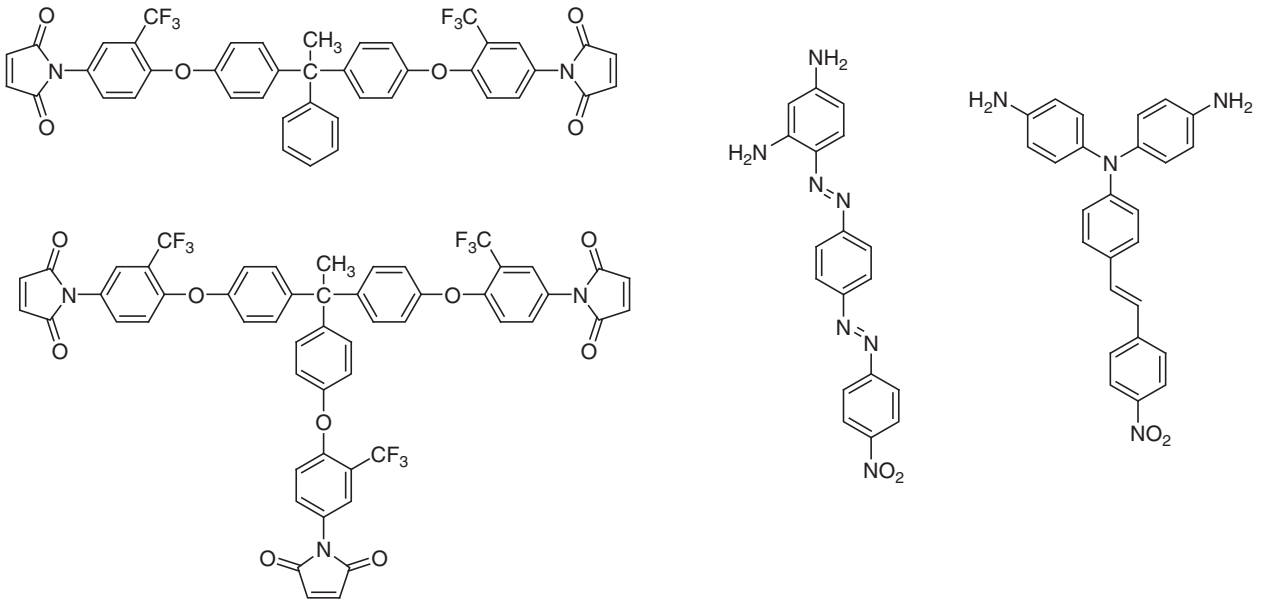


Scheme 40

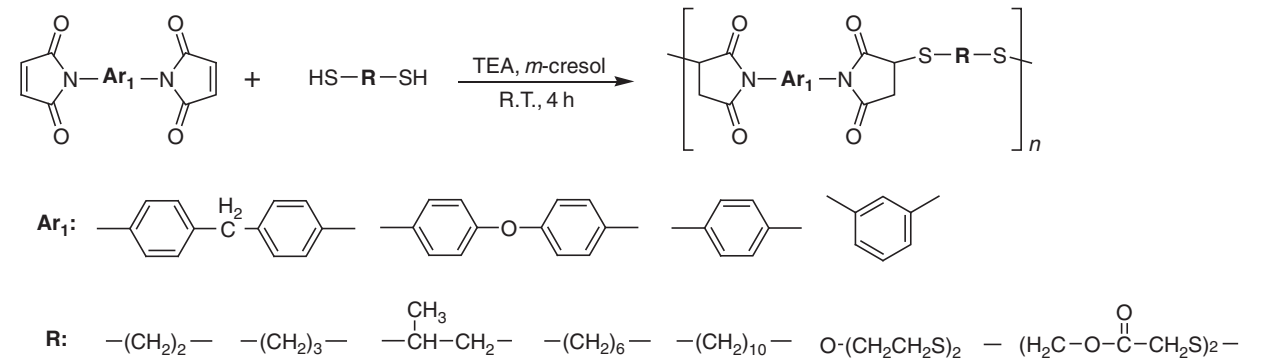
DMSO. By incorporating the polyaspartimide structure into the NLO-active hyperbranched polymers, thermal stability was greatly enhanced. All the hyperbranched polymers exhibited better NLO properties than their corresponding linear analogues due to the presence of a spherical shape and site isolation effect. Waveguide properties could be also achieved for all the NLO polymers.

The condensation of maleimide compounds with hydrogen sulfide and bisthiols was studied in several model systems by Crivello[143] in 1976 (Scheme 41). BMI compounds undergo rapid, exothermic polymerization with thiol-containing compounds in *m*-cresol and basic catalyst to give linear PITEs with high viscosity. PITE copolymers can readily be prepared by mixing two BMI monomers together in solution and then adding a catalyst and hydrogen sulfide. Random copolymers were obtained in this manner and revealed properties as a combination of those of the two homopolymers; they exhibited only one glass transition temperature and one melting point.

Yen and Liou,[144] therefore, used this facile approach to prepare a series of thermoplastic PITEs (Scheme 42). These polymers were highly soluble in various organic solvents and showed useful thermal stability associated with high glass transition temperatures. These optically isotropic thermoplastic PITEs exhibiting well-balanced optical properties are promising candidates for optical waveguide or encapsulant materials in advanced optical applications for both solution casting and injection molding techniques.

5.20.2.7 PI Copolymers

The intractable characteristics of aromatic PIs are major problems as a result of high melting points and insolubility. To overcome this drawback, copolymerization is an effective approach and various copolyimides have been developed. For example, poly(ester imide)s, **PAI**s, poly(pyrrolone imide)s (**PPI**s), poly(benzimidazole imide)s (**PBII**s), poly(benzoxazole imide)s (**PBOI**s), and poly(benzothiazole imide)s (**PBTI**s) have been developed as an alternative material offering a compromise between excellent thermal stability and processability. Some of the representative copolyimides were selected and summarized as follows.



Scheme 41

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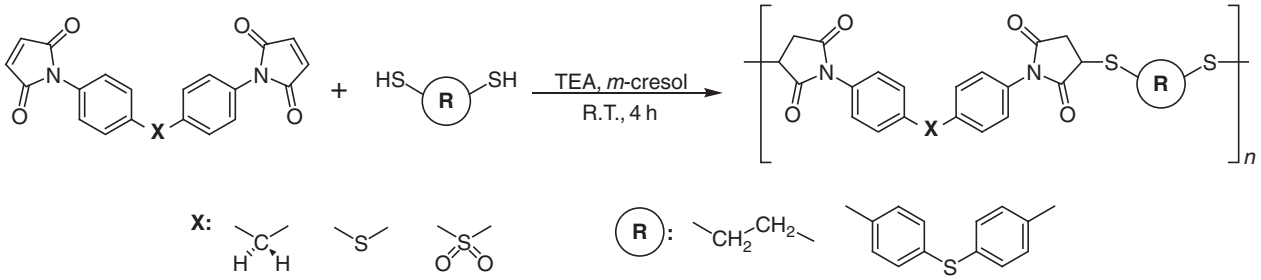
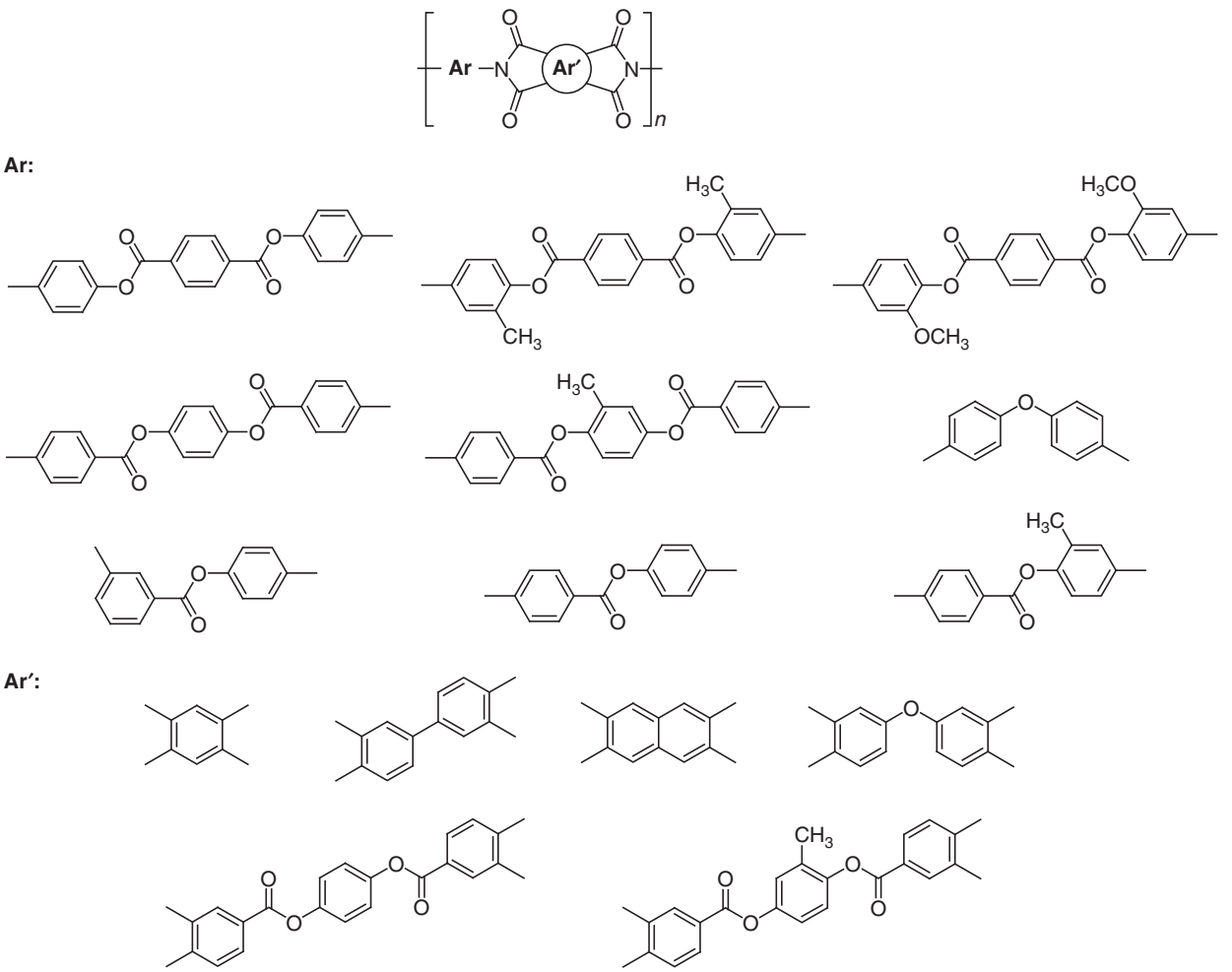


Scheme 42

5.20.2.7.1 Poly(ester imide)s

One of the applications in the greatest demand of PIs is a use as dielectric layers (base film materials) in copper clad laminates (CCLs), from which FPC boards, tape-automated bonding, and chip-on-film assembly systems are fabricated. Thermo-dimensional stability of PI films is one key parameter for realizing higher density assembly in FPC. For this purpose, to use PI films possessing lower in-plane CTE (simply called CTE) is the most effective approach. Particularly in the two-layered CCL, CTE values of the PI base films must be precisely controlled to practically the same value as that of the copper layer (17.7 ppm K^{-1}); otherwise the CCL undergoes curling. In this regard, many PI systems are not applicable because of their much higher CTE values (40–70 ppm K^{-1}). Therefore, considerable efforts have been made for reducing CTE of PI films. Schematic investigations on the structure–CTE relationships revealed that PI systems possessing linear and stiff backbone structures tend to show low CTE characteristics.[145,146]

Hasegawa *et al.*[147–149] reported the investigations of various poly(ester imide)s for FPC applications. Ester-containing tetracarboxylic dianhydrides and diamines were used to obtain a low CTE and low water absorption (Scheme 43). The resultant poly(ester imide)s showed high dimensional stability, high T_g, low CTE, high



Scheme 43

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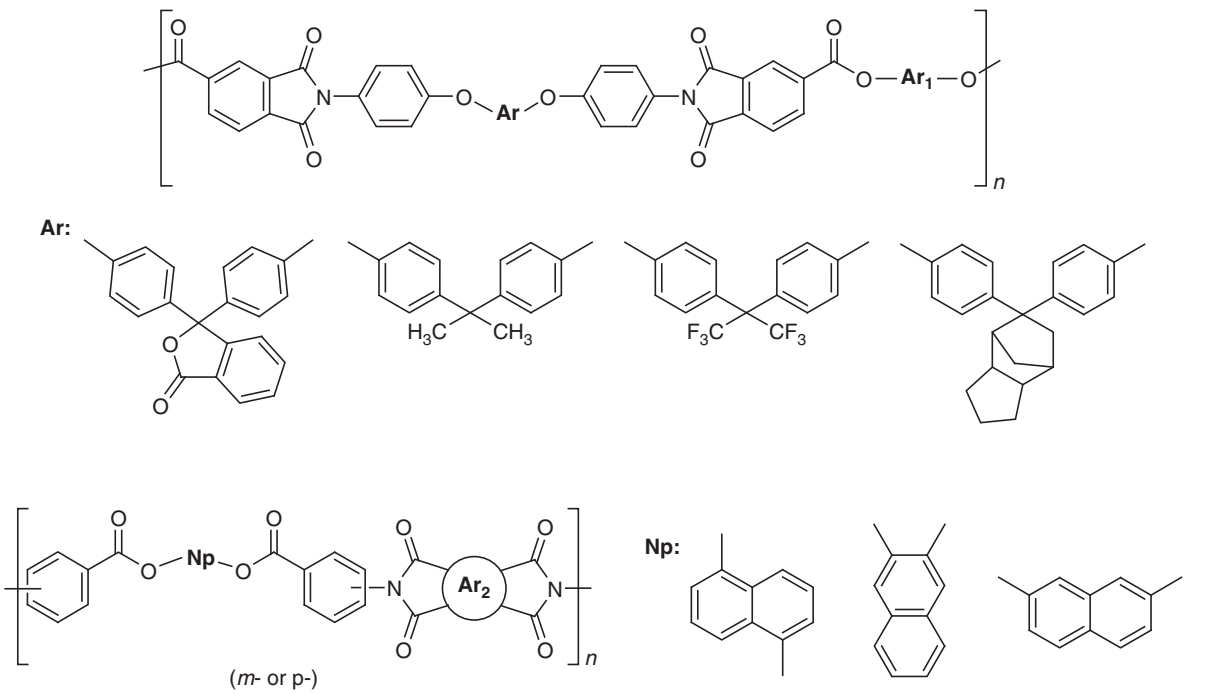
modulus, low water absorption, and lower coefficients of humidity expansion (CHEs) at the same time. The results revealed that the *para*-aromatic ester units contribute very effectively to the acquisition of low CTE and low water absorption. Moreover, the copolymer system achieved excellent combined properties: a very high T_g at 410 °C, a slightly lower CTE (10.0 ppm K^{-1}) than that of copper foil, suppressed water absorption (0.35%), an extremely low CHE (3.4 ppm per RH%), and good film toughness. Thus, these poly(ether imide)s can be promising candidates as the next generation of FPC-based film materials.

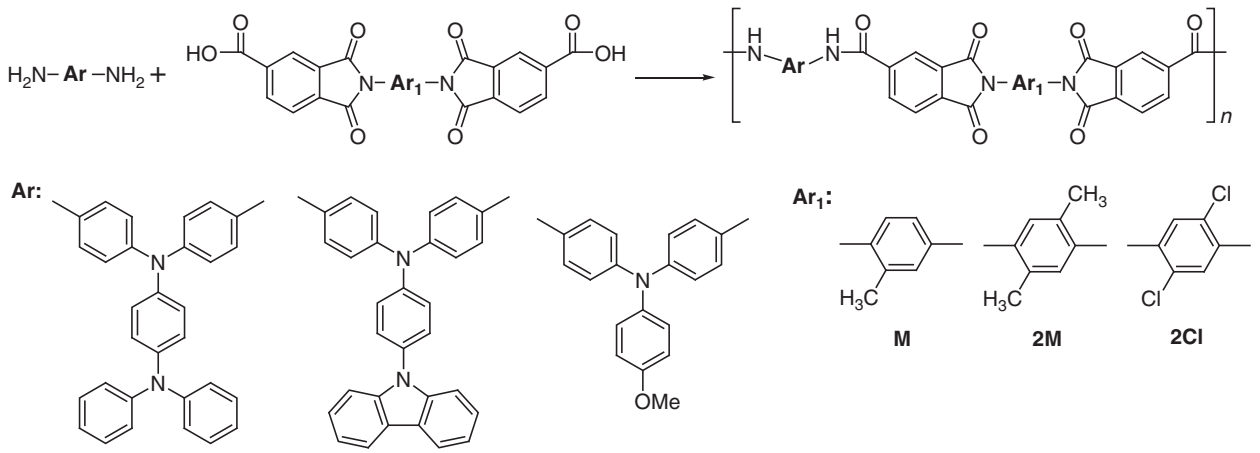
Yang *et al.*[150,151] synthesized high-molecular-weight aromatic poly(ester imide)s from bis(trimellitimide)-diacids and various bisphenols by direct polycondensation using diphenyl chlorophosphate and pyridine as condensing agents (Scheme 44). Hsiao *et al.*[152–154] also reported the synthesis of soluble and light-colored poly(ester imide)s using naphthalene ring-containing bis(ester-amine)s and various tetracarboxylic dianhydrides by conventional polycondensation (Scheme 44). All polymers showed good thermal stability, high optical transparency, low dielectric constant, and low water absorption. Some of the polymers exhibited good solubility in organic solvents and could be cast into tough and flexible films, which could be considered as new candidates for processable high-performance polymeric materials.

5.20.2.7.2 Poly(amide imide)s

Liou *et al.*[155–157] reported aromatic poly(amine-amide-imide)s having *para*-methoxy substituent, pendant TPA and *N*-carbazolylphenyl units from the phosphorylation polyamidation of the synthesized diamine with imide ring-preformed dicarboxylic acids (Scheme 45).



Scheme 44



Scheme 45

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All polymers are highly soluble in polar organic solvents. Flexible, amorphous, and deep reddish films of poly(amine-amide-imide)s can be obtained by solution casting and showed useful levels of thermal stability associated with high glass transition temperatures and degradation temperatures. The poly(amine-amide-imide) films exhibited reversible electrochemical oxidation redox couples, good electrochromic stability, and high contrast of optical transmittance change.

5.20.2.7.3 Poly(pyrrolone imide)s

The copolymer consisting of pyrrolone and imide units exhibited enhanced solubility without sacrificing thermal and mechanical properties.

Yang *et al.*[158] prepared **PPI** matrix resin by using PMR (*in situ* polymerization of monomer reactants) process in anhydrous ethyl alcohol and NMP (Scheme 46). The homogeneous matrix resin solution (40–50% solid) was stable for a storage period of 2 weeks and showed good adhesion with carbon fibers which ensured production of prepregs. Thermosetting **PPI** as well as short carbon fiber-reinforced polymer composites could be accomplished at optimal thermal curing conditions. The resulting copolymer showed excellent thermal stability with a high initial decomposition temperature and good mechanical properties.

Burns and Koros[159] examined PPI copolymers 6FDA-TAB/DAM for the application of O_2/N_2, CO_2/CH_4, and C_3H_6/C_3H_8 separation by controlling the TAB/DAM ratio to quantitatively alter the structure of the polymer matrix (Scheme 47). Combining these two classes of polymers could also be used to design to provide rigidity and desirable mechanical properties in addition to high-quality gas transport properties.

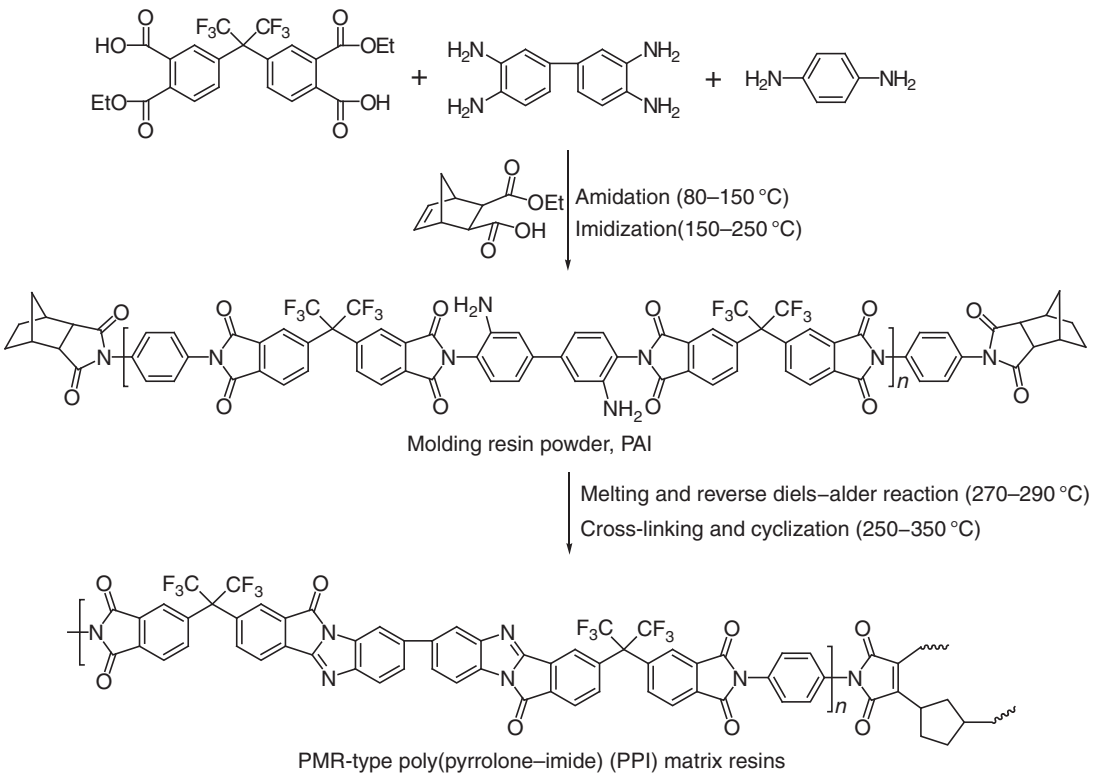
Choi *et al.*[160] reported poly(benzoxazole-*co*-pyrrolone) copolymers in various compositions by thermal rearrangements from their precursors of hydroxyl-containing PPIs (Scheme 48). All the copolymers showed higher gas permeability as well as gas selectivity than their corresponding polybenzoxazole or polypyrrolone homopolymers.

5.20.2.7.4 Poly(benzimidazole imide)s

The thermal and mechanical properties of PBII copolymers could be further increased comparing to the corresponding PIs. The route to obtaining these copolymers involved the synthesis of benzimidazole-based diamine compounds, which react with aromatic tetracarboxylic anhydrides to yield benzimidazole-imide copolymers (Scheme 49).[161]

The benzimidazole-containing aromatic PIs prepared from synthesized 5,4′-diamino-2-phenyl benzimidazole (49) and commercial tetracarboxylic dianhydrides by the conventional two-step polymerization were amorphous and could afford flexible, transparent, and tough films with outstanding thermal and mechanical properties (Scheme 50).[162] In addition, they showed high levels of tensile strength of up to 234 MPa and modulus of up to 5.6 GPa, although the values of the elongation at the break were rather low. Excellent properties of these copolyimides are attributed to the rigid-rod structure and interchain hydrogen bonding.

Acid–base blend membranes prepared by a combination of polymeric nitrogen-containing bases (N bases) and polymeric sulfonic acids are new class of interesting materials that exhibit improved thermal stability and good resistance to swelling. In a similar manner, polymers bearing both sulfonic acid groups and N bases should possess the improved hydrolytic stability.



Scheme 46

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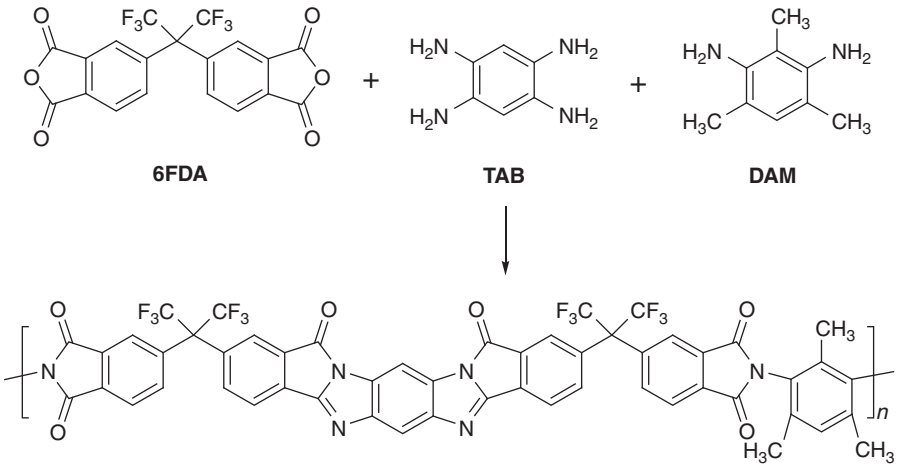
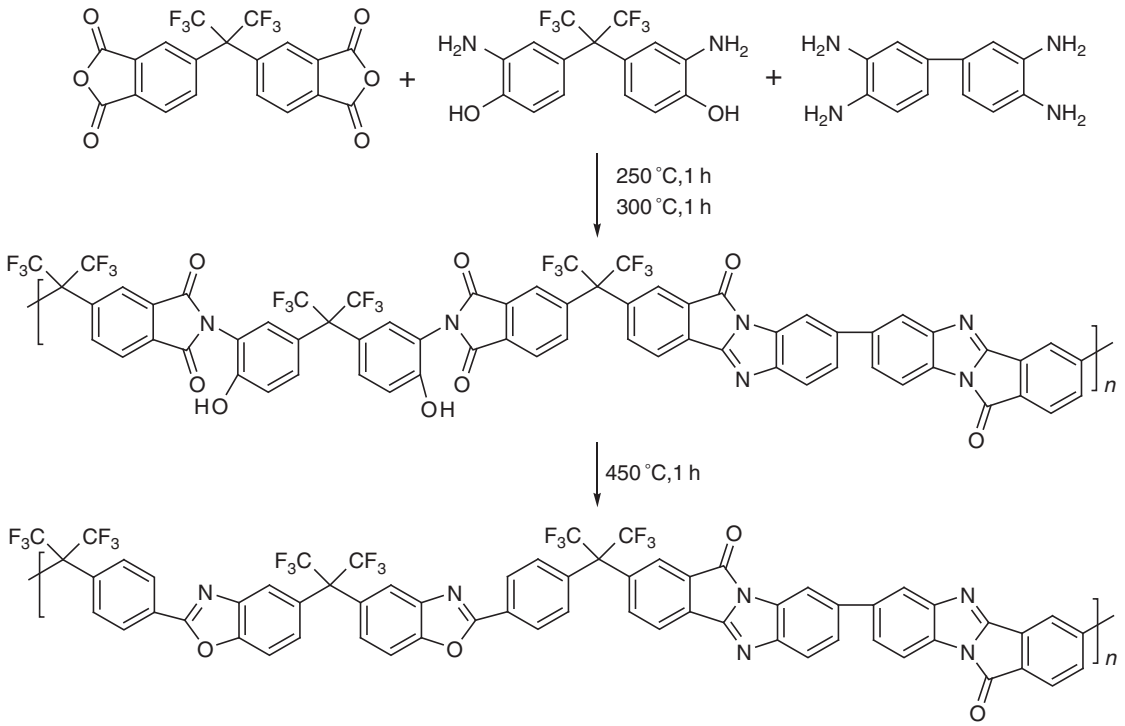
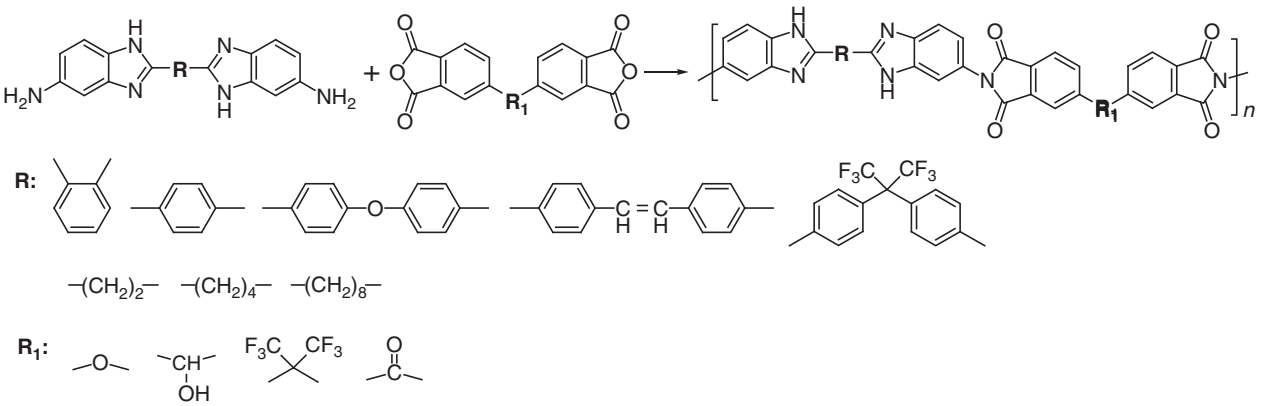


Scheme 47



Scheme 48



Scheme 49

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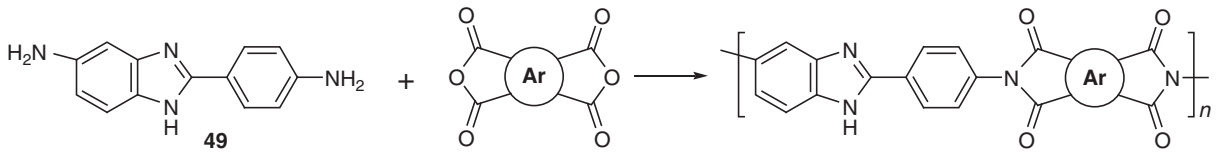
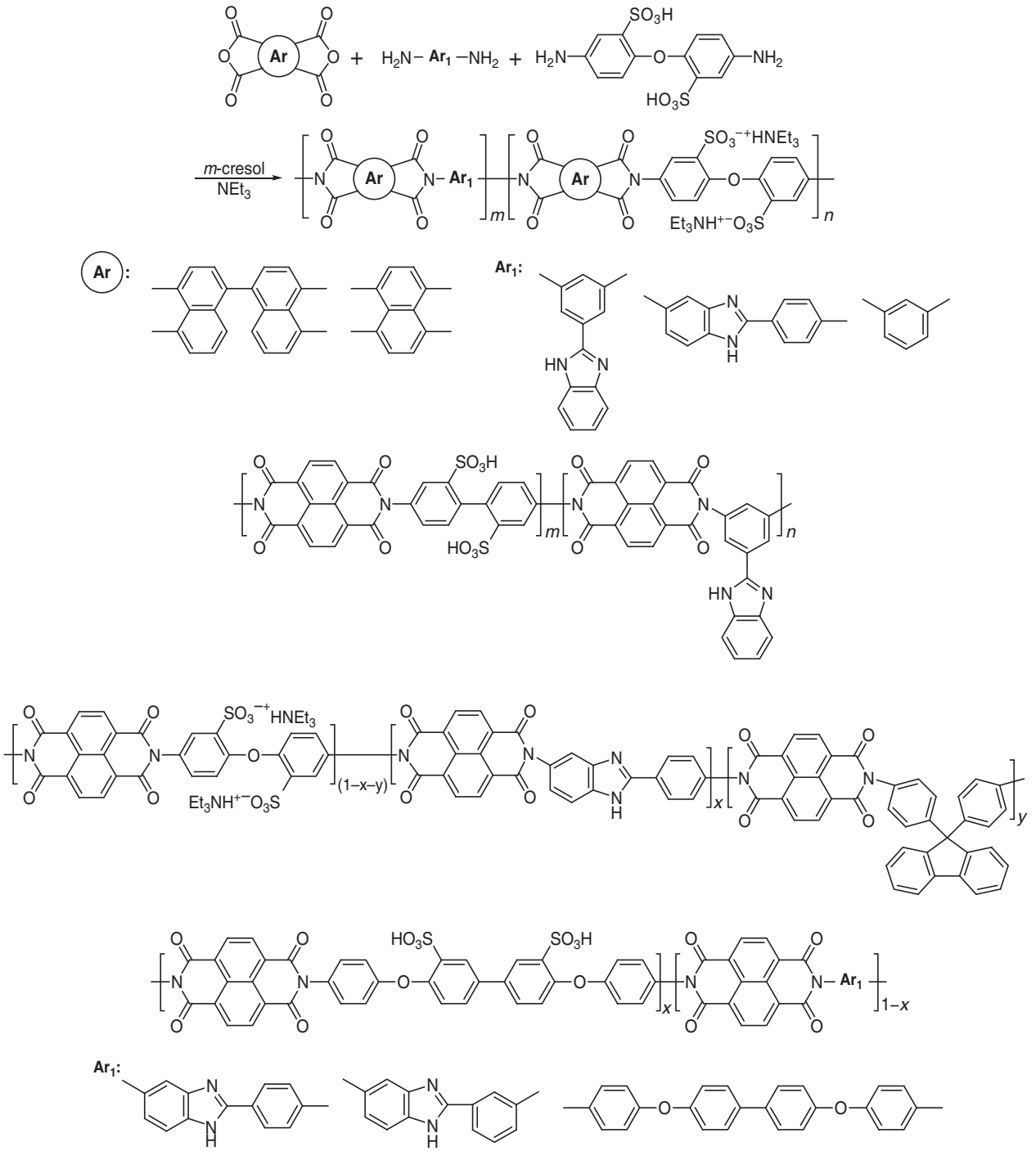


Scheme 50

In view of this consideration, efforts have been made to develop membrane materials based on sulfonated PIs (SPI) containing benzimidazole groups (Scheme 51).[163–166] SPI membranes incorporated with basic benzimidazole groups showed enhanced thermal and hydrolytic stability at the expense of some proton conductivity. Furthermore, the low methanol permeation rate was also achieved by introducing the benzimidazole into the SPI backbone.



Scheme 51

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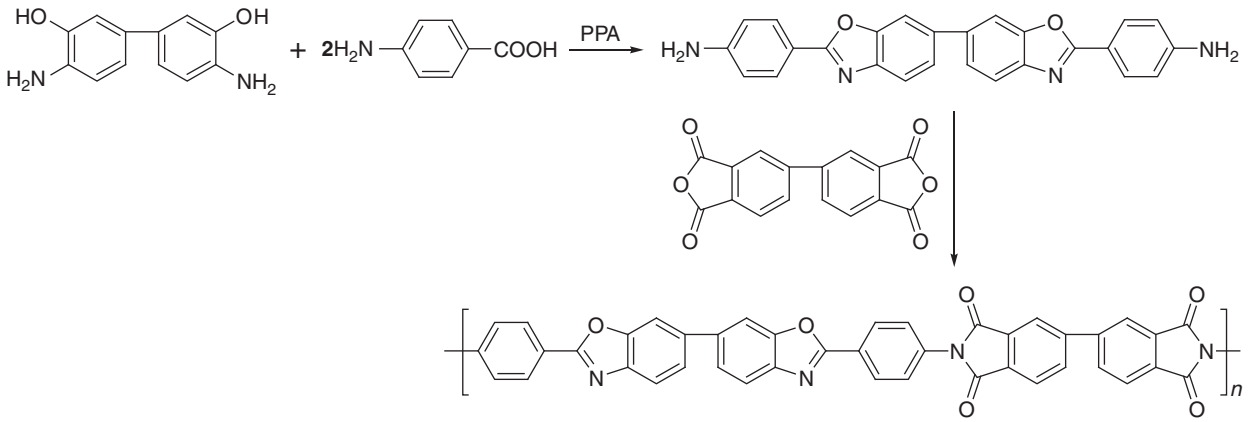
5.20.2.7.5 Poly(benzoxazole imide)s

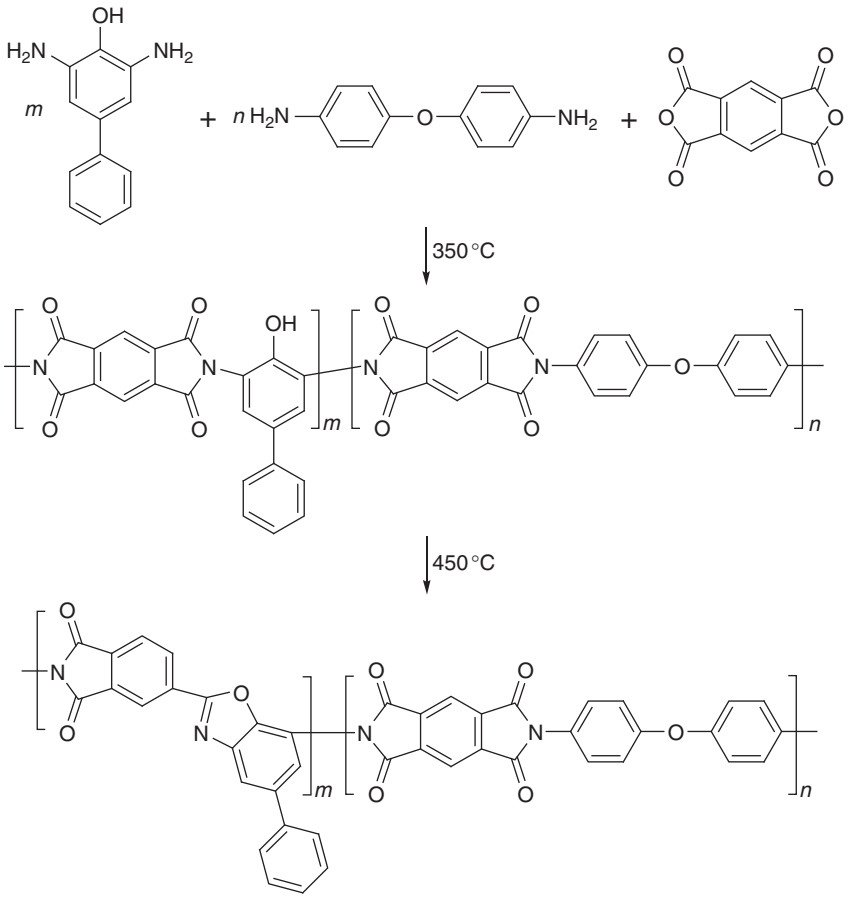
Aromatic polybenzoxazoles (PBOs) possess superior thermal and chemical properties to other engineering plastics such as polysulfone and polyetheretherketone (PEEK). The preparation of PBOIs has been developed by using benzoxazole-preformed diamines and tetracarboxylic dianhydrides or thermal conversion of hydroxyl-containing PIs to polybenzoxazole imides (Schemes 52 and 53).[167,168]

The synthesis of poly(*o*-hydroxy-amide-imide)s with high molecular weights by low-temperature solution polycondensation from imide-preformed diacid chlorides having chloro- or methyl-substituted *p*-phenylene units and three bis(*o*-amino phenol)s has been reported by Liou[169,170] (Scheme 54). Subsequent thermal cyclodehydration of the poly(*o*-hydroxy-amide-imide)s afforded novel PBOIs. These intrinsic alternating copolymers exhibited high glass transition temperatures over 300 °C and were stable up to 500 °C in air or nitrogen.

Hsu *et al.*[171] reported a novel positive-working and alkali-developable photosensitive PBOI precursor based on



Scheme 52



Scheme 53

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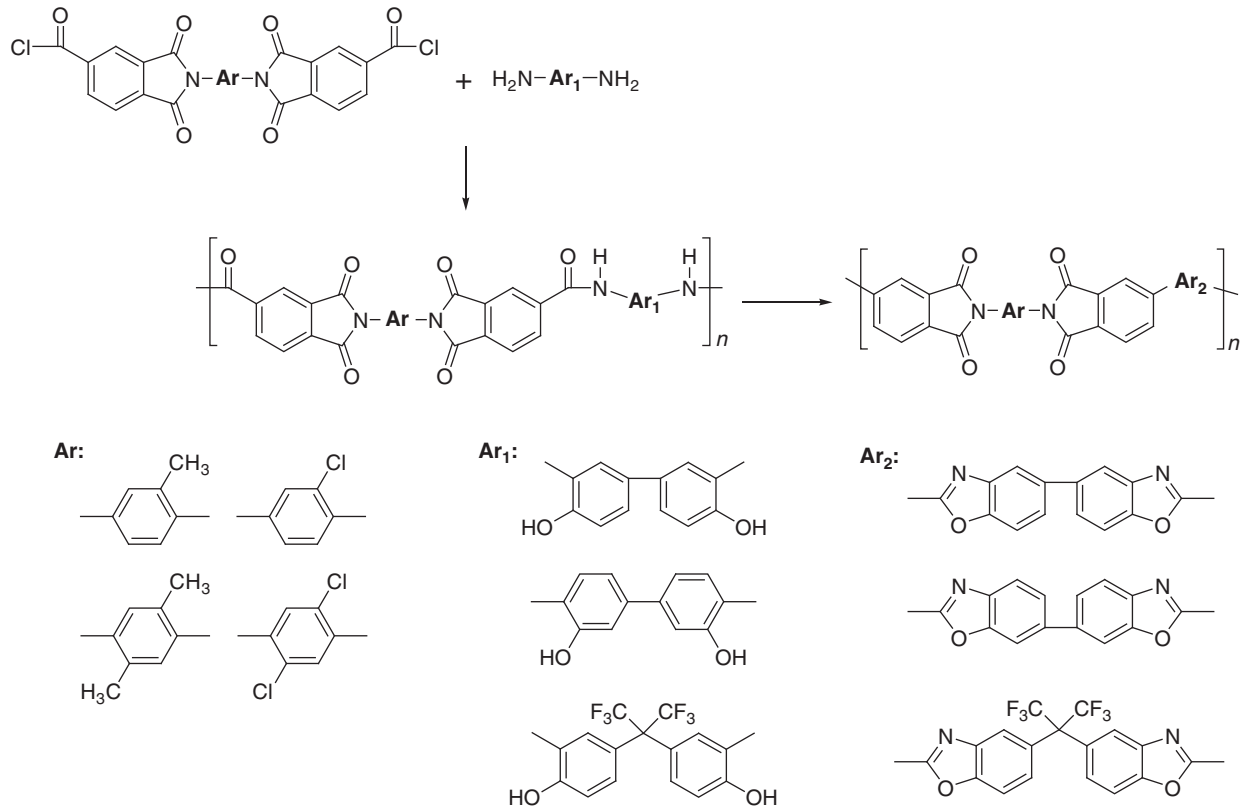
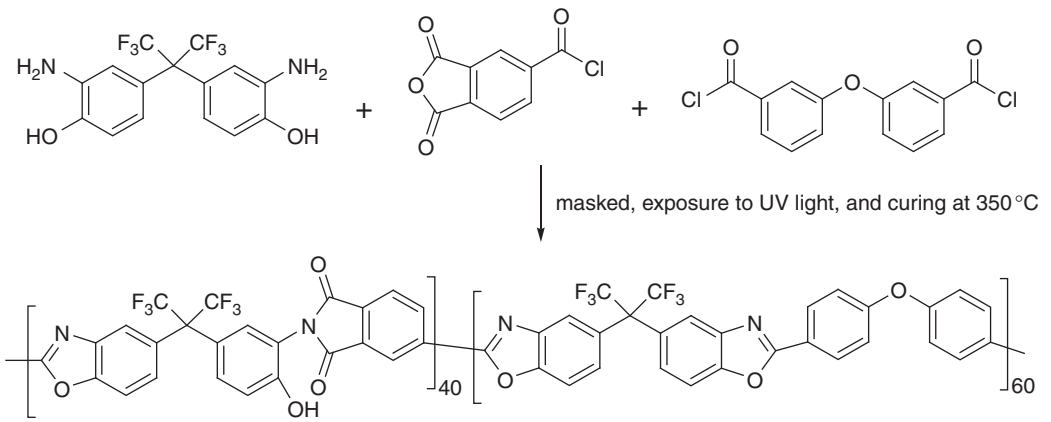


Scheme 54



Scheme 55

a poly(amic acid hydroxyamide) bearing phenolic hydroxyl groups and carboxylic acid groups (Scheme 55). By using the photosensitive compound diazonaphthoquinone and 0.6 wt.% tetramethylammonium hydroxide as the developer, the resulting patterns with a resolution of 5 μm were achieved.

5.20.2.7.6 Poly(benzothiazole imide)s

Rigid-rod and extended chain-containing poly(benzothiazoles)s (**PBTs**) have very high moduli, low CTEs, exceptional thermal stability, and many other desirable properties. The high degree of molecular rigidity in these systems dominates the morphology and subsequent mechanical properties. The poly(benzothiazoles)s are generally processed from nematic liquid crystalline solutions in polyphosphoric acid into highly ordered or semicrystalline fibers. A drawback of these rigid-rod polymers is their limited solubility and intractability, precluding their uses in many applications. The PBTIs prepared from benzothiazole-preformed diamines and tetracarboxylic dianhydride could enhance solubility without sacrificing thermal stability (Scheme 56).[172]

PI-based second-order NLO materials were usually synthesized from poly(hydroxy imide)s, followed by the Mitsunobu

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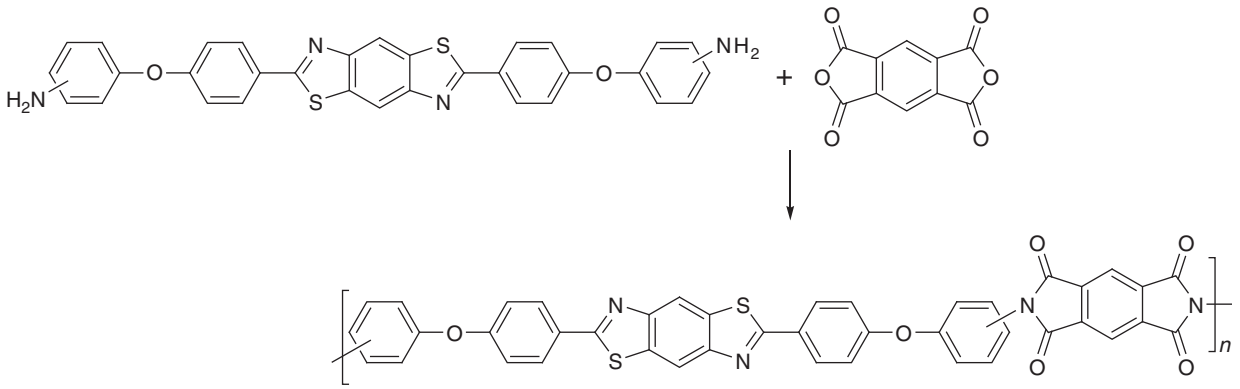
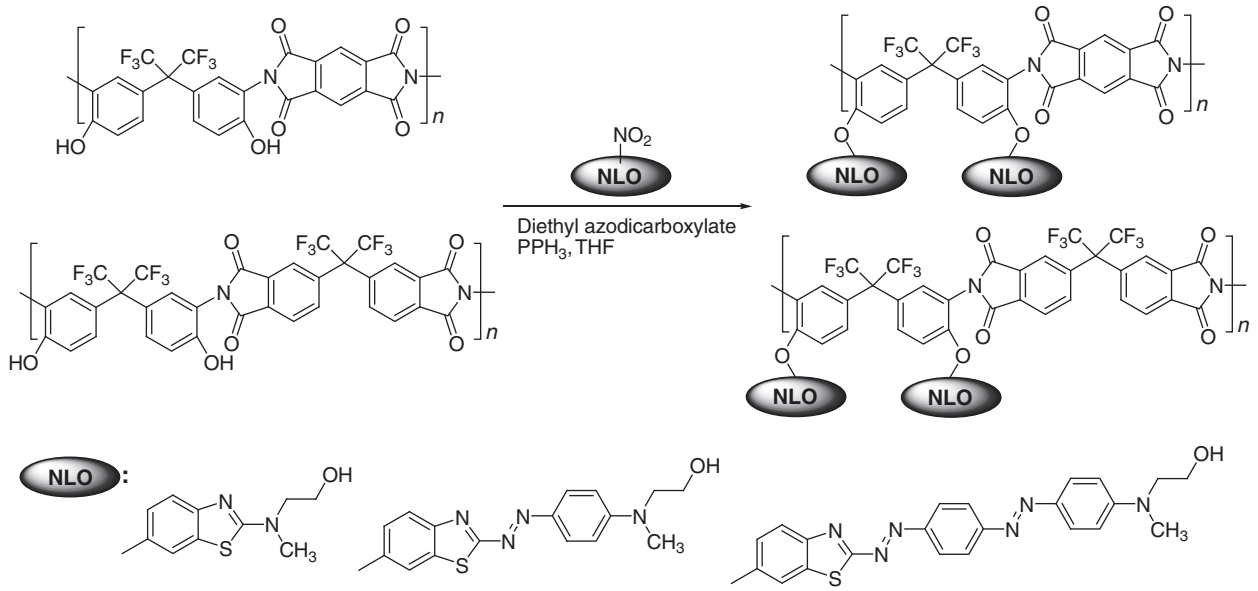


Scheme 56



Scheme 57

reaction with NLO chromophores (Scheme 57).[173] In addition, benzothiazole-based diamines with nitro group were also used to prepare the NLO PIs (Schemes 58 and 59).[174,175] These benzothiazole chromophores containing an electron-withdrawing nitro end group have been developed as donor–π-bridge–acceptor NLO units. The resulting copolyimides with side-chain benzothiazole groups showed good solubility in aprotic polar solvents such as DMF, DMAc, and NMP. It was also found that the stability of the NLO chromophore increased with increasing the glass transition temperatures of the PBTIs. The versatility of the reaction scheme and the ease of processing ensure this series of materials for further use.

In 2008, a series of PI/benzothiazole silica NLO hybrid materials were synthesized from PMDA, 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane, and an NLO benzothiazole molecule via a sol–gel process; the tetraethoxysilane content in the hybrid films varied from 0% to 22.5% (Scheme 60).[176] The NLO experimental results suggest that the hybrid thin films have potential applications as passive films for optical devices.

5.20.3 Functional PI

5.20.3.1 Electrochromic PI

Since 2005, the first electrochromic aromatic poly(amine imide)s with pendant TPA units were reported by Liou *et al.*[103] from the newly synthesized diamine, *N,N*-bis(4-aminophenyl)-*N′,N′*-diphenyl-1,4-phenylenediamine, and various tetracarboxylic dianhydrides by either a one-step or a conventional two-step polymerization process (Scheme 61). All the poly(amine imide)s were amorphous showing high solubility in many organic solvents and could be solution cast into transparent, tough, and flexible films with good mechanical properties. They had useful levels of thermal stability associated with relatively high glass transition temperatures. The poly(amine imide) films exhibited two reversible oxidation redox couples and revealed good stability of electrochromic characteristics with a drastic color change from pale yellowish to green and blue when oxidized.

In the following years, organosoluble aromatic PIs and poly(amine-amide-imide)s bearing pendant *N*-carbazolylphenyl,

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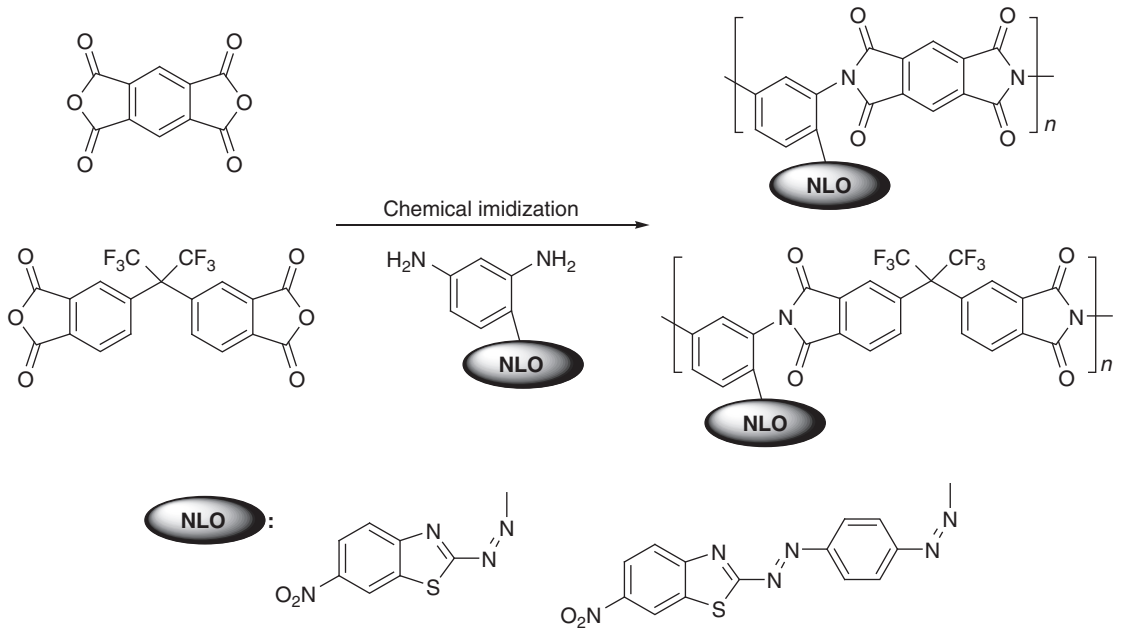
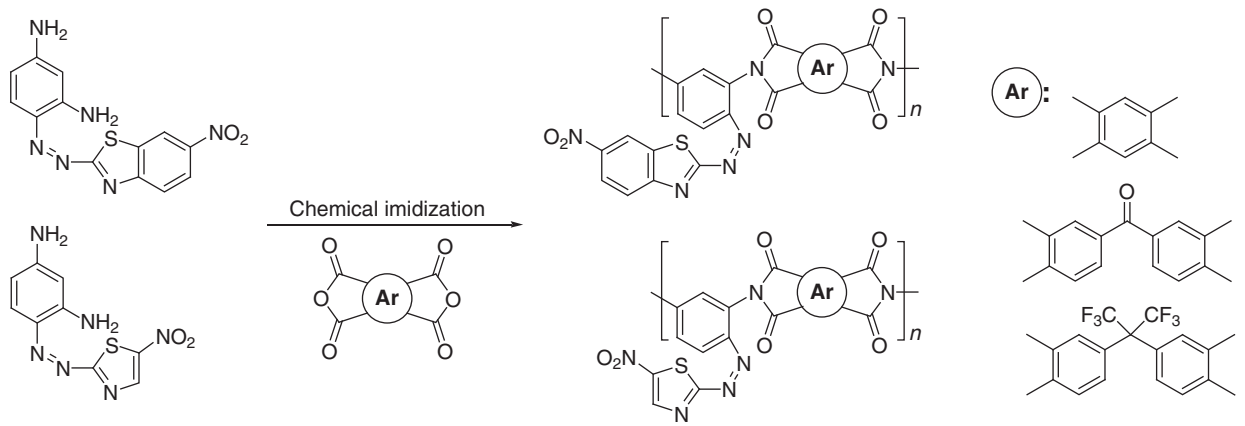
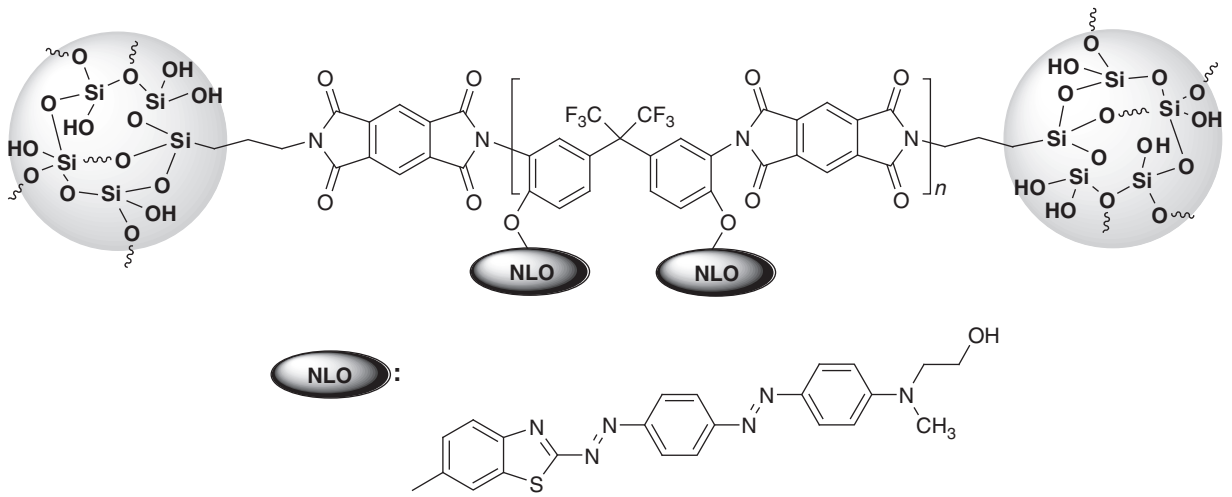


Scheme 58



Scheme 59



Scheme 60

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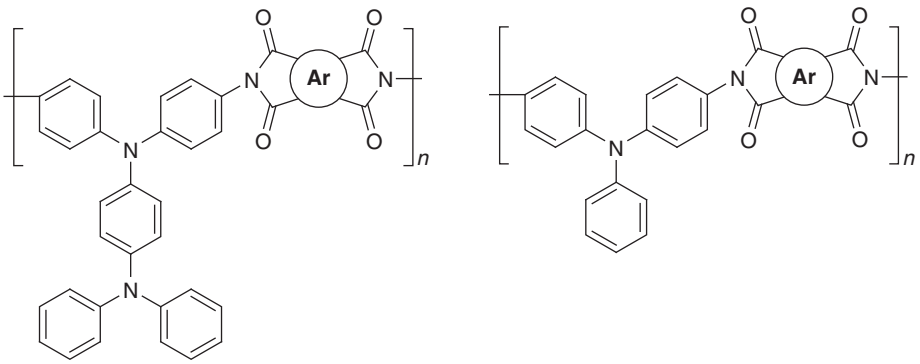
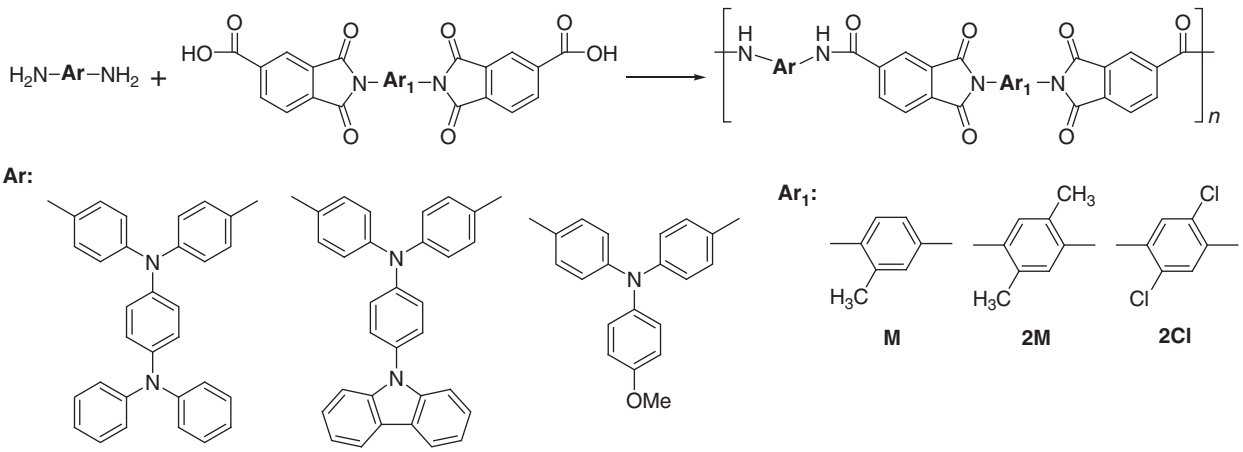


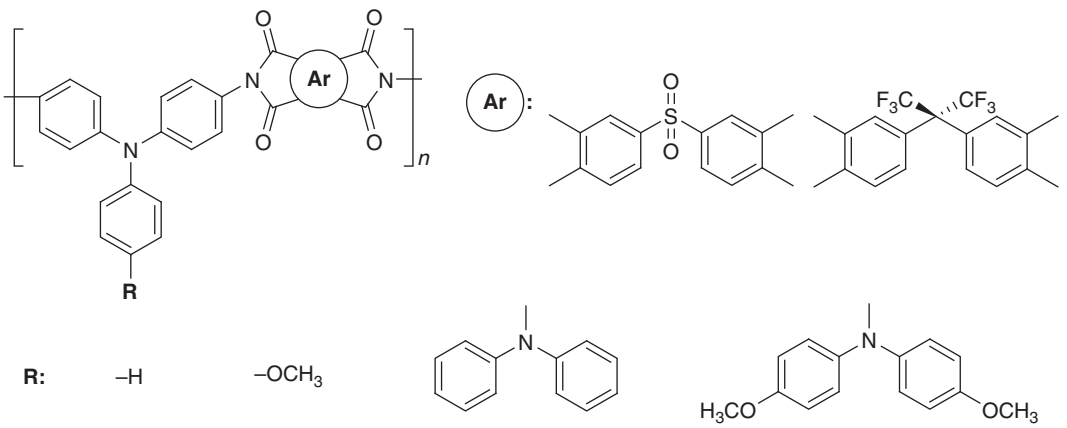
Scheme 61



Scheme 62

TPA and methoxy-substituted TPA moieties were also developed from the corresponding diamines (Scheme 62).[155–157] All the PIs were highly solution processable and exhibited excellent thermal stability with high T_s. The PI films showed good adhesion with indium tin oxide (ITO)-coated glass electrode and good electrochemical stability and also revealed electrochromic characteristics changing color from the original pale yellowish to green or blue when scanning potentials positively. Thus, the TPA-based PIs could be good candidates as anodic electrochromic materials because of their proper oxidation potentials, electrochemical stability, and thin film formability.

Gas transport properties of the PIs for CO_2, CH_4, O_2, and N_2 were also investigated (Scheme 63).[105] It was shown that the introduction of the bulky TPA unit into aromatic PIs can improve gas transport properties by increasing permeability at the slight expense of a decrease in permselectivity. The combination of electrochromic and gas permeability properties along with excellent thermal stability makes these new PIs as newly processable high-performance polymers with multifunction.



Scheme 63

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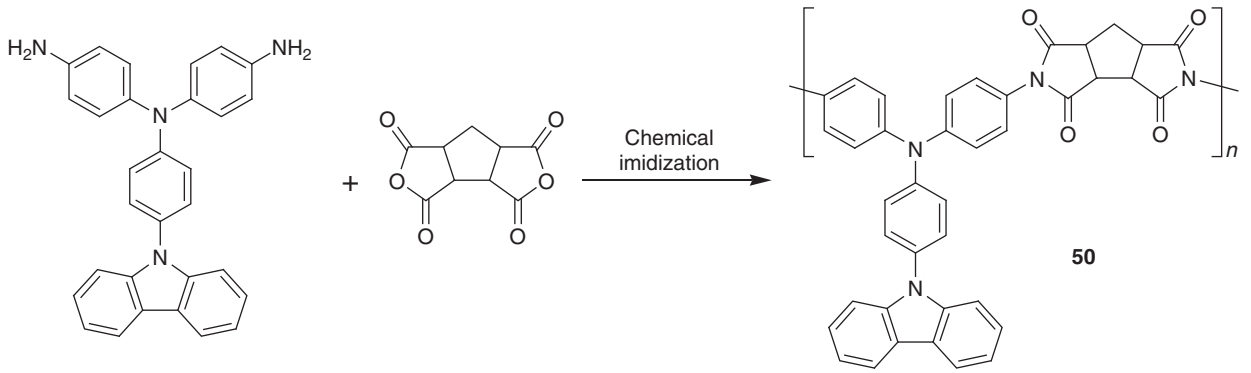
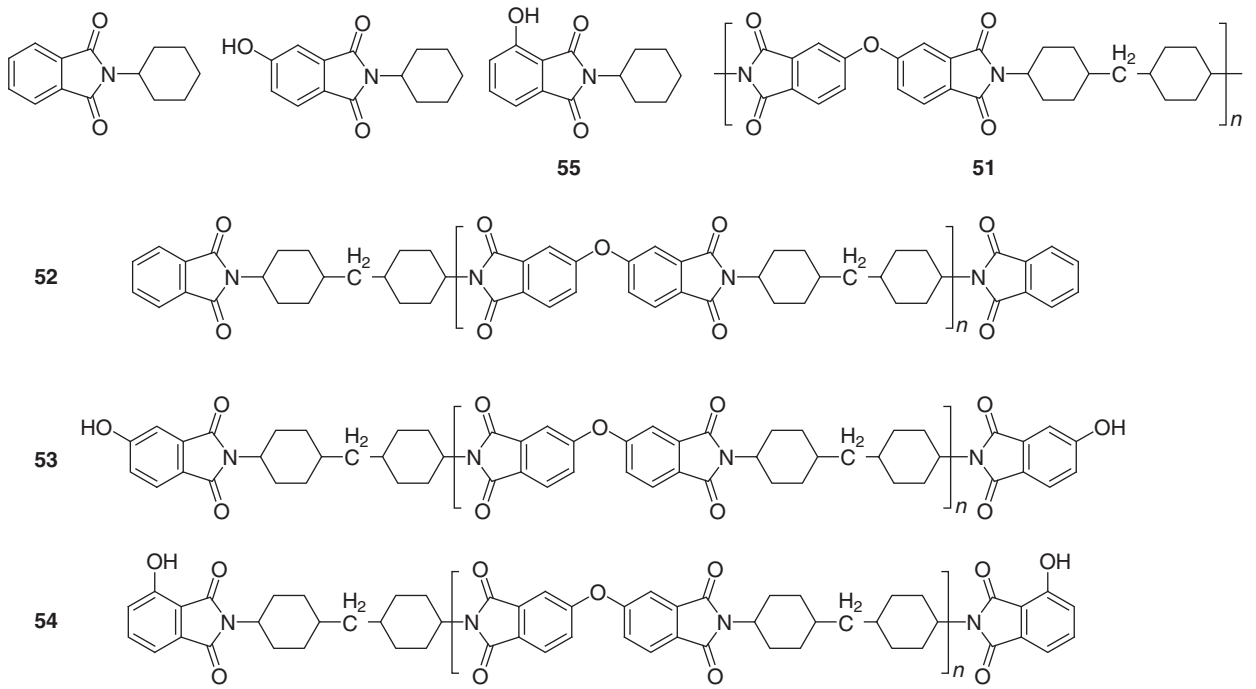
5.20.3.2 Photoluminescent PI

Carbazole is a conjugated unit that has interesting optical and electronic properties such as photoconductivity and photorefractivity. In the field of electroluminescence, carbazole derivatives are often used as the materials for hole-transporting and light-emitting layers because of their high charge mobility and thermal stability, and show blue electroluminescence due to the large bandgap of the improved planar biphenyl unit by the bridging nitrogen atom. Poly(amine imide)s bearing pendant *N*-phenylcarbazole units were prepared by the two-step method starting from the diamine, 4,4′-diamino-4″-*N*-carbazolyltriphenylamine, and various tetracarboxylic dianhydrides (Scheme 64).[104] All the poly(amine imide)s were amorphous with high T_g, excellent thermal stability, and useful mechanical properties (e.g., flexibility). The semiaromatic poly(amine imide) (50) showed light color and high optical transparency and exhibited violet–blue photoluminescence both in film state and in NMP solution with about a quantum yield of 4.54%. The poly(amine imide) films showed good adhesion with ITO and were found to be electroactive. The polymer films exhibited multicolor behavior, that is, pale yellow, green, and blue in color when various potentials were applied. All the obtained poly(amine imide)s revealed good stability of electrochromic characteristics for the first oxidation state, changing color from the yellowish neutral form to the green oxidized forms when scanning potentials positively. The poly(amine imide)s can be used as potential candidates in the development of dynamic electrochromic and electroluminescent devices due to their suitable highest occupied molecular orbital (HOMO) levels, excellent thermal stability, and reversible electrochemical behavior.

Ando *et al.*[177] examined the UV/vis absorption and fluorescent properties of imide compounds and PIs having a hydroxy group at the terminal anhydride moiety extensively, and a new molecular design concept for controlling the emission colors of fluorescent PIs was established (Scheme 65). The synthesized PIs (51–54) showed high transparency in the visible region. The



Scheme 64



Scheme 65

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fluorescence lifetime of imide moieties in the main chain decreased with increasing the (55) terminal group, indicating that the intra- and/or interchain energy transfer should occur from the PI main chain to the terminal group. As a result, the emission color of 54 was successfully controlled from blue to light green by varying the amount of terminal groups while maintaining the inherent high transparency of the PIs. The molecular design concept established in this study should be beneficial for developing a new class of superengineering plastics for advanced optical and electronic applications.

5.20.3.3 PI for Memory Device

Resistive switching behavior has been primarily studied in amorphous silicon-based materials for the past 30 years. It was found that the digital data could be stored by applying or discharging electrical charges through a simple device configuration consisting of two electrode layers sandwiching the storage medium. As compared to the traditional inorganic semiconductor-based memories, polymeric memory devices are extensively attractive today because of the advantages of structural flexibility, low cost, solution processability, and three-dimensional stacking capability. The recently studied polymer systems exhibit memory switching characteristics, including conjugated polymers, functional PIs, polymers with specific pendant chromophores, and polymer nanocomposites (metal nanoparticle and fullerene embedded). The electrical switching phenomena in polymers and the corresponding polymer electronic memories as an emerging area in organic electronics have been reviewed by Kang *et al.*[178] recently.

Organic and polymer materials are promising candidates for future molecular-scale memory applications. Their attractive features include good processability, miniaturized dimensions, and the possibility for molecular design through chemical synthesis. Among all the studied polymer systems, PIs are promising candidates for memory device applications because of their excellent physical and chemical properties in addition to the electrical switching behavior. Functional PIs containing both electron donor and acceptor moieties within a repeating unit contribute to electronic transition between the ground and excited states, which could be manipulated by the induced charge transfer (CT) from donor (D) to acceptor (A) under applied electric fields. Among the studied functional PIs, the TPA-based PIs prepared by Liou *et al.*[103] since 2005 attracted significant attention. For example, the memory device of a TPA-functionalized PI (56)[179] exhibited dynamic random access memory (DRAM) behavior, whereas a device based on 57[180] showed the improved DRAM performance as reported by Kang and coworkers. And an oxadiazole-containing PI (58)[181] was found to reveal a static random access memory (SRAM) behavior (Scheme 66).

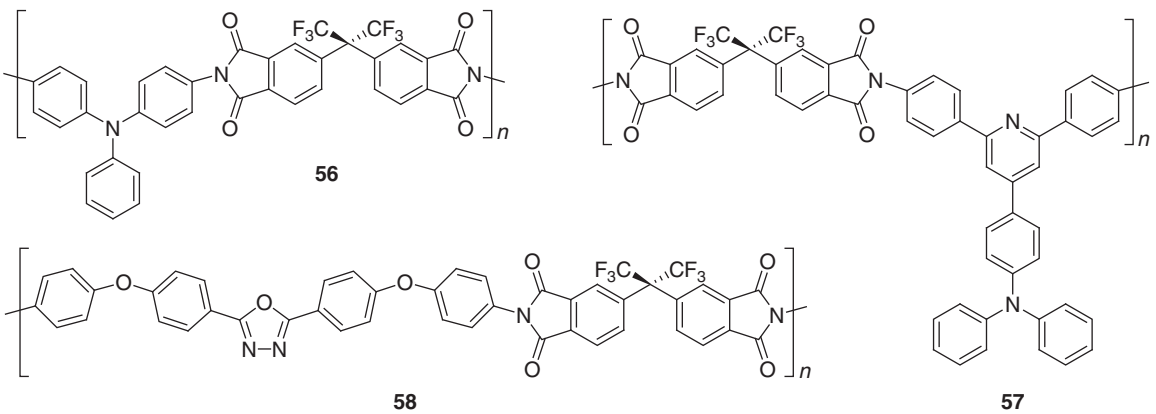
Meanwhile, Lee *et al.*[182] also proposed a series of TPA-based PIs for memory characteristics. They found that 59 (two connected TPA rings) showed stable digital nonvolatile write-once-read-many-times (WORM) and volatile DRAM memory characteristics depending on film thickness. Moreover, a flash-type memory of 60[183] bearing two pendant TPA groups and a unipolar WORM memory of 61[184] having an attached hydroxyl group on TPA were also reported recently (Scheme 67).

Ueda and Chen[185,186] prepared sulfur-containing PIs (62 and 63), and found that the relatively high dipole moments of the sulfur-containing PIs provided a stable CT complex for the flash memory device with nonvolatile memory characteristics and low turn-on threshold voltages. They further synthesized two functional PIs (64 and 65) consisting of electron-donating TPA with single and double isolated ether linkage, respectively, and electron-accepting phthalimide moieties. The memory devices with the configuration of 64/Al or ITO/65 exhibited distinct volatile memory characteristics of DRAM and SRAM, respectively. The result provides the strategies for the design of functional PIs for advanced memory device applications (Scheme 68).

5.20.3.4 High Refractive Index PI

5.20.3.4.1 Sulfur-containing high refractive index PI

Sulfur-containing linear thioether and sulfone, cyclic thiophene, thiadiazole, and thianthrene are the most commonly used moieties for increasing refractive index of polymers. Recently, systematic work by the Ueda group revealed the influence of sulfur groups on the refractive indices and optical dispersion of polymers. First, a series of sulfur-containing PIs were developed to increase the n values of polymers. The average n values (n_{av}) are all higher than 1.72 and increase with an increase in the sulfur content of the PIs. In addition, the flexible thioether or sulfonyl linkages in PIs endow lower



Scheme 66

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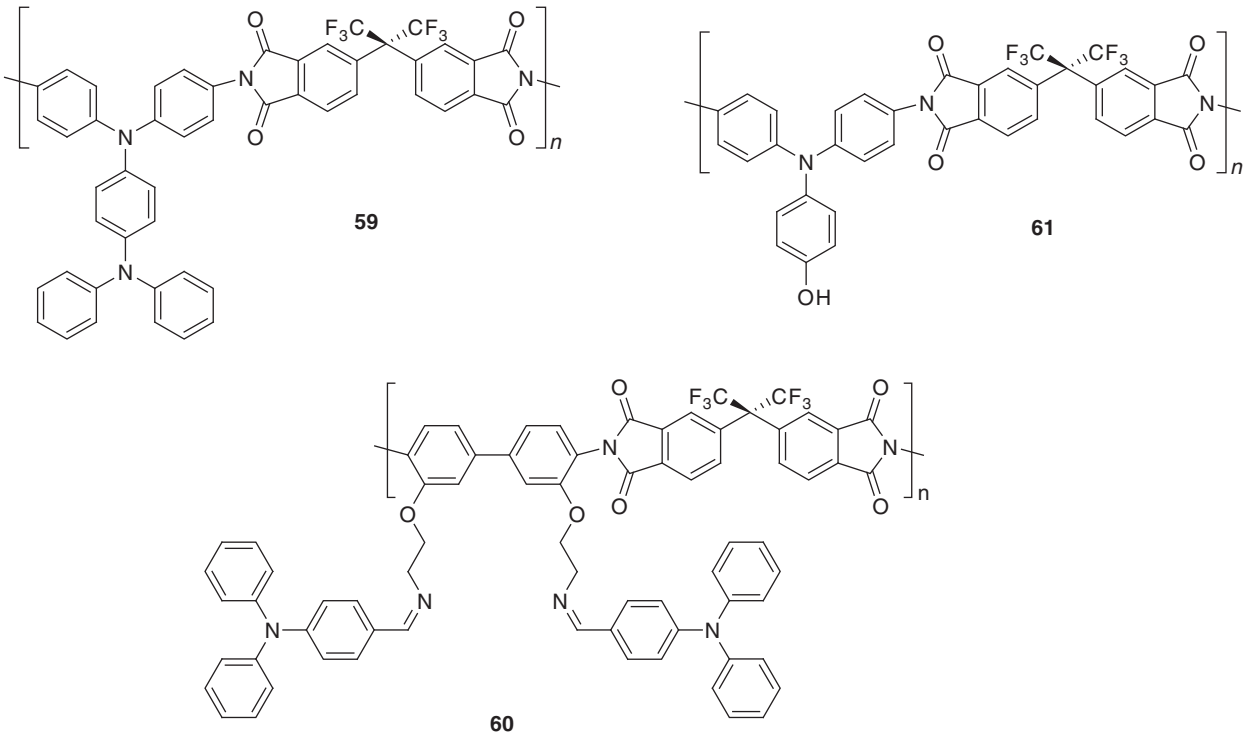
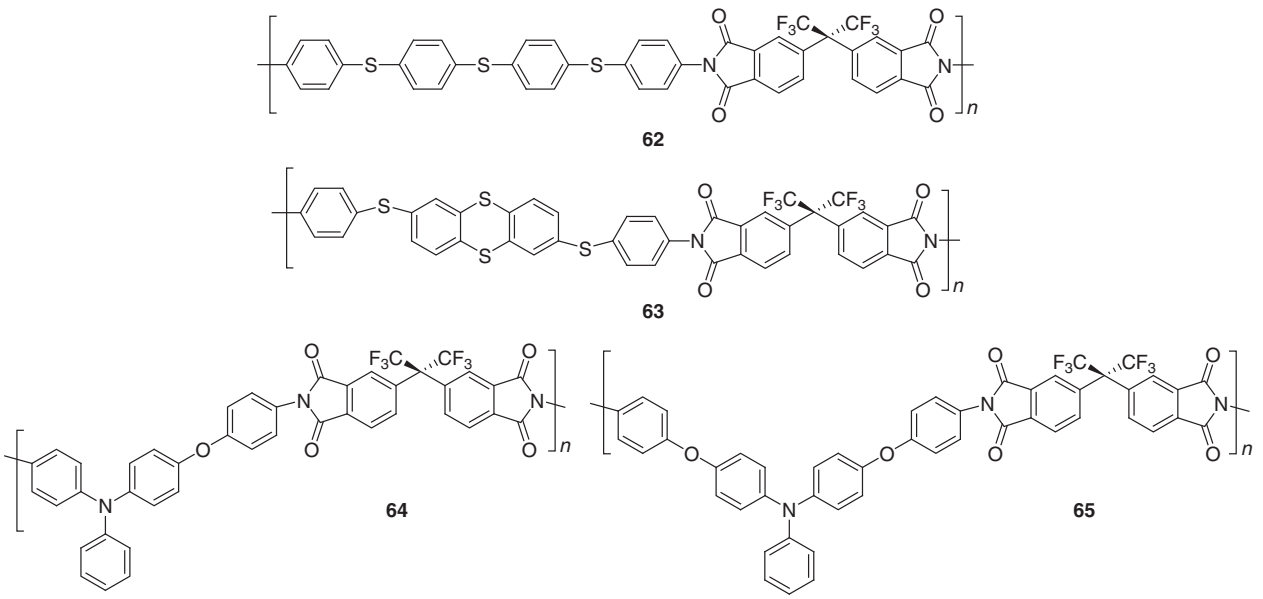


Scheme 67



Scheme 68

birefringence (Δn) less than 0.01. PIs containing sulfur-rich thianthrene and tetrathiaanthracene moieties in the repeating units exhibited the highest n_{av} values among previously reported PI systems in the literature.

Optical properties of the PIs prepared from various tetracarboxylic dianhydrides are summarized in Table 1.[114–117] **PI-a** and **PI-d** showed the highest n_{av} and optical transparency, respectively. These results provide the strategies for the design of high refractive PIs for optical applications.

5.20.3.4.2 PI/inorganic hybrid materials

Recently, polymer–inorganic hybrid materials have attracted considerable interest owing to their enhanced mechanical, thermal, magnetic, optical, electronic, and optoelectronic properties when compared to the corresponding individual polymer or inorganic component.[187] Chemical methods based on hybridization approach by *in situ* sol–gel reaction made it possible to manipulate the organic/inorganic interfacial interactions at various molecular and nanometer length scales,

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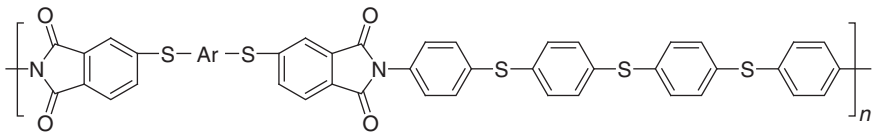
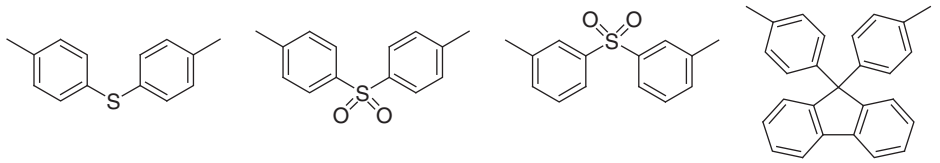
Table 1 Optical properties of PIs



PI

Ar:



(a) (b) (c) (d)

		Optical Properties		
Index	*d(μm)*	λ_0 *(nm)*	n_{av}	Δn
PI-a	9.3	402	1.748 2	0.006 8
PI-b	7.4	~380	1.731 9	0.006 5
PI-c	5.4	374	1.730 9	0.005 9
PI-d	6.6	367	1.725 5	0.005 9

resulting in homogeneous structures and thus overcoming the problem of nanoparticle agglomeration. For optical applications, such as high refractive index materials, optical waveguides, and antireflective films, the inorganic domains of these hybrid materials must be less than 40 nm to avoid scattering loss and retain optical transparency.[188] Precise control of the morphology and the phase separation is critical in preparing transparent hybrid films, and the sol–gel reaction was widely used for making transition metal oxide solids with fine-scaled microstructures. Particle sizes less than a couple of nanometers could easily be achieved in the derived gels, and microstructural dimensions could also be maintained when subsequently crystallized at elevated temperatures.

In 1992, Imai *et al.*[189] prepared the PI–silica hybrid films with ethoxysilyl groups in the polymer backbone. The polyamic acid–silica gel mixtures can be cast onto glass plates, and then be heated to 300 °C to convert the component matrix polymers to PIs (**Scheme 69**). The PI–silica hybrid films containing 70 wt.% of the silica obtained were self-standing and tough. The silica particles were dispersed homogeneously in the matrix PIs as observed by SEM. The size of the silica particles increased with increasing silica content, and decreased with increasing ethoxysilyl content. Results of the dynamic-mechanical analysis indicate that movement of the PI chain in the matrix is restricted, especially when the PIs contain higher amounts of ethoxysilyl. The report is very beneficial for the designing of PI–inorganic hybrid films.

In 2008, Ueda *et al.*[190] successfully prepared a PI–TiO_2 hybrid film containing 45 wt.% silica-modified anatase-type TiO_2 nanoparticles with a refractive index of 1.81 at 632.8 nm (**Scheme 70**). In addition, Su and Chen[191] developed a new synthetic route to prepare PI–nanocrystalline–titania hybrid materials with a relatively high titania content (up to 90 wt.%) (**Scheme 71**). This approach demonstrates a new route for preparing high refractive index PI–nanocrystalline–titania hybrid materials for optical applications.

Recently, Liou *et al.*[192,193] successfully synthesized highly transparent and tunable refractive index PI–titania hybrid optical films from hydroxy-containing organosoluble PIs and titanium butoxide by controlling the organic/inorganic mole ratio (**Scheme 72**). The hybrid thin films had good surface planarity, high thermal stability, tunable refractive indices, and high optical transparency in the visible range. Moreover, the thick titania hybrid films could be achieved even with a relatively high titania content. The refractive index (up to 1.92) and titania content (50 wt.%) are highest among the highly optical transparent polymer–titania hybrid thick films (20–30 μm thick). The three-layer antireflective coating based on the hybrid films exhibited a reflectance of less than 1.0% in the visible range. It suggested potential optical applications of the novel PI–titania hybrid optical films.

5.20.3.5 PIs for Fuel-cell Application

Fuel cells have the potential to become an important energy conversion technology. Research efforts directed toward the widespread commercialization of fuel cells have accelerated in light of ongoing efforts to develop a hydrogen-based energy economy to reduce pollution. Proton exchange membrane (also termed 'polymer electrolyte membrane') (PEM) fuel cell employing a solid polymer electrolyte to separate the fuel from the oxidant was first deployed in the Gemini space program in the early 1960s using cells that were extremely expensive and

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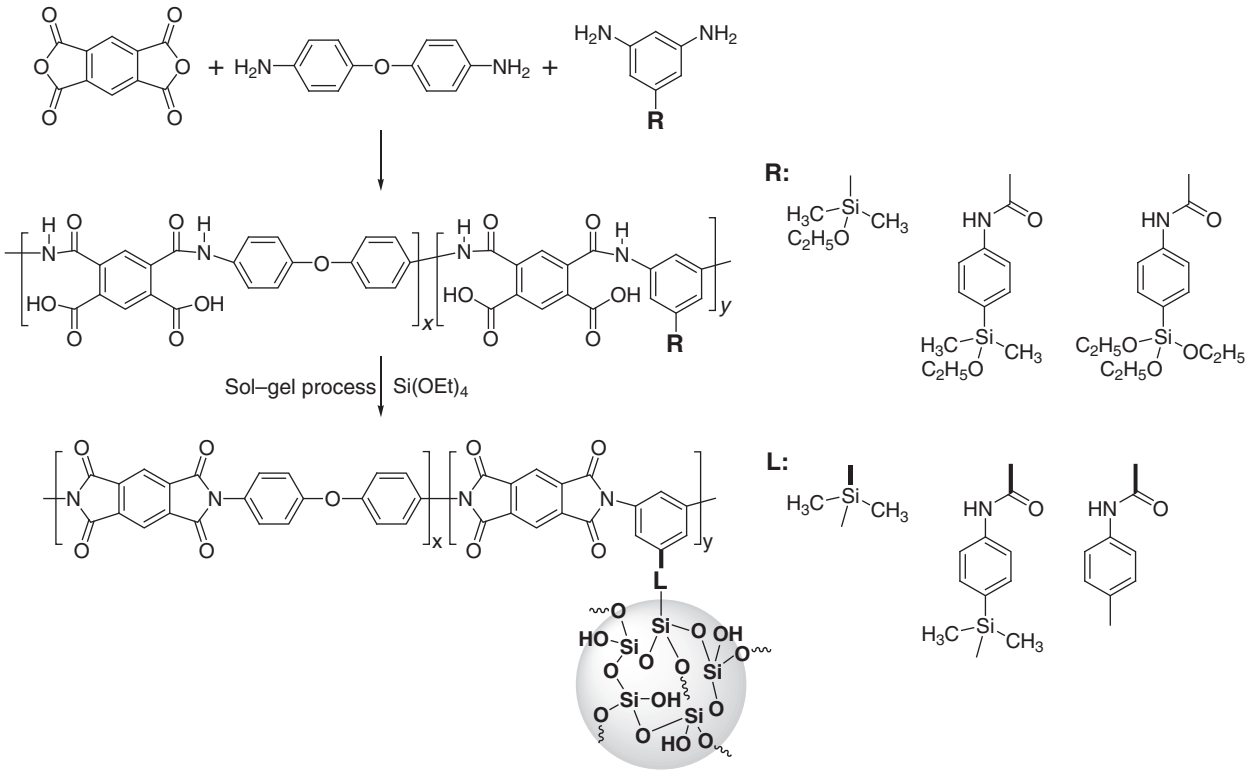
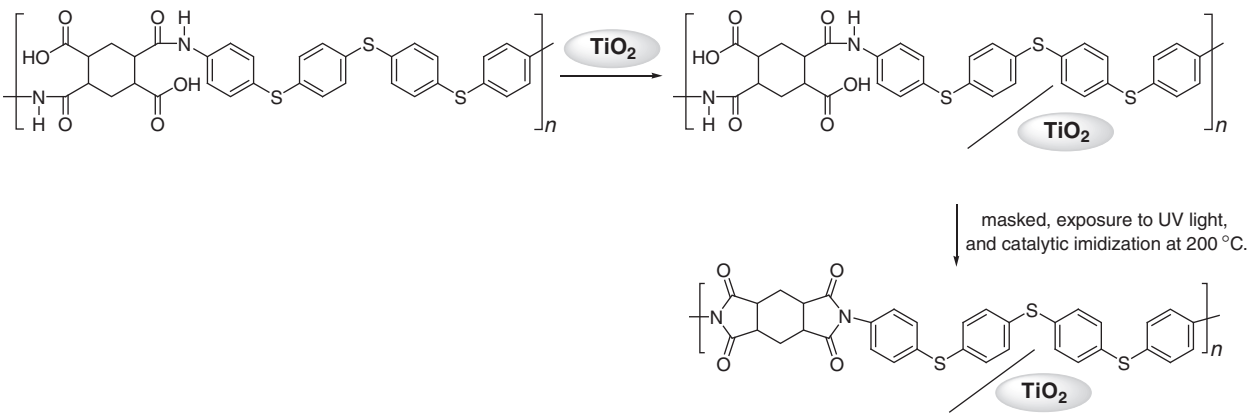
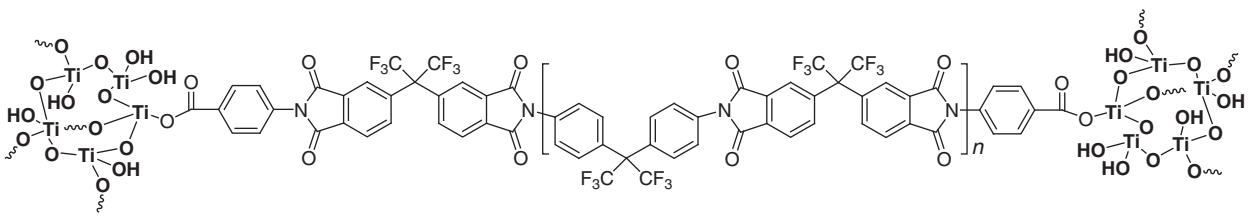


Scheme 69



Scheme 70



Scheme 71

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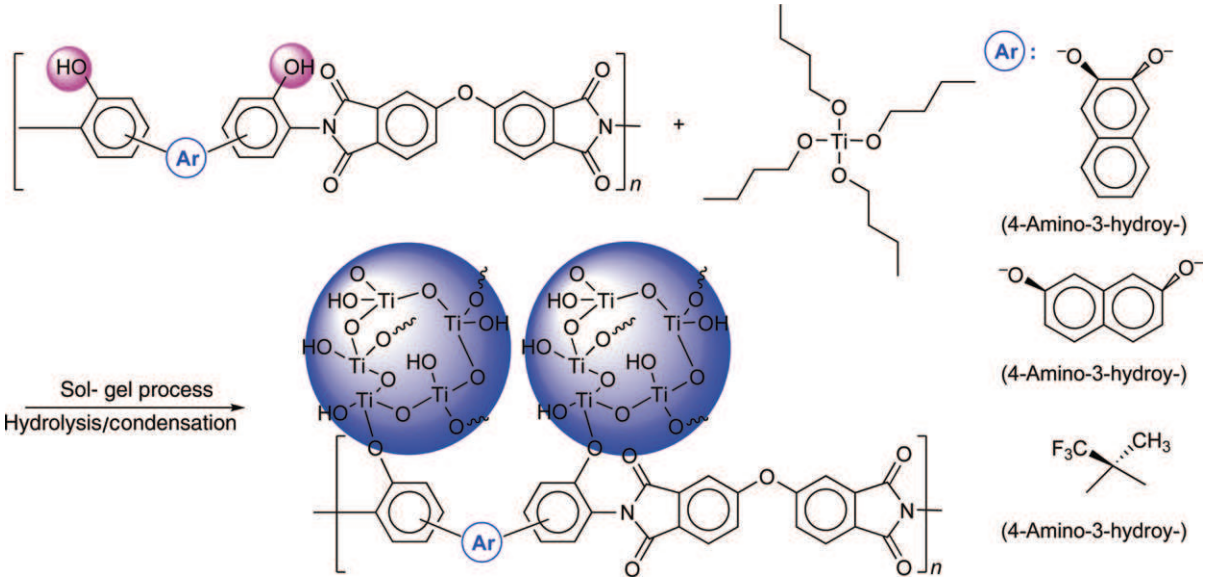


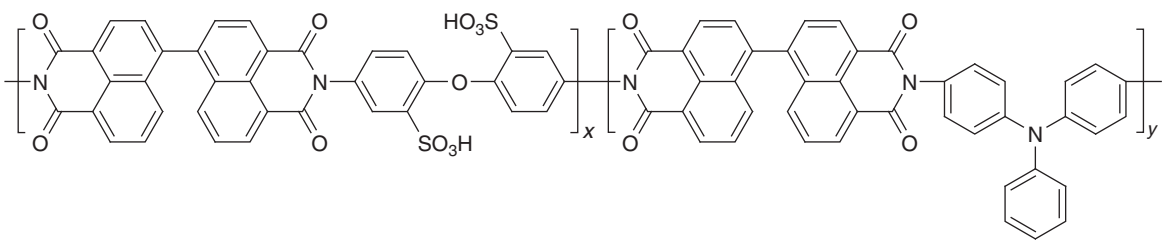
Scheme 72

had short lifetimes due to the oxidative degradation of the sulfonated polystyrene–divinylbenzene copolymer membranes. The commercialization of Nafion by DuPont in the late 1960s helped to demonstrate the potential interest of fuel cells in terrestrial applications.[194]

PEM fuel cells have been developed for three main applications: automotive, stationary, and portable power. Each of these applications has its unique operating conditions and material requirements. Common themes critical to all high-performance proton exchange membranes include (1) high protonic conductivity, (2) low electronic conductivity, (3) low permeability to fuel and oxidant, (4) low water transport through diffusion and electroosmosis, (5) oxidative and hydrolytic stability, (6) good mechanical properties in both a dry and a swollen state, (7) cost, and (8) capability for fabrication into membrane electrode assemblies (MEAs). Most of all the membrane materials for PEM fuel cells rely on absorbed water and its interaction with acid groups to produce protonic conductivity. Due to the large fraction of absorbed water in the membrane, both mechanical properties and water transport become key issues. Devising systems that can conduct protons with little or no water is perhaps the greatest challenge for new membrane materials. Specifically, for automotive applications the US Department of Energy has currently established a guideline of 120 °C and 50% relative humidity as target operating conditions, and a goal of 0.1 S cm^{-1} for the protonic conductivity of the membrane.[194,195]

Zhang *et al.*[196] reported a series of SPI bearing basic groups from binaphthy-based tetracarboxylic dianhydride, a sulfonated diamine, and a TPA-based diamine for proton exchange membranes (**Scheme 73**). The electrolyte properties of the synthesized PIs were investigated and compared to those of PIs based on NTDA. The SPI exhibited much better water stability than those based on NTDA. Such improvement in stability could be attributed to the excellent hydrolytic stability of the binaphthalimide moieties. The basic TPA groups introduced in the main chains could effectively improve the proton conductivity and dimensional stability of PIs. Furthermore, the low methanol permeation rate was achieved by introducing the TPA into the SPI backbone.

Watanabe *et al.*[197–199] demonstrated that the introduction of aliphatic segments in both the main and side chains could effectively improve the hydrolytic stability of PI ionomers without sacrificing other preferable properties (proton conductivity, oxidative and mechanical stability). Both electronic and steric effects are crucial for the hydrolytic and oxidative stability. A significant decrease in the conductivity at low humidity observed for the linear ionomers was improved to the level nearly required for the practical fuel-cell applications by increasing the ion exchange capacity (IEC) and introducing a branching structure. Scanning transmission electron microscope (STEM) images have revealed that aggregation of ionic groups was suppressed by the branching and therefore small (<5 nm) and well-dispersed hydrophilic domains distributed throughout the



Scheme 73

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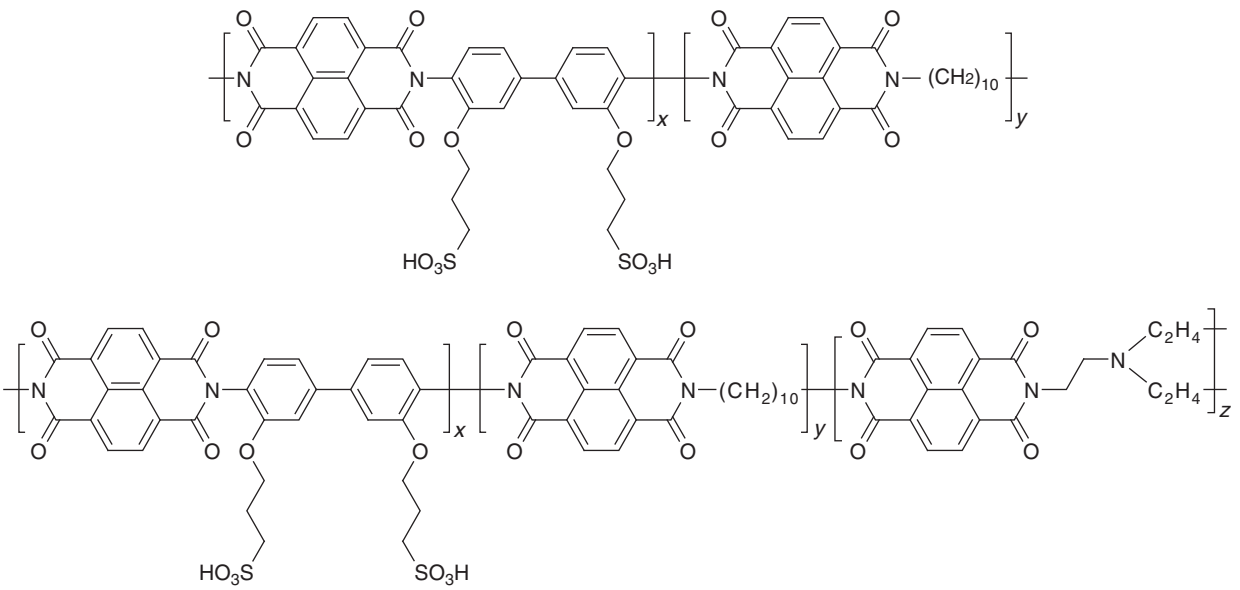
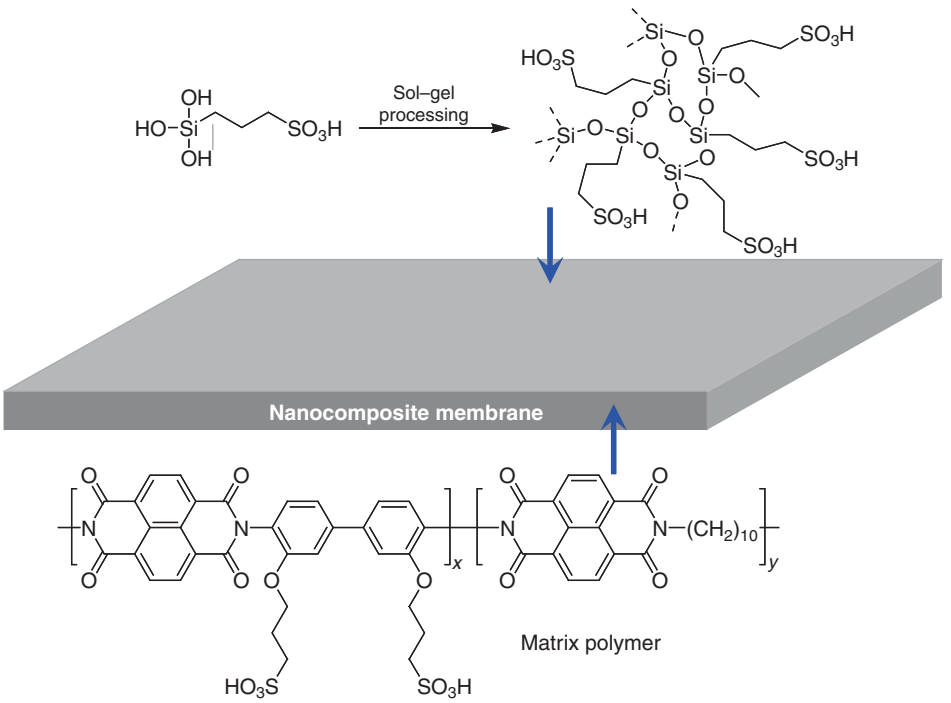
membrane. The morphology is distinctive from that of the perfluorinated ionomers (in which 5–10 nm-sized hydrophilic clusters are observed) and is likely to contribute better proton–conducting properties. Hydrogen and oxygen permeability of SPI membranes was more than 1 order of magnitude lower than that of Nafion under a wide range of conditions (40–120 °C and 0–90% RH). High-performance fuel cells have been achieved with the PI ionomer membrane. As evidenced in little changes in open circuit voltage (OCV) during the operation, the SPI membrane was durable for 5000 h, which is the longest fuel-cell operation reported for an alternative electrolyte membrane (Scheme 74).[199,200]

In addition, Watanabe *et al.* also developed an effective approach to improve the proton conductivity of polymer electrolyte membranes by simply incorporating acid-functionalized polysilsesquioxane (Scheme 75).[201] Nanocomposite membranes prepared by *in situ* sol–gel processing showed much higher proton conductivity (up to 30 times) than that of the original membranes and less dependence of the conductivity on the humidity. The nanocomposite membranes are expected to



Scheme 74



Scheme 75

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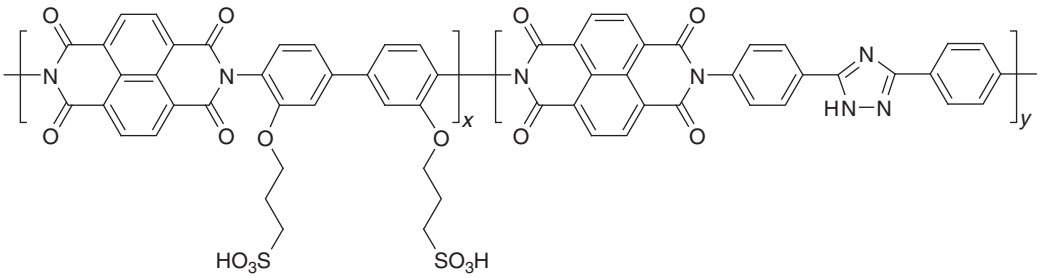

Scheme 76

have an impact on the field of solid electrolyte science, especially conductive membrane materials.

Recently, novel SPI ionomer containing triazole groups has also been proposed. The SPI membranes exhibit high proton conductivity, and thermal, oxidative, chemical, and good mechanical stability (Scheme 76).[202,203] The aim of this work was to evaluate the durability of the SPI membrane in polymer electrolyte fuel-cell (PEFC) operation. Watanabe *et al.* have confirmed that the triazole-based membrane could also be durable for 5000 h at 80 °C in single fuel-cell operation. Changes in the terminal voltage at constant current density, OCV, mass activity, and ohmic cell resistance were monitored during cell operation. Posttest analyses of the membrane characteristics were carried out, including thickness, IEC, and molecular weight.

5.20.4 Conclusions

PI synthesis has been explored to a significant extent as solution–processable high-performance polymers with superior properties such as high thermal stability, exceptional mechanical properties, and outstanding optical characteristics along with electrical and chemical resistance. An excellent combination of these properties makes them suitable for a wide range of applications from engineering plastics in aerospace industries to membranes for fuel-cell applications and gas or solvent separation. The functional PIs having potential applications such as electrochromic, luminescent, memory devices, high refractive, and fuel-cell materials were introduced and discussed.

This chapter also covered a majority of the works in the recent decade involving the synthesis and property evaluation of functional PIs as well as their structural design by using the respective monomers. This summarized information may be helpful for scientists to extend further research related to high-performance polymers and develop novel polymeric materials with an even wider range of useful properties.

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5.21 High-Performance Heterocyclic Polymers

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5.21.1 Introduction

The quest for high-performance/high-temperature organic polymers, materials that perform at 200 °C or higher, began in the late 1950s to meet the demands primarily of the aerospace and electronic industries.[1,2] Since then, many families of high-performance/high-temperature polymers have been reported. Several of these have reached commercialization. In 1988, the market for high-performance/high-temperature organic polymers was estimated at $2.3 billion and it comprised 90 million kilograms;[3] in 2000, the market was estimated at $4.36 billion and it comprised 206.7 million kilograms.[2] With an improvement in the world economy, the market is predicted to grow substantially.[2]

Of the most popular high-performance/high-temperature polymers (e.g., poly(arylene ether)s, poly(phenylene sulfide)s, polyamides, resins from cyanates, organofluoro polymers, certain silicones, and aromatic heterocyclic polymers), aromatic heterocyclic polymers have received much attention because they have proven to be among the most thermally stable materials produced to date.[1,2,4–12]

Among aromatic heterocyclic polymers, polyazoles,[13–15] polybenzazoles,[13,14,16,17] polyquinoxalines,[18–21] polyimides,[22–43] and ladder polymers[41,42,44–50] are exceptionally interesting and have been studied adequately.

[†] Deceased.

5.21.2 Polyazoles

Polyazoles consist of azole cycles – five-membered aromatic cycles containing at least two nitrogen atoms – connected with different aromatic units.[13–15] The most important classes of polyazoles are isomeric polyoxadiazoles, polythiadiazoles, polytriazoles, and polypyrazoles.

Most of the information on polyazole synthesis appeared at the beginning of the 1940s,[51–53] but significant progress in this field was achieved in the 1960s when new methods for polymer synthesis – low-temperature solution polycondensation,[54–60] solid-phase polycyclocondensation,[17,59–62] high-temperature solution polycyclocondensation in acidic solvents,[63–65] and 1,3-dipolar polyaddition[66] – had come into use.

The most important method for the preparation of polyazoles is polycyclocondensation, which can be realized as a one-stage or a two-stage process, the formation of an individual polymer being regarded as a stage.

One-stage syntheses are carried out in most cases in a solvent although the reaction can be performed in the melt. The main requirement both in industrial processing and in successfully conducting these reactions is the solubility and fusibility of starting monomers and/or target polymers, respectively. In general, the one-stage method is simpler than the two-stage method from the technological point of view.

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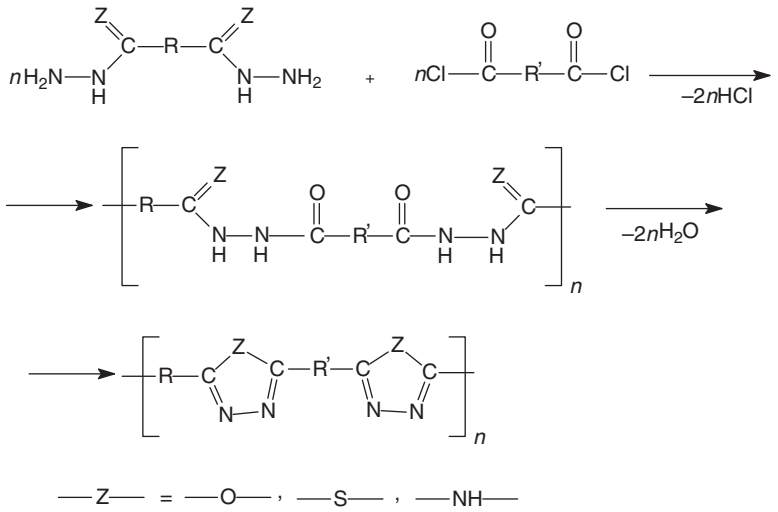


Scheme 1

The most universal two-stage synthesis consists of the formation, at the first stage, of a high-molecular-weight prepolymer, which is converted to polyazole on heating or by the action of chemical reagents.

The most important polyazoles – poly-1,3,4-oxadiazoles,[67–79] poly-1,3,4-thiadiazoles,[80] and poly-1,2,4-triazoles[81] – can be prepared in accordance with **Scheme 1** including the formation of polyhydrazides,[67–79] polythiohydrazides,[80] and polyacyoylhydrazides[81] followed by polycyclocondensation of these prepolymers.

5.21.2.1 Polyoxadiazoles

5.21.2.1.1 Poly-1,3,4-oxadiazoles

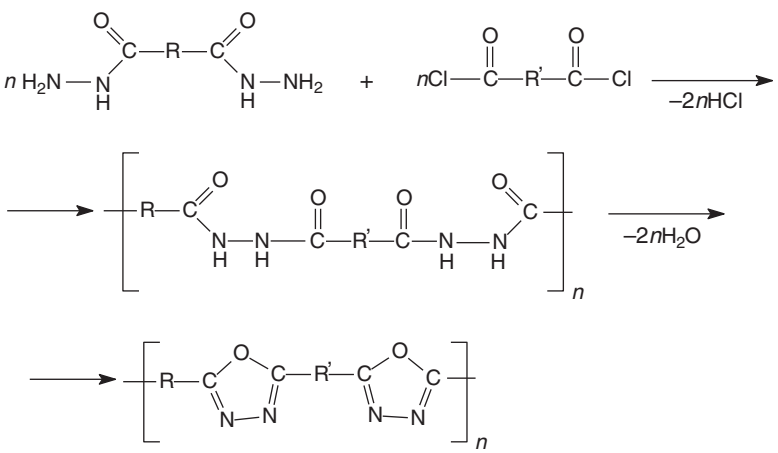
The 1,3,4-isomer of the oxadiazole family is far more widely utilized in polymer backbones than the 1,2,4- or 1,2,5-isomer.[15] The oxadiazole ring has been known for some time but it was not until about 1958 that Huisgen and co-workers[82,83] began a detailed exploration.

In 1964, Frazer and co-workers[67–69] developed one of the most popular synthetic routes through the cyclization of polyhydrazides (**Scheme 2**). This method offered the advantage of a soluble and processable intermediate polyhydrazide polymer that can be cast into films, spun into fibers, and so on. Once formed, the precursor polymers are converted by heat treatment to more thermally stable and less soluble poly-1,3,4-oxadiazoles.

The best method for the preparation of high-molecular-weight aromatic polyhydrazides is low-temperature solution polycondensation using dipolar aprotic solvents – hexamethylphosphoramide (HMPA), *N,N'*-dimethylacetamide (DMAc), N-methylpyrollidone (NMP)/LiCl, and so on. These reactions proceed under homogeneous conditions and result in high-molecular-weight polyhydrazides soluble – depending on their structures – in dipolar aprotic solvents – dimethylsulfoxide (DMSO), Hexamethylphosporamide (HMPAm), DMAc, and so on.

Polycyclization of polyhydrazides to the corresponding poly-1,3,4-oxadiazoles is realized by heating up to 300 °C under vacuum.[69]

The kinetics of the thermal cyclodehydration reaction of poly(arylene hydrazide)s to poly-1,3,4-oxadiazoles have been studied in detail by Gebben *et al.*[84] By using the isothermal method, it was found that the reaction kinetics depend on the physical state of the polymer, rubbery or glassy, with higher isothermal conversion rates in the rubbery state. There are also



Scheme 2

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considerable differences in kinetics between the film and powder forms of the polyhydrazides. The films show much higher conversion rates than powders.

The thermal properties of aromatic poly-1,3,4-oxadiazoles are summarized in Table 1.

Full conversion of flexible polyhydrazide films resulted in shrunken and brittle poly-1,3,4-oxadiazole films without any mechanical strength.[92]

Embrittlement of converted polyhydrazide films has been reported by Frazer and Sarasohn;[85] this is in contrast to flexible converted polyhydrazide fibers reported.[89,93]

Macroscopic shrinkage of the polymer films is caused by shrinkage of polyhydrazide macromolecules upon conversion into poly-1,3,4-oxadiazoles. Shrinkage of these macromolecules is caused by the ring closure of the hydrazide groups into 1,3,4-oxadiazole groups (Figure 1).

X-ray analysis showed that upon ring closure the carbon–carbon distance in hydrazide segment decreases by 30%.[94,95]

Therefore, the observed brittleness of the fully converted polyhydrazide films is likely to be caused by chain shrinkage upon conversion, a low molecular weight, a lack of orientation, or possibly a combination of these phenomena.

To overcome the abovementioned disadvantages of the two-step method, an alternative one-step process for the preparation of poly-1,3,4-oxadiazoles was developed.

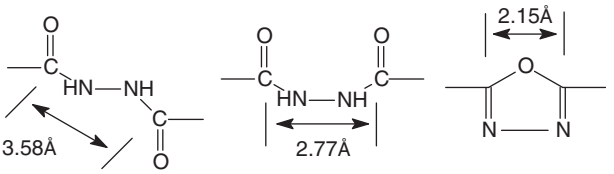


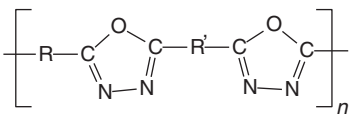
Figure 1 Decrease in intramolecular carbon–carbon distance due to cyclodehydration.

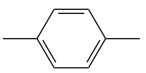
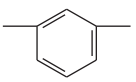
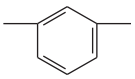
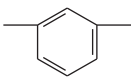
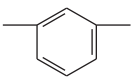
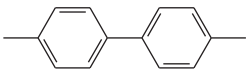
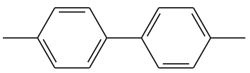
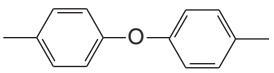
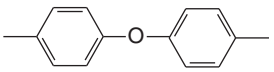
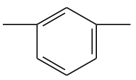
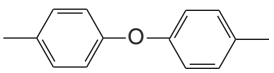
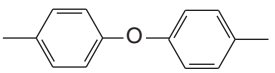
High-molecular-weight poly-1,3,4-oxadiazoles were easily prepared by a one-step synthesis in polyphosphoric acid (PPA) using dicarboxylic acids and hydrazine as monomers, as originally reported by Iwakura *et al.*[96] Whereas polyhydrazide synthesis requires high-purity monomers and complete exclusion of water, the direct formation of poly-1,3,4-oxadiazoles from dicarboxylic acids and hydrazine sulfate is relatively simple.

Scheme 3 shows the two-step mechanism by which the reaction is believed to occur.

Using polycyclocondensation reaction in PPA, high-molecular-weight poly[(*p*-phenylene)-1,3,4-oxadiazole]s and poly[(*m*-phenylene)-1,3,4-oxadiazole]s were prepared.[84] Flexible asymmetric membranes were prepared from solutions of the polymers in concentrated sulfuric acid followed by coagulation in water.

Table 1 Thermal properties of aromatic poly-1,3,4-oxadiazoles of general formula



–R–	–R′–	$T_{soft.}$ (°C)	MP (°C)	$T_{degr.}$ (°C)	References
				447	75
			>400	450	69, 75, 85–90
	-		>400	275	69, 85
			>400	450	69, 91
			440	400	90
		430		470	75, 90
		380		430	69, 75, 90
		370		430	69, 75, 90

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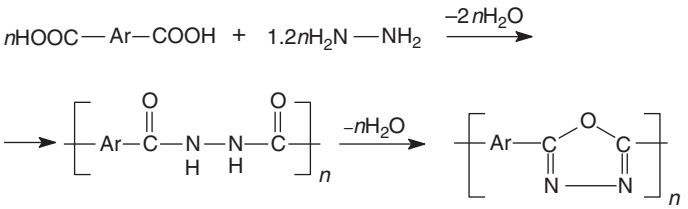

Scheme 3

The disadvantages of PPA as a condensation agent are the high viscosity of the reaction solution and incomplete cyclization of intermediate hydrazide bonds in the main chains. A convenient method for the synthesis of poly(arylene-1,3,4-oxadiazole)s that have high molecular weights has been developed by Ueda and Sugita.[97] The polymers were prepared by one-step direct polycyclocondensation of dicarboxylic acids with hydrazine sulfate by using phosphorus pentoxide/methanesulfonic acid (PPMA, Eaton's reagent[65]) as both a condensation agent and a solvent. The reaction requires a temperature of only 80 °C and 0.5–2.0 h and yields polymers with high molecular weights. The main advantages of this method are the rapidity and simplicity of the procedure and milder reaction conditions compared with the PPA method.

One additional polycondensation medium for the preparation of poly(1,3,4-oxadiazole)s is fuming sulfuric acid (oleum).[98]

Polycondensation of dicarboxylic acids and hydrazine sulfate in oleum is influenced by many reaction parameters such as the concentration of free SO_3, the absolute concentration of the monomers, the molar ratio of the diacid and hydrazine salt, the molar ratio of free SO_3 and monomers, and temperature. It was also shown that homogeneity of the reaction mixture markedly influences the reproducibility of the polycondensation as well as the molecular weight of the resulting polymers.[99] A homogeneous solution at the beginning of polycondensation is necessary for an exact temperature regime, and it can be realized by a special mechanochemical activation of the monomer powders before their addition to the reaction vessel.[100] This is also important for technical polycyclocondensation reactions and for the production of fibers from the reaction solution.

Because oleum is an aggressive medium, an alternative approach for the synthesis of poly(arylene-1,3,4-oxadiazole)s was developed.[101] This method uses amidosulfonic acid (ASA) as a SO_3 donor. If 1 mol of ASA reacts with 1 mol of sulfuric acid, free SO_3 is formed at an elevated temperature (Scheme 4).

It was found that SO_3 formed *in situ* is able to cause polycyclocondensation of aromatic dicarboxylic acids and hydrazine sulfate with the same reaction mechanism as observed in the classic oleum route.[98] There are two advantages of the ASA method compared with the reaction in oleum: (1) much smaller amounts of sulfuric acid are necessary for the whole process, and (2) the synthesis can be made in an extruder.[102]

Poly(arylene-1,3,4-oxadiazole)s are soluble in strong acid solvents such as sulfuric acid, PPA, and trifluoromethane sulfonic acid; in addition, they are soluble in an aprotic solvent system consisting of a nitroalkane and a Lewis acid.[98] None of the poly(arylene-1,3,4-oxadiazole)s based on the simplest

$$(NH_2)SO_3H + H_2SO_4 \longrightarrow SO_3 + (NH_4)HSO_4$$

Scheme 4

dicarboxylic acids – terephthalic, isophthalic, 4,4′-dicarboxydiphenyl – are soluble in organic solvents. This substantially limits both the possibility of their detailed investigation and, sometimes, the field of their application. As a result, significant attention was paid to the elaboration of organosoluble poly(1,3,4-oxadiazole)s.

Several organosoluble poly(1,3,4-oxadiazole)s were prepared using monomers containing diphenyl ether, 1,1,1,3,3,3-hexafluoroisopropylidene, and tetraphenylsilane groups; all of these fragments improve the solubility of the aromatic polymers.[103]

Poly(4,4′-diphenyl ether oxadiazole) (Figure 2) demonstrating solubility in formic acid, DMSO, and NMP was prepared by Hensema *et al.*[78] and Sena and Andrade.[104,105]

Flexible films were obtained from a formic acid solution.

As it is known that 1,1,1,3,3,3-hexafluoroisopropylidene unit improves the solubility of different aromatic polymers,[103,106,107] different research groups have incorporated this unit in poly-1,3,4-oxadiazole chains (Figure 3).

Russian workers[108] have prepared poly-1,3,4-oxadiazole by cyclodehydration of polyhydrazide, which in turn was prepared by a low-temperature polycondensation of the dihydrazide and dichloride of 1,1,1,3,3,3-hexafluoro-2,2-(4-carboxyphenyl) propane.

Hensema *et al.*[78] and Sena and Andrade[104] prepared the same polymer directly by the less laborious one-step synthesis using 1,1,1,3,3,3-hexafluoro-2,2-bis(4-carboxyphenyl)propane and hydrazine as monomers. Solubility tests showed that this polymer is soluble in tetrahydrofuran (THF), chloroform, NMP, *o*-dichlorobenzene, and trifluoroacetic acid. Flexible films were cast from the polymer solution in trifluoroacetic acid.

Incorporation of tetraphenylsilane groups in poly(1,3,4-oxadiazole)s led to the formation of a polymer (Figure 4) demonstrating solubility.[109–112]

Copoly(1,3,4-oxadiazole)s containing hexafluoroisopropylidene and tetraphenylsilane groups (Figure 5) were

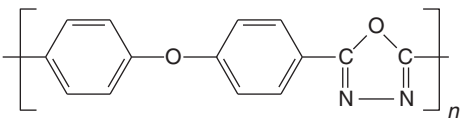

Figure 2 Poly(4,4′-diphenyl ether oxadiazole).

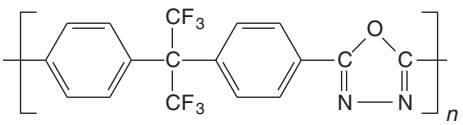

Figure 3 Poly[1,3,4-oxadiazole-2,5-diyl-1,4-phenylene[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,4-phenylene].

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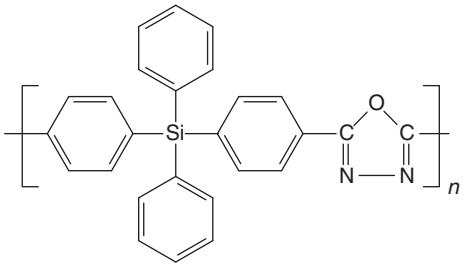

Figure 4 Poly(1,3,4-oxadiazole), containing tetraphenylsilane group.

synthesized by Fitch *et al.*[113] These copolymers are soluble in common organic solvents such as THF and $CHCl_3$ and are stable up to 500 °C.

Korshak *et al.* have developed the so-called 'cardo' poly (1,3,4-oxadiazole)s. Polymers of this type, containing at least one element in the repeating unit, which is included in the cyclic side group, might be considered as loops (Latin cardo) in the backbone of the macromolecules.[114,115] The most typical representatives of the cardo groups are given in Figure 6.

One of the most available monomers containing cardo group is 4,4′-diphenylphthalidedicarboxylic acid; this monomer and its derivatives (dichloride and dihydrazide) were used for the synthesis of cardo poly(1,3,4-oxadiazole)s.[116–120] The synthesis of cardo poly(1,3,4-oxadiazole) in PPA was carried out in accordance with Scheme 5.

The regularities of cardo poly(1,3,4-oxadiazole) formation in PPA have been studied in detail.[119–121] It was found that the ratio of starting monomers, reaction temperature and reaction duration, concentration of starting compounds, and the content of phosphoric anhydride in phosphoric acid strongly affect the results of polycondensation (the yield and the molecular mass of polymers) and the possibility of side reactions. Thus, a soluble polymer of the highest molecular mass may be obtained from an equimolar ratio of monomers. An excess of acid decreases the molecular mass, while an excess of dihydrazide leads to the formation of insoluble polymer due to a side reaction of the lactone cycle. If the process is performed at 140 °C, it is advisable to continue the reaction for approximately 5 h. Polymers of the highest molecular mass are obtained when the concentration of the starting compounds is approximately 0.3 mol kg^{-1} of PPA.

The molecular mass of poly(1,3,4-oxadiazole) strongly depends on the concentration of PPA. It considerably increases on increase of phosphoric acid anhydride content from 82% to 86%. However, technologically it is preferable to carry out the polycyclocondensation reaction in phosphoric acid containing about 84% of phosphoric acid anhydride.

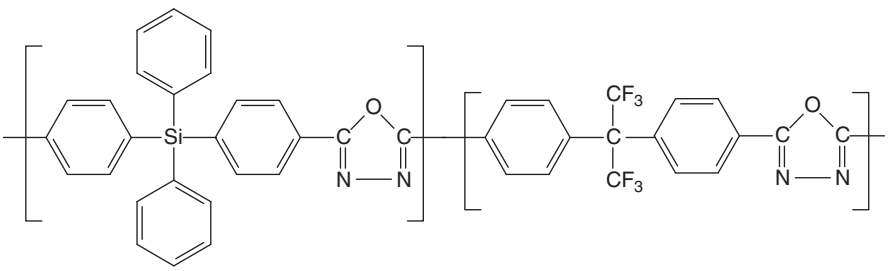

Figure 5 Copoly(1,3,4-oxadiazole), containing tetraphenylsilane and hexafluoropropylidene groups.

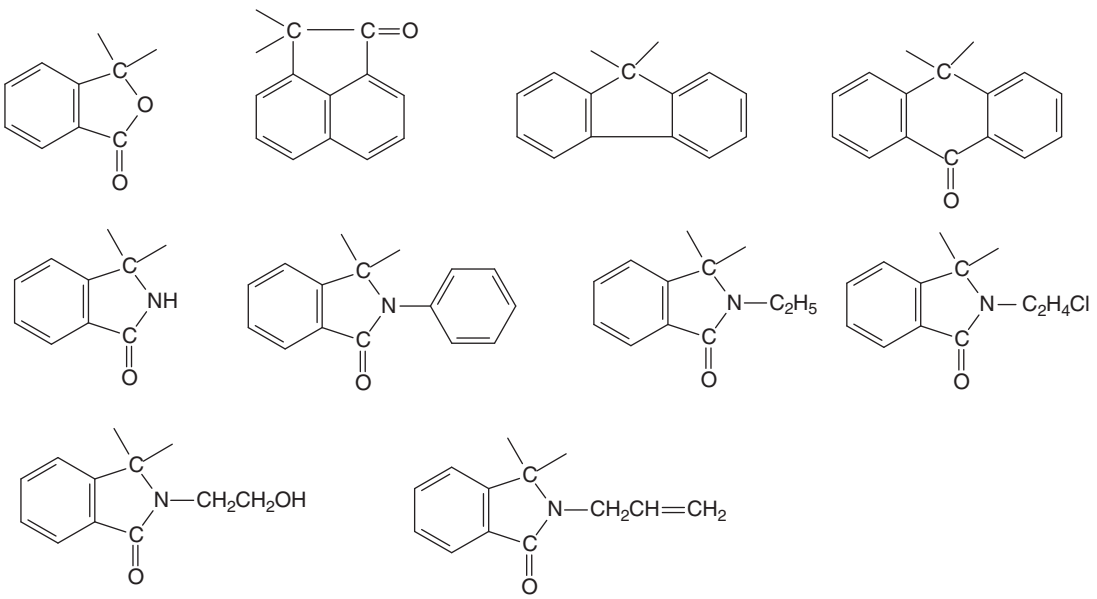

Figure 6 Cardo groups, included in the backbone of the poly(1,3,40oxadiazole)s.

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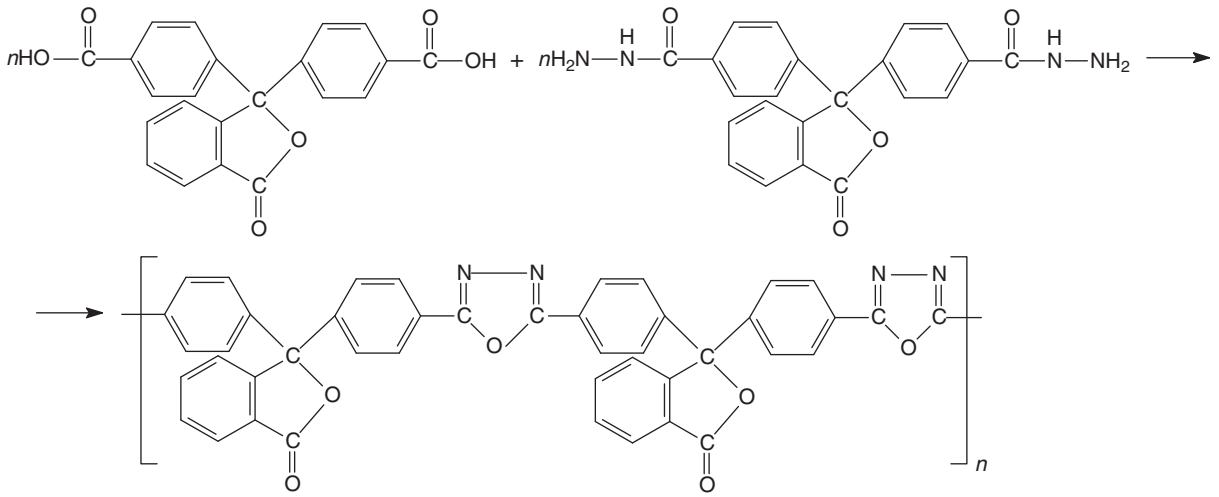
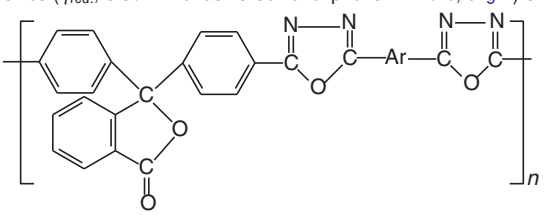


Scheme 5

By replacing one of the starting monomers with appropriate derivatives of aromatic dicarboxylic acids such as isophthalic, terephthalic, 4,4′-dicarboxydiphenyl, and 4,4′-dicarboxydiphenyl ether, mixed poly(1,3,4-oxadiazole)s are obtained.

A comparison of three different methods for the preparation of poly(1,3,4-oxadiazole)s – two-stage method including formation of polyhydrazides and their subsequent polycyclization (thermal or in the presence of catalytical complex DMF · SO_3) and one-stage method in PPA – has demonstrated that polymers of the highest mass (up to 300 000) are obtained under the conditions of one-step polycyclocondensation in PPA[119,120] (Table 2).

Table 2 Reduced viscosities ($\eta_{red.}$, 0.5% in tetrachloroethane–phenol mixture, dl g^{-1}) of poly(1,3,4-oxadiazole)s of general formula



prepared by various methods

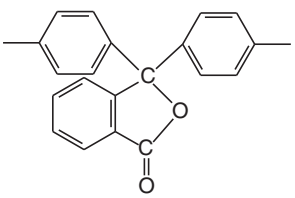
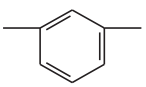
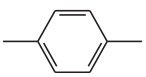
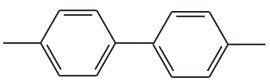
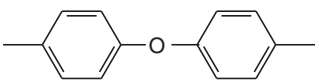
–Ar–	Method for the preparation of polymers		
	Thermal cyclization of polyhydrazides	*Catalytic cyclization of polyhydrazides using DMF·SO_3*	*One-step synthesis in PPA*
	1.74	0.60	5.30
	0.70	0.60	1.00
	0.58	0.70	1.90
	1.15	1.13	4.75
	1.75	0.87	3.78

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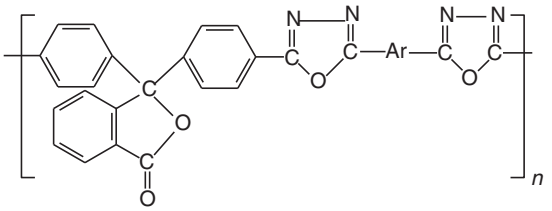
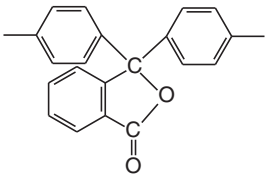
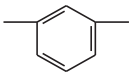
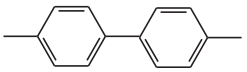
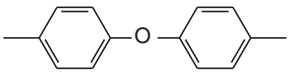
Table 3 Thermal and mechanical properties of the cardo poly(1,3,4-oxadiazole)s of general formula



–Ar–	$T_{soft.}$ (°C)	$T_{degr.}$ (°C)	Mechanical properties of nonoriented films (25 °C) σ (MPa)	ε (%)
	390	400	120	8
	360	400	120	10
	390	430	220	80
	400	430	240	75
	340	430	140	100

Some properties of the cardo poly(1,3,4-oxadiazole) series synthesized are listed in Table 3.[114,115]

Among various poly(1,3,4-oxadiazole)s with phthalide groups, poly[2,5-(4′,4″-diphenylphthalide)-1,3,4-oxadiazole] possesses the highest solubility – it is soluble in such solvents as methylene chloride, tetrachloroethane (TCE), DMAc, HMPA, pyridine, benzyl alcohol, and NMP.

All the abovementioned information demonstrates that poly(1,3,4-oxadiazole)s possess a number of useful properties and considerable potential for practical application.

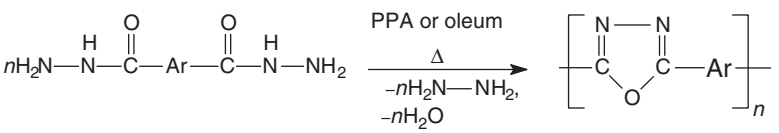
Along with polycyclocondensation of dicarboxylic acid with hydrazine in acetic solvents for the preparation of poly(arylene-1,3,4-oxadiazole)s, self-polycondensation of aromatic dicarboxylic acid dihydrazides in PPA or fuming sulfuric acid was used.[122,123] This reaction was carried out in accordance with Scheme 6.

Presumably, this reaction proceeds through an intermediate polyhydrazide formed by elimination of hydrazine. Fuming sulfuric acid is preferred for the synthesis of aromatic poly (1,3,4-oxadiazole)s.

An interesting one-step preparation of poly (1,3,4-oxadiazole) using NMP and lithium chloride in place of strong acid has been reported[124] (Scheme 7).

The molecular weight of the poly(1,3,4-oxadiazole) obtained was 6000. The reaction is made possible by the greater reactivity of hydrazide groups toward cyclodehydration when they are adjacent to each other.

One additional method for the preparation of poly (1,3,4-oxadiazole)s is based on cyclodeamination of poly(*N*-acetylhydrazidines), also referred to as poly(*N*-acylamidrazones), by heating in strong acids such as refluxing trifluoroacetic acid or PPA at 200 °C[124–126] (Scheme 8).



Scheme 6

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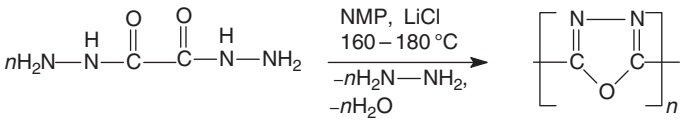
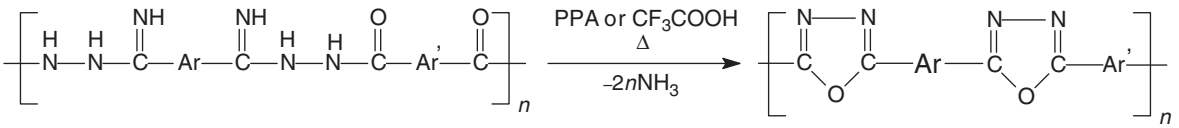
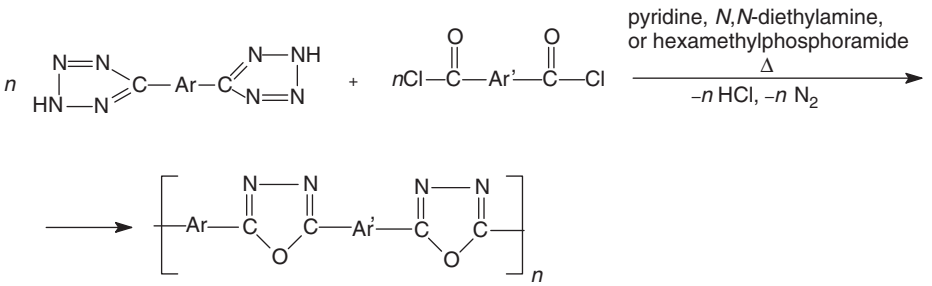


Scheme 7



Scheme 8



Scheme 9

For example, poly[2,2′-(2,6-pyridinediyl)-5,5′-(*m*-phenylene)-di-(1,3,4-oxadiazole)] was obtained in near quantitative yield by refluxing hydrazidine in trifluoroacetic acid for 18 h.

One additional method for the preparation of poly (1,3,4-oxadiazole)s is based on the interaction of bis-tetrazoles with dicarboxylic acid dichlorides[85,127,128] (Scheme 9).

Abshire and Marvel[127] synthesized a series of poly(1,3,4-oxadiazole)s by reaction of bis-tetrazoles with diacid dichlorides in pyridine. For example, they obtained poly-[*p*-phenylene-2,5-(1,3,4-oxadiazole)] by refluxing in dry pyridine for 72 h a mixture of *p*-phenylene-bis-tetrazole and terephthaloyl chloride. Unfortunately, all polymers obtained by this route were of low molecular weight as evidenced by inherent viscosities under 0.2 dl g^{-1} as measured in concentrated sulfuric acid.

Similar polycondensation processes have since been carried out by reaction of *m*-phenylene-bis-tetrazole with terephthaloyl chloride in HMPA[128] and by reaction of *p*-phenylene-bis-tetrazole with 1,1′-ferrocenedicarboxylic acid dichloride in *N,N*-diethylaniline.[76]

Generally, poly(arylene-1,3,4-oxadiazole)s are thermally stable up to 450 °C[102] and have good stability toward hydrolytic attack.[85,129–131] By dynamic-mechanical investigations of poly(arylene-1,3,4-oxadiazole)s, no typical glass transition temperature was observed up to 400 °C.[132]

The most widely known uses of poly-1,3,4-oxadiazoles are in films and fibers. Poly-1,3,4-oxadiazoles form yellow or brown transparent films with a percent elongation-to-break reported commonly in the 25–50% range. Tensile strengths are near 120 MPa and upon weathering or heat aging this value drops to about 80 MPa. By immersing the poly-1,3,4-oxadiazole film in DMAc followed by drying, the tensile properties can be increased significantly.[15,133]

Table 4 Miscellaneous applications of poly-1,3,4-oxadiazoles

Application	*References*
Glass laminate composite	139
Metal adhesive	140, 141
Dyeable films and fibers	142
Cation exchange resin	142
Weather-resistant, pigmented film	143, 144
Graphitized fibers	145
Ultrafiltration membranes	146

Fibers of poly(arylene-1,3,4-oxadiazole)s are spun from sulfuric acid solution[134] and they have a denier of 2–3. They demonstrate tensile strengths from 1.4 to 5.2 g den^{-1}, elongation 5–40%, and Young's modulus of 42–54 g den^{-1}, values that depend on the composition of connecting units and processing variables.[134,135] Poly(arylene-1,3,4-oxadiazole) fibers have a combination of good properties (i.e., strength, stiffness, resistance, and low density).[136–138]

Table 4 gives applications that have been developed for poly-1,3,4-oxadiazoles.[15]

5.21.2.1.2 Poly-1,2,4-oxadiazoles

The poly-1,2,4-oxadiazole systems have received very little attention since the mid-1960s when synthesis of many high-temperature polymers was rampant. The most well known method for the preparation of poly-1,2,4-oxadiazoles is polycyclocondensation reaction using bis-amidoximes and dicarboxylic acid dichlorides as starting reagents[74,75,147,148] (Scheme 10).

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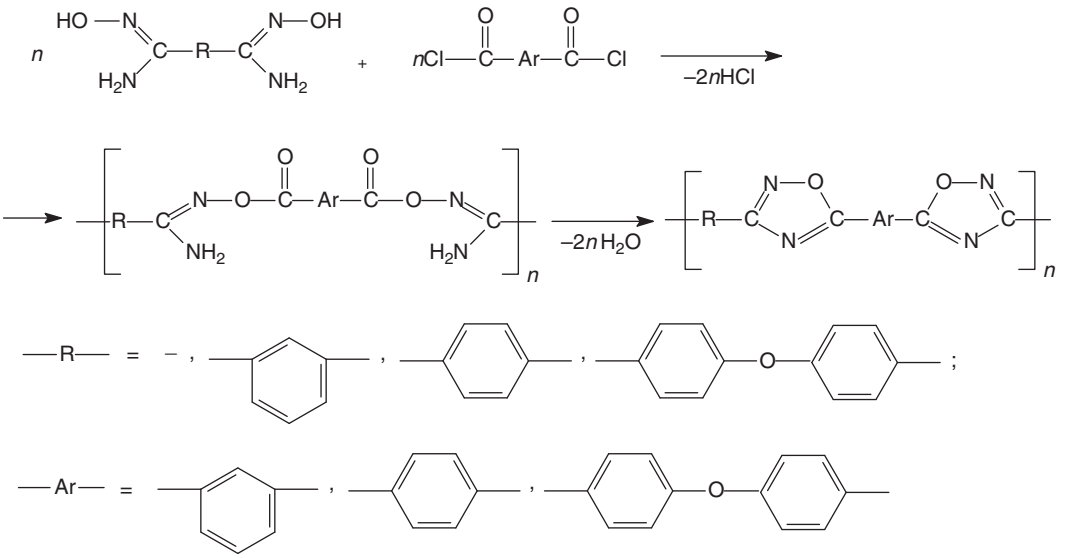


Scheme 10

By performing an initial condensation at low temperatures, side reactions are obviated. For example, the acid chloride could be envisioned to react with the amide nitrogen of the amidoxime to give the acylamidoxime instead of the *O*-acyl isomer.[148]

The cyclization mechanism involves nucleophilic attack of the free amine on the carbonyl carbon (Scheme 11).

In terms of solubility and tractability these polymers are quite similar to poly-1,3,4-oxadiazoles; however, they possess considerably less thermal stability and lower T_g. For example, poly(diphenylether-1,2,4-oxadiazole) begins to decompose at 310 °C in air (incipient weight loss by thermogravimetric analysis (TGA)),[148] whereas the analogous poly-1,3,4-oxadiazole decomposes above 400 °C.

Poly-1,2,4-oxadiazoles were also prepared using 1,3-dipolar polyaddition reactions in accordance with Scheme 12.[149–152]

Cycloaddition reactions proceed at low temperatures in diluted solutions.

One additional process for obtaining poly-1,2,4-oxadiazoles by 1,3-dipolar polyaddition is based on solid-state self-polymerization of *p*-cyanobenzonitrile-*N*-oxide upon standing at room temperature (Scheme 13).[153,154] Heat or UV light may be used to accelerate the reaction.

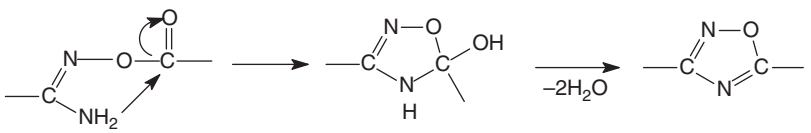
Little work has appeared that relates to the processing and use of these materials. A perfluoroether–1,2,4-oxadiazole polymer has been synthesized as a tough, crepe gum that can be cross-linked for use as an oil-resistant, low-temperature, flexible and thermooxidatively stable elastomer.[15,155]

The third approach to poly-1,2,4-oxadiazoles reported by Hong[156] may be quite similar to the dipolar addition of nitrile oxide to nitrile. The reason is that the terephthaloylhydroxamoyl chloride can undergo basic dehydrochlorination to the dinitrile oxide (Scheme 14).[140,157]

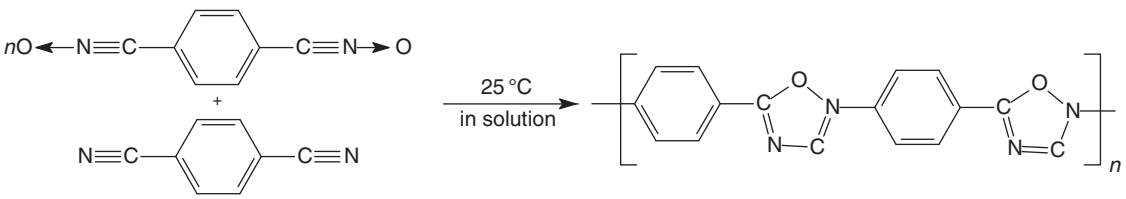
It is not clear whether this occurs or whether the dihydroxamoyl chloride reacts directly with terephthalonitrile or phthalaldehyde dioxime.[15]

5.21.2.1.3 Poly-1,2,5-oxadiazoles

Dinitrile-*N*-oxides have been shown to self-condense by 1,3-dipolar cycloaddition to 1,2,4- or 1,2,5-oxadiazole-*N*-oxide polymers, also known as polyfuroxanes (Scheme 15).[149,154,157–160]



Scheme 11



Scheme 12

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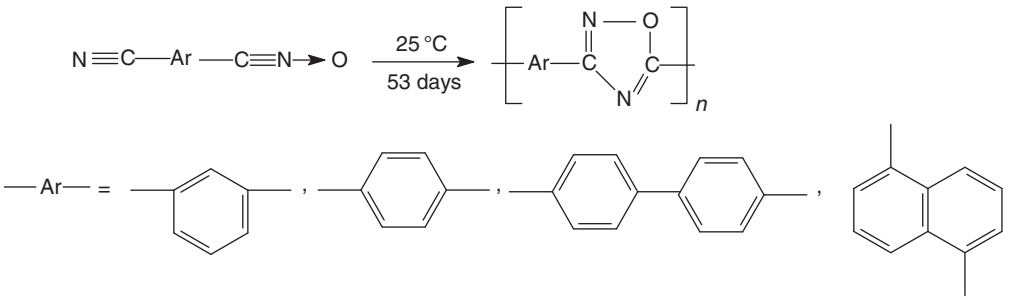
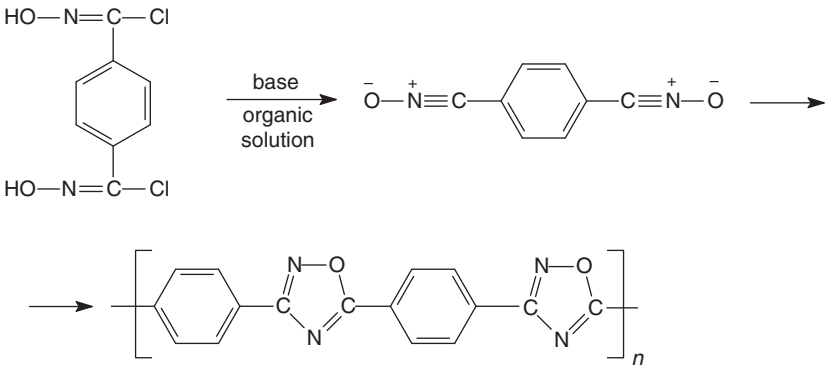
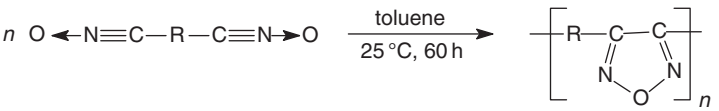


Scheme 13



Scheme 14



Scheme 15

The reaction can be carried out in solution with or without Lewis acid catalyst, to result in 1,2,5-system. The polymers are yellow-brown with a decomposition temperature of 217–223 °C and inherent viscosities up to 0.18 dl g^{-1} in sulfuric acid. The low decomposition temperature is not unexpected in view of the fact that the simplest polymer, poly(1,2,5-oxadiazole-*N*-oxide) (–R=– in Scheme 15), explodes when heated.[160]

5.21.2.2 Polythiadiazoles

Two isomers of the thiadiazole rings have been incorporated into the backbone of polymers.[15] They have either a 1,2,5- or 1,3,4-structure (Figure 7).

The polythiadiazoles exhibit the same desirable chemical and thermal stability as the poly-1,3,4-oxadiazoles but are somewhat more tractable.

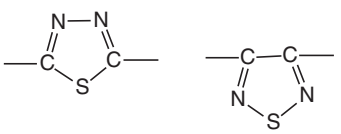


Figure 7 The fragments of the polythiadiazoles.

Polythiadiazoles have received much less attention than polyoxadiazoles because precursors for the thiopolymers are less accessible.

5.21.2.2.1 Poly-1,3,4-thiadiazoles

The simplest method for the preparation of poly-1,3,4-thiadiazoles is exactly like that used in making poly-1,3,4-oxadiazoles, that is, cyclodehydration of polyhydrazides. Frazer[161] used this approach to obtain poly(1,3,4-thiadiazole)s prior to 1965. Thus, by reacting tetrathiodicarboxylic acids with aromatic acids dithiohydrazides polythiohydrazides were obtained; they were converted to the corresponding poly (1,3,4-thiadiazole) by heating under vacuum (Scheme 16).

A typical example of such reactions is the interaction of dimethyltetrathioisophthalate with isophthalic acid dithiohydrazide in HMPA followed by the conversion of the polyhydrazide thus formed to the corresponding poly (1,3,4-thiadiazole) by heating at 285 °C under vacuum for 18 h (Scheme 17).[80]

In the reaction in Scheme 17, the diesters of tetrathiodicarboxylic acids may be replaced with diimidates (Scheme 18).[162]

One additional method for the preparation of poly(1,3,4-thiadiazole)s from polyhydrazides is based on the treatment of 'normal' polyhydrazides with P_2S_5 in pyridine[163] (Scheme 19).

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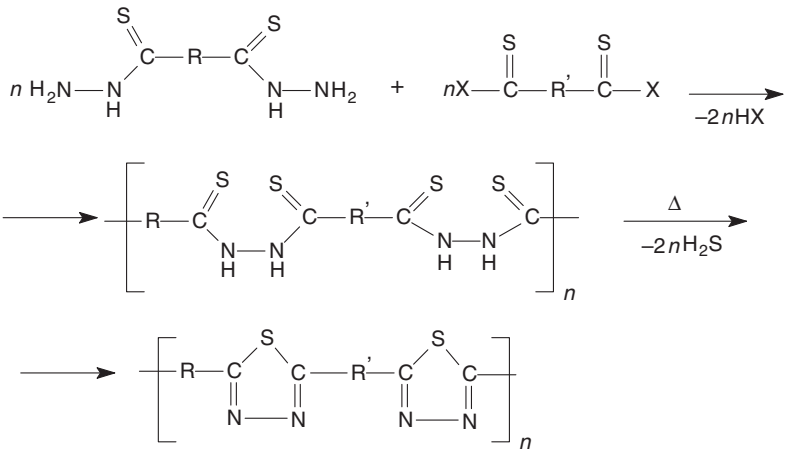
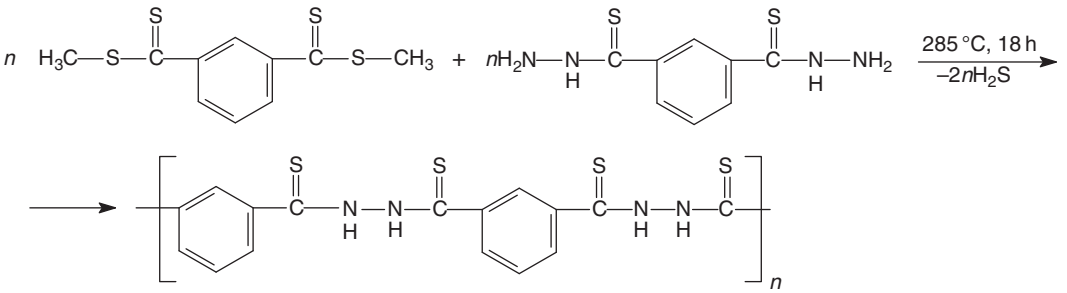
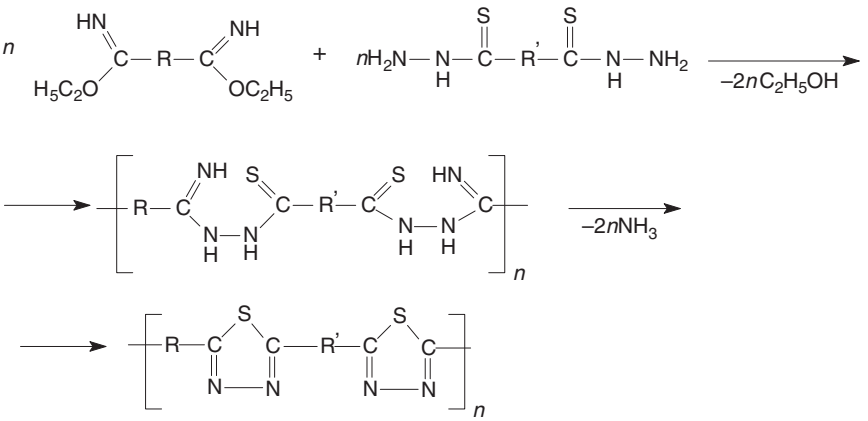


Scheme 16



Scheme 17



Scheme 18

Frazer[161] and Frazer and Memger[163] obtained patents for various aromatic and aliphatic poly(1,3,4-thiadiazole)s which can be cast into films and spun into fibers.

The majority of the polymers containing 1,2,5-thiadiazole rings were prepared using difunctional monomers containing the abovementioned rings – diamines, dicarboxylic acid dichlorides, or diesters, and so on – and formally belong to polyamides, polyesters, polyurethanes, and polyhydrazides containing 1,2,5-thiadiazole units.[164–166]

5.21.2.3 Polytriazoles

Among the polytriazoles, unsubstituted and N-substituted poly-1,2,4-triazoles are the most important systems.

5.21.2.3.1 Unsubstituted poly-1,2,4-triazoles

Unsubstituted poly-1,2,4-triazoles were prepared by the interaction of different dicarboxylic acid bis-amidrazones[126] with aromatic dicarboxylic acid dichlorides with subsequent thermal dehydration of polyacylamidrazones thus obtained[71,81,124,125,167] (Scheme 20).

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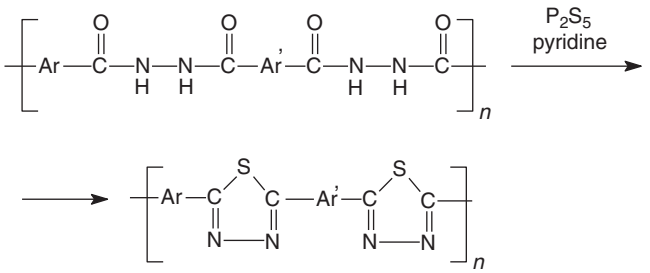
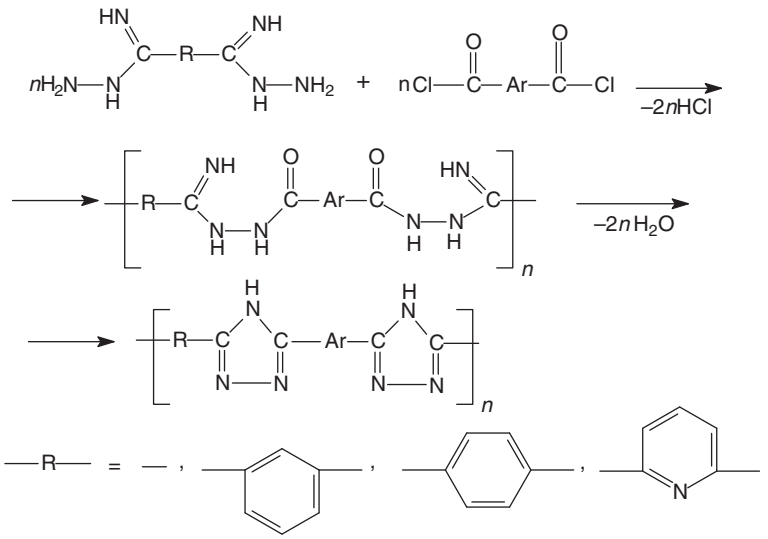


Scheme 19



Scheme 20

Interaction of bis-amidrazones with aromatic dicarboxylic acid dichlorides was carried out under the conditions of interfacial polycondensation and low-temperature solution polycondensation. Cyclization of polyacylamidrazones thus obtained in *m*-cresol[167] or in solid state at temperatures exceeding 250 °C led to the formation of unsubstituted poly-1,2,4-triazoles. Polymers obtained are soluble in conc. H_2SO_4 and start to decompose in air at 420 °C.

Poor solubility of unsubstituted poly-1,2,4-triazole prompted some research groups to incorporate aryl substituents in position 4 of 1,2,4-triazole rings.

5.21.2.3.2 Poly(4-aryl-1,2,4-triazole)s

The simplest poly(4-aryl-1,2,4-triazole)s containing phenyl substituents in position 4 of 1,2,4-triazole cycle were prepared by a reaction of aromatic polyhydrazides[77,78,92,168] and poly(1,3,4-oxadiazole)s[77,78,92,169,170] with aniline in PPA (**Scheme 21**).

The synthesis of poly(4-phenyl-1,2,4-triazole) can be further simplified by performing the complete reaction as a one-pot synthesis.[171] First the reaction between dicarboxylic acid and hydrazine yielding a poly(1,3,4-oxadiazole) is carried out in PPA. When this polycondensation reaction is complete, extra PPA is added to the reaction mixture followed by the addition of aniline. The reaction temperature is increased and the poly(1,3,4-oxadiazole) is converted into the corresponding poly(4-phenyl-1,2,4-triazole).

The reaction between poly(1,3,4-oxadiazole) and aniline is believed to occur via an intermediate (**Scheme 22**).[95]

If the reaction is not completed, unclosed 1,2,4-triazole rings are present in the final product. These unclosed rings can be closed by means of heat treatment at 350 °C for 24 h.

Poly(4-phenyl-1,2,4-triazole)s demonstrate improved solubility and decreased T_g's when compared to polyhydrazides and corresponding poly(1,3,4-oxadiazole)s. For poly[*p*-phenylene-(4-phenyl)]-1,2,4-triazole, a theoretical glass transition temperature of 380 °C was obtained upon extrapolation.[78]

In addition, a series of poly(1,2,4-triazole)s were prepared in which *p*-phenylene and *m*-phenylene units were incorporated alternately in the polymer backbone. Poly(1,2,4-triazole)s were prepared by reaction of the corresponding polyhydrazides with aniline and substituted anilines. Upon incorporation of aniline, *p*-toluidine, *p*-chloroaniline, and *p*-fluoroaniline as pendant groups, glass transition temperatures were obtained between 254 and 283 °C while the inherent viscosities η_{inh} ranged from 0.8 to 1.12 dl g^{-1}.[78,92]

The aromatic poly-(4-phenyl-1,2,4-triazole)s are promising new gas separation membrane materials since they combine excellent gas separation properties with a high thermal stability and a good chemical resistance.[172–176] Possible applications include the separation of air into oxygen and nitrogen and the separation of carbon dioxide from methane. These

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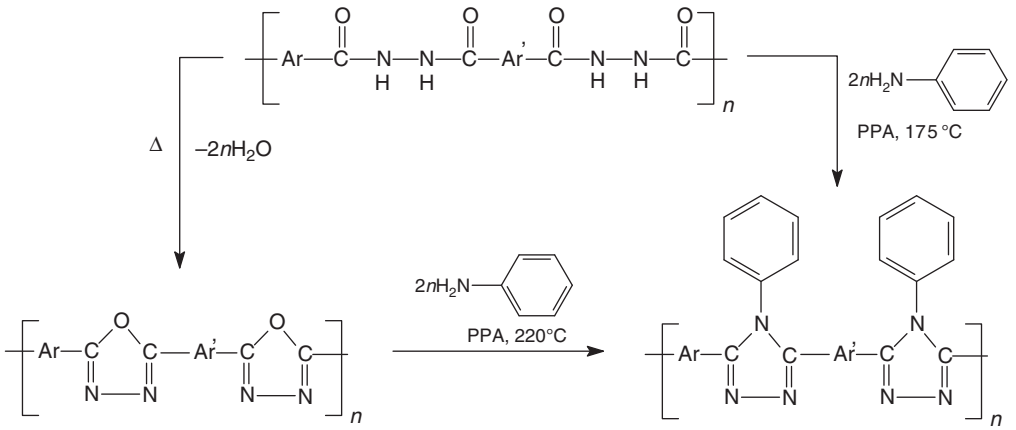
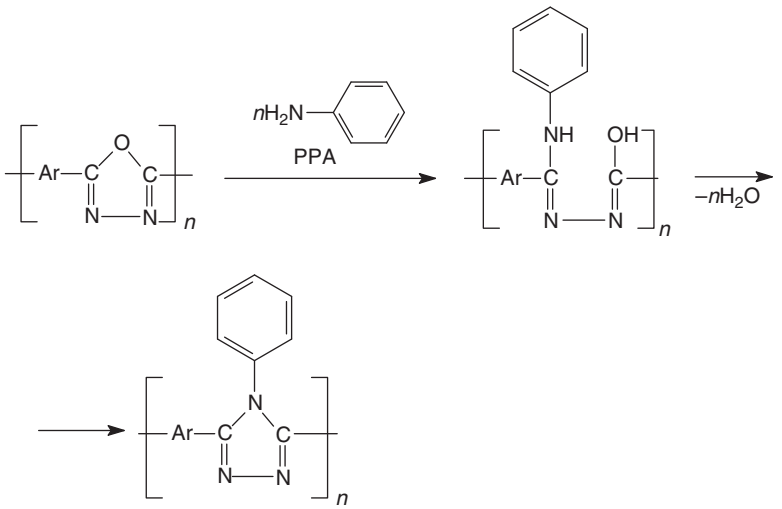


Scheme 21



Scheme 22

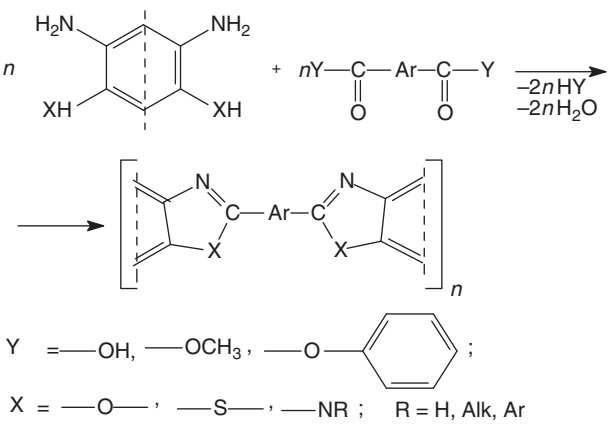
membranes combine high permeability and high selectivity.[92] The high permeability of these polymers is mostly explained in terms of their high free volume, which is due to their bulky groups preventing efficient packing, while their high selectivity is related to their rigid structure.[78,176,177]

5.21.3 Polybenzazoles

All aromatic polybenzazoles are known over the past five decades as a class of aromatic heterocyclic polymers that exhibit high thermal stability.[6,8–10,12–15] The most important representatives of polybenzazoles are polybenzimidazoles,[178] polybenzoxazoles (PBOs),[179] and polybenzothiazoles.[180]

The most widely adopted method for the synthesis of polybenzazoles is the interaction of *o,o′*-disubstituted aromatic diamines with aromatic dicarboxylic acids or their derivatives[14,17] (Scheme 23).

Reactions presented in Scheme 23 may be carried out (1) in the melt (Marvel reaction),[181–186] (2) in organic solvents using high-temperature solution polycyclocondensation process, or (3) in PPA (Iwakura reaction)[63,64] or in Eaton's reagent,[65] as two-stage polycyclocondensation, the first stage of which is low-temperature polyamidation and the second solid-phase polycyclodehydration of the prepolymers.[6,8–16]



Scheme 23

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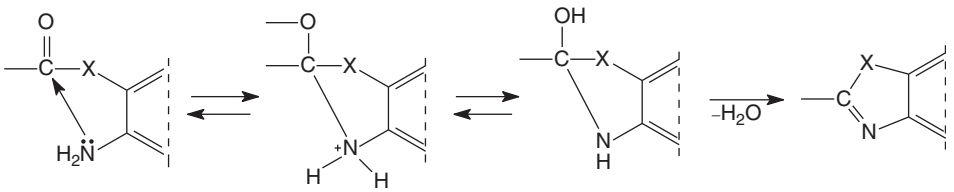


Scheme 24

A further common method for the synthesis of polybenzazoles well developed in the last three decades is the reaction of reductive polyheterocyclization.[187–189]

Each of these processes is being used more or less successfully to obtain particular polybenzazoles.

In many cases, researchers working in the field of polybenzazoles synthesis have consciously or inadvertently used catalytic methods of these polymers resorting in most cases to acid catalysts. This situation is quite natural considering the fact that the ease of benzazole cycle formation in the electrophilic reactivity of the carbon atom of carbonyl group protonated by the acid catalyst is a fact well known in the chemistry of individual heterocyclic compounds[190,191] (Scheme 24).

5.21.3.1 Polybenzimidazoles

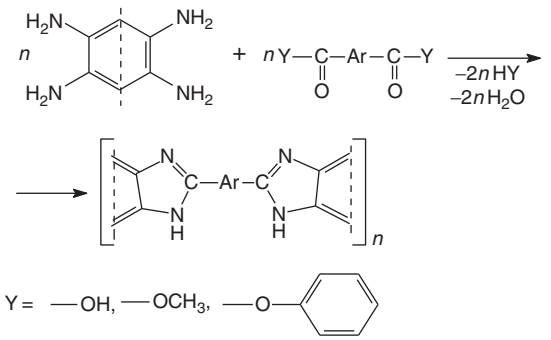
Polybenzimidazoles are a class of linear heterocyclic polymers that contain benzimidazole nuclei as a repeating unit. Benzimidazole groups exhibit excellent inherent thermal stability and resistance to hydrolysis by chemicals, acids and bases, and temperatures. These polymers can be divided into two general groups – unsubstituted polybenzimidazoles (NH benzimidazoles) and N-substituted polybenzimidazoles.

5.21.3.1.1 Unsubstituted polybenzimidazoles

Partially aromatic polybenzimidazoles were first invented by Brinker and Robinson[192] in 1959. One year later, wholly aromatic polybenzimidazoles having excellent thermal and chemical stabilities were reported by Vogel and Marvel.[61]

Unsubstituted polybenzimidazoles are usually prepared by the reaction of bis(*o*-phenylenediamine)s with dicarboxylic acids or their derivatives in accordance with Scheme 25.

The Marvel reaction considered in advance of the other processes of synthesis of polybenzazoles consists in the fusion of *o,o′*-disubstituted aromatic diamines with aromatic dicarboxylic acids or their derivatives followed by solid-phase thermal treatment of the reaction products in a medium of an inert gas or *in vacuo*. The most commonly used derivatives of aromatic dicarboxylic acids are dimethyl or diphenyl esters,[181–186,193] with the best results being obtained in the second case.[193]



Scheme 25

The mechanism of the formation of the polybenzimidazoles under the conditions of the Marvel reaction was studied.[61,194–199] According to the results, at least two alternative mechanisms of the formation of polybenzimidazoles may be postulated. The first of them[61,195] adds up to the formation at the first stage of the reaction of poly-*o*-aminoamides later undergoing cyclodehydration with the formation of polybenzimidazoles (Scheme 26).

A similar scheme was detailed by Gray *et al.*,[198,199] who represented the reaction of formation of the polybenzimidazoles in the following developed form (Scheme 27).

As may be seen, this reaction includes nucleophilic attack by the amino group on the carbon atom of the carbonyl with formation of a compound of the aldol type, which with the release of phenol is converted to an *o*-aminoamide structure. The free amino group of the latter undergoes intramolecular acylation of the amide by the carbonvl group with formation of the 2-hydroxybenzimidazoline structure (a) partially converted as a result of the cyclodehydration process at a temperature of 300 °C to benzimidazole (b). Continuation of the polycyclodehydration process with the rise in temperature to 400 °C gives polymers mostly of the polybenzimidazole type. The alternative mechanism proposed by Wrasidlo and Levine[196,197] also includes at the first stage nucleophilic attack by the amino group on the carbonyl carbon atom with formation of a compound of the aldol type although its further conversion is linked with dehydration leading to the formation of the polymeric Schiff base. The *syn* form of the latter is stabilized by the formation of a hydrogen bond and may in the view of the authors form, as a result of intramolecular acylation of the amino group, the 2-phenoxybenzimidazoline structure undergoing splitting off of phenol with formation of the target polybenzimidazole (Scheme 28).

The Marvel reaction with the use of diphenyl esters of aromatic dicarboxylic acids has been successfully used for the synthesis of the nonsubstituted polybenzimidazoles.[61,62,200–209]

The far more successful synthesis of the polybenzazoles using as starting compounds diphenyl esters of aromatic dicarboxylic acids is related to a number of factors: (1) the higher electrophilic reactivity of diphenyl esters of the dicarboxylic acids as compared with the dicarboxylic acids themselves or their dimethyl esters;[210] (2) the plasticizing effect of the phenol released into the polymeric system formed determining the rise in its mobility and facilitating both the course of the reactions via the terminal groups increasing the molecular weights of the polymers and intensification of the reactions of intramolecular

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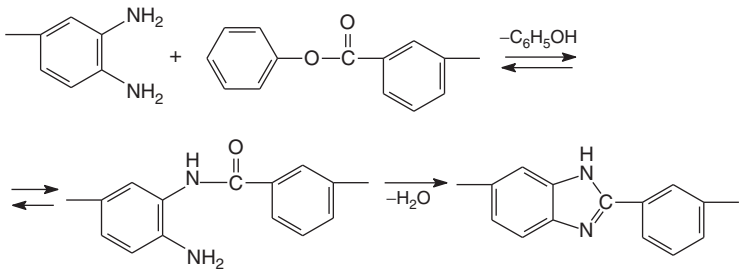
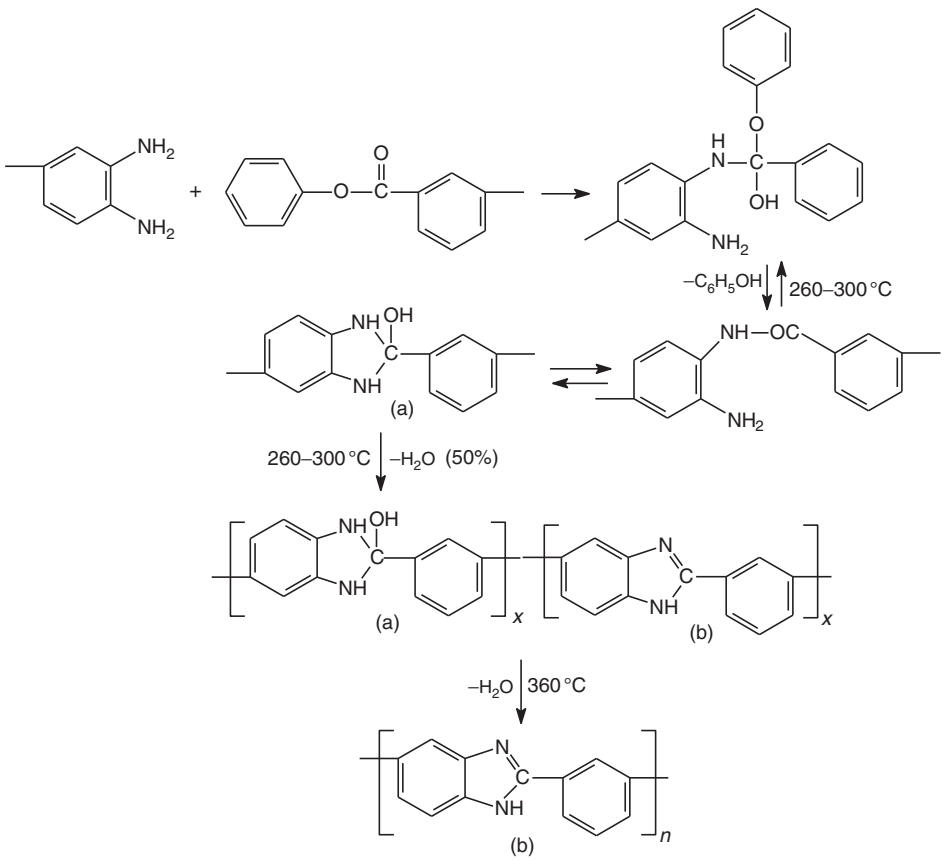


Scheme 26



Scheme 27

cyclization raising the degree of cyclization of these systems;[61,210] and (3) the catalytic action of the phenol released as a by-product and promoting both an increase in the molecular weights and an increase in the degree of cyclization of the polybenzazoles.

The catalytic activity of phenol, not previously emphasized while discussing the results of synthesis of the polybenzazoles using the conditions of the Marvel reaction, is quite natural in view of the protonogenic properties of this compound and does not contradict any of the above mechanisms of the reaction of formation of the polybenzazoles. Thus, the Marvel reaction may be regarded as one variant of the catalytic method of synthesizing the polybenzazoles with the use of a comparatively weak acid catalyst – phenol.

Synthesis of the polybenzazoles under the conditions of the Marvel reaction has such merits as carrying out the process in the absence of solvents and the possibility of reaching high molecular weights and high degree of cyclization of the polymers. However, this process also has some shortcomings including, in particular, the following: (1) There is a need to use as starting compounds free *o,o′*-disubstituted aromatic diamines, individual representatives of which are very unstable to oxidation. This factor, in particular, using the conditions of the Marvel reaction hampers the synthesis of polybenzazoles based on tetrafunctional nucleophilic compounds containing all functional groups in one benzene nucleus, for example, 1,2,4,5-tetraaminobenzene and isomeric dihydroxydiaminobenzenes. (2) In order to obtain polybenzazoles of high degree of cyclization and molecular weight, there is a need to use a high (up to 673 K) temperature and desirably a vacuum which *in toto* creates considerable difficulties in the designing of the apparatus for the processes. In addition, the

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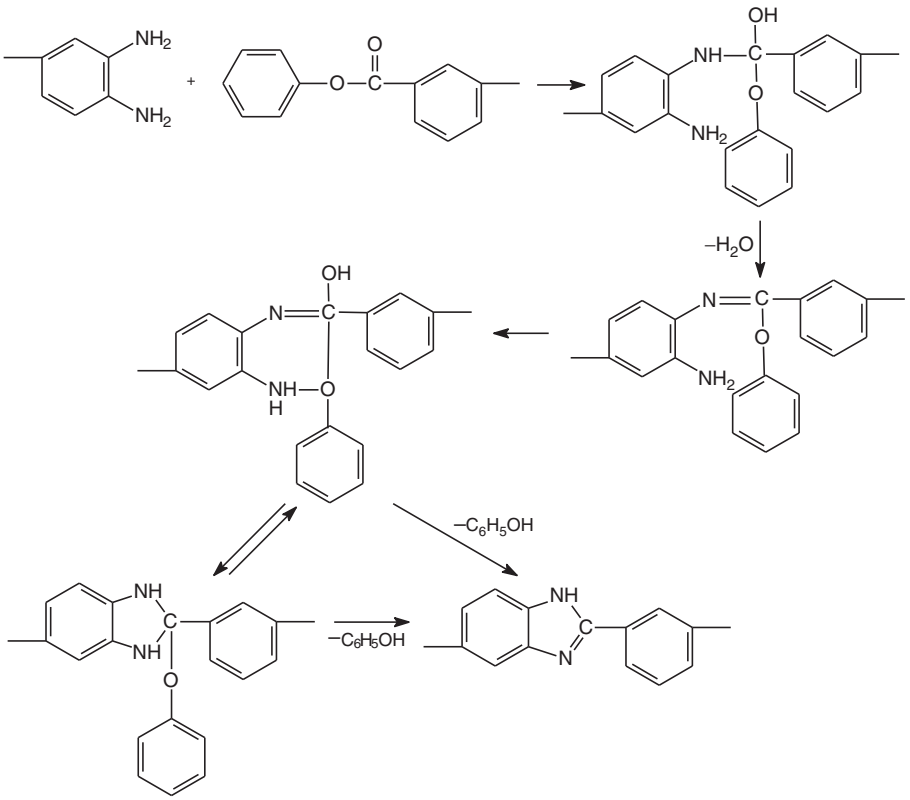

Scheme 28

synthesis of the polybenzazoles at such high temperatures leads to undesirable subsidiary and secondary processes (cross-links, degradation, etc.) often adversely affecting the properties of the target polymers.

Apparently one may with some confidence predict that replacement in the Marvel reaction of the diphenyl esters of the dicarboxylic acids by diesters of more acidic phenols will lead to appreciable intensification of this process and give high-molecular-weight and well-cyclized polybenzazoles in far milder conditions.[62] However, such an approach involves some complication of structure and less accessibility of the electrophilic monomers used for the synthesis of the polybenzazoles.

The catalytic action of phenol and its homologs has been used in relation to the synthesis of the polybenzazoles by various authors conducting this process under conditions of high-temperature polycyclocondensation in phenolic solvents mostly at the boiling points of the latter.

Synthesis of the polybenzazoles in phenol and isomeric cresols has been successfully undertaken in relation to the PBOs,[63] polybenzthiazoles,[64–66] and nonsubstituted polybenzimidazoles.[67–73]

Synthesis of the polybenzazoles in phenolic solvents usually occurring homogeneously is a quite technological process though characterized by a number of serious drawbacks: like the synthesis of the polybenzazoles under the conditions of the Marvel reaction, this process implies the need to use as starting compounds free *o,o′*-disubstituted aromatic diamines; the need to use comparatively toxic phenolic solvents and accordingly the need to include in the technological cycle of obtaining polymers the stage of precipitation of the polybenzazoles; a combination of the temperature of the processes (~473 K) and the catalytic activity of the phenols is sometimes not enough to reach high molecular weights and high degree of cyclization of the polybenzazoles.

Nevertheless, the synthesis of the polybenzazoles in phenolic solvents is typical of catalytic polycondensation in which phenol and its homologs perform the functions of both catalysts and solvents. Also related to such processes is the widely used method of synthesis of the polybenzazoles – the polycyclocondensation in PPA or the 'Iwakura reaction'.[14] Synthesis of the polybenzazoles by the Iwakura reaction is carried out in line with **Scheme 29**.

It is known that PPA acts simultaneously as a strong protonic acid and a Lewis acid.[63,64] As a consequence, it increases the positive charge on the carbon atom of the carbonyl group and thereby raises its electrophilic reactivity.[211] Taking this fact into account, the overall mechanism of the formation of the polybenzimidazoles in PPA was represented by Imai *et al.*[211] as shown in **Scheme 30**.

Synthesis of the polybenzimidazoles in PPA is carried out in homogeneous conditions in the interval 150–200 °C and gives high-molecular-weight and well-cyclized products. This process has been successfully employed to obtain nonsubstituted polybenzimidazoles.[64,211–215] Thermodynamically, the driving force of the reaction of synthesis of the polybenzazoles in PPA is the formation of aromatic heterocycles.[216] Taking into account the possibility of dissociation of the amide bonds in PPA to the starting amines and carboxylic acids, it must be assumed that the rise in the molecular weights of the

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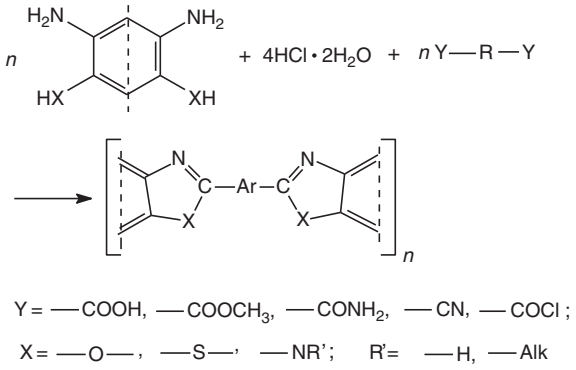


Scheme 29

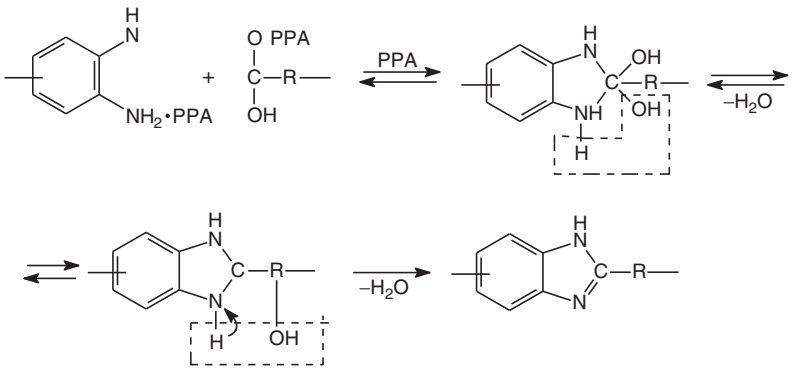
polybenzimidazoles in PPA is brought about by the formation of heterocyclic fragments.

Synthesis of the polybenzimidazoles in a PPA medium has a number of specific drawbacks: the high corrosive activity of PPA; PPA not available as a commercial product and accordingly the need to prepare it extemporaneously before the synthesis of polyheteroarylenes; the need to dilute the reaction solutions of PPA before precipitating them to obtain them in the form of comparatively finely dispersed powders, which sharply increases the volume of both the solvents and the precipitants of the polyheteroarylenes; and the action of PPA as a phosphorylating agent[63,64] leading to phosphorylation of the polybenzazoles and hence some fall in their thermal characteristics.

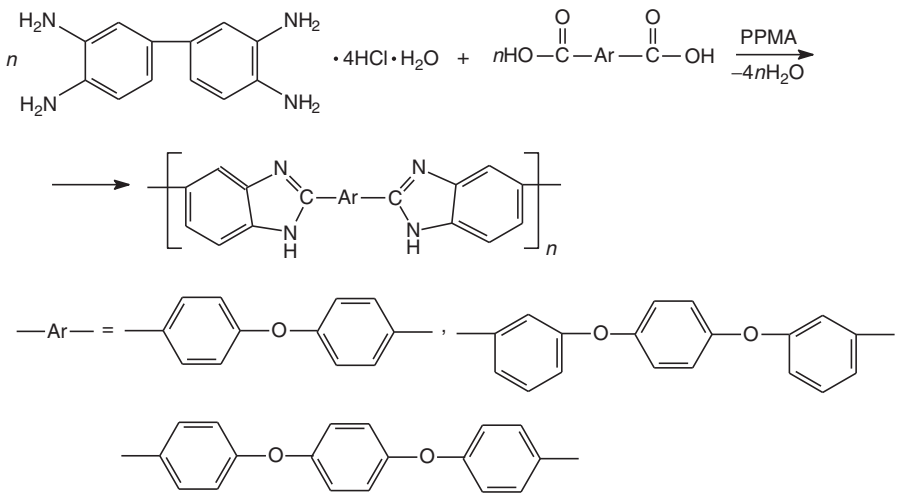
A convenient method for the synthesis of certain polybenzimidazoles of high molecular weights is based on direct polycondensation of aromatic dicarboxylic acid with bis(*o*-phenylenediamine)s using PPMA (Eaton's reagent) as condensing agent and solvent.[65,217] Polycondensation of aromatic dicarboxylic acids containing phenyl ether groups with 3,3′-diaminobenzidine tetrahydrochloride (**Scheme 31**) proceeded very quickly; it was completed within 80 min at 140 °C, and produced polybenzimidazoles with inherent viscosities up to 5.8 dl g^{-1}.

This method is advantageous to the formation of polybenzimidazoles because of the rapidity and simplicity of the reaction and milder reaction conditions compared to conventional methods.

A universal method of synthesizing polybenzazoles is the two-stage polycyclocondensation[6,8–10] presupposing clear separation of the stages of synthesis of the prepolymers and their cyclization. Usually the first stages of such processes are carried out through the interaction of the *o,o*′-disubstituted



Scheme 30



Scheme 31

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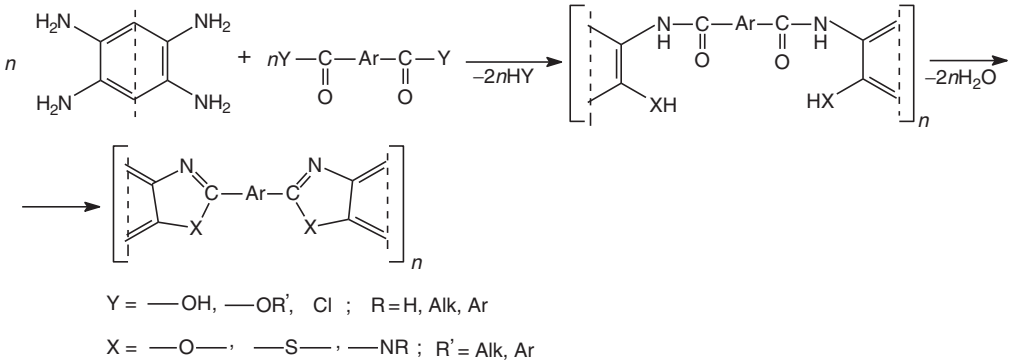


Scheme 32

aromatic diamines with the dichlorides of the aromatic dicarboxylic acids in a medium of amide solvents at temperatures not above 25 °C after which the prepolymers formed are worked up to products or are released from the reaction solutions, carefully washed free of solvents and the by-products of the reaction, and subjected to thermal solid-phase polycyclodehydration or chemical polycyclodehydration (Scheme 32).

A necessary condition for the successful course of this process is the selectivity of low-temperature polyamidation determined by the comparative nucleophilic reactivity of the neighboring functional groups of the *o,o'*-disubstituted aromatic diamines and the electrophilic reactivity of the acylating agents.[218,219] It is quite obvious that the selectivity of such processes is higher the greater the difference in the nucleophilic reactivities of the neighboring functional groups in the disubstituted aromatic amines and the lower the electrophilic reactivity of the dichlorides.

The processes of selective polyacylation of bis(*o*-phenylenediamine)s[218–220] characterized by the comparable reactivity of the neighboring nucleophilic centers present great difficulties.

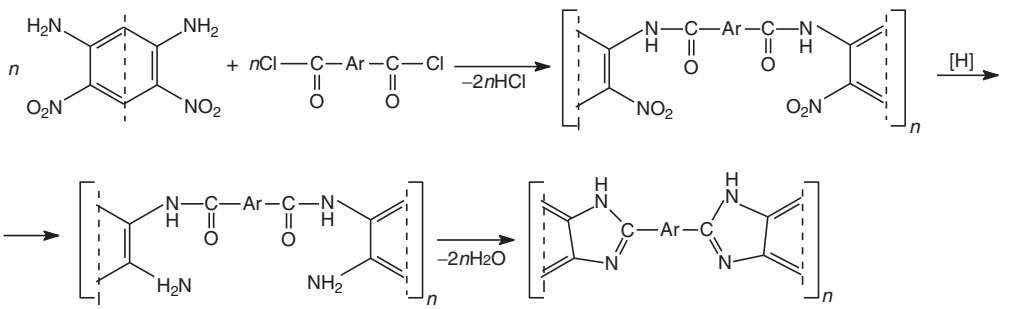
A detailed study of the possibility of conducting selective acylation of bis(*o*-phenylenediamine)s showed that this problem may be solved by very careful dosing of the dichlorides into the reaction solution[220] replacing the dichlorides of the dicarboxylic acids by the less reactive difluorides[221] or by blocking two of the four amino groups of bis(*o*-phenylenediamine) by hydrogen chloride.[222–224] It should be noted that each of the approaches greatly complicates synthesis of the polybenzazoles.

The reactions of thermal solid-phase polycyclodehydration of *o*-substituted polyamides leading to the formation of the target polybenzazoles are usually undertaken by a stepped rise in temperature from room temperature to 573–623 K and are conducted *in vacuo* or in an inert medium.

The approach considered, in principle, yields products of all the polybenzazoles irrespective of their structure through the stage of soluble prepolymers although the process has a number of serious shortcomings: the problematical nature of conducting selective polyamidation; the need to conduct the process of solid-phase polycyclodehydration of the prepolymers at high temperatures (300–350 °C) *in vacuo* which seriously complicates the choice of apparatus for the process; and the problematical nature of reaching a high degree of cyclization of the polybenzazoles in conditions of solid-phase polycyclodehydration.

An attempt to fundamentally improve the existing methods of synthesis of the polybenzimidazoles was made by Korshak *et al.*[187,188] and Rusanov *et al.*[189] in a series of studies of reductive polyheterocyclization. Synthesis of the polybenzimidazoles by this method was undertaken by obtaining o-nitrosubstituted aromatic polyamides followed by reduction of the nitro groups to amino group and simultaneous cyclization of the reduced polymers in line with Scheme 33.

Comparison of the schemes of polybenzimidazoles synthesis by the traditional method and reductive polyheterocyclization points to the presence in the latter of a number of important advantages. The starting compounds used in the reaction of reductive polyheterocyclization are bis(*o*-nitroaniline)s, which are far more accessible, cheaper, and more resistant to oxidation than the bis(*o*-phenylenediamine)s used in the traditional method of synthesis of the polybenzimidazoles.



Scheme 33

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The use of bis(*o*-nitroamide)s allows the first stages of synthesis of the polybenzimidazoles (selective polyamidation) to be run without subsidiary processes. This determines the possibility of using in all cases as acylating agents accessible and reactive derivatives of dicarboxylic acids – their dichlorides.

A by-product of the first stage of the reaction (hydrogen chloride) may be directly used in combination with different metals and primarily with activated iron to reduce the nitro to amino groups and also for the catalysis of benzimidazole cycle formation.[225–227]

It is better to conduct such reactions in the form of continuous processes in the medium of methylpyrrolidone, an effective solvent of heterochain and heterocyclic polymers. An essential condition for the successful course of the process is the solubility of the polymers at all stages of the process since otherwise the polymer released from the solutions would coat the activated iron, which would hamper the further progress of the process.

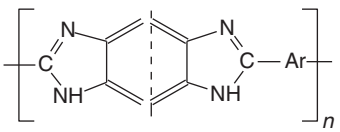
The processes of reductive polyheterocyclization were studied in the greatest detail in relation to the synthesis of nonsubstituted polybenzimidazoles.[228–232]

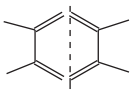
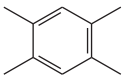
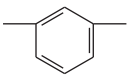
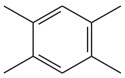
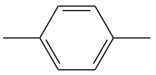
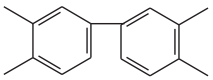
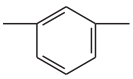
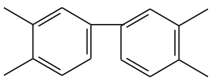
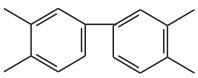
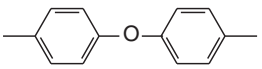
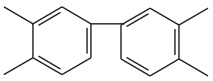
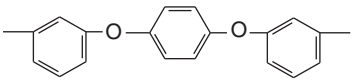
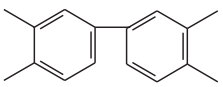
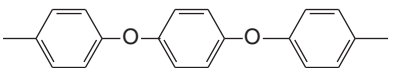
The synthesis of nonsubstituted polybenzimidazoles with high-viscosity (molecular weight) characteristics involves considerable difficulties due to a fall in the nucleophilic reactivity of the aromatic diamines as a result of the introduction of electron-withdrawing o-nitro substituents. Nucleophilic reactivity of bis(*o*-nitroaniline)s can be increased using silylation of these monomers.[232–235]

The most widely used bis(*o*-phenylenediamine)s for the preparation of polybenzimidazoles are 1,2,4,5-tetraminobenzene tetrahydrochloride, 3,3′,4,4′-tetraminodiphenyl, 3,3′,4,4′-tetraminodiphenyl ether, 3,3′,4,4′-tetraminodiphenyl sulfone, 3,3′,4,4′-tetraminodiphenyl methane, and so on. Some properties of the polybenzimidazoles based on 1,2,4,5-tetraminobenzene tetrahydrochloride, 3,3′-diaminobenzidine, and aromatic dicarboxylic acids (or their derivatives) are listed in Table 5.

Polybenzimidazoles listed in Table 5 which are free of ether groups and *m*-phenylene units belong to rigid-rod polymers.[236–238] All these polymers were prepared using solution polycyclocondensation reactions in PPA or in Eaton's reagent. The polymers did not display sufficient solubility in acidic solvents to exhibit mesogenic behavior. Polymerizations utilizing 1,2,4,5-tetraaminobenzene tetrahydrochloride or 1,3-diamino-4,6-(*p*-toluenesulfamido)benzene at low concentrations (1–2%) provide low-molecular-weight polymers with intrinsic viscosities between 2 and 4 dl g^{-1}. Polymerizations above the theoretical critical concentration result in the polymer crystallizing out of solution and being completely

Table 5 Some properties of the polybenzimidazoles of general formula



	–Ar–	η_{inh}	$T_{10\%}$, TGA (°C) In air	In N_2
				
				
				
				
		3.63 ($H_3C—SO_3H$)	465	540
		0.94 ($H_3C—SO_3H$)	440	500
		5.84 ($H_3C—SO_3H$)	470	540

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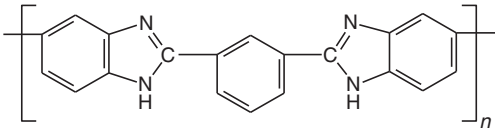


Figure 8 Poly[2,2'-(m-phenylene)-5,5'-bisbenzimidazole] (PBI).

insoluble in all acidic solvents. A variety of high-molecular-weight rigid-rod polybenzimidazoles containing various pendant benzazole groups have been obtained.[239–244] It is felt that the pendant groups retard the crystallizing process by preventing the close packing of chains.

Some alternative approaches to the improvement of polybenzimidazoles solubility are based on the incorporation of ether,[217] *m*-phenylene, hexafluoroisopropylidene,[245] and *m*-carboranylene[246] groups in the macromolecular chains of these polymers.

Hoechst Celanese Corporation commercialized one of the aromatic polybenzimidazoles, poly[2,2′-(*m*-phenylene)-5,5′-bibenzimidazole], under the trade name PBI® (Figure 8).

An extensive study was carried out on this polymer because of its toughness, no flammability, thermal and chemical stabilities, and processability.[247] Because of these unique properties, PBI has been used to form membranes,[248] electrically conductive materials,[249–252] fire-resistant materials,[253] ultrafilters,[254] and other types of separatory media.[255–259]

The thermal stability and no flammability of PBI are attractive for many industrial and aerospace applications. PBI fiber was produced by the dry spinning of a 23% solution of PBI in DMAc containing 2% LiCl. The retention of fiber strength versus the exposure temperatures in air was excellent. The fiber began to lose its strength above 300 °C and had about a 50% retention of properties at 500 °C. The fibers provided comfort through their high moisture retaining properties, no flammability in air and low shrinkage when exposed to flame, and chemical resistance.[260]

Polybenzimidazole was used as support for the preparation of polymer-supported catalysts for both reduction and oxidation. The high thermal stability of PBI support at high temperatures is an extremely valuable feature for this application. The imidazole ring in PBI was used for direct coordination to transition metals. Polybenzimidazole was complexed with $PdCl_2$ and reduced to PBI/Pd^0 using hydrogen and methanol/NaOH in nitrobenzene. PBI–Pd^0 catalyst is extremely active and thermally stable, and is recyclable without loss of activity. PBI/Pd^0 catalyst is very effective in the reduction of nitro compounds to the corresponding amines or of alkenes to the corresponding alkanes.[261–266]

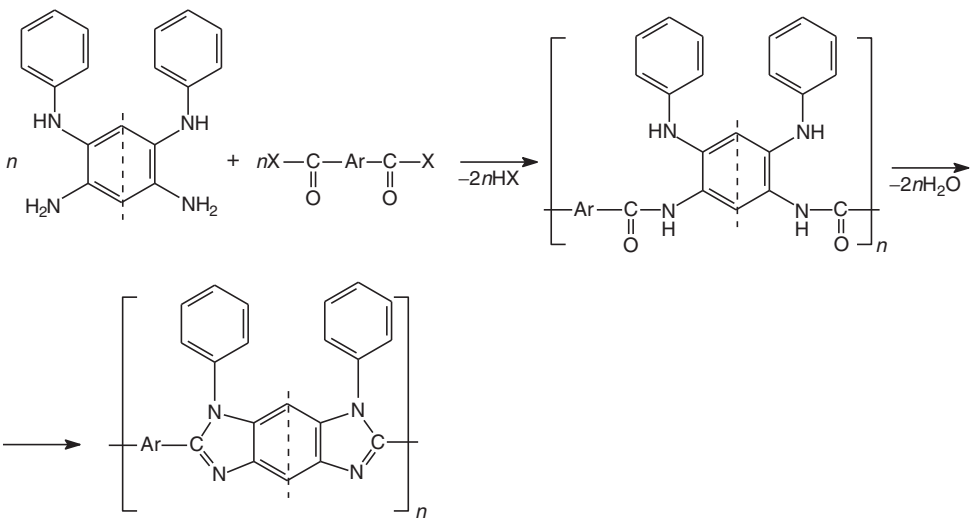
In the past several years, there has been a major emphasis on the development of high-temperature (>100 °C) polymer-based proton exchange membrane fuel cells.[267,268] In 1995, Wainright *et al.*[269] first described a polybenzimidazole–phosphoric acid complex for use in high-temperature fuel cells. It has been reported that these membranes exhibit high ionic conductivities at high temperatures, low gas permeability, excellent chemical and thermal stability in the fuel cell environment, and nearly zero water drag coefficient.[270–274]

5.21.3.1.2 Phenyl-substituted polybenzimidazoles

The most important polymers among phenyl-substituted polybenzimidazoles are poly(*N*-phenyl)benzimidazoles, products of the interaction between *N*,*N*′-diphenyl-substituted bis(*o*-phenylenediamine)s and aromatic dicarboxylic acid derivatives[62,275–285] (Scheme 34).

For the preparation of poly(*N*-phenyl)benzimidazoles, 'Marvel reaction' was used, that is, – interaction of *N*,*N*′-diphenyl-substituted bis(*o*-phenylenediamine)s with the diphenyl esters of aromatic dicarboxylic acids in melt followed by solid-state cyclodehydration;[62,280,284] however, the most effective method for the preparation of these polymers is the two-stage process including low-temperature solution polycondensation of *N*,*N*′-diphenyl-substituted bis(*o*-phenylenediamine)s with aromatic dicarboxylic acid dichlorides followed by thermal or chemical cyclization of the poly(*o*-phenylamino)amides thus formed[281–283,285] (Scheme 35).

The high-molecular-weight polymer precursors ($\eta_{red.}$ up to 2.5 dl g^{-1}) were prepared by low-temperature solution polycondensation (0–20 °C) in DMAc or NMP. In contrast with



Scheme 34

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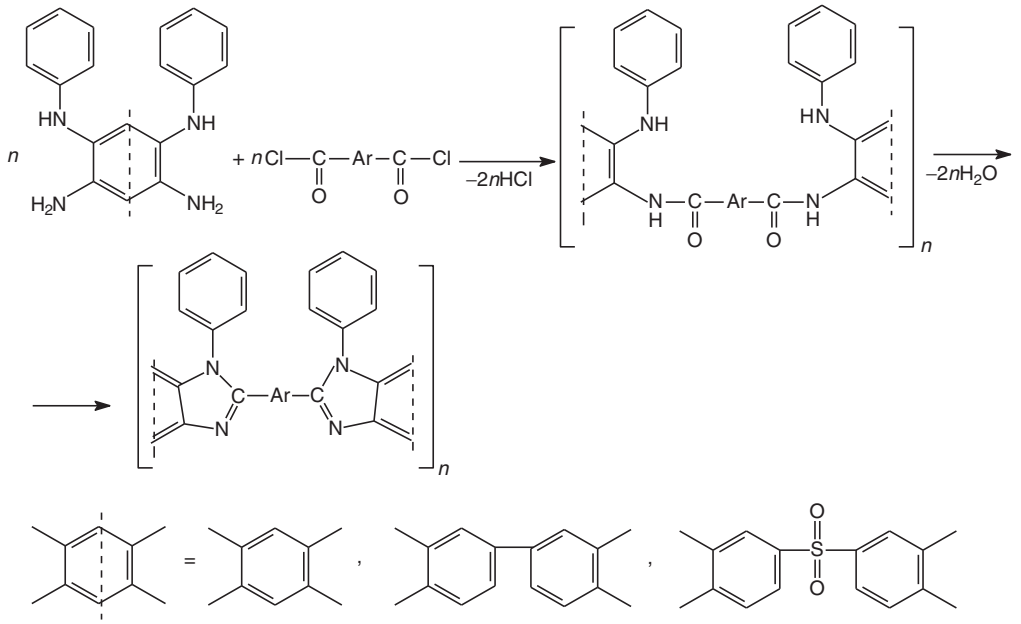

Scheme 35

unsubstituted bis(*o*-phenylenediamine)s, the tetramines used in these reactions behave differently in the nucleophilic reactivities of the amino and imino groups doubly joined in positions ortho to each other.[286,287] As a result, it is possible to add the solid dicarboxylic acid dichloride to the solution of bis (*N*-phenyl-*o*-phenylenediamine) without any gelation. The reactions of poly(*o*-phenylaminoamide) synthesis proceed with a high rate.[283]

All poly(*o*-phenylaminoamide)s are soluble in highly polar solvents such as dimethylformamide (DMF), DMAc, pyridine, DMSO, NMP, and HMPA, forming solutions of 20–25% concentration. Almost all the poly(*o*-phenylaminoamide)s were of sufficiently high molecular weight to form films from 8–10% solutions in DMAc.

The conversion of the poly(*o*-phenylaminoamide)s to the corresponding poly(*N*-phenyl)benzimidazoles was effected by solid-state polycyclocondensation. On conducting the cyclization, some 1–2% DMAc was left to plasticize the polymers and to facilitate their cyclization. The optimum cyclization conditions are temperatures of 300—310 °C and reaction periods of 5–6 h.

All poly(*N*-phenyl)benzimidazoles are soluble in formic acid and in the TCE–phenol (3:1) mixture. These polymers were of sufficient molecular weight to form strong films, cast from 10–12% solutions in TCE–phenol (3:1) mixture.

Good solubility of all poly(*N*-phenyl)benzimidazoles is due to the beneficial effect of the phenyl substituents, as has been demonstrated for many polyheteroarylenes.[103]

Selected properties of poly(*N*-phenyl)benzimidazoles based on 1,3-diamino-4,6-di(phenylamino)benzene are listed in Table 6.

In accordance with isothermal aging results in air at 400 °C, poly(*N*-phenyl)benzimidazoles exhibit superior thermooxidative stability, but in an inert atmosphere they are less stable when compared to their nonphenylated analogues. Their degradation begins with the scission of the phenyl side groups[288] because of the absence of conjugation between the phenyl group in position 1 and the imidazole ring.[289]

Along with solid-state polycyclization for the transformation of poly(*o*-phenylaminoamide)s to poly(*N*-phenyl) benzimidazoles, catalytical methods including cyclization of poly(*o*-phenylaminoamide)s under the action of PPA,[276,283] formic acid, and dichloroacetic acid were used.[276]

A very simple method for the poly(*N*-phenyl) benzimidazoles synthesis includes low-temperature solution polycondensation resulting in poly(*o*-phenylaminoamide)s formation and their treatment in reaction solutions with gaseous HCl. The reactions were carried out in NMP at temperatures of 170–180 °C and they proceeded homogeneously.[17]

Poly(*C*-phenyl)benzimidazoles were prepared using multistep method based on the interaction of activated bis-*o*-nitrohalogen arylenes with aromatic diamines, reduction of the poly-*o*-nitroamines thus obtained, benzoylation of the reduction products via the primary amino groups followed by catalytic cyclization of poly-*o*-benzamidoimines[228,290–292] in line with Scheme 36.

Unlike the previously considered reactions of reductive polyheterocyclization characterized by the advent of cyclization processes immediately after reduction of the nitro to the amino groups, the reactions of synthesis of poly-*C*-phenylbenzimidazoles presuppose separation of the stages of reduction and cyclization by a further reaction – usually the reaction of acylation. As a consequence, such reactions have been called processes of modified reductive polyheterocyclization.[228,290–292]

With the condition that one uses as bis-*o*-nitrohalogen arylenes the corresponding derivatives of the diphenylsulfone and benzophenone series and as aromatic diamines the corresponding derivatives of the diphenyl oxide and diphenyl methane series, high-molecular-weight poly-*C*-phenylbenzimidazoles very soluble in organic solvents are formed possessing a valuable complex of high thermal and strain strength characteristics.[228,290–292]

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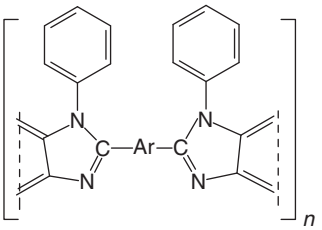
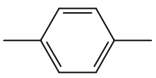
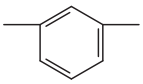
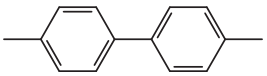
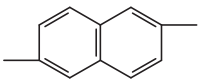
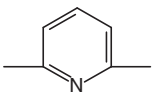
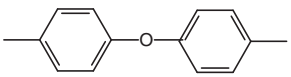
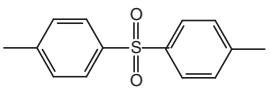
Table 6 Selected properties of poly(*N*-phenyl)benzimidazoles of general formula



–Ar–	$\eta_{red.}$ (0.5% in TCE–phenol (3:1)) (dl g^{-1})	$T_{soft.}$ (°C)	$T_{degr.}$ (5%, air) (°C)	Films tensile strength, σ (MPa)
	9.90	380	450	135
	7.20	370	490	110
	8.40	390	430	120
	5.20	390	480	120
	1.00	330	420	90
	1.20	320	480	95
	1.10	345	430	95

5.21.3.1.3 Poly(1,2-diarylbenzimidazoles)

Poly(1,2-diarylbenzimidazoles) are the products of the interaction of the *o*-substituted diamines of the general formula shown in Scheme 37 with aromatic dicarboxylic acid dichlorides followed by thermal treatment of the polymers thus obtained[293,294] Scheme 38.

Thermal treatment was accompanied by polymer degradation and drop of the mechanical properties of the films therefrom.

5.21.3.2 Polybenzoxazoles

All aromatic PBOs have been known over the past four decades as a class of aromatic heterocyclic polymers that exhibit high thermal stability.[5,6,8–10]

There have been several methods for the preparation of aromatic PBOs: one involves a two-step method starting from bis(*o*-aminophenol)s[295] or their trimethylsilyl-substituted derivatives[296] with aromatic dicarboxylic acid dichlorides with subsequent cyclization of the poly(*o*-hydroxy)amides thus formed. Another is a one-step method from combinations of bis(*o*-aminophenol)s and aromatic diacid diphenyl esters[193] or from aminohydroxybenzonitriles.[297] The high-temperature solution polycyclocondensation of the bis(*o*-aminophenol) monomers with aromatic dicarboxylic acids has also been known with use of PPA,[298] Eaton's reagent,[299] and a mixture of trimethylsilyl polyphosphate and chlorobenzene.[300] High-molecular-weight PBOs were also prepared using reductive polyheterocyclization reaction, including low-temperature solution polycondensation of bis(*o*-nitrophenol)s with aromatic diacid dichlorides followed by reduction of the nitro groups in the macromolecules of poly(*o*-nitro)esters thus formed and subsequent polycyclization of poly(*o*-amino)esters.[228,301,302]

The two-step method for the preparation of PBOs is based on mild interaction of bis(*o*-aminophenol)s with aromatic dicarboxylic acid dichlorides followed by thermal polycyclization of poly(*o*-hydroxy)amides thus formed[193,295,303–315] (Scheme 39).

The most widely used bis(*o*-aminophenol)s are 4,6-diamino-1,3-benzenediol dihydrochloride, 3,3′-diamino-4,4′-dihydroxy-biphenyl, 3,3″-dihydroxybenzidine, 3,3′-diamino-4,4′-dihydroxydiphenyl sulfone, 3,3′-diamino-4,4′-dihydroxydiphenylmethane, 2,2-bis(3-amino-4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane, and 2,2-bis(3-amino-4-hydroxyphenyl)-2-phenyl-1,1,1,3,3,3-hexafluoropropane.

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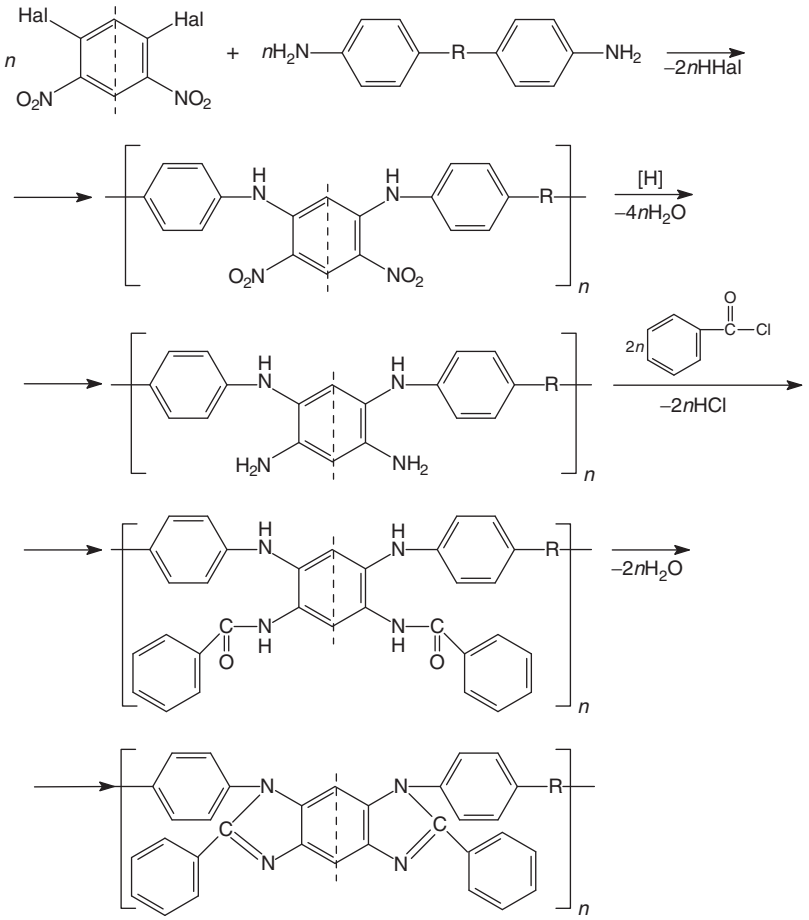
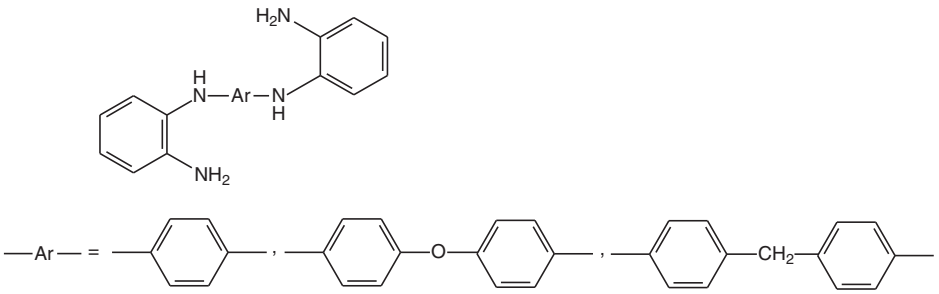


Scheme 36



Scheme 37

PBOs based on bis(*o*-aminophenol)s containing flexibilizing groups demonstrate solubility in organic solvents (Table 7) and, as a result, can be synthesized using high-temperature solution polycyclocondensation in organic solvents using acidic catalysts.

The method of catalytic polycyclodehydration in solution was investigated in more detail by Korshak *et al.* in a cycle of studies of catalytic polycyclodehydration of poly-*o*-hydroxyamides.[227,316–319] The polycyclodehydration process was conducted directly in the reaction solutions of poly-*o*-hydroxyamides[227] using hydrogen chloride – a by-product in the synthesis of poly-*o*-hydroxyamides – as a catalyst of cyclization.

Mikhina *et al.*[318] established that acid catalysts including hydrogen chloride catalyze not only the process of cyclization but also hydrolysis of the *o*-hydroxyamide bonds. The rate constant of the cyclization process is at least 20 times greater than that of hydrolysis; nevertheless, cyclization is accompanied by fall in the molecular weights of the target PBOs. Polymers with an optimal combination of degree of cyclization and molecular weights are obtained with the use of hydrogen chloride in amounts not exceeding 0.125 mol per elementary polymer unit. An excess of hydrogen chloride (on synthesis of poly-*o*-hydroxyamides 2 mol of HCl per elementary polymer unit is released) is neutralized by the α-oxides of the olefins.[227]

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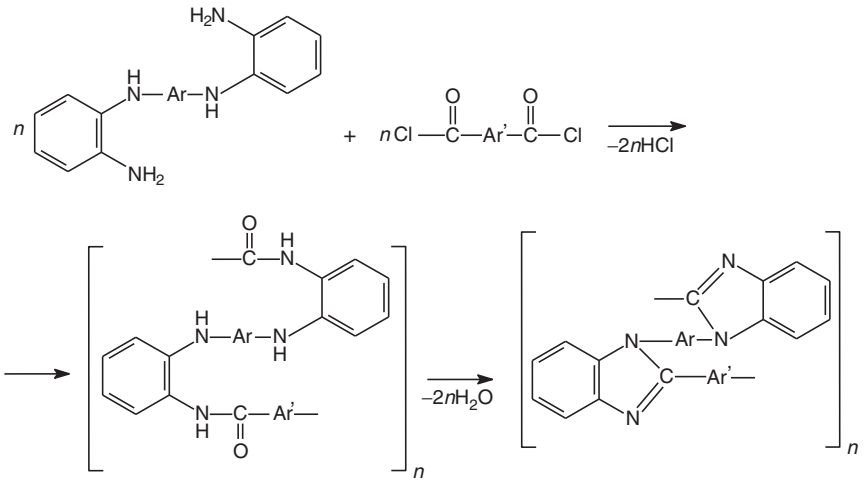
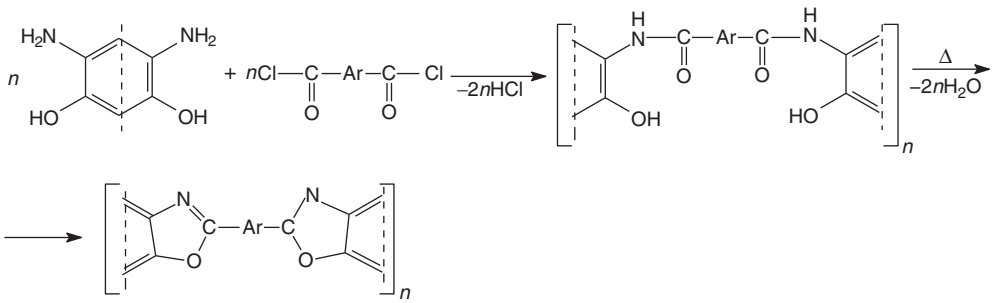


Scheme 38



Scheme 39

When compared with the traditional two-stage method of synthesis of polybenzazoles, catalytic polycyclodehydration in solution has the following advantages: exclusion from the technological cycle of such laborious and energy-consuming stages as dilution of the reaction solution and precipitation, washing, drying, and comminution of the prepolymer; the possibility of synthesizing the PBOs on standard equipment; the mild conditions of conducting catalytic polycyclodehydration make it possible to obtain target polymers with a lower degree of unit heterogeneity, that is, as close as possible to their idealized structures, which improves solubility and the capacity for processing the polymers.[319]

Along with improved solubility in organic solvents, incorporation of flexibilizing group in PBO macromolecules results in decrease of T_g's (Table 7).[320,321]

Certain PBO material properties, such as the dielectric properties, hydrolytic stability, and possibly thermooxidative stability and mechanical properties, would be expected to be equivalent or even superior to existing high-performance aromatic polyimides (APIs).

Despite extensive development of organosoluble PBO, the main attention was paid to rigid-rod PBO and polybenzothiazoles as well as the molecular composites therefrom.

5.21.3.2.1 Rigid-rod polybenzoxazoles and polybenzothiazoles

Poly(benzoazols) (PBAz, see Figures 9 and Figures 10) and in particular poly(benzobisazoles) (PBBAz; see Figures 11) belong to the series of rigid-rod polyheteroarylenes (Figures 9–11).

High-temperature polycyclocondensation of 4,6-diaminodihydroxybenzene[322] and 2,5-diaminobenzene-1,4-dithiol hydrochloride[323,324] with terephthalic acid on PPA is the most popular procedure for the synthesis of the polymers (Figure 11) Scheme 40.

If the synthesis is performed at polymer concentrations that are high enough for the formation of anisotropic solutions, the resulting polymeric solutions can be used directly for the preparation of high-modulus fibers[324] and films.[325]

Because of high oxidizability of the tetrafunctional nucleophilic monomers, these are used in the form of hydrochlorides or other salts rather than as free bases. The process is performed in two steps. In the first step, which is carried out at 60–80 °C, the nucleophilic monomers are subjected to dehydrochlorination; in the second step, terephthalic acid is added and the mixture is slowly heated to 190–200 °C and stirred at this temperature for 8–10 h.

In the course of polycyclocondensation, the content of P_2O_5 in PPA decreases, and its properties as a solvent, catalyst, and cyclodehydrating agent deteriorate. The addition of P_2O_5 to the solutions results in both acceleration of the polycyclodehydration reaction and an increase in the molecular mass of the target polymers.[326,327] In addition to dicarboxylic acids, the respective acid chlorides are also used for the synthesis of poly(benzobisazoles) (PBBAzs) in a PPA medium.[328] Since the glass transition temperatures of PBBAz often exceed their decomposition temperatures,[329] the fibers

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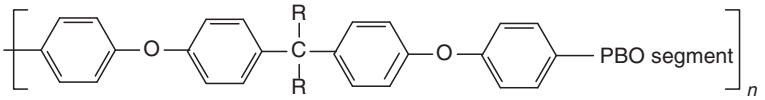
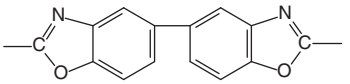
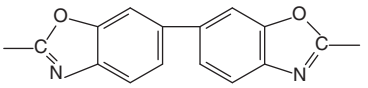
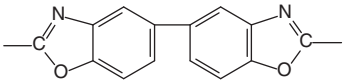
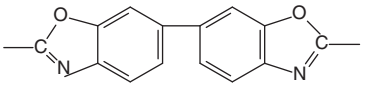
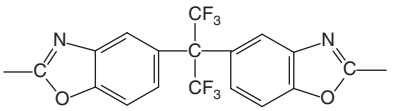
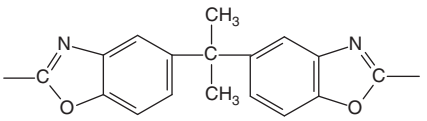
Table 7 Solution and thermal properties of various fluorine-containing PBOs of general formula



–R–	η_{inh} ($dl\,g^{-1}$)	PBO segment	T_g (°C)
—CH_3	Dec. (H_2SO_4)		224
—CF_3	0.53 (DMAc)		231
—CH_3	Dec. (H_2SO_4)		223
—CF_3	1.03 (DMAc)		225
—CH_3	Dec. (H_2SO_4)		218
—CH_3	0.53 (DMAc)		218

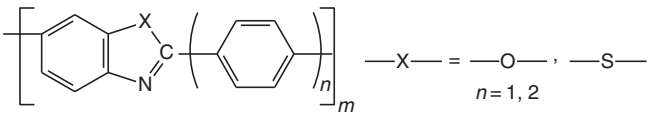


Figure 9 Rigid-rod poly(benzoxazole)s and poly(benzothiazole)s.

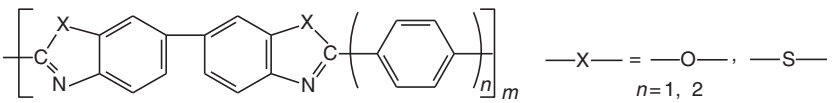


Figure 10 Poly(benzoxazole)s and poly(benzothiazole)s.

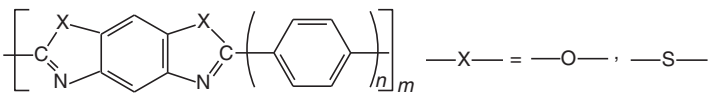


Figure 11 Poly(benzoxazole)s and poly(benzothiazole)s.

and films are usually prepared directly from the solutions of these polymers.

PBBAzs are soluble in strong acids, for example, PPA, methanesulfonic acid, chlorosulfonic acid, 100% H_2SO_4, and Lewis acids (e.g., $BiCl_3$ or $SbCl_3$). Recently,[330] it was shown that poly(benzobisthiazole) (PBBT) forms liquid crystalline solutions in nitromethane-containing $AlCl_3$ or GaC_3. Liquid crystalline solutions of PBBAz yield high-strength and high-modulus films and fibers. Very often, the deformation strength characteristics of PBBAz fibers even surpass those of

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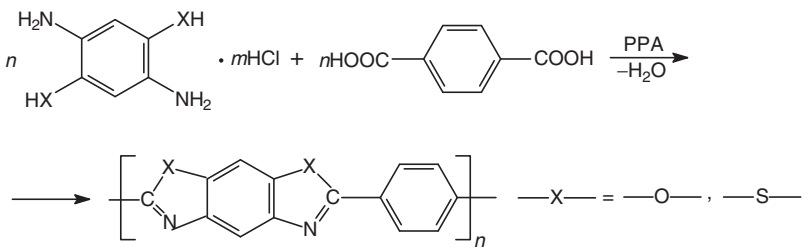


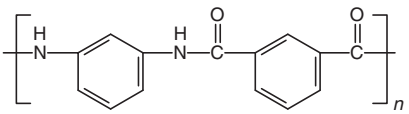
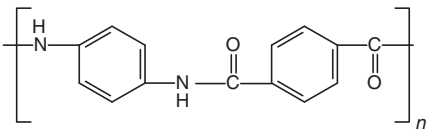
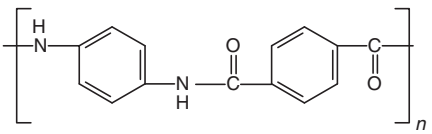
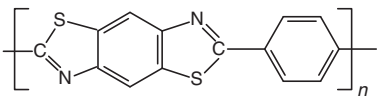
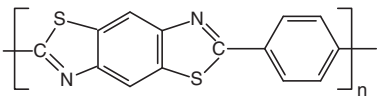
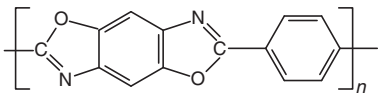
Scheme 40

Kevlar polyamide fibers, which is attributed, in particular, to the greater values of the Kuhn segments in PBBAz (Table 8 and Figure 11).

The films with controlled planar orientation based on PBBT and poly(benzobisoxazole) (PBBO) have specific strengths of 2 GPa and moduli of elasticity of 270 GPa.

PBBAzs are distinguished by extremely high thermal stabilities, namely, under the conditions of a dynamic TGA in air ($\Delta T = 10\,\text{deg min}^{-1}$), they begin to lose weight at temperatures above 600 °C. Under the conditions of an isothermal analysis in circulating air at 371 °C, their thermal characteristics markedly exceed those of poly(*p*-benzamide). PBBT is much more resistant to heating than PBBO (Figure 11, X = –S–; Figure 11, X = –O–).

Table 8 The ultimate rupture strength (σ), the moduli of elasticity (E), the elongation at rupture (ε), and values of the Kuhn segment (A) of fibers based on rigid-rod polymers

Polymer	*Σ (GPa)*	E *GPa*	*ε (%)*	*A (Å)*	*References*
 (Nomex)	0.70	17.3	22	47	236
 (Kevlar 29)	2.64	58.9	4	300	331
 (Kevlar 49)	2.64	127.5	2.4	300	332
 (PBBT 3c)[a]	0.5–2.2	50–76	4.5	1060	332, 333
 (PBBT 3c)[b]	0.8–2.5 (4.2)	76–265 (< 300)	1.0–1.5	1060	334
 (PBBO 3b)[b]	2.8–3.4	467		-	335

[a] Freshly formed.
[b] Heat-treated.

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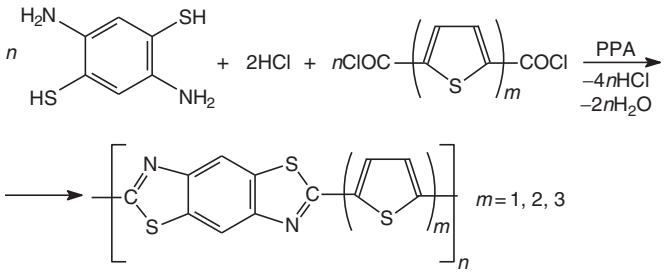


Scheme 41

A significant disadvantage of all PBBAzs is their low compression strength. Modification of the basic chains of their macromolecules and the introduction of bulky substituents into macromolecules were undertaken in order to enhance this parameter, to improve the solubility of PBBAz, and to impart specific properties to these systems.

Thus, the *p*-phenylene residues of terephthalic acid in the basic chains of PBBAz were replaced by thiophene-2-5-diyl,[336–338] fluorene-2,7-diyl,[339] adamantanediyl,[340] bicyclo[2,2,2]octanediyl,[341,342] and 2,2′-bipyridinediyl[343] fragments. In particular, the reaction of the 2,5-diaminobenzene-l,4-dithiol dihydrochloride with thiophene-, bithiophene-, and terthiophenedicarbonyl dichlorides afforded PBBT soluble in methanesulfonic and sulfuric acids[336] (Scheme 41).

A similar approach was used for the synthesis of a thiophene-containing PBBO.[338] Although PBBT and PBBO are characterized by much lower values of the Kuhn segment than those of the analogous polymers based on terephthalic acid, the majority of their solutions in various acids manifest liquid crystalline properties.

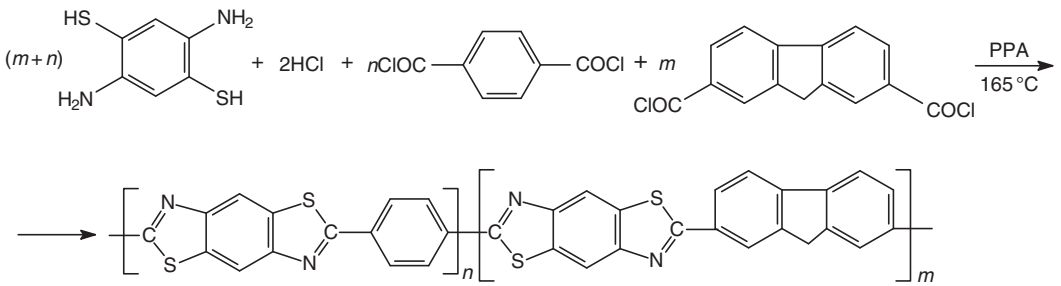
A certain deviation from a strictly straightened chain was also observed in the case of PBBT prepared from the 2,5-diaminobenzene-1,4-dithiol dihydrochloride in PPA after partial substitution of fluorene-2,7-dicarbonyl dichloride for the terephthaloyl dichloride[339] (Scheme 42).

Polycyclocondensation at 165 °C results in the formation of high-molecular-weight polymers that are completely soluble in methanesulfonic and sulfuric acids. At higher temperatures, this reaction is accompanied by the formation of insoluble polymers, which can be due to the five-membered ring opening in the fluorene fragment.

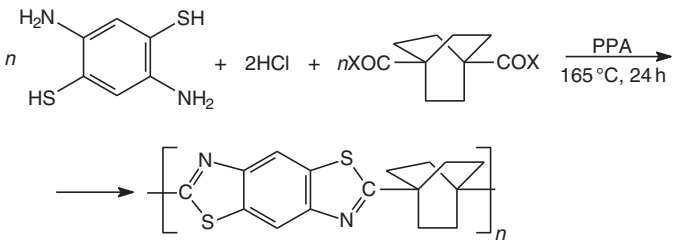
The colorless PBBT was obtained by the reaction of the 2,5-diaminobenzene-1,4-dithiol dihydrochloride with bicyclo [2,2,2]octane-1.4-dicarboxylic acid, its dimethyl ester, or the dichloride in PPA (Scheme 43).[341,342]

The resulting polymer is soluble in methanesulfonic and sulfuric acids. In terms of thermal stability, the rupture strength, and modulus of elasticity, the polymer ranks below PBBT based on terephthalic acid but considerably surpasses it in compression strength.

PBBOs and PBBTs containing 2,2′-bipyridinediyl residues were obtained by the reaction of 2,2′-bipyridine-4,4′-dicarboxylic acid or 2,2′-bipyridine-5,5′-dicarboxylic acid with various mononuclear diaminodiols and diaminodithiols (Scheme 44).[344]



Scheme 42



Scheme 43

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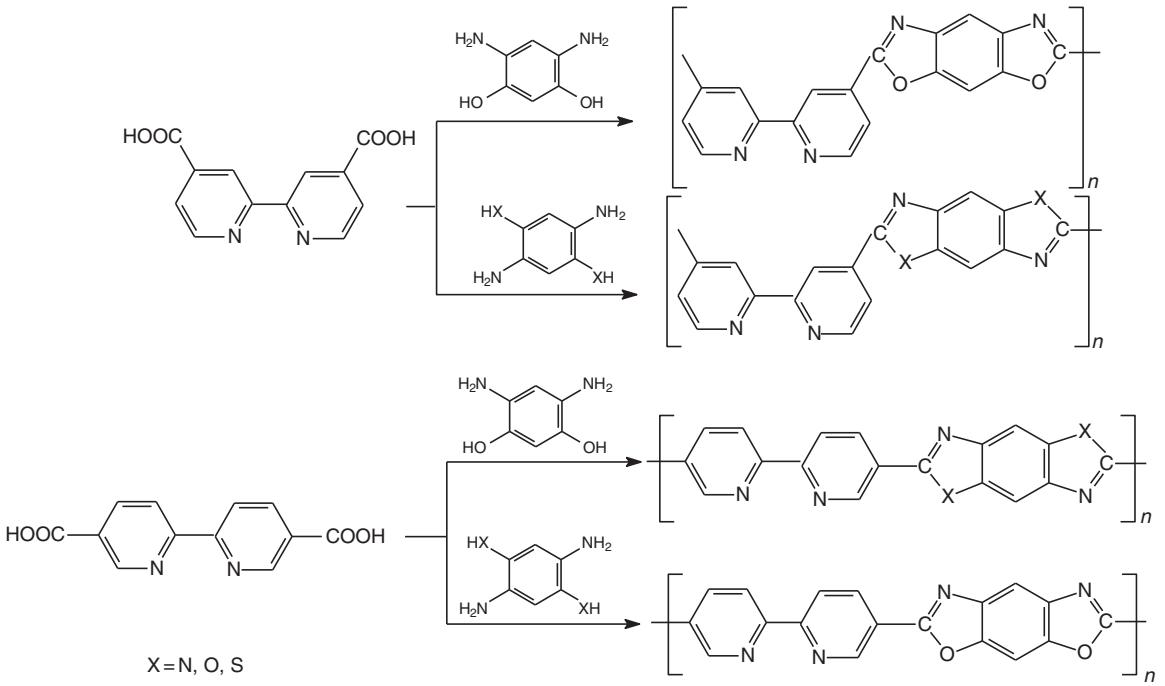


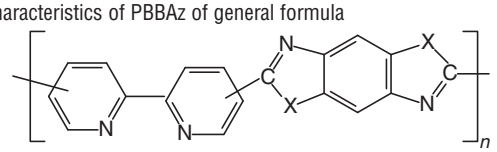
Scheme 44

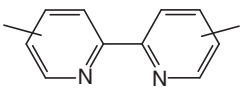
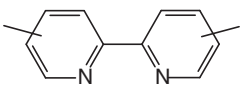
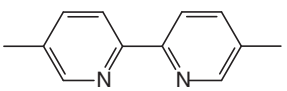
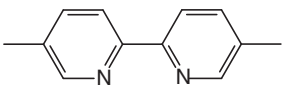
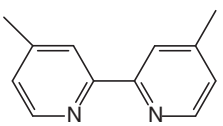
The 4,4′-substituted PBBAzs are soluble in methanesulfonic, sulfuric, trifluoroacetic, and formic acids as well as in a mixture of nitromethane with $AlCl_3$. They form strong films. The 5,5′-substituted polybenzazoles are soluble only in methanesulfonic acid and in a mixture of nitromethane with $AlCl_3$. The solutions of PBBAz form lyotropic mesophases in methanesulfonic acid.

The PBBAzs manifest extremely high thermal stabilities in inert media and in air (Table 9).

Much attention has been given to the synthesis of PBBAz with bulky substituents in the carbocyclic fragments of the macromolecules. Such structures are usually synthesized by polycyclocondensation of dicarboxylic acids or their derivatives containing the corresponding substituents.

Table 9 Some characteristics of PBBAz of general formula



	–X–	η_{inh} ($dl\,g^{-1}$) ($MeSO_3H$)	$T_{degr.}$ (air) (°C) In air	In N_2	Yield (%)
	–O–	3.1	591	668	82
	–S–	3.7	537	585	83
	–O–	1.7	586	648	86
	–S–	2.1	569	597	87

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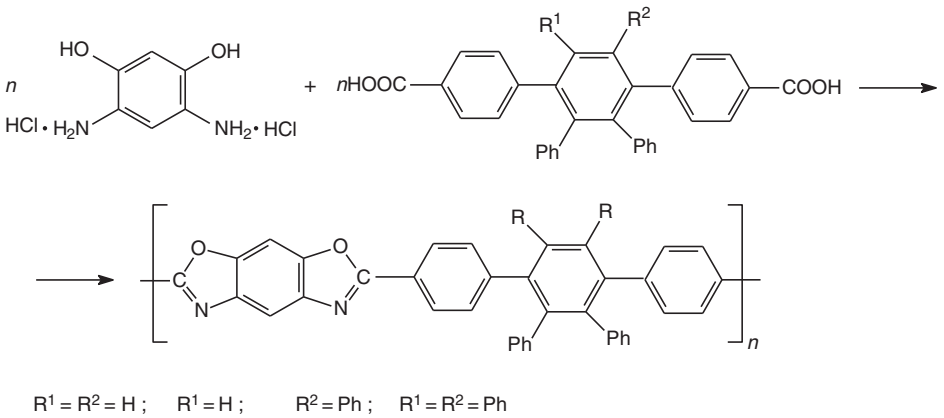


Scheme 45

Wolfe and Arnold[322] were among the first to have synthesized PBBO based on di-, tri-, and tetraphenyl-*p*-terphenyl dicarboxylic acids Scheme 45.

The solubility of the phenyl-substituted polymers exceeds markedly that of the unsubstituted PBBO. In addition to methanesulfonic and chlorosulfonic acids, they are soluble in benzenesulfonic acid and a 7:3 mixture of *m*-cresol with dichloroacetic acid as well as in a 9:1 mixture of dichloroacetic acid with methanesulfonic acid.

An analysis of the thermal stabilities of the substituted PBBO containing a triphenyl-substituted central fragment revealed that the latter is more resistant to isothermal aging at 316 °C than PBBO, but is decomposed more rapidly at 371 °C due to the splitting of the phenyl groups.

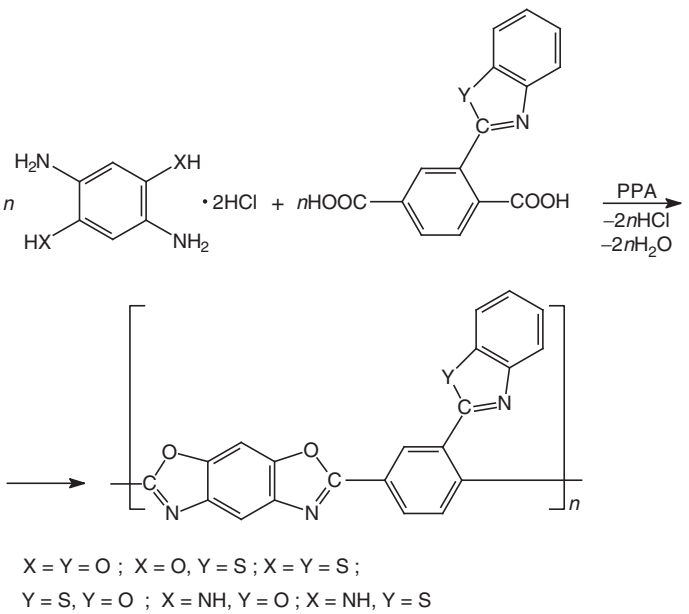
The PBBO and PBBT containing benzooxazol-2-yl or benzothiazol-2-yl substituents in the phenyl fragment were obtained using the corresponding substituted terephthalic acids[345,346] (Scheme 46).

The PBBAzs thus formed were soluble in sulfuric and methanesulfonic acids; the specific viscosities of their solutions in methanesulfonic acid varied from 4 to 19 dl g^{-1}. The anisotropic polymeric solutions (10%, w/w) were used to obtain fibers. The fibers from PBBT manifested the most valuable properties, namely, stability of 2.4 GPa and specific modulus of elasticity of 172–207 GPa. Their compression strengths (380 MPa) exceed that of the unsubstituted PBBT.

2,5-Di(benzothiazolyl)terephthalic acid was used together with 2-benzoazolylterephthalic acids in the synthesis of PBBAz[346] (Scheme 47).

Dicarboxylic acids were used as acid components in the synthesis of PBBO in order to achieve an even greater disturbance of the close packing of PBBAz and to increase the compression strength[347,348] (Scheme 48).

It should be noted that high-molecular-weight PBBAz a–d were obtained only in those case where polycyclocondensation was carried out at very low concentrations of the



Scheme 46

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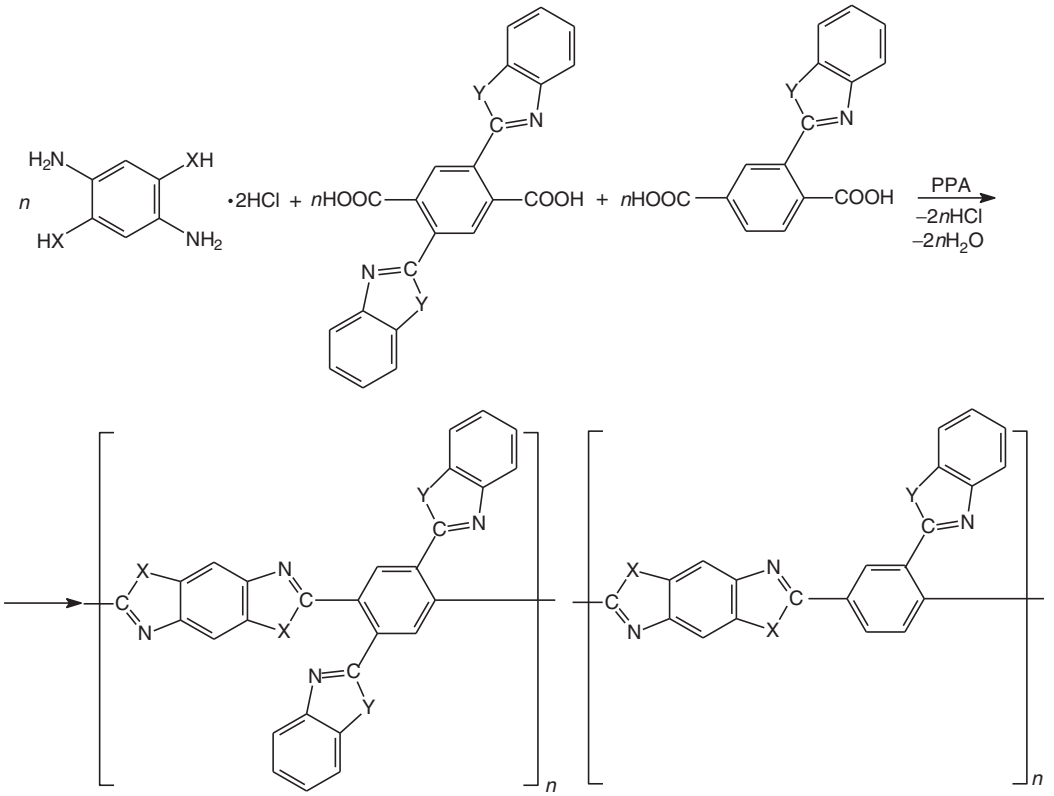


Scheme 47

monomers in PPA (< 1%), whereas with an increase in their concentration to 10% only low-molecular-weight oligomers could be isolated from their solutions (Scheme 48).[347]

The PBBAz a–d are soluble in sulfuric, methanesulfonic, and trifluoromethanesulfonic acids. The intrinsic viscosities, [η], of the polymers a–d measured in methanesulfonic acid at 30 °C were equal to 12.0, 7.7, 11.4, and 8.7 dl g^{-1}, respectively.

The presence of extended side groups in the PBBAz synthesized prevents the straightening of the basic chains of the macromolecules and the formation of anisotropic solutions, as a result of which the attempt to prepare high-quality fibers based on them failed.

The introduction of insignificant amounts (1–2 mol.%) of benzothiozolylphenyl-substituted *p*-terphenyldicarboxylic acid as a comonomer to terephthalic acid results in the copolymer[348] (Scheme 49).

The polycyclocondensation at concentrations of 10% (w/w) yielded copolymers with intrinsic viscosities of 20–28 dl g^{-1}. The fibers prepared from the copolymers manifested a specific strength of 2.5 GPa, a modulus of elasticity of 193–283 GPa, and compression strengths of 344–482 MPa.

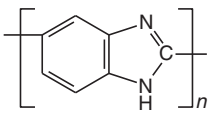
The PBBAzs with aryloxide and arylthio substituents were obtained by the reactions of 4,6-diaminoresorcinol, 2,5-diaminohydroquinone, 4,6-diaminobenzene-1,3-dithiol, and 2,5-diaminobenzene-l,4-dithiol hydrochlorides with 4,8-diaryloxy(arylthio)naphthalene-2,6-dicarboxylic acids in PPA[349] (Scheme 50).

5.21.4 Molecular Composites Based on Rigid-Rod Polybenzazoles

The term molecular composites is usually applied to describe systems that consist of rigid-rod molecules dispersed in matrices of flexible-rod molecules at the molecular level; in this case, rigid-rod molecules play the role of reinforcing elements.

Molecular composites can be prepared both by mixing rigid- and flexible-rod polymers at the molecular level and by synthesizing block and graft copolymers containing rigid- and flexible-rod fragments.

Among the first molecular composites were those based on PBBT as a rigid-rod component and polybenzoimidazole (ABPBI) as a flexible-rod component.[350,351]



ABPBI was obtained by homocondensation of 3,4-diaminobenzoic acid in PPA.[352,353]

Mixtures of these polymers at the molecular level were prepared from solutions with concentrations below those required for precipitation.[351] The mechanical properties of PBBT–ABPBI molecular composites (both as fibers and as films) are listed in Table 10.

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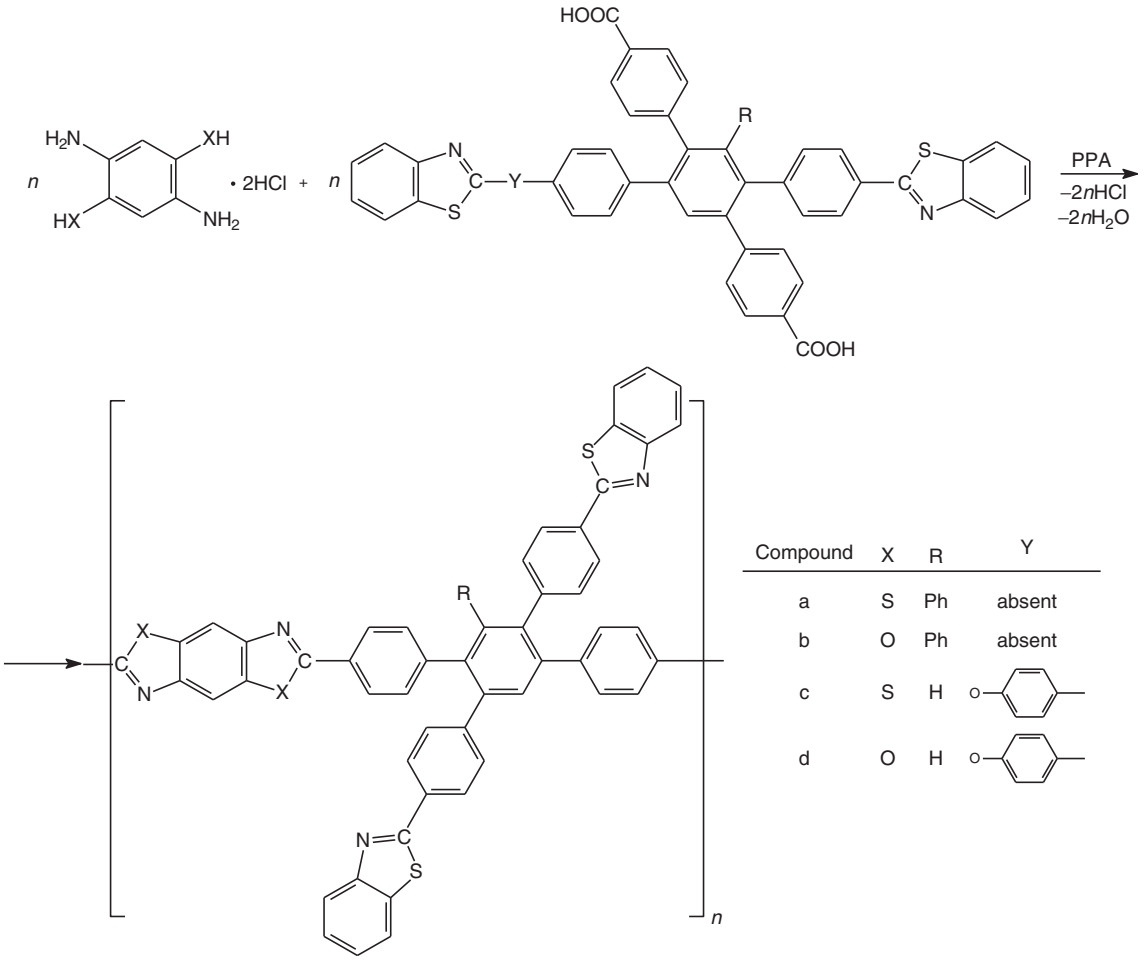
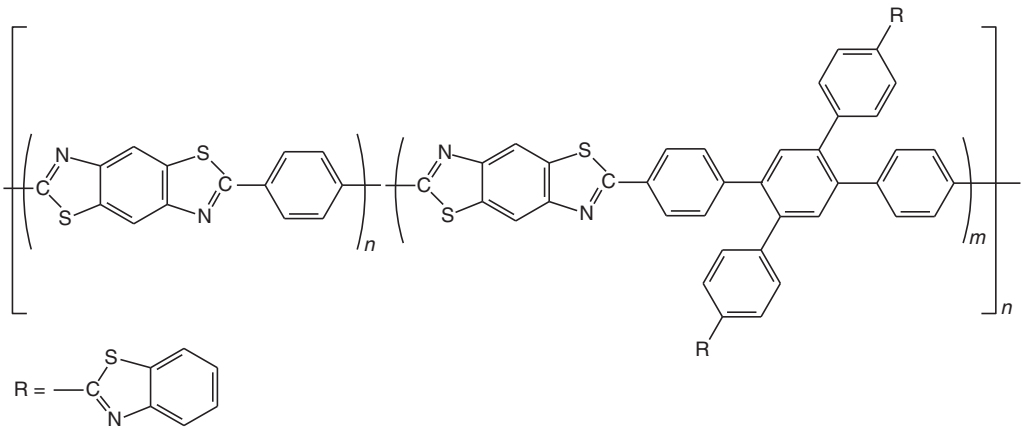


Scheme 48



Scheme 49

As can be seen from Table 10, the introduction of 30% PBBT into the matrices of ABPBI enhances significantly the deformation strength characteristics of the material. The results of morphological studies of these mixtures, namely, low- and wide-angle X-ray scattering, optical microscopy, and scanning electron microscopy, suggest the absence of phase separation.[350]

The processability of molecular composites could be improved using thermoplastic polymers, for example, amorphous and partially crystalline polyamides,[357,358] polyphenylquinoxalines,[359] and poly(ether ether ketones),[360] as flexible-rod matrices. The mechanical characteristics of the molecular composites based on thermoplastic polymers and PBBT are listed in Table 11.

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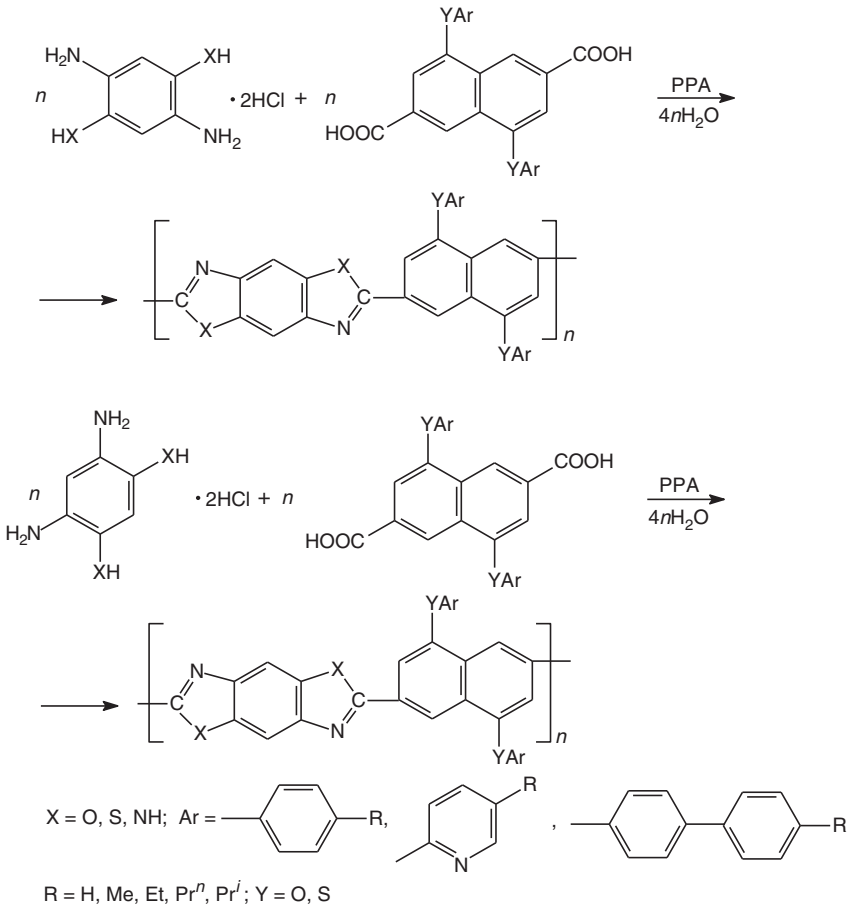

Scheme 50

Table 10 Mechanical characteristics of fibers and films based on the PBBT–ABPBI molecular composites

Composition	*Product*	*E (GPa)*	*σ (MPa)*	*ε (%)*	*References*
PBBT	Fiber	300	3000	1.1	354
ABPBI[a]	Fiber	16.8	675	29	350
ABPBI[b]	Fiber	36.0	1110	5.2	354
PBBT–ABPBI (30:70)[a]	Fiber	16.8	1161	7.2	350
c	Fiber	71.7	1215	2.5	350
d	Fiber	109.7	1283	1.8	355
PBBT–ABPBI (30:70)[a]	Film	30.4	690	55	355
e	Film	88.2	918	2.4	356

[a] Freshly formed.
[b] Heat-treated.
[c] Heat-treated at 427 °C.
[d] Heat-treated at 525 °C.
[e] Heat-treated at 540 °C.

Thus the mechanical properties of the PBBT–nylon system exceed those of a monoaxially oriented fibrous composite of identical composition by 50–300%.

In addition to the construction of composites at the molecular level, the design of molecular composites by the synthesis of block and graft copolymers has become a very popular approach.

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Table 11 Mechanical characteristics of molecular composites based on PBBT and thermoplastic polymers

Thermoplastics	*Composition (w/w)*	*Product*	*E (GPa)*	*σ (MPa)*	*References*
Polyphenylquinoxaline	30:70	Fiber	17.5	355	359
Nylon	30:70	Fiber	36.0	345	359
Poly(ether ether ketone)	50:50	Film	11.0	248	360
		Block	15.8	105	360
Nylon-6,6	50:50	Block	20.8	183	358

Whereas in the molecular composites prepared by mechanical mixing of flexible- and rigid-rod components the reinforcing macromolecules are bound to the matrices exclusively due to physical interactions, in block copolymer-based molecular composites the flexible- and rigid-rod fragments are linked by covalent bonds. As a result, the transfer of strains from the rigid-rod fragments to the flexible-rod matrices occurs more effectively; hence, the block copolymer-based molecular composites manifest higher deformation strengths and dimensional stabilities.

The block copolymers of the ABA type[361] which contain rigid-rod blocks B and flexible-rod blocks A[361] were synthesized as model systems. Macromolecules of PBBT with carboxy-terminal groups ($[\eta] = 10–24\ \mathrm{dl\,g^{-1}}$) used as rigid-rod blocks were introduced into copolycondensation with 3,4-diaminobenzoic acid hydrochloride, which resulted in the formation of benzoimidazole rings and simultaneous binding of the individual blocks (**Scheme 51**).

The compositions of the blocks were varied by changing the content of 3,4-diaminobenzoic acid used for copolycondensation. As can be seen from **Table 12**, the moduli of elasticity of the block-copolymeric molecular composites are comparable with those of the dynamic mixtures; their magnitudes depend on the ratios of the rigid- and flexible-rod components. The values of the moduli suggest that the reinforcement does not necessarily require highly extended macromolecules of PBBT. Comparison of the breaking strengths (see **Table 12**) points to a much higher (up to 33%) deformation strength of the block-copolymeric molecular composites compared with the materials prepared from mechanical mixtures.

The polybenzobisthiazoles carrying terminal carboxy groups were introduced into the Friedel–Crafts polycondensation reaction with *m*-phenoxybenzoic acid in a P_2O_5–$MeSO_3H$ mixture.[362] This reaction yielded block copolymers of the ABA type which contained flexible-rod polyether ketone blocks and rigid-rod PBBT blocks.

Table 12 Some characteristics of the block copolymers and mixed molecular composites[361]

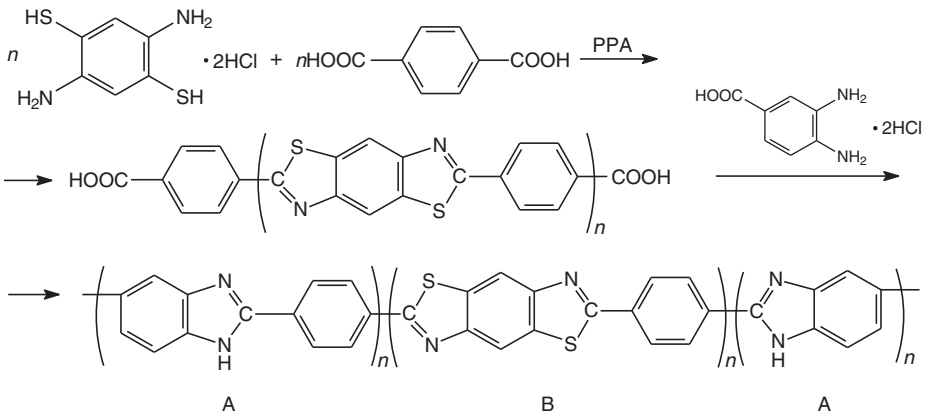
Ratios	*[η] (dl g⁻¹) PBBT*	*[η] (dl g⁻¹) Copolymer*	*E (GPa)*	*σ (MPa)*	*ε (%)*
30:70	10.7	8.5	102.7	1696	2.3
25:75	12.9	10.7	94.5	1566	2.5
30:70	17.7	7.3	115.8	1600	1.4
30:70	*a*	*b*	116.5	1268	1.4

[a] The PBBT:ABPBI ratios for the polymer.
[b] A physical mixture comprising 30% (w/w) PBBT ($[\eta] = 31\ \mathrm{dl\,g^{-1}}$) and 70% (w/w) ABPBI ($[\eta] = 31\ \mathrm{dl\,g^{-1}}$).

In addition to block-copolymeric molecular composites, much attention has been given to the synthesis of molecular composites based on graft copolymers containing rigid- and flexible-rod macromolecules. In particular, benzothiazol-2-yl-substituted PBBI was metallated using NaH in DMSO with subsequent treatment with acrylamide[363] or with propylene oxide[363–365] (**Scheme 52**).

The grafted copolymer is soluble in methanesulfonic, 97% formic, and trifluoroacetic acids much more easily than PBBI.

Although the softening of these polymers could not be detected by differential scanning calorimetry, their solid melts could be obtained by compaction at 190–232 °C. The introduction of polypropylene oxide side chains is accompanied by



Scheme 51

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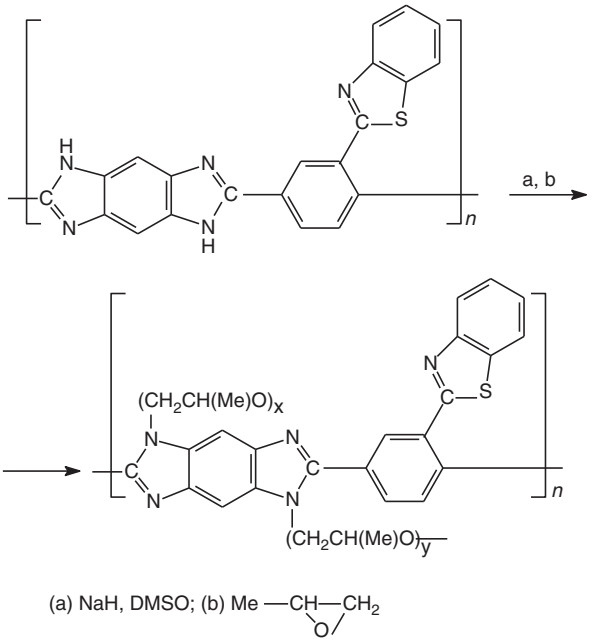


Scheme 52

a significant decrease in their thermal stabilities in comparison with that of the starting compound, namely, poly(benzobisimidazole) (PBBI).

Of special interest is the synthesis of molecular composites based on grafted copolymers with heat-resistant side chains. Since rigid-rod PBBAzs are soluble only in acidic solvents, the set of reactions used for the grafting is rather limited. Evers and co-workers[355,366] used the Friedel–Crafts reaction of *m*-phenoxybenzoic acid with PBBT in $MeSO_3H$–P_2O_5 (10:1, w/w) for the synthesis of grafted copolymers of the AB type. Thus the reaction of the polybenzobisthiazole copolymer containing 4,4′-(*o*-diphenoxyphenylene) groups, which are distributed statistically among the fragments of the rigid-rod PBBT, with *m*-phenoxybenzoic acid afforded the copolymer[367] (**Scheme 53**).

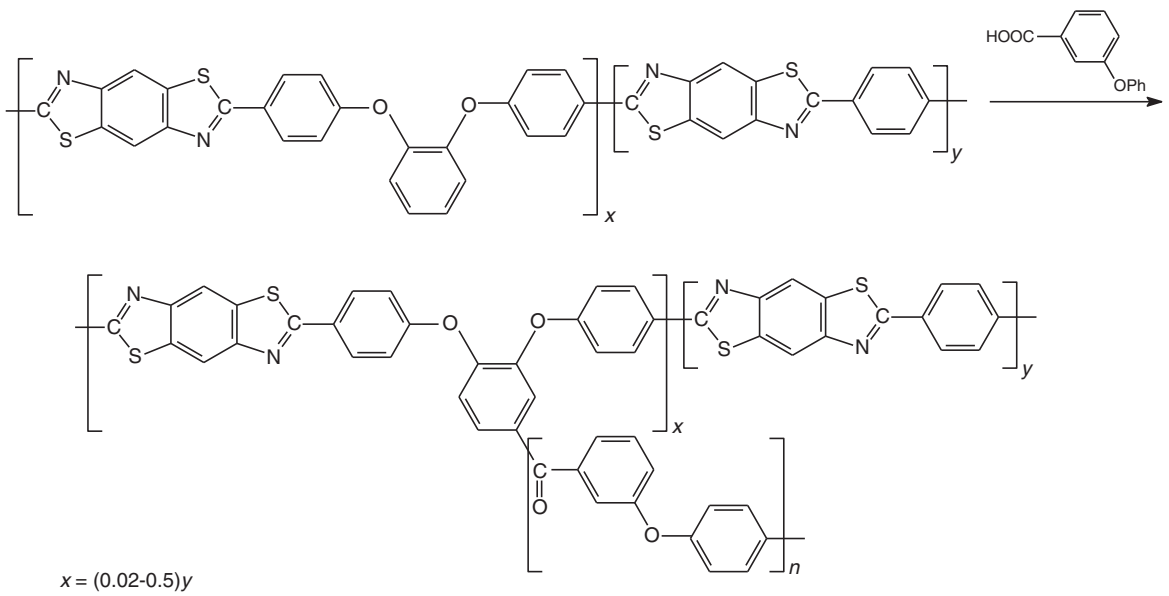
Compaction at high temperatures and pressures (285 °C, 6.9 MPa) is employed for the preparation of bulk products possessing isotropic properties. The main disadvantage of this approach is the low elasticity of the grafted fragments.

An alternative approach is based on the use of polybenzobisthiazole copolymers containing 2,6-dimethylphenoxide side groups as the basic macromolecular chains.[367,368] Treatment of these systems with *m*-phenoxy benzoic acid in P_2O_5–$MeSO_3H$ was accompanied by the formation of the grafted copolymers (**Scheme 54**).

According to the dynamic mechanical analysis data, the softening of the grafted copolymers occurs at 180–265 °C depending on the value of γ.[369] Their secondary processing into bulk products is carried out at pressures up to 40 MPa and at temperatures which are 40–50 °C higher than the softening temperature. A specimen containing 46% (w/w) of PBBT and 54% (w/w) of the copolymer manifests a rupture strength of 40 MPa and a modulus of elasticity of 9.7 GPa.

Rigid-rod PBBAzs are the most promising materials in those fields where small weight, high deformation strength, rigidity, thermal and chemical stability as well as radio transparency are the critical factors. The latter property is especially important, and in this respect PBBAz fibers have an indisputable advantage over graphite fibers. PBBAz fibers manifest greater elongation at rupture in comparison with graphite fibers and possess higher thermal and thermooxidative stabilities in comparison with Kevlar fibers. This altogether demonstrates their usefulness for aeronautical, aerospace, and electronic engineering. Yet another field of application in which PBBAzs have obvious advantages over glass, Kevlar fibers, and coal plastics is thermostable membranes and filters. Further progress in this area will largely depend on the cost of the monomers and the 'cost–property' ratios of these systems.

The main drawback of the materials based on PBBAz is their low compression stability. In recent years, increasing attention



Scheme 53

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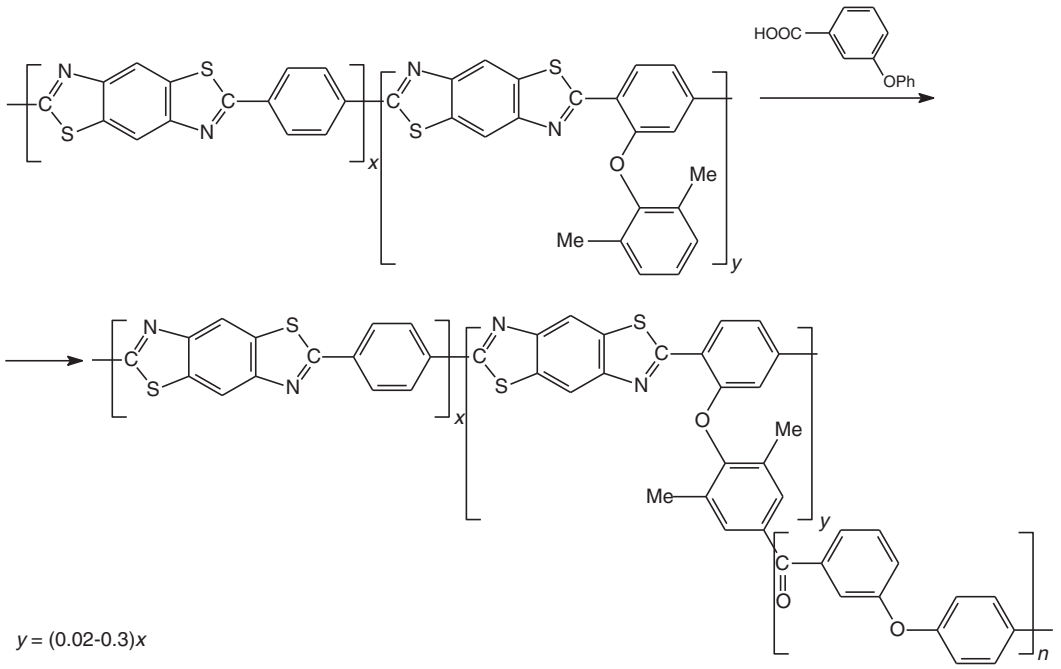

Scheme 54

has been given to the construction of PBBAz that can be cross-linked to form three-dimensional structures.[370–372] Further developments in this field will obviously be aimed at the construction of systems whose solidification is not accompanied by the evolution of volatile by-products.

5.21.5 Aromatic Polyimides

The development of the chemistry of APIs[28–32] led to the formation of a large number of polyheteroarylenes exhibiting significantly different properties. One of the most important factors influencing the properties of API is the rigidity of their macromolecules. In terms of this feature, the API may be divided into two principal groups: flexible-chain and rigid-chain polyimides.

The development of the flexible-chain polyimides was stimulated by the need to obtain easily processed polyimides soluble in the usual organic solvents and having wide gaps between the glass transition and decomposition temperatures.[36–38] The development of the chemistry of the rigid-chain polymers was in turn determined by the need to create very strong and high-modulus materials.[373,374]

The molecular designs of the flexible- and rigid-chain polyimides are different. The flexible-chain API contains in the main chain asymmetric phenylene (*m*-phenylene) rings and groups that increase the flexibility of the chain (ether, thioether, isopropylidene, hexafluoroisopropylidene, etc.),[36–38] whereas in the rigid-chain API the macromolecular chains are extended to the maximum extent and contain predominantly symmetrical *p*-phenylene fragments and heterocycles without any groups that increase the flexibility of the chains.[375]

5.21.5.1 Flexible-Chain Aromatic Polyimides

The most important flexible-chain APIs are polyimides with ether groups in the main chain, the so-called polyetherimides (PEIs). A wide range of PEIs have been obtained as a result of the interaction of various aromatic diamines containing ether groups and the dianhydrides of aromatic tetracarboxylic acids without the same groups in accordance with **Scheme 55**.

The values of the Kuhn segment (A_f/A), calculated and determined experimentally,[376,377] for certain PEIs based on the dianhydride of oxybis(benzene-3,3′,4,4′-dicarboxylic) acid and the properties of these PEIs are presented in **Table 13**.

The use of diamines with *p*-phenylene fragments and of dianhydrides containing only one ether group led to PEIs with a 30–37 Å Kuhn segment and a glass transition temperature of 255–290 °C. When the 'dianhydride A' was used instead of oxybis(benzene-3,3′,4,4′-dicarboxylic) acid, PEIs with a 26–32 Å Kuhn segment and a glass transition temperature of 175–215 °C were synthesized.

In order to obtain PEIs with a smaller Kuhn segment and lower glass transition temperatures, it appeared useful to introduce the largest possible number of ether groups into the macromolecule, which increases the flexibility of the chain, as well as *m*-phenylene fragments. A large group of bis(phthalic anhydrides), containing at least two ether groups – bis(etherphthalic anhydrides) (BEPAs) – were synthesized. The dianhydrides were obtained by the aromatic nucleophilic nitro-displacement reaction between bisphenoxides and nitrophthalimides or nitrophthalonitriles (**Scheme 56**).[36–38,378–383]

The reactions of the BEPA with aromatic diamines (*m*-phenylenediamine, bis(4-aminophenyl)ether, bis(4-aminophenyl)methane, etc.) were carried out in accordance with **Scheme 57**.[384–396]

The PEIs were synthesized in the melt,[384–388] in amide solvents (high-temperature polycondensation),[389,390] or in nonpolar organic[384,385,391,392] and phenolic[393–396] solvents.

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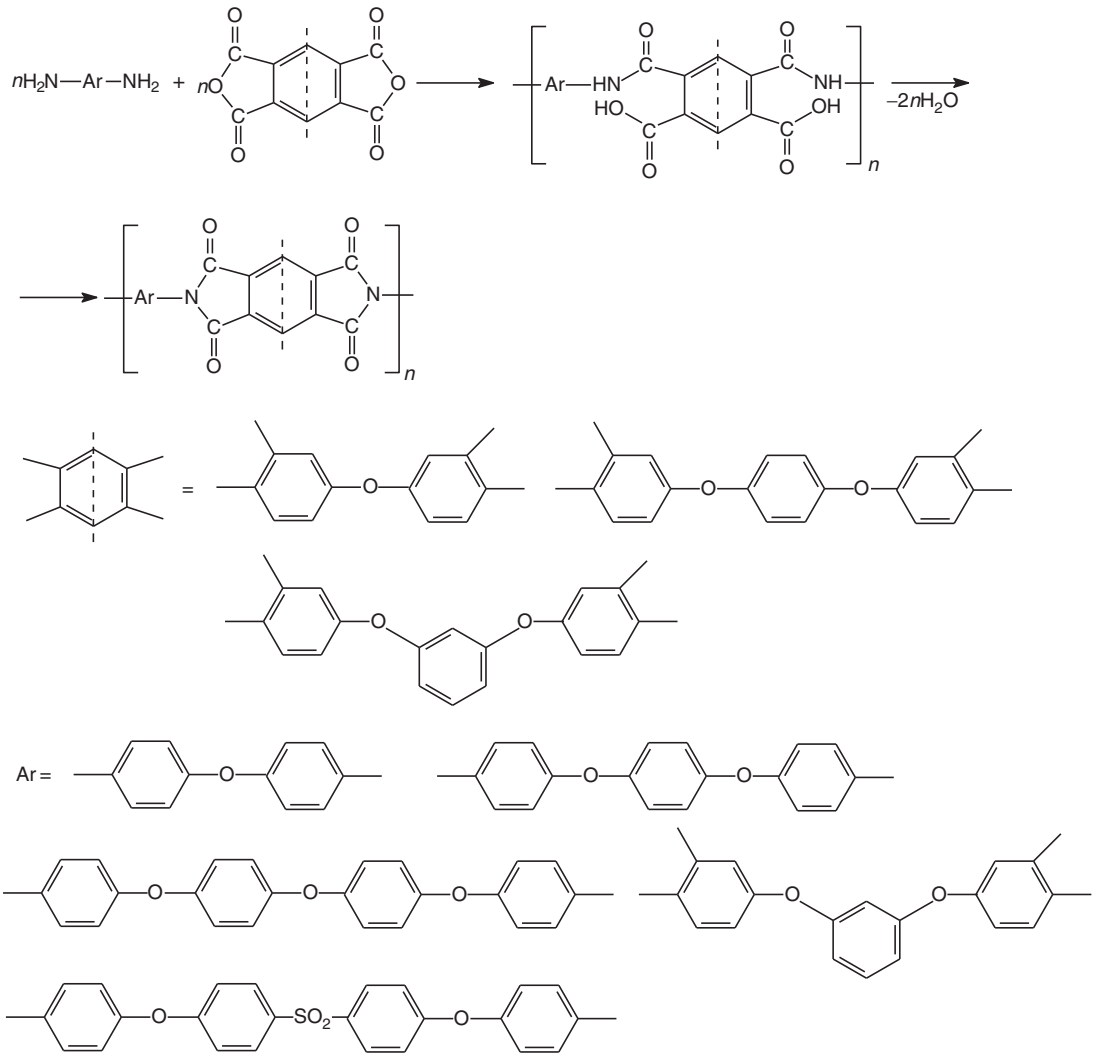
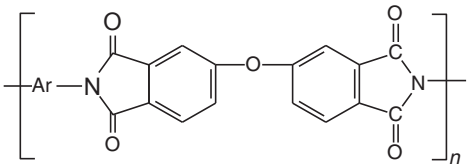
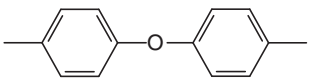
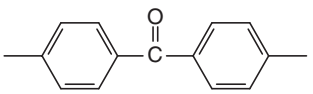
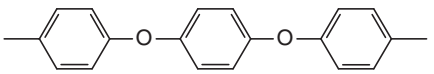


Scheme 55

Table 13 The properties of polyimides based on the dianhydride of oxybis(benzene-3,3′,4,4′-dicarboxylic) acid[376,377]



–Ar–	T_g (°C)	$T_{10\%}$ (°C)	Properties of films: E (GPa)	σ (MPa)	ε (%)	A_f (Å)
	270	450–500	3.2	160–200	50–100	36.4
	290	445	3.1	141	16	36.3
	255	460	2.7–3.2	140–170	50–75	29.9

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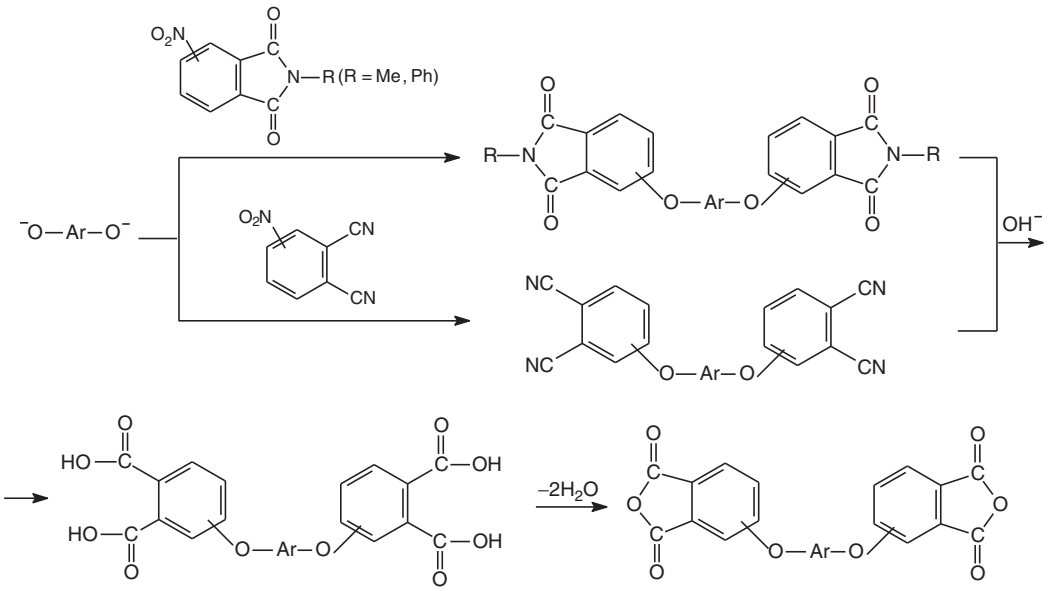
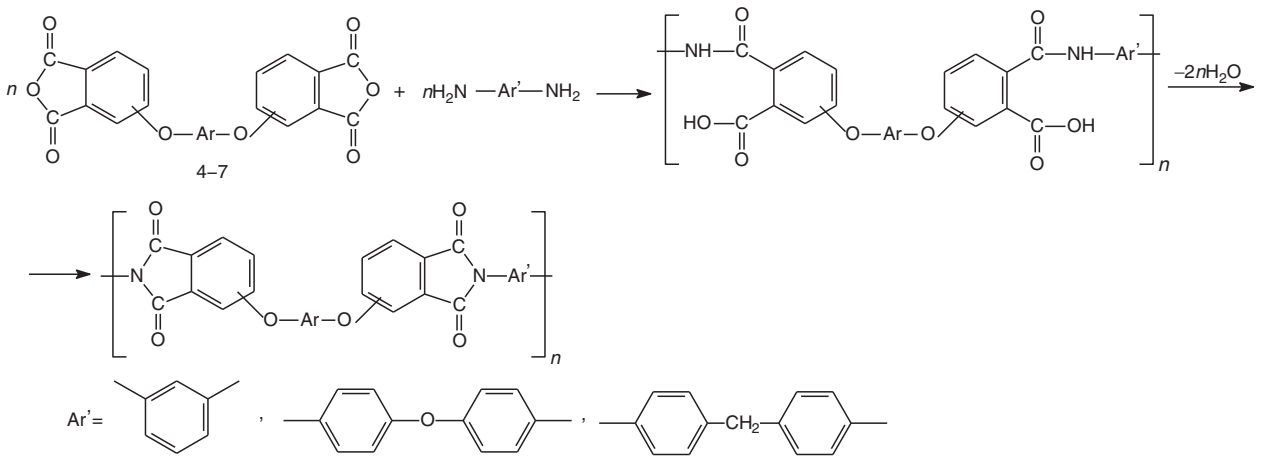


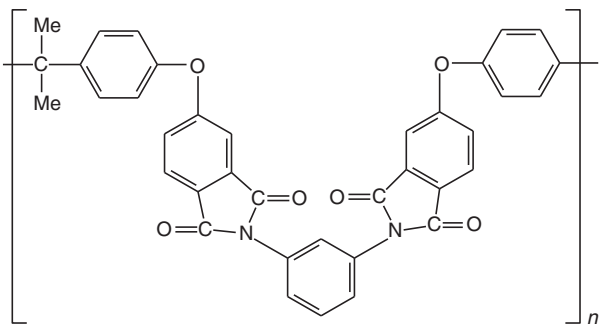
Scheme 56



Scheme 57

Particular attention was focused on the polymers obtained on the basis of the cheap and readily available *m*-phenylenediamine.

Among the PEIs, the polymer synthesized from the 'dianhydride A' is the most important and is most readily available.



This polymer, containing *m*-phenylene ring, ether, and iso-propylidene groups in the main chain, is extremely flexible – its Kuhn segment is 19 Å long.[397] It was selected as the starting material for the preparation of the ULTEM plastic, which is produced by the General Electric Company.[36] Certain properties of ULTEM are listed in Table 14.

Another approach to the synthesis of flexible-chain readily processable PEI is based on the use of aromatic diamines containing several ether groups and *m*-phenylene fragments in the structure of the molecule. A large group of these diamines have been obtained by the interaction of various bisphenoxides with unsubstituted and substituted *m*-dinitrobenzenes[398–419] by the aromatic nucleophilic nitro-displacement reaction (Scheme 58).

As a rule, the aromatic nucleophilic nitro-displacement reaction takes place readily, provided that the activating groups are located in the ortho- and para-positions relative to the nitro group, but in certain cases meta-substituted dinitro compounds can also be involved in the reaction.[29]

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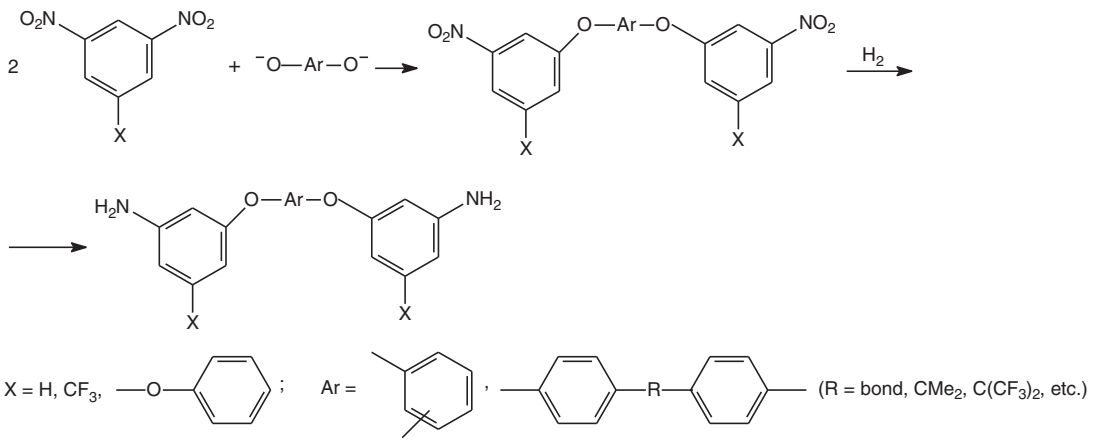
Table 14 The properties of the ULTEM polyimide[36]

Mechanical properties		*Thermal properties*	
Tensile strength at yield (yield point)	105 MPa	Glass transition temperature	217 °C
Tensile modulus	3000 MPa	Heat deflection temperature	
		1.85 MPa	200 °C
		0.46 MPa	210 °C
Tensile elongation, ultimate	60–80%	Limited oxygen index	47
Flexural strength	45 MPa	Burn bending UL 94 v-O at (vertical)	0.64 mm
Flexural modulus	3300 MPa	Smoke evolution according to the NBS method	
		D_s after 4 min	0.7
		D_{max} after 20 min	30
Compressive strength	140 MPa		
Compressive modulus	2900 MPa		
Gardner impact strength	36 Nm		
Izod impact strength			
Notched	50 J m^{-1}		
Unnotched	1300 J m^{-1}		



Scheme 58

Numerous studies[398–411] have been devoted to the preparation of diamines from *m*-dinitrobenzene. Among them, products with the isopropylidene and hexafluoroisopropylidene 'bridging' groups are of greatest interest. The PEIs involving these diamines have been synthesized in accordance with Scheme 59.

The reactions were carried out in NMP at room temperature; the intermediate poly(*o*-carboxy)amides were cyclized directly in the reaction solution using as the catalyst either a 1:1 pyridine–acetic anhydride mixture or orthophosphoric acid or adding compounds that form azeotropic mixtures with the water evolved during cyclization. All the reactions took place under homogeneous conditions. Under the conditions of catalysis by orthophosphoric acid or without the use of any catalyst, high-molecular-mass PEIs with a high degree of cyclization were obtained as a rule.

The polyimides obtained are readily soluble in organic solvents – NMP, *m*-cresol, methylene chloride, chloroform, and so on. The ready solubility of the polymers is determined by their structure and method of synthesis. The polymers synthesized under mild conditions are known to be more soluble than the polymers obtained at high temperatures.[420] Thus the polyimides, obtained in accordance with Scheme 59, are readily soluble in NMP and DMAc, while the polyimides based on 2,2-[bis(*p*-aminophenoxy)phenylene]propane,[421] obtained using solid-phase high-temperature cyclization of polyamidoacids, are insoluble in these solvents. The polyimides based on diamines with trifluoromethyl groups in the benzene ring are even more soluble.[413,414] The corresponding diamines were obtained in accordance with Scheme 58; 3,5-dinitro-*l*-trifluoromethylbenzene and various bisphenoxides were used as the starting compounds.[412–414] Attention has been concentrated on the diamine with the isopropylidene bridging group.

The polyimides were synthesized from this diamine and the dianhydrides of the simplest dinuclear tetracarboxylic aromatic acids in NMP without a catalyst in accordance with Scheme 59.[414] The polyimides have low glass transition temperatures (180–210 °C) combined with high decomposition temperatures. The polymers are soluble not only in amide, phenolic, and chlorinated solvents but also in cyclohexanone and butyrolactone.

3,5-Dinitrodiphenyl ether can also be used to obtain the diamines. The interaction of the ether with various

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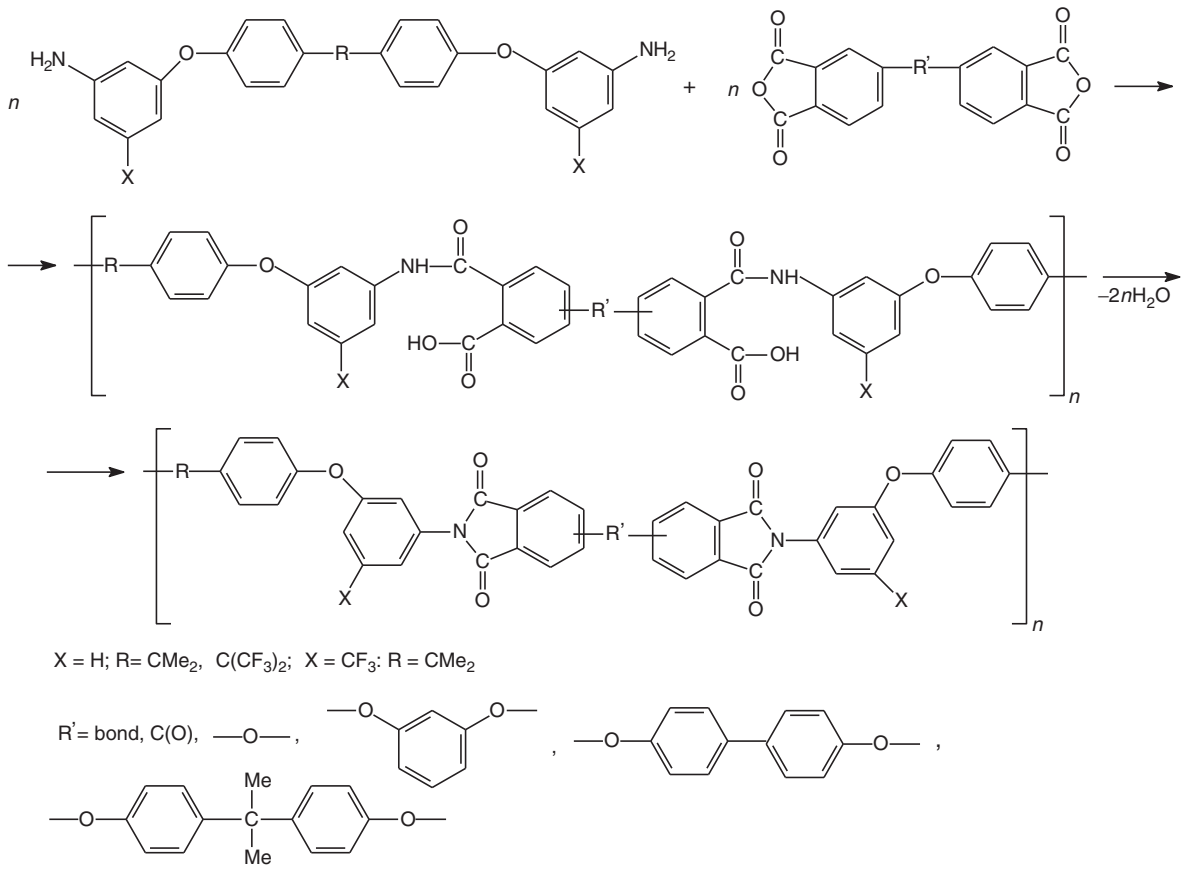
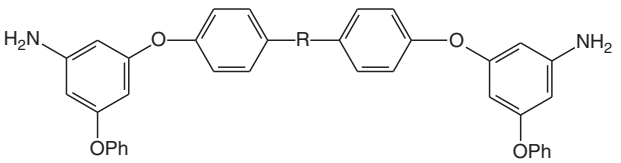


Scheme 59

bisphenoxides leads to nitro compounds with phenoxide side groups,[415,416] the reduction of which results in the formation of the corresponding amines with phenoxide side groups.[417] The polyimides have been synthesized from a diamine containing a hydroquinone residue.[418] The synthesis was based on Scheme 60. All the reactions were carried out homogeneously and led to high-molecular-mass polyimides with a high degree of cyclization. The polyimides obtained were distinguished by relatively low glass transition temperatures combined with high decomposition temperatures and a ready solubility in organic solvents, which led to their being easily processed into articles.

Almost all the polymers are soluble in amide, phenolic, and chlorinated solvents, and also in cyclohexanone, acetone, and butyrolactone. The polyimides based on the diamines having the following general formula are even more easily processed into articles.



R = CMe_2, $C(CF_3)_2$

5.21.5.2 Rigid-Chain Aromatic Polyimides

As mentioned above, the macromolecules of rigid-chain APIs must be extended to the maximum extent and must contain symmetrical *p*-phenylene fragments and heterocyclic units without 'flexibilizing bridges'. The simplest APIs with a 'rod' geometry may be obtained from pyromellitic dianhydride or the dianhydride of biphenyl-3,3′,4,4′-tetracarboxylic acid and carbocyclic (*p*-phenylenediamine, benzidine, 4′,4″-diaminoterphenyl, etc.) or heterocyclic [2,5-bis(*p*-aminophenyl)pyrimidine]diamines[422–426] in accordance with Scheme 61.

The high-molecular-mass poly(*o*-carboxy)amides formed in the first stage (in various amide solvents) undergo chemical or thermal cyclodehydration in the second stage, which results in the formation of insoluble polyimides. The value of the Kuhn segment was 625 Å for the polypyromellitimide based on 4′,4″-diaminoterphenyl and 1750 Å for the polypyromellitimide based on 2,5-bis(*p*-aminophenyl)pyrimidine, which indicates a high rigidity of the macromolecules.[423]

It is noteworthy that the evolution of gaseous products during the high-temperature thermal cyclodehydration limits the use of these materials in the industrial manufacture of thick-walled articles.[423]

The studies by various research groups on the problem of the removal of water stimulated investigations of the synthesis of rigid-chain polyimides soluble in organic solvents. Bulky side groups are usually introduced into the macromolecule in

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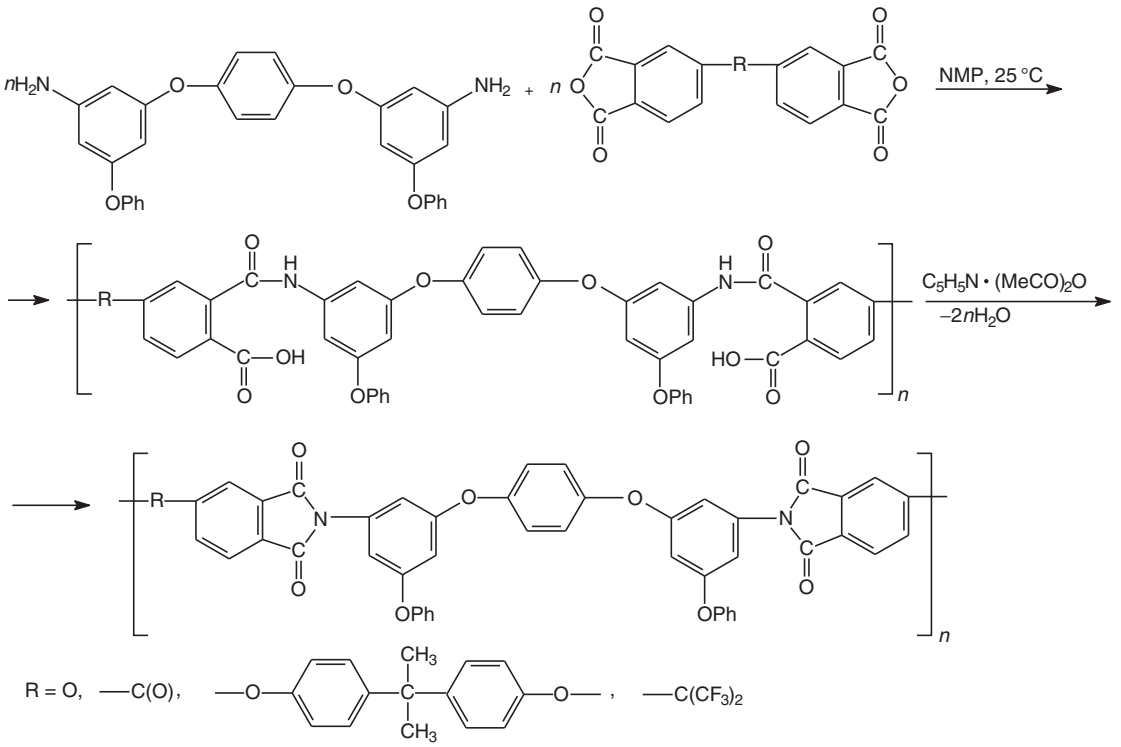
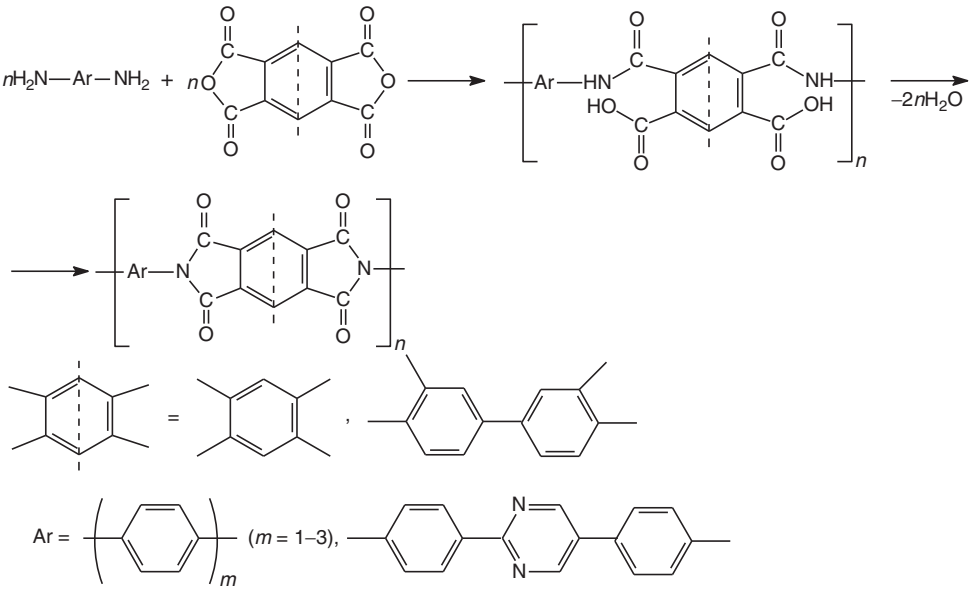


Scheme 60



Scheme 61

order to improve the solubility of polymers. Typical representatives of such groups are long aliphatic segments, for example, dodecyl fragments.[427–430] The reaction of 4,4″-diamino-2,5,2′,5′,2″,5″-hexadodecyl-*p*-terphenyl with pyromellitic dianhydride in *m*-cresol at 200 °C using isoquinoline as the catalyst was carried out in accordance with Scheme 62.

The polyimide obtained as a result of this reaction was soluble in various organic solvents. However, it is noteworthy that the introduction of aliphatic fragments into the molecules of APIs appreciably lowers their thermal stability – the polymers rapidly lose weight starting from 380 °C.

Better results were obtained when diamines and/or dianhydrides with trifluoromethyl side groups were used as the starting components.[431–438] Polyimides based on 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl and the dianhydrides of pyromellitic, biphenyl-3,3′,4,4′-tetracarboxylic,

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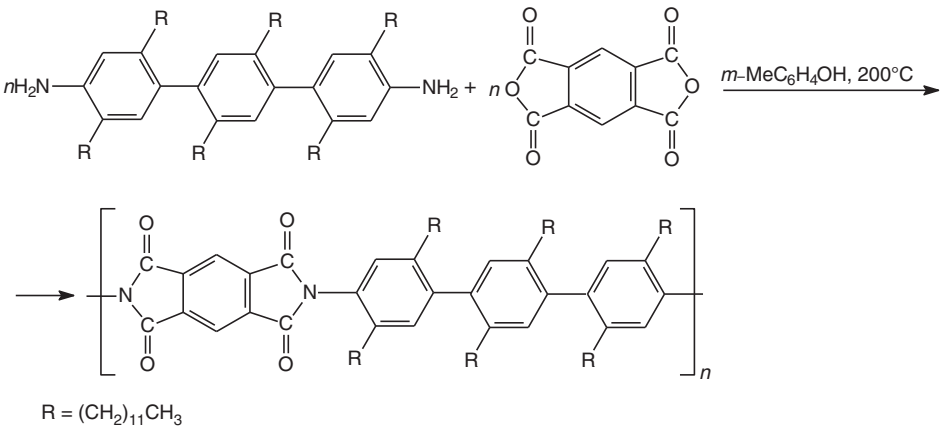
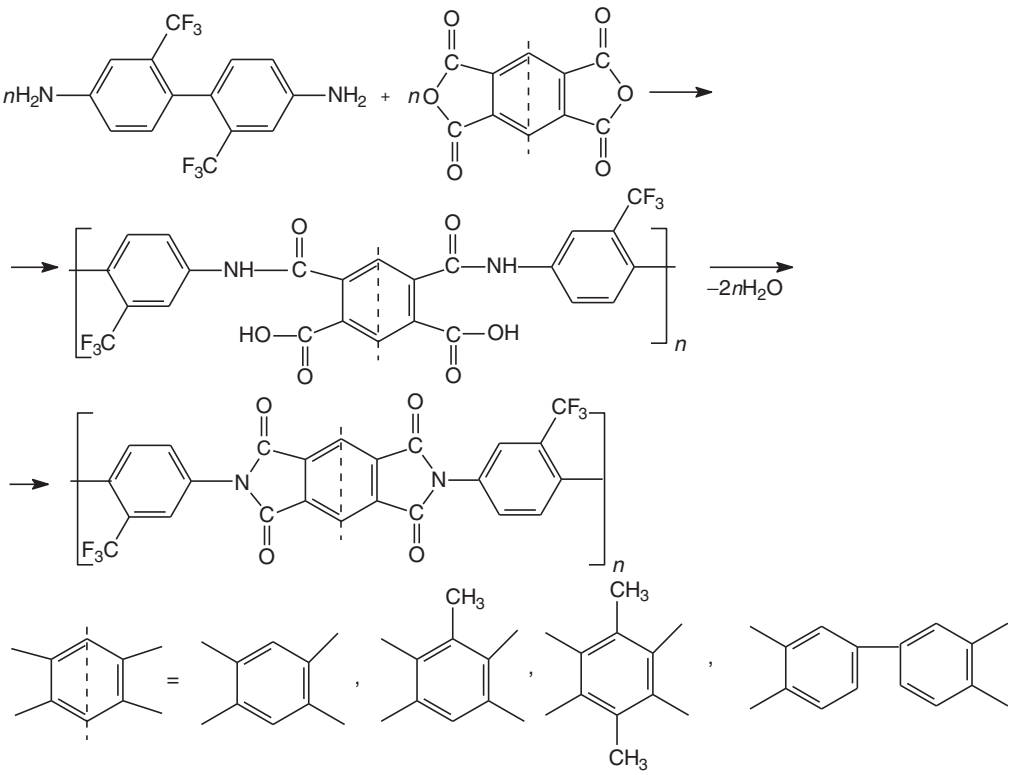


Scheme 62



Scheme 63

1-(trifluoromethyl)benzene-2,3,5,6-tetracarboxylic, and 1,4-bis(trifluoromethyl)benzene-2,3,5,6-tetracarboxylic acids have been synthesized by this procedure (Scheme 63).

The synthesis is carried out in two ways – by a two-stage reaction involving the low-temperature synthesis of poly (*o*-carboxy)amides in DMA with subsequent thermal cyclization in the solid state at 350 °C[432,433] and by a single-stage polycyclocondensation in boiling *m*-cresol.[434–438] The polyimide obtained from 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl and the dianhydride of biphenyl-3,3′,4,4′-tetracarboxylic acid by polycondensation in *m*-cresol is of greatest interest.[434–438] This polymer is soluble in hot *m*-cresol. Fibers with a low strength and low elasticity modulus have been obtained by spinning its isotropic solution, but after 10-fold drawing at a temperature above 380 °C the strength and the modulus of elasticity improved greatly when a load was applied. The fibers drawn in this way had a tensile strength of 3.2 GPa and an initial modulus of elasticity in excess of 130 GPa. The fibers had excellent thermal stability and retained a high strength and modulus of elasticity at elevated temperatures.

Rigid-chain polyimides soluble in phenolic solvents have been obtained by the interaction of the dianhydride of biphenyl-3,3′,4,4′-tetracarboxylic acid with 2-phenyl-*p*-phenylenediamine and 4,4′-diamino-1,1′-binaphthyl[439] in accordance with Scheme 64.

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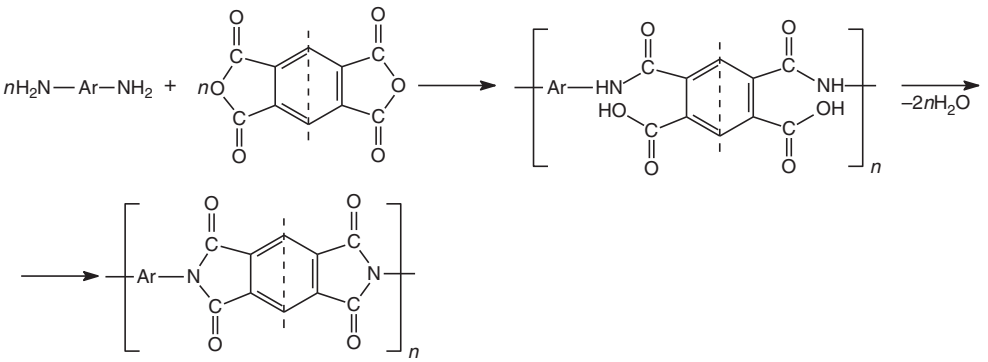


Scheme 64

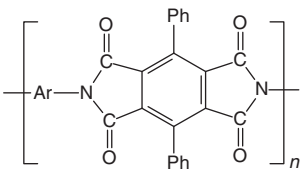
The reaction was carried out in *m*-cresol or *p*-chlorophenol at 200 °C using isoquinoline or tertiary amines as catalysts. The polyimides are soluble in *m*-cresol and *p*-chlorophenol and have a high viscosity combined with high glass transition temperatures and decomposition temperatures. The same diamines have been used in the reactions with the dianhydrides of 3-phenyl- and 3,6-diphenylpyromellitic acids (Scheme 64).[440]

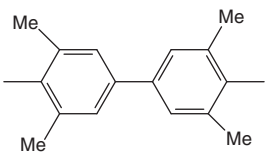
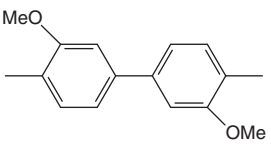
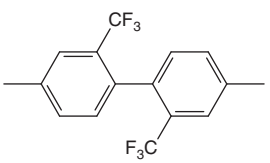
The dianhydride of 3,6-diphenylpyromellitic acid was also made to react with *p*-phenylenediamine, 1,4-diamino-2,3,5,6-tetramethylbenzene, benzidine, 4,4′-diamino-3,3′,5,5′-tetramethylbiphenyl, 4,4′-diamino-3,3′-dimethoxybiphenyl, and 4,4′-diamino-2,2′-bis(trifluoromethyl)biphenyl.[441] The corresponding polyimides were obtained in two ways – by a two-stage synthesis (low-temperature synthesis of poly-*o*-carboxyamides in NMP with subsequent chemical or thermal imidization) and a single-stage high-temperature polycyclocondensation in boiling *m*-cresol with isoquinoline as the catalyst. Best results were achieved when the single-stage process was used.

Among the rigid-chain polyimides synthesized in this way, three polymers (based on dinuclear diamines) proved soluble in *m*-cresol. It is most likely that the improvement of the solubility of these polymers is associated with the nonplanarity of the bisphenylene fragments (especially 2,2′-substituted ones).[442]

The intrinsic viscosities of the polymers soluble in *m*-cresol (Table 15) are in the range of 0.91–2.63 dl g^{-1}; these are

Table 15 Some properties of polyimides having the general formula



–Ar–	[η] (dl g^{-1})	$T_{5\%}$ (TGA) (°C) N_2	Air
	0.91	520	440
	2.63	475	425
	2.40	585	585

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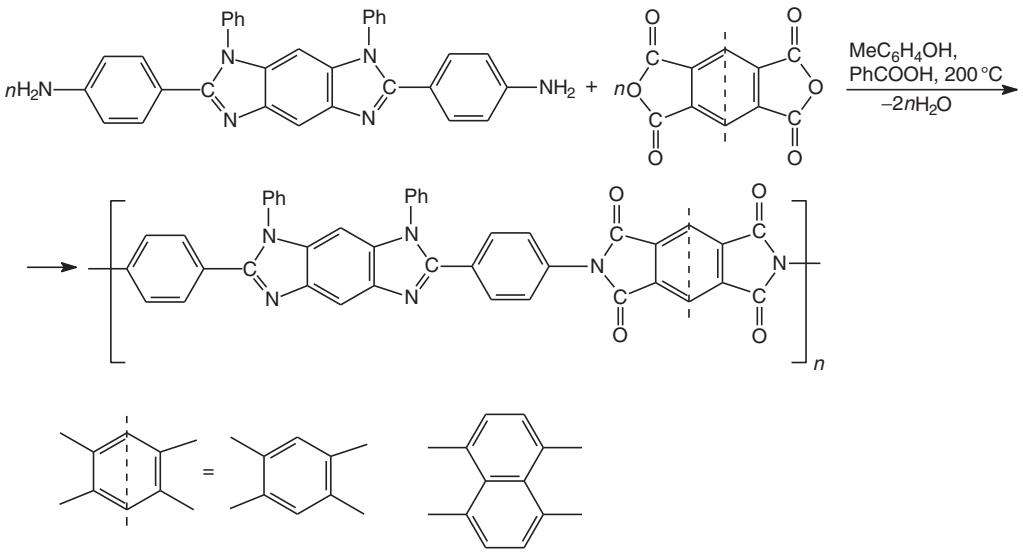

Scheme 65

relatively low values for rigid-chain polymers. The mass-average molecular masses of these polymers are 10 000–12 000.

Fibers have been obtained from the polyimide with trifluoromethyl side groups by wet spinning from a hot *m*-cresol solution. The thermooxidative stability of the polyimides synthesized from 4,4′-diamino-3,3′,5,5′-tetramethylbiphenyl and 4,4′-diamino-3,3′-dimethoxybiphenyl is relatively low – thermograms indicate 5% weight losses in air at 425 and 440 °C respectively. The low thermal stability of these polymers may be associated with the lack of resistance of the methoxy and methyl groups to oxidation. The thermal stability of the same polymers under nitrogen is much higher (the thermograms indicate 5% weight losses at 475 and 520 °C, respectively, in this instance). The presence of trifluoromethyl side groups in polyimides increases the thermooxidative and thermal stabilities of the polymers. Thermograms indicate a 5% weight loss at 585 °C in air and under nitrogen.[441]

The rigid-chain polyimide (a) was obtained from 2,6- di (p-aminophenyl)-1,7-diphenylbenzo[1,2-d:4,5-d']bisimidazole and pyromellitic dianhydride by high-temperature polycondensation in phenolic solvents (Scheme 65).

Despite the presence of phenyl substituents, the polyimide 20 hardly dissolves in organic solvents. A polymer with a better solubility was synthesized by the interaction of the same diamine and the dianhydride of naphthalene-1,4,5,8-tetracarboxylic acid.[443] The resulting polynaphthylimide 21 dissolved not only in sulfuric acid but also in trifluoroacetic acid as well as the TCE–phenol mixture. The ready solubility of the polyimide is combined with the high viscosity of the solution and the very high glass transition temperature and decomposition temperature (540 °C).

Polynaphthylimides have a number of advantages over polyphthalimides (e.g., they are more stable under the conditions of hydrolysis and thermolysis)[444] and therefore investigators have devoted much attention to the synthesis of soluble polynaphthylimides. The most significant and to some extent unexpected result was obtained in the synthesis of the polyimide from the dianhydride of naphthalene-1,4,5,8-tetracarboxylic acid and an asymmetric diamine – 2-(*p*-aminophenyl)-5(6)-aminobenzimidazole – in accordance with Scheme 66.[445]

Despite the absence of substituents of any kind in the diamine and the dianhydride, the reaction occurred homogeneously and led to the high-molecular-mass polymer 22 ($M = 120\,000$),[446] which is soluble (before isolation from the reaction solution) in phenolic solvents. The polymer is moderately rigid – its Kuhn segment is 320 Å.[347] Strong and elastic films have been cast from the reaction solutions of the polyimide (Table 16). After heat treatment at 140 °C for 12 h with subsequent maintenance *in vacuo* at 250 °C for 3 h, the properties of the films improved and after stretching the tensile strength was 930 ± 10 MPa and the modulus of elasticity was 20 + 1 GPa.

The partial replacement of 2-(*p*-aminophenyl)-5 (6)-aminobenzimidazole by benzidine led to a polymer with a larger Kuhn segment and a greater strength and modulus of elasticity (Table 17).

5.21.6 Ladder and Semi-ladder Polymers

The trend toward the synthesis of polyheteroarylenes with enhanced thermal properties involves the development of systems containing highly condensed heterocyclic fragments which predetermine a partially 'ladder' structure of the polymers. The greatest effort[46,448] has been devoted to those ladder or semi-ladder polymers formed from the reaction of aromatic tetracarboxylic acid dianhydrides with aromatic tetramines. Although the products have been given various names, they are more generally classified as polyaroylenebenzimidazoles.[448] The major distinction is between those systems that incorporate fused imidazole-pyrrolone five-membered rings (polybenzoylenebenzimidazoles) and fused imidazolepiperidone five- and six-membered rings (polynaphthoylenebenzimidazoles (PNBIs)) in the macromolecular chains. Soon after the demonstration of superior thermal properties of PNBIs, considerable activity has centered around these polymers.

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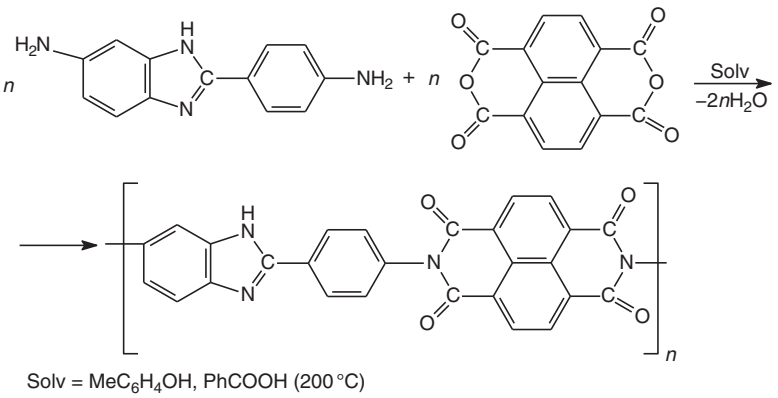
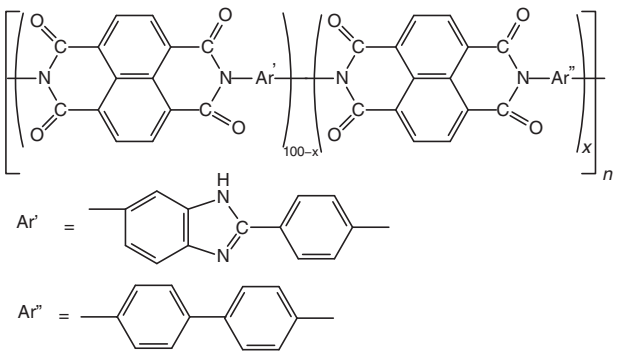


Scheme 66

Table 16 The properties of a polynaphthylimidobenzimidazole film[347]

Test specimen	*σ (MPa)*	*ε (%)*	*E (× 10⁻³ MPa)*
Film after casting	320 ± 10	25 ± 5	4.5 ± 0.5
Film after heating (140 °C/12 h and 250 °C/3 h *in vacuo*)	470 ± 10	15 ± 5	4.6 ± 0.5
Stretched film	930 ± 10	8 ± 1	20 ± 1

Table 17 The properties of copolymers having the general formula[447]



X (mol.%)	*[η] (dl g⁻¹) (H₂SO₄)*	*σ (MPa)*	*ε (%)*	*E (× 10⁻³ MPa)*
0	9.8	320 ± 10	25 ± 5	4.5 ± 0.5
5	11.5	384 ± 21	17 ± 4	10.0 ± 0.5
10	13.0	443 ± 9	17 ± 1	12.9 ± 0.5
15	8.9	417 ± 19	17 ± 2	12.0 ± 0.8
20	11.2	446 ± 19	17 ± 2	15.2 ± 1.6
20	11.2	1174[a]	4[a]	29.9[a]
25	9.4	418 ± 14	20 ± 4	10.7 ± 0.3
30	15.3	418 ± 33	20 ± 4	10.4 ± 0.2
30	15.3	1500[a]	4[a]	38.0[a]

[a] Data for oriented (60%) films are presented.

Considerable effort has been directed toward the synthesis of ladder and semi-ladder PNBIs following the predictions made by Tessler[449,450] that the double-strand polymers would prove to be more resistant to thermal and thermooxidative breakdown than comparable single-strand polymers. Ladder and semi-ladder PNBIs have been produced mainly from the reaction of 1,4,5,8-naphthalenetetracarboxylic acid dianhydride and the appropriate tetramines 1,2,4,5-tetraminobenzene and 3,3′-diaminobenzidine[451–454] (Scheme 67).

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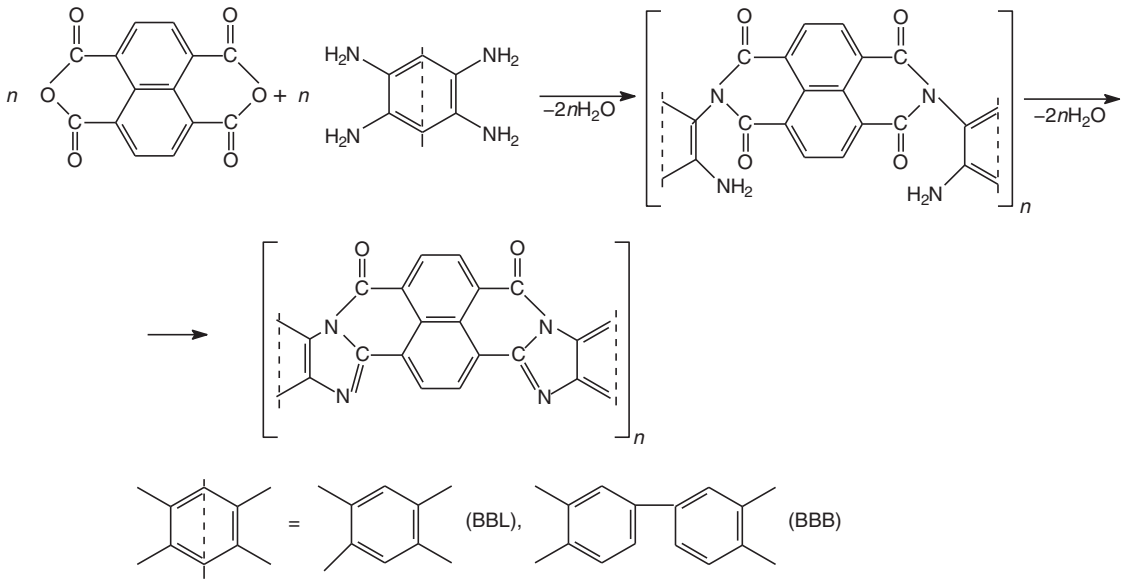

Scheme 67

The most frequent process has involved the single-stage solution polycondensation in PPA at a temperature of 150 °C.[451–454] The conditions of typical polycondensation reactions in PPA and inherent viscosities of the polymers obtained are given in Table 18.

PNBIs synthesized in accordance with Scheme 67 are high-molecular-weight polymers soluble in strong acids (PPA, H_2SO_4, H_3CSO_3H) only.

Poly(benzobisimidazobenzophenanthroline) ladder (BBL) and semiladder (BBB) polymers have been studied in the greatest detail. Investigation of the thermal properties of these polymers using the isothermal aging procedure has demonstrated that after aging at 316 °C in air during 500 h, BBL and BBB retained 87% and 57% of their initial weight.[455–457] At a higher temperature (425 °C), BBB is comparable with polybenzimidazoquinazoline, the most thermally stable organic polymer.

The general volatile products that are eliminated during the degradation of BBB are CO, CO_2, and H_2O;[458,459] at high temperatures (>525 °C), an additional volatile compound – CH_4 – was observed (Table 19).

The advantage of ladder PNBIs over other organic polymers in reference to their heat stability seems to be rather significant; in particular, as shown by investigations of serviceability ranges for this polymers, the BBB markedly excels in heat stability over organic polymers and is comparable with sodium silicate and potassium silicate glasses.

Although fibers based on BBL were basically accessible[453], mostly the properties of BBB fibers were investigated.[452,453,460–463] The fibers were spun from H_2SO_4 (97%) solution and after being stretched up to 80–120% at 500–600 °C, the room temperature tenacity was 44 cN Tex^{-1} with an extension to break of 5%. Other textile properties such as moisture sensitivity, loop strength, and knot strength were good and UV resistance was excellent. In air, 55–60% of the initial strength was retained after 30 h at 360 °C.

Some other ladder PNBIs of general formula were synthesized by the interaction of 1,4,5,8-naphthalenetetracarboxylic acid dianhydride with 1,2,5,6-tetraminonaphthalene, 2,3,7,8-tetraminophenazine, and 2,3,7,8-tetraminodibenzofuran. The polycondensation processes were carried out in PPA and molten Lewis acids ($SbCl_3$, $BiCl_3$) and led to the formation of PNBIs with intrinsic viscosities shown in Table 20.

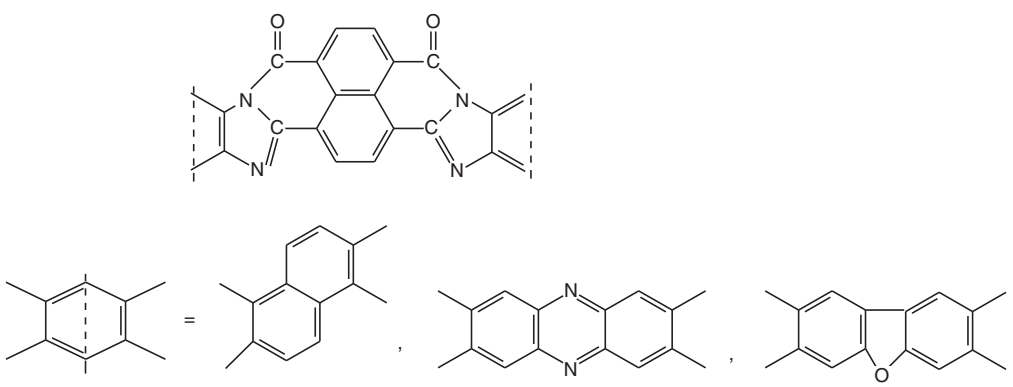

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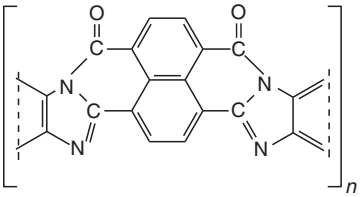
Table 18 Conditions of polycondensation and η_{inh} of the PNBIs of general formula



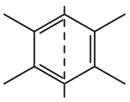
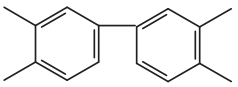
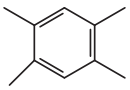
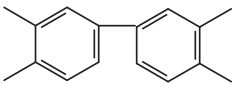
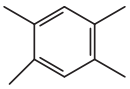
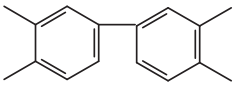
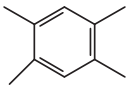
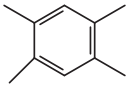
	*Monomer concentration (mol l^{-1})*	*Reaction conditions*		*Viscosity (H_2SO_4)*
		Temperature (°C)	*Time (h)*	
	0.40	110–120	18	0.57
	0.20	100–130	18	0.28
	0.22	180–190	20	1.35
	0.18	180–190	20	0.63
	0.40	200–220	3.5	0.75
	0.19	200–220	4.5	0.34
	0.13	190–195	24	0.90

Table 19 The volatile products that are eliminated during the degradation of BBB (for 1 h at each temperature)

Temperature (°C)	*The total amount of the volatile products (%)*	*The amount of volatile degradation products (mol mol^{-1})*			
		CO_2	*CO*	*H_2*	*CH_4*
In vacuo					
400	0.4	-	-	-	-
450	0.9	-	-	-	-
500	3.1	-	Traces	Traces	-
550	4.9	-	0.09	0.04	0.01
600	5.7	-	0.16	0.07	0.02
In the presence of O_2					
300		0.12	Traces	-	-
350		0.20	0.05	-	-
400		0.50	0.15	-	-
450		1.38	0.23	-	-
500		1.47	0.34	-	-

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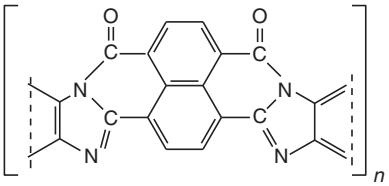
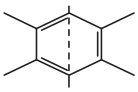
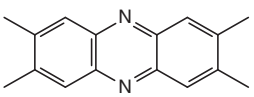
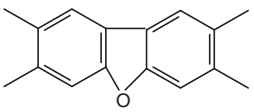
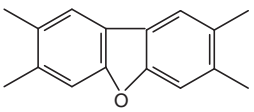
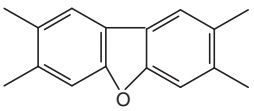
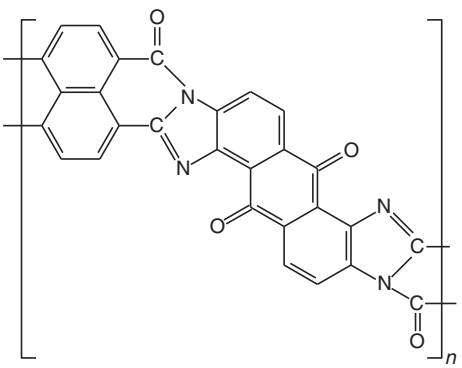
Table 20 Reaction conditions and intrinsic viscosities of the PNBIs of general formula



	Reaction conditions			
	Solvent	*Time (h)*	*Temperature (°C)*	*[η] (dl g^{-1}) (H_3CSO_3H)*
	PPA	10	180	0.8
	PPA	10	180	1.1
	PPA	10	180	1.0
	$SbCl_3$	12	140	2.0
	$BiCl_3$	8	160	1.7

The thermal stabilities of the polymers were good, showing initial weight loss by TGA in the region of 450 and 650 °C in air and nitrogen, respectively. Another ladder PNBI with an intrinsic viscosity of 2.4 dl g^{-1} was prepared[464] on the basis of 1,2,5,6-tetraminoanthraquinone. The polymer can be wet spun into pliable fiber from methanesulfonic acid. The TGA curve in air shows little weight loss below 550 °C.



In general, ladder and semi-ladder PNBIs are extremely thermally stable polymers; the wide use of these systems is restrained by the difficulties in the processing of the PNBIs arising from their solubility in organic solvents and nearly equal temperatures of softening and thermal degradation. One of the promising approaches to PNBIs with improved processability is the incorporation of different flexibilizing groups in their macromolecular chains.

5.21.6.1 Polynaphthoylenebenzimidazoles Containing the Flexibilizing Groups in Their Macromolecules

Different PNBIs containing bridging flexibilizing groups have been produced from the reaction of 1,4,5,8-naphthalene tetracarboxylic acid dianhydride and the appropriate tetramines – 3,3′,4,4′-tetraminodiphenyl ether, 3,3′,4,4′-tetraminodiphenylmethane, 3,3′,4,4′-tetraminodiphenylsulfone, and 3,3′,4,4′-tetramino (diphenyl ether of hydroquinone) (Scheme 68).

The most frequent process has involved the single-stage solution polycondensation in PPA.[465–467] Limited examples exist for the synthesis of PNBIs by a two-stage process in dipolar aprotic solvents.[466,468–472] According to recent studies, high

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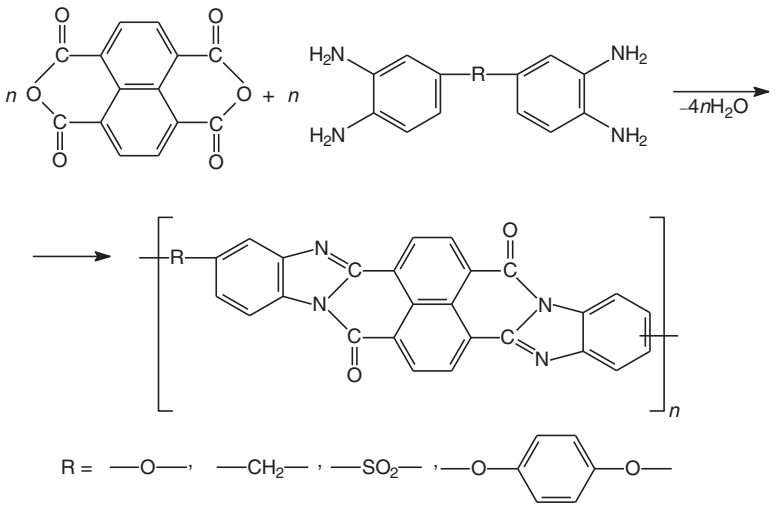


Scheme 68

molecular PNBIs can be obtained in comparatively mild conditions, for instance, by polycondensation in phenolic solvents at 160–180 °C.[473] It should be noted that the synthesis of PNBIs in phenolic solvents served as the first example of producing high molecular cyclized systems in the conditions of the so-called precipitative polyheterocyclization.[474] This process, which involves the precipitation of PNBIs from solution in the course of polycyclocondensation, appears to be technologically attractive, since it avoids the use of solvents and precipitants in high volumes in obtaining final polymers as finely dispersed powders, which are especially convenient for subsequent processing into final products.

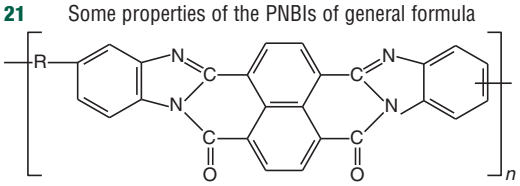
The PNBIs prepared in PPA and phenolic solvents are high molecular weight and almost completely cyclized polymers; some of their properties are given in Table 21.

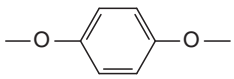
The introduction of flexibilizing linking groups into the amine component leads to a marked lowering of T_g and serviceability ranges of the PNBIs from values above 550 °C for the completely ladder[475,476] or rigid semi-ladder polymers.

Nevertheless, the advantage of the PNBIs containing flexibilizing groups over traditional polyheteroarylenes, such as polyimides and polyphenylquinoxalines; in particular, as shown by investigations of serviceability ranges for these polymers, the PNBIs markedly excel in their heat stability over traditional polyheteroarylenes, polyimides, and polyphenylquinoxalines.

Among the PNBIs demonstrated in Table 26, the PNBI derivative based on the available and highly nucleophilic 3,3′,4,4′-tetraaminodiphenyl ether is of great interest.

Table 21 Some properties of the PNBIs of general formula



–R–	$\eta_{red.}$, H_2SO_4, 25 °C (dl g^{-1})	$T_{10\%}$ (°C)[a]
—O—	4.0[b]	520
—O—	3.4[c]	
—CH_2—	2.2[b]	500
—CH_2—	1.9[c]	
—O—  —O—	1.8[b]	520
—SO_2—	0.6[b]	510
—SO_2—	1.4[c]	

[a] Temperatures of the 10% weight loss in air (TGA, $\Delta T = 4.5$ °C min^{-1}).
[b] Viscosities of PNBIs prepared in PPA.
[c] Viscosities of PNBIs prepared in *m*-cresol.

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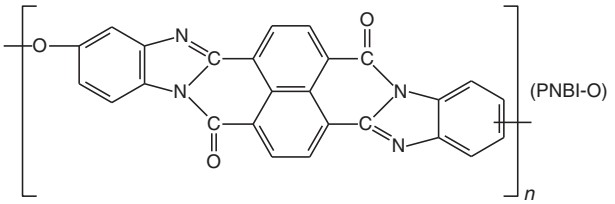

This polymer having an extremely high molecular weight (M = 100 000–700 000)[478,479] is completely soluble in H_2SO_4 and some other strong acids; it forms solutions of relatively high concentrations. PNBI-O is less thermally stable than BBB (Tables 22 and 23).

Nevertheless, the fibers spun from H_2SO_4 solutions of the PNBI-O are close to BBB fiber[480–482] (Table 24).

The introduction of additional ether groups combined with the asymmetric aromatic units into the amine component[454] led to the formation of PNBIs of general formula soluble in phenolic solvents and having lowered T_g's. Some properties of these polymers are given in Table 25; the properties of BBB and PNBI-O polymers are given for comparison.

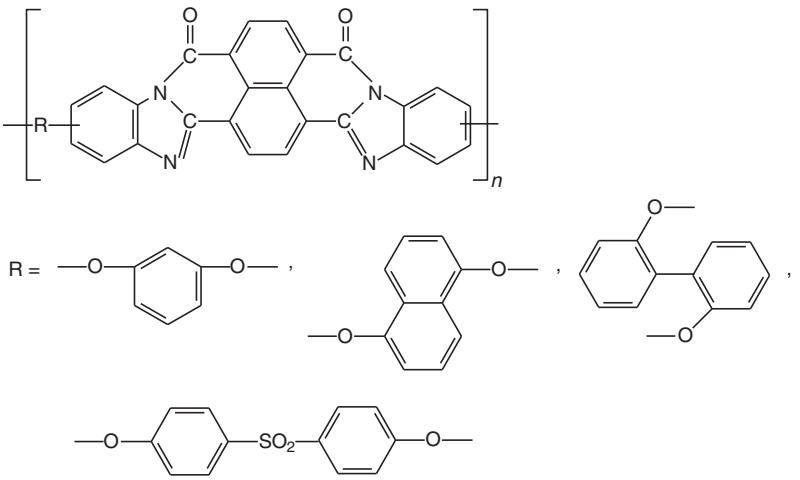

Table 22 The volatile products eliminated during the degradation of PNBI-O for 1 h at each temperature

Temperature (°C)	*The total amount of the volatile products (%)*	*The amount of volatile degradation products (mol mol^{-1})*		
		CO_2	*CO*	*H_2*
In vacuo				
400	0.7	-	-	-
450	0.8	-	-	-
550	1.3	-	0.01	Traces
600	6.7	0.15	0.20	0.01
	9.0	0.18	0.59	0.06
In the presence of O_2				
250		0.02	-	-
300		0.12	0.04	-
350		0.32	0.15	Traces
400		1.37	0.40	0.01
450		2.63	0.73	0.01
500		2.87	1.17	0.01

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Table 23 PNBI's degradation temperature range (isothermal condition) and activation effective energies of the degradation processes

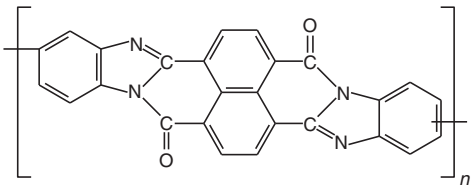
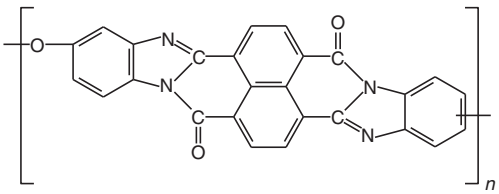
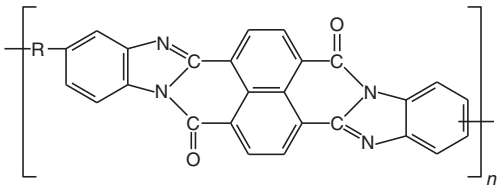
Polymer	*Degradation temperature range (°C)*	*E (kcal mol^{-1})*
	450–475	51 ± 5
	400–425	46 ± 5

Table 24 Some properties of PNBI-O fibers

	Initial fiber	*Oriented fiber*
Room temperature tenacity (cN Tex^{-1})	15–20	35–40
Extension to break (%)	15–25	2–6
Initial modulus (acoustic), 10^6 Pa	9000	28 000
Density (kg m^{-3})	1450	1350

Table 25 Intrinsic viscosities and glass transition temperatures of the PNBIs of general formula



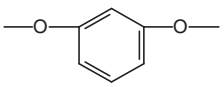
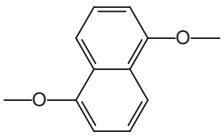
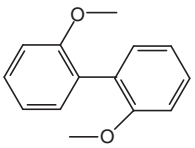
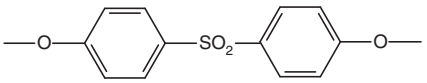
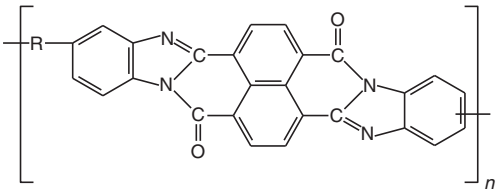
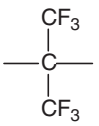
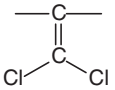
–R–	*[η] (dl/g)*	*T (°C)*
–	1.3	550
—O—	0.62	405
	0.82	325
	0.33	308
	0.41	310
	9.56	294

Table 26 Some properties of the PNBIs of general formula



–R–	*$\eta_{red.}$, H_2SO_4, 25 °C (dl g^{-1})*	*$T_{soft.}$ (°C)*	*$T_{10\%}$ (°C)*	*Film properties at 25 °C*	
				σ (kg cm^{-2})	*ε (%)*
	3.1		515	980	60
	1.0	450	510	1300	15

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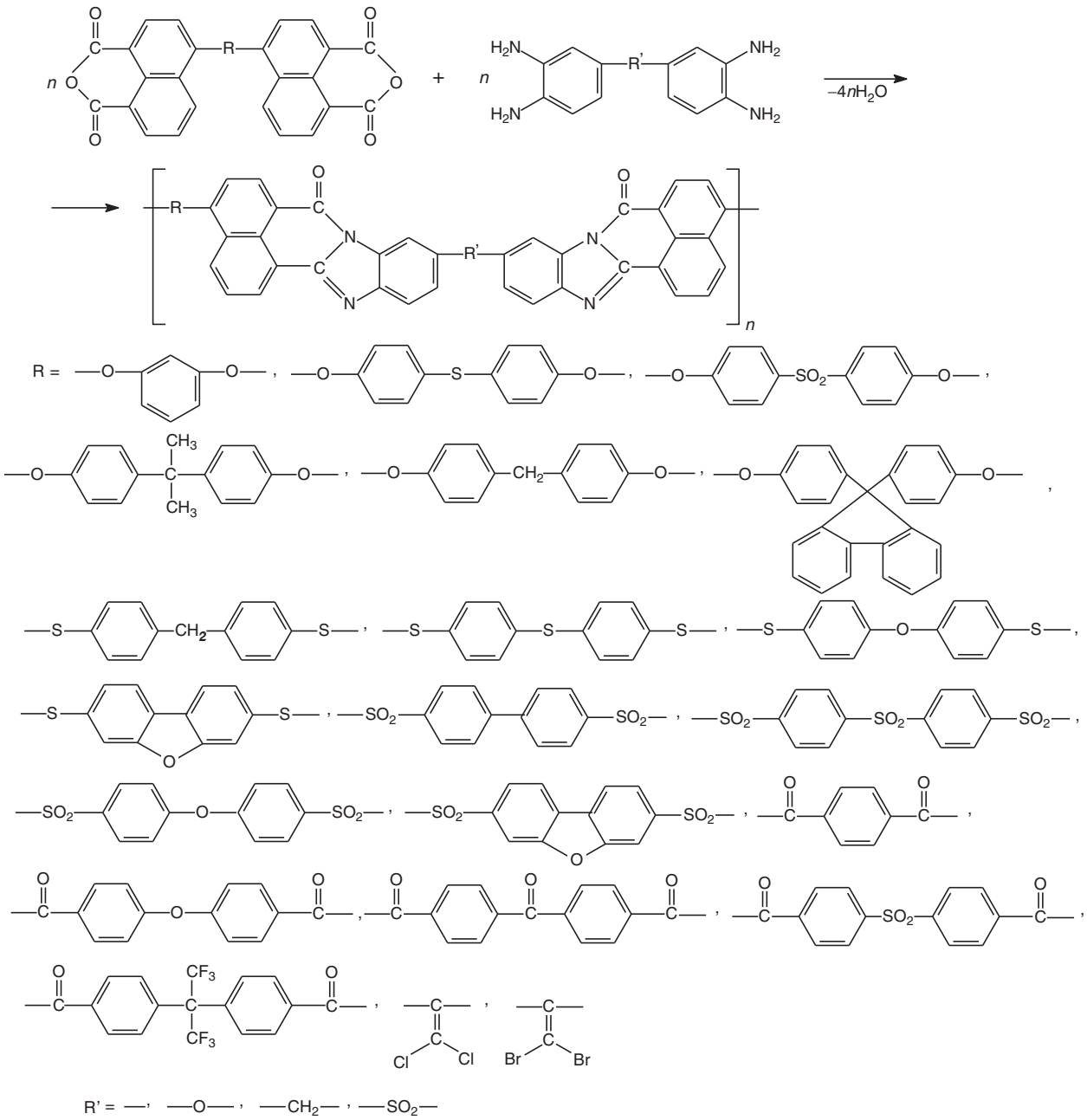

Scheme 69

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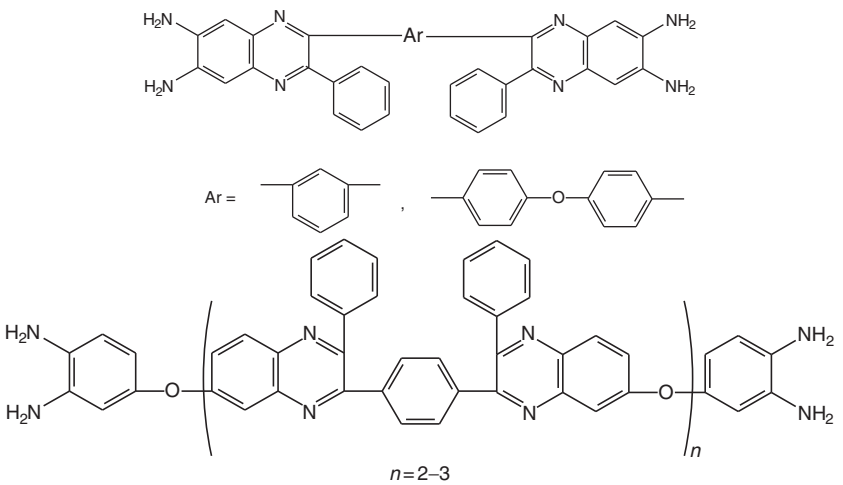
PNBIs soluble in the same solvents but having much higher T_g's were obtained on the basis of tetramines containing hexafluoroisopropylidene[106,483] and 1,1-dichloroethylene linking groups. Some properties of these polymers and films made therefrom are given in Table 26.

Some PNBIs soluble in phenolic solvents and having very high T_g's and degradation temperatures were prepared on the basis of 1,4,5,8-naphthalenetetracarboxylic acid dianhydride and individual isomeric[484] tetramines containing phenylquinoxaline units or oligomeric products containing *o*-phenylenediamine end groups and phenylquinoxaline moieties.[485]

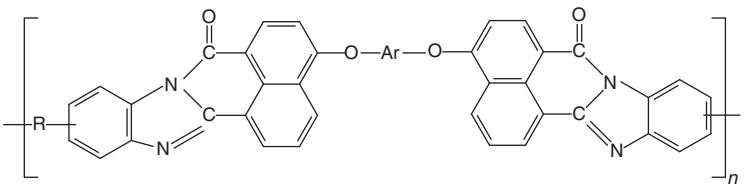
The large variety of such monomers was obtained on the basis of acenaphthene and its simplest derivatives.[486–495] These bis(naphthalic anhydrides) containing arylenedioxy-, arylenedisulfide-, arylenedisulfo-, arylenediketo-, and 1,1-dihalogenethylenic flexibilizing groups were reacted with various bis(*o*-phenylenediamine)s in accordance with Scheme 69.

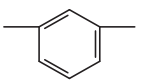
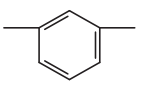
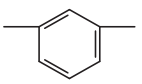
The most frequent process involved the single-stage solution polycondensation in phenolic solvents using benzoic acid as a catalyst. PNBIs synthesized in accordance with Scheme 69 are high-molecular-weight polymers soluble in strong acids and in phenolic solvents; some properties of the PNBIs containing arylenedioxy[493,495] and arylenediketo groups are given in Tables 27–29.



An alternative approach to the PNBIs providing satisfactory processing properties is based on the utilization of the bis (naphthalic anhydrides) having different flexibilizing groups.

Table 27 Some properties of the PNBIs of general formula



–R–	–Ar–	$\eta_{red.}$, H_2SO_4, 25 °C (dl g^{-1})	T_g (°C)	$T_{degr.}$ (°C) In Ar	$T_{degr.}$ (°C) In air
-		1.10	395	490	470
—O—		0.68	368	490	490
-		0.29	-	460	440

(*Continued*)

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Table 27 (*Continued*)

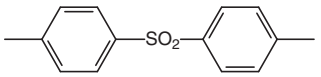
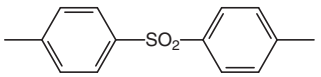
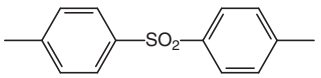
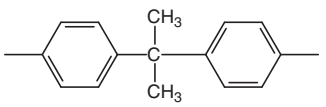
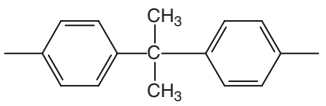
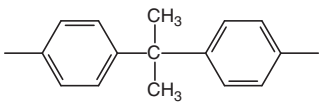
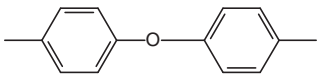
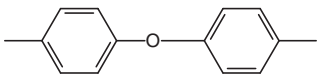
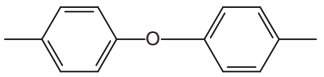
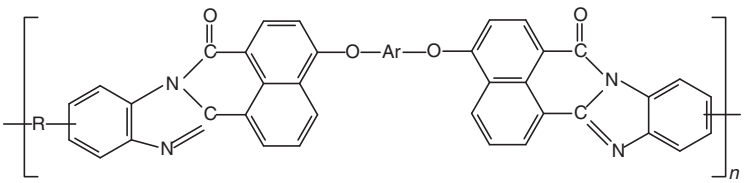
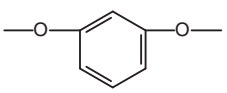
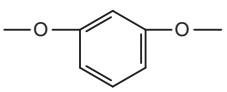
–R–	–Ar–	$\eta_{red.}$, H_2SO_4, 25 °C (dl g^{-1})	T_g (°C)	$T_{degr.}$ (°C) In Ar	$T_{degr.}$ (°C) In air
-		0.49	404	450	430
—O—		0.30	360	460	430
—CH_2—		0.20	380	450	430
-		1.00	373	460	450
—O—		0.75	312	460	450
—CH_2—		0.37	355	460	440
-		0.40	340	-	520
—O—		0.50	320	-	500
—CH_2—		0.70	320	-	480

Table 28 Mechanical and electrical properties of the films on the basis of PNBIs of general formula



–R–	–Ar–	Tensile strength (kg cm^{-2})	Limit elongation at break (%)	Volume resistivity (ohm cm)	tg δ at 50 Hz, 20 °C
-		1120	85	2×10^{16}	0.0017
—O—		1080	85	7×10^{16}	0.0014

(*Continued*)

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Table 28 (*Continued*)

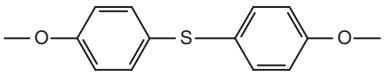
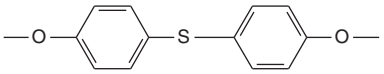
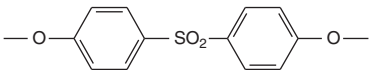
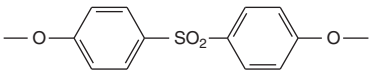
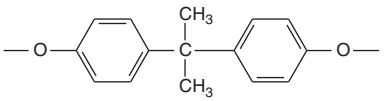
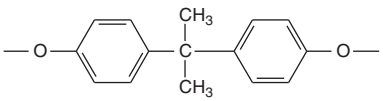
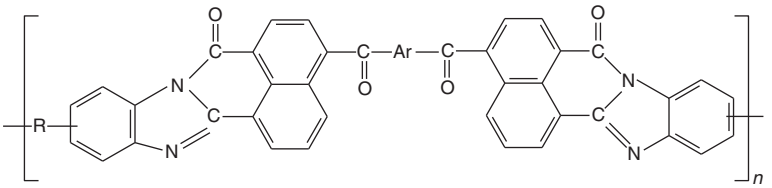
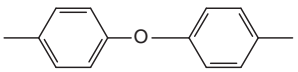
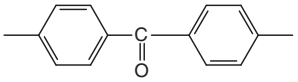
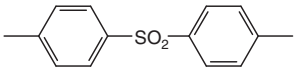
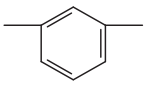
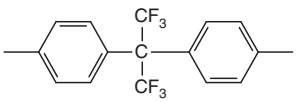
–R–	–Ar–	Tensile strength ($kg\,cm^{-2}$)	Limit elongation at break (%)	Volume resistivity (ohm cm)	tg δ at 50 Hz, 20 °C
-		1350	70	3×10^{16}	0.0012
—O—		910	75	4×10^{16}	0.0014
-		920	60	1×10^{16}	0.0015
—O—		1110	80	3×10^{16}	0.0014
-		950	70	6×10^{16}	0.000 94
—O—		980	113	1×10^{16}	0.0016

Table 29 Some properties of the PNBIs of general formula



–Ar–	$\eta_{red.}$, H_2SO_4, 25 °C ($dl\,g^{-1}$)	T_g (°C)	$T_{degr.}$ in air (°C)	Film properties at 25 °C: σ ($kg\,cm^{-2}$)	Film properties at 25 °C: ε (%)
	1.00	345	550	1260	15
	1.40	355	520	1100	13
	1.35	375	525	1000	11
	3.90	370	530	1040	11
	0.53	-	490	-	-
	1.80	360	545	1080	13

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The abovementioned PNBIs seem to be very promising film- and fiber-forming systems demonstrating outstanding thermal properties.

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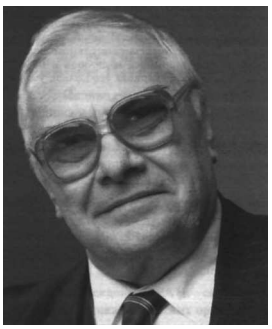
Biographical Sketches



Aleksandr L'vovich Rusanov (1939–2010), a well-known authority in the field of polymer chemistry, an honored scientist of the Russian Federation, a doctor of science in chemistry, and professor and head of the Laboratory of Macromolecular Compounds at the A.N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences, passed away on 16 November 2010 at the age of 71. Rusanov's entire life was associated with the A.N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences, where he worked his way from a postgraduate student to the head of the laboratory.

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He made a substantial contribution to the development of a universal method for synthesizing heterocyclic polymers – reductive polyheterocyclization – which is unique in world science. This method makes it possible to prepare polyheteroarylenes on the basis of more accessible, inexpensive, and stable compounds than substances used in traditional methods of synthesis of these polymers.

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5.22 Polyphenylenes, Polyfluorenes, and Poly(phenylene vinylene)s by Suzuki Polycondensation and Related Methods

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5.22.1 Introduction

Polyphenylenes (PPs), polyfluorenes (PFs), and poly(phenylene vinylene)s (PPVs) have been intensively studied over the past decades and have grown up into important classes of polymers (for a review, see Reference 1). They attract great interest particularly as active materials for electronic devices (for a review, see Reference 2) such as light-emitting diodes (for example, see Reference 3), photovoltaic cells (for example, see Reference 4), and field-effect transistors (for example, see Reference 5). Among these polymers, poly(*para*-phenylene)s (PPPs) can be considered a protopype; they have a stiff backbone consisting of benzene rings that are directly *para*-linked to one another by carbon–carbon bonds (**Figure 1**(**a**)). Depending on the dihedral angle between consecutive phenylene units, there can be some π-conjugation along the backbone, which is of relevance to issues associated with the spatial extension of electronic excitation. The stiff chain can also promote intermolecular interactions, leading to liquid crystalline (LC) phases as well as attractive engineering properties in bulk. In addition, the backbone is all-hydrocarbon and hydrophobic and, therefore, practically unaccessible to hydrolytic degradation as is encountered, for example, for aromatic polyesters. All these aspects make PPPs and related polymers attractive not only for basic research but also for technical application. Note that PFs are a subclass of PPPs in which adjacent phenylenes are pairwise bridged with a methylene group (**Figure 1**(**b**)). This clamp forces the two phenylene ring of each pair into a coplanar conformation. In the PPVs, on the other hand, the vinylene bridges between the aromatic rings represent structural units that allow coplanarization of the polymers' π-electron systems and hence quite efficient and long-range π-electron conjugation along the chains (**Figure 1**(**c**)).

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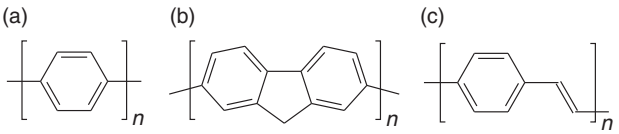


Figure 1 Chemical structures of (a) poly(*para*-phenylene) (PPP), (b) poly(2,7-fluorene) (PF), and (c) poly(*para*-phenylene vinylene) (PPV).

The polymers this chapter are dealing with are intrinsically neither soluble nor meltable, and progress in terms of synthesis, characterization, and processing could only be achieved after measures had been implemented to increase their solubility and to reduce their melting temperatures. These measures, known as the 'hairy rod' concept,[6] were taken in the late 1980s and the 1990s and, in retrospect, were key to the considerable success these polymers experienced in the years to come. This concept involves the decoration of conformationally restricted polymers such as PPs (particularly PPPs), PFs, and PPVs with flexible chains. These chains act as the 'solvent' for the rods and increase their solubility mainly for entropic reasons but also by reducing the crystallization energy. Consequently, growing chains stay in solution and do not precipitate anymore at an early stage of growth. In the case of PPVs, moreover, side chains not only lead to improved solubility, but additionally represent powerful tools for adapting the (opto)electronic properties. Hypsochromic shifts of the emitted light toward the blue regime are observed for PPVs whose aromatic moieties bear alkyl, aryl, or silyl substituents. Alkyloxy groups, on the other hand, induce bathochromic shifts, leading to yellow, reddish-orange (e.g., poly(2-methoxy-5-(2′-ethylhexoxy)-*para*-phenylene vinylene)), or red emission (e.g., poly(2-methoxy-5-(3′,7′-dimethyloctoxy)-*para*-phenylene vinylene)). Alternatively, modification of the (opto)electronic properties can also be achieved by substituting the vinylene moieties by, for example, cyano or fluoro substituents.

From the many synthesis methods that were tried over the years, the polycondensation protocol based on the Suzuki–Miyaura cross-coupling reaction[7] proved most effective and widely applicative. It is commonly referred to as Suzuki polycondensation (SPC),[1] and is the method this chapter puts its focus on. Only for PPVs, some further transition metal-mediated coupling methods could gain relevance so far for the synthesis of well-defined and high-molecular-weight macromolecules of tailored properties. These coupling methods complement the established precursor routes to PPVs through chain-growth pathways, which include Gilch and Wessling processes, and the classic step-growth polymerizations following, for example, Wittig, Horner–Wadsworth–Emmons (HWE), Siegrist, and Knoevenagel protocols. The modern step-growth methods leading to PPVs will be treated in a separate section.

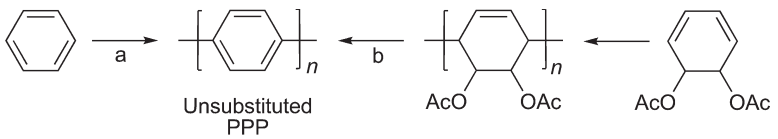
This chapter reviews the synthesis of PPs, PFs, and PPVs including underlying ideas on how to design structure and how to improve synthesis. It also guides through several synthetic issues relevant to those considering using SPC. Finally, a collection of recent examples will be presented that not only mirrors where the present interest concentrates but also shows where the field is going to in future.

5.22.2 Synthesis Background and Strategy

5.22.2.1 Polyphenylenes

Earlier attempts to synthesize unsubstituted PPP had started directly from benzene that was treated with Friedel–Crafts catalysts under oxidative conditions[8,9] ('Kovacic method', Scheme 1(**a**)); other methods made use of variations of the Ullmann reaction,[10] the Wurtz–Fittig reaction,[11] or the Kumada coupling.[12] Further, an indirect method by a soluble precursor polymer that in a final step was converted into the insoluble 'PPP' was reported by Ballard *et al.*[13] and thereafter also by Gin *et al.* (Scheme 1(**b**)).[14] Not unexpectedly, the inherent insolubility of the unsubstituted PPP turned out to be the insurmountable complication in all of these attempts, leading to incomplete reaction, formation of only oligomers, premature precipitation of the intermediate reaction products, and various side reactions.

In 1989, the first synthesis of a PPP that applied the 'hairy rod' concept was reported by Rehahn *et al* (for a review on the birth of SPC, see Reference 15). It was based on SPC using an AB monomer (Scheme 2(**a**)) that carried two flexible alkyl chains. Note that for SPC, 'A' represents halogenide or triflate, and 'B' corresponds to boronic acid or boronate. This PPP was fully soluble in organic solvents and, therefore, characterizable, features which at that time were unheard of. It was structurally well defined, particularly it was exclusively 1,4-connected, and had average molar masses in the range of 6000–8000 g mol^{-1}. While this was clearly not high-molar-mass material, the mass was in a range considered promising for implementation of substantial improvements. The same group also reported SPC using AA/BB monomers, which led to an alternating sequence due to the copolymerization of the two different kinds of monomers (Scheme 3).[16,17] These two findings triggered worldwide research activity into SPC, both in academia and in industry, and led to the situation that SPC nowadays is considered the most reliable method for the synthesis of high-molar-mass substituted PPs and related other aromatic polymers. As alternative, Yamamoto protocol using dihalobenzene with nickel (0) is also often used in academic research (Scheme 2(**b**)). This protocol is indeed attractive compared to SPC particularly as far as the ease of monomer synthesis is concerned. There is, however, a price to be paid that includes (1) no



Scheme 1 Idealized representations of (a) the direct method and (b) the precursor route to unsubstituted PPP.

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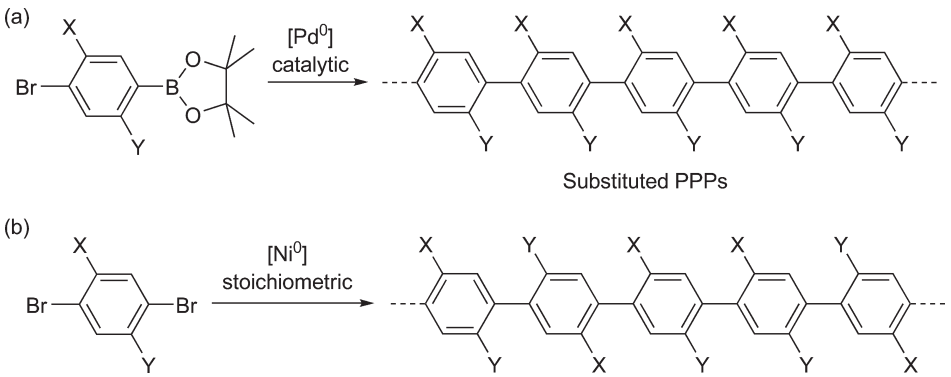
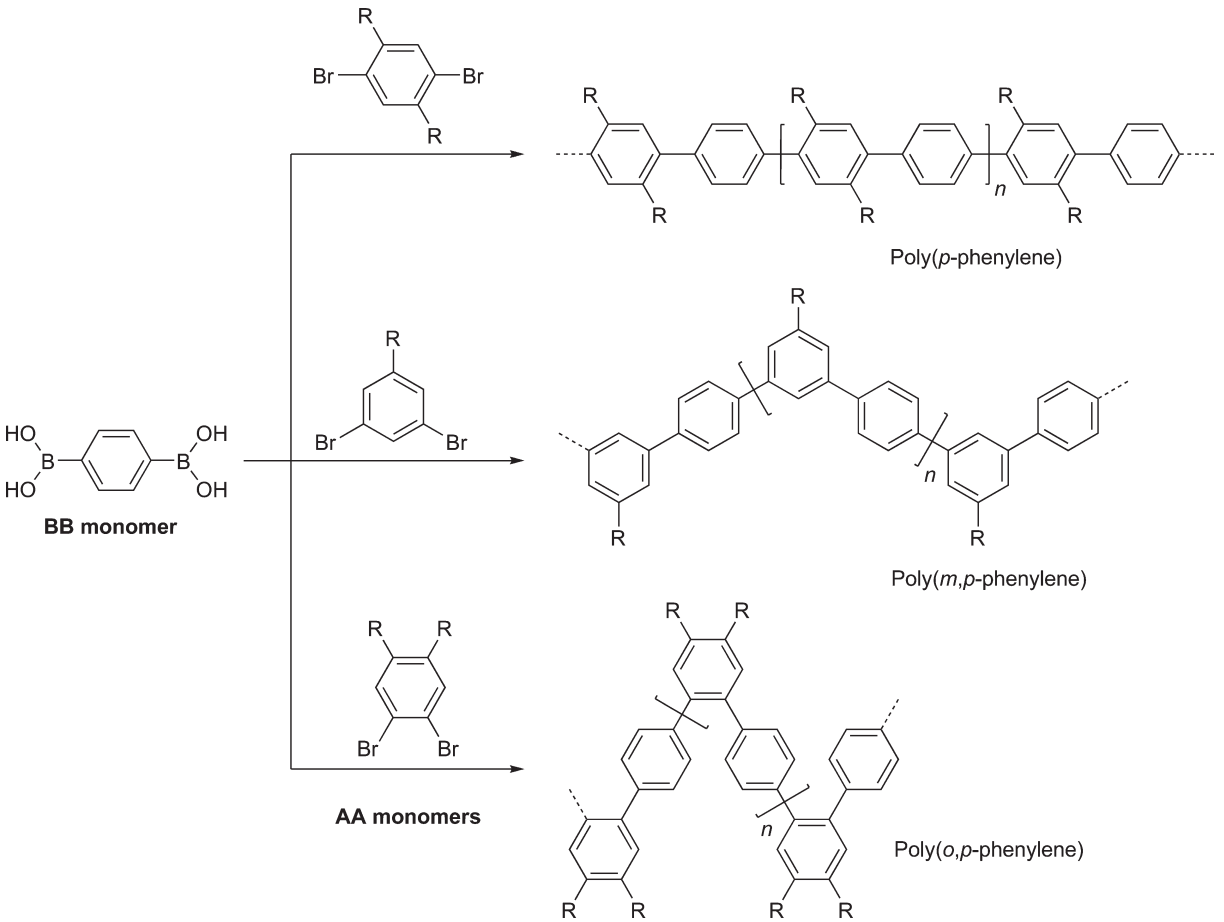


Scheme 2 SPC and Yamamoto protocol for the synthesis of substituted PPPs.



Scheme 3 Example of possible structural variations by SPC using AA/BB monomers.

head-to-tail control of monomer incorporation (and thus no chain directionality), (2) no possibility to achieve an alternating sequence, (3) the necessity for stoichiometric use of an expensive nickel reagent, and (4) the difficulty in removal of the residual metal from products.

For SPC, both AB and AA/BB approaches can be used, which allows for considerable structural variations. From the latter, entire families of closely related PPs were obtained by typically keeping the BB monomer constant while varying AA. This proved to be an attractive feature for industrial applications where properties could be fine-tuned by slight variations in AA or by using mixtures of different AAs. Furthermore, phenylene-1,4-diboronic acid is commercially available and can conveniently be used as the BB monomer as is or in the corresponding diboronate form. Note that SPC is not restricted to the synthesis of PPPs but it can also be used for a variety of related aromatic polymers, including kinked PPs that are composed of *meta*- and *ortho*-phenylene units (Scheme 3).[19,20]

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5.22.2.2 Polyfluorenes

Soon after the discovery of the first polymer-based organic light-emitting diodes (OLEDs) by Burroughes *et al.*,[21] PF derivatives were tested in such devices.[22] After considerable optimization, they then gained commercial relevance.[23] PFs are usually synthesized by either SPC or the Yamamoto protocol, whereby the former is favored for technical scale application. PFs (Figure 2) represent a subclass of PPPs. Substituents on PPPs *ortho* to the connecting C–C bond force the adjacent phenlyene units to be twisted relative to one another even more so than for the unsubstituted case. Obviously, this leads to a disruption of π-conjugation (Figure 3(a)). Bridging of consecutive phenylene units with methylene groups reduces the dihedral angle between them to almost 0° (see Section 5.22.5.3). Exceptional electrical, optical, and optoelectronic properties are the result: PFs can act simultaneously as semiconductors and efficient electroluminescent emitters. The bridge also forces the backbone out of linearity. Each repeat unit's director has the angle 2α to the next director, resulting in a reduced persistence of PF as compared with PPP. Another important feature of the PFs is that lateral substituents can be introduced at position C-9. Only if affixed at this position, any substituent has only little influence on the dihedral angle between consecutive fluorene units. This thus remains to be largely determined by the steric repulsion between the *ortho* hydrogens of consecutive repeat units, which leads to an optimum dihedral angle in terms of achieving the desired blue emission (Figure 3(b)).

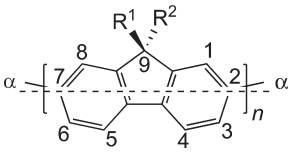

Figure 2 Chemical structure of a PF substituted at position C-9 with two groups R^1 and R^2, which serve the purpose to increase the parent polymer's solubility and processability. The bridging of the two phenylene units by carbon C-9 causes the PF repeat unit to deviate from linearity by the angle α.

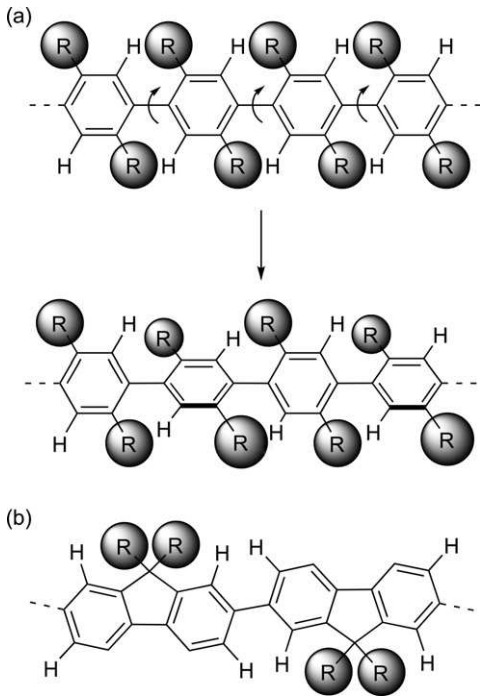

Figure 3 (a) Steric repulsion between consecutive phenylene units of a PPP as a result of substitutions *ortho* to the connecting C–C bonds, which causes larger dihedral angles and less cross-conjugation. (b) For PFs, the bulky substituents can be installed at C-9 positions whereby the dihedral angles between repeat units remain basically unaffected (at least in solution).

Poly(9,9-dialkyl-2,7-fluorene)s (alkyl > C_6) are soluble in organic solvents such as chloroform at room temperature. This not only allows to prepare films by spin- or drop-casting techniques but also to characterize the polymers. Light-scattering measurements gave a persistence length of around 7 nm,[24] which is approximately half than that obtained for a soluble PPP derivative (see Section 5.22.3.5). This value reflects the semirigid nature of PFs, which is the reason why gel permeation chromatography (GPC) studies with polystyrene (PS) calibration tend to overestimate molar masses.[24] The semirigidity also leads to thermotropic phase behavior of some 9,9-dialkyl-PF derivatives.[25] Depending on the lengths of the side chains, transitions into the nematic phase were found in the range of 100–180 °C.[26] Moreover, for monoalkylated PFs sandinic mesophases were reported, and enantiomeric side groups can induce chiral mesophases.[27] Based on this LC behavior, PFs were fabricated into OLEDs exhibiting polarized electroluminescence.[28]

Photoluminescence spectra of PFs from dilute solution show emission peaks with well-resolved vibronic fine structure.[29–31] Also the bulk material emits a bright sky-blue light when excited by ultraviolet (UV) irradiation. This intense blue emission combined with a large photoluminescence quantum efficiency (> 50%)[32,33] is the main reason why PF homo- and copolymers are being studied extensively as functional materials for OLEDs. Because of the stiff industrial competition in the field of OLEDs, an enormous variety of derivatives and modifications including copolymers and blends were published in both the open and patent literature, which cannot possibly be covered here. For more details, the interested reader is rather referred to pertinent recent reviews.[1,34,35]

5.22.3 Fundamental Synthetic Aspects

5.22.3.1 General Remarks

SPC is usually believed to be a step-growth process based on Suzuki–Miyaura cross-coupling. The AA/BB approach has been used more frequently than the AB approach mainly because of the greater simplicity of monomer synthesis. For the former, a commercially available phenylene-1,4-diboronic acid can be used as BB monomer, which grossly reduces the synthetic effort. For the latter, the monomer structure must be desymmetrized and borylation is inevitably the last step. The boron functionality is often introduced by halogen–metal exchange followed by quenching with trialkylborates and acidic workup (Scheme 4(a)).[10] If chromatographic purification is necessary, the boronic acid is further esterified to the corresponding pinacolate whereby any eventual complication caused by

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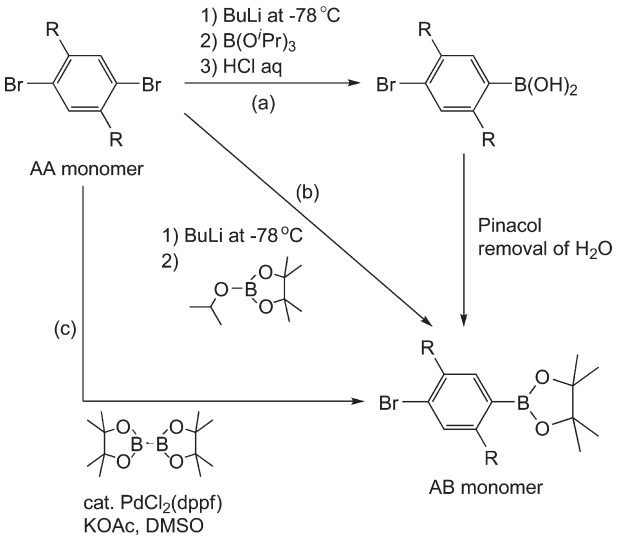

Scheme 4 Synthetic routes to AB-type SPC monomers with boronic ester functionality.

boroxine formation from free boronic acid can be circumvented. The pinacolate is among the most highly stable boronate against silica gel. The boron pinacolate is also accessible directly from the halogenide by using isopropyl pinacolyl borate (**Scheme 4(b)**).[11] However, because of the aggressive nature of the lithiated or Grignard-type intermediates, quite a few substitution patterns on monomers are excluded from the very beginning by these protocols. It is, therefore, of continued importance to develop other routes to boronic esters under mild conditions. For example, Ishiyama *et al.*[36] reported mild palladium (Pd)-catalyzed incorporations of boronic pinacolate to aromatic units by reacting the corresponding aromatic halogenide with pinacoldiboron (**Scheme 4(c)**).

Despite its popularity, the AA/BB approach suffers from a major disadvantage: the necessity to strictly control the stoichiometric balance between the two monomers. While the stoichiometrical balance between A and B functionalities is intrinsically achieved for AB, in the AA/BB approach, this must be guaranteed through several measures. Carothers equation describes the dramatic reduction in molar mass caused by stoichiometry mismatch.[37] Though one may think that this is a simple task, in reality these measures turn out to be everything else but simple. Control of stoichiometry is in fact a major challenge in the SPC of AA/BB systems. Like any other step-growth polymerization, great care must be taken with monomer purity, storage, weighing, transfer to reactor, stirring, and related issues. In many publications using SPC, such aspects, which are so critical to success, are not described. Even worse, it seems that they are sometimes not sufficiently considered in the experimental realization. This is why the reader will be briefly guided through this matter in Section 5.22.3.2. Recent attempts to develop chain-growth SPC will also be introduced in Section 5.22.4.4.

5.22.3.2 Monomer Purity and Stoichiometry

Like for any other step-growth polymerization, monomer purity is a key also for SPC, specifically as far as the AA/BB approach is concerned. (In the AB approach, impurities that do not interfere with the polycondensation reaction, e.g., residual solvents but not monofunctional compounds causing chain termination, can be tolerated.) The degree of purity can be quantified by high-resolution nuclear magnetic resonance (NMR) spectroscopy (**Figure 4**), gas chromatography (GC), or high-performance liquid chromatography (HPLC) analysis and should be far beyond 99%. If the presence of certain impurities cannot be avoided, for example, for noncrystallizable monomers, at least their nature must be known and their mole fraction be considered when it comes to matching stoichiometry.

In cases where the amount and/or the nature of the impurities are unclear, series of test polycondensations need to be performed in which the proportions of both monomers are gradually changed. From the respective molar masses, it can then be back-concluded which proportion best mirrored the exact 1:1 stoichiometry. Bo and Schlüter[38] reported such a series in which the weight-average degree of polymerization (P_w) differed by a factor of more than 10, just by changing the apparent monomer ratio from 1.000:1.000 to 1.000:1.005.

Larger scale reactions reduce weighing errors and transfer losses, which make it easier to precisely control stoichiometry. For a research laboratory investigating complex monomers requiring multistep syntheses, 500 mg of monomer is a reasonable compromise between synthetic effort and the need for large scale to achieve stoichiometric control. We find that SPC on the 5 g scale and above causes the least problems and that those on the 50 mg scale produce basically meaningless results. This shows a delicacy in the evaluation of the intrinsic potential of SPC for a given system. It is difficult to conclude for a given set of monomers and conditions whether high molar masses can be achieved or not, if all data are only based on small-scale experiments. Apropos intrinsic potential of SPC: Often respectable molar masses are discussed referring to polymers that were isolated in yields below 100%, say 60–70%. According to Carothers equation, high molar mass can only be reached for extremely high conversions, which normally should go hand in hand with high isolated yields. Mass losses during workup of 5% can be considered normal and, in special cases, perhaps even 10% are understandable. (Some losses may be due to low-molar-mass cyclic products that do not precipitate during polymer recovery.) Losses of 30–40%, however, can be an indication that substantial amounts of the lower molecular weight chains were removed by inadvertent fractionation. For an adequate description of actual and representative molar masses, molar masses from reactions with low yields (60–70%) can neither be reasonably used nor compared with one another. (According to Carothers equation, polymers with, e.g., P_n's of 50 and 100 require conversions of 98% and 99%, respectively. Claiming a $P_n = 50$ and stating a yield of 65%, e.g., does therefore not make sense.)

Having now talked so much about the need for matching stoichiometry, it may sound like a contradiction to point out that several laboratories doing SPC use the boron-based monomer in slight excess. This may be done to offset protolytic and other losses of boron-containing monomers.

5.22.3.3 Polymerization and End-Capping

By far, most of the optimization of SPC conditions has been done in industry. Given its considerable technological

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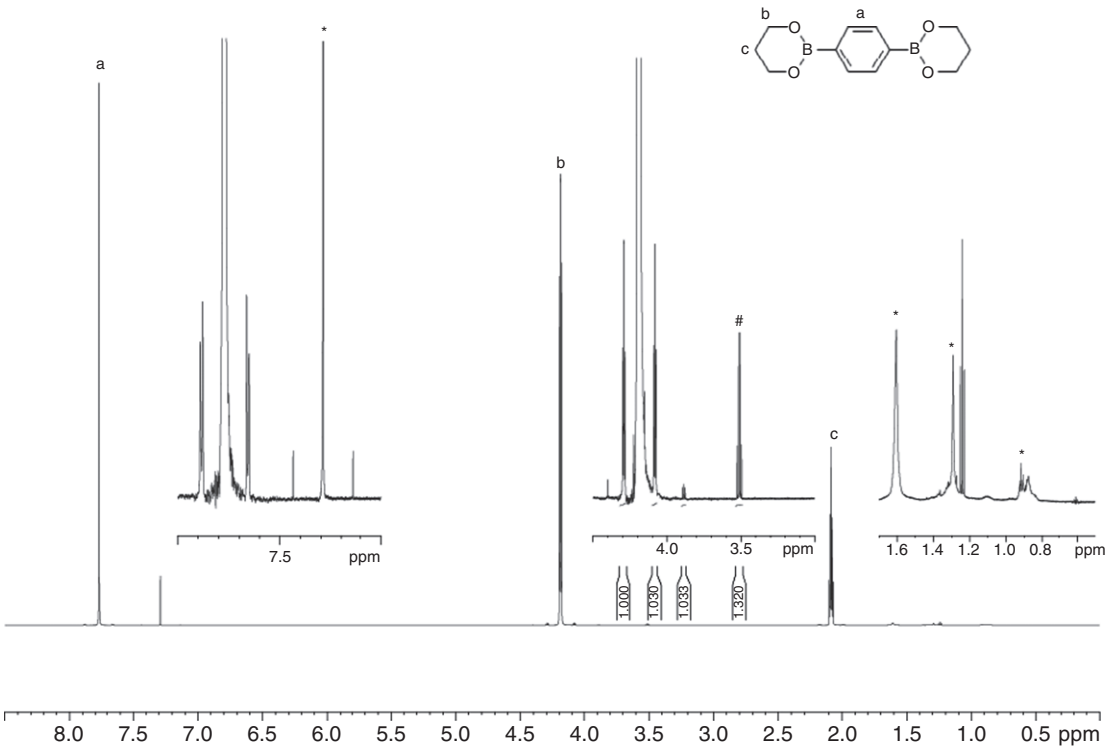

Figure 4 ^{1}H NMR spectrum (700 MHz) of benzene-1,4-diboronic ester to illustrate the level of purity considered sufficient. The signals of the NMR solvent ($CDCl_3$) and impurities contained in it are marked (*). The signals of residual solvent (diethylether), the monomer was recrystallized from, are also marked (#). The insets show strongly amplified regions to check for trace impurities that are practically absent (except for some unknown compound causing the signal at $\delta = 3.9$ ppm). The ^{13}C satellites, each of which has 0.5% of the corresponding main signal's intensity, are used to determine the content of ether by integration to be 0.3 mol.% in the present case.

importance, PF was used as the prototype polymer for these studies. One of the earliest studies on improving the molar mass of PF used phase-transfer catalysts.[39] It was assumed that these catalysts facilitate the transfer of the anionic boron species from the aqueous into the organic layer, where the coupling reaction between the boronate and the halide–palladium complex takes place. Best results were obtained using tetra-*n*-butylammonium halides, benzyltriethylammonium halides, and tricaprylammonium chlorides (Aliquat® 336). The reaction leading to polymer **3** was studied most intensively (**Scheme 5**).

The GPC molar masses of the fibrous polymer **3** (100% yield) were $M_w \approx 148\,000\,g\,mol^{-1}$ and $M_n \approx 48\,000\,g\,mol^{-1}$, and its inherent viscosity amounted to $[\eta] = 1.50\,dl\,g^{-1}$. Without Aliquat® 336, polymer **3** had $M_w \approx 13\,000\,g\,mol^{-1}$, $M_n \approx 9\,000\,g\,mol^{-1}$, and $[\eta] = 0.22\,dl\,g^{-1}$. Polymers **4–6** were synthesized similarly. Their inherent viscosities amounted to 0.94, 0.39, and 1.84 $dl\,g^{-1}$, respectively, indicative of significant molar masses. Later, Towns and O'Dell[40] described disadvantages of this procedure. They included (1) slowing of the reaction when toluene is used, (2) discoloration of the product, (3) decomposition of the catalyst, (4) poor reproducibility of the polymerization, and (5) foaming. These authors claimed in the same patent to having overcome these problems by the use of 'organic bases' (This includes alkylammonium hydroxides, alkylammonium carbonates, alkylammonium biscarbonates, alkylammonium borates, 1,4-diazabicyclo[2.2.2]octane (DABCO), dimethylaminopyridine, pyridine, trialkylamines, and alkylammonium fluorides.) instead of the commonly used inorganic ones. When studying the same reaction to polymer **3** (**Scheme 5**) in the presence of 'organic bases' after only 2 h reaction time, high molar masses of 204 000–370 000 were observed by GPC. Even higher molar mass can be found in another patent.[41] Monomers **7** and **8** were polymerized in a reaction mixture containing dioxane, toluene, water, K_3PO_4, and 0.025 mol.% of a tris-*ortho*-tolylphosphine palladium catalyst (**Scheme 6**). By adding a small additional quantity of monomer **7** after 6 h, doing an end-capping procedure after 7 h using bromobenzene, treating the reaction mixture with aqueous NaCN, followed by twofold precipitation of the raw polymer resulted in a 88% yield of polymer **9** as a colorless solid. GPC analysis gave $M_w = 814\,000\,g\,mol^{-1}$ and $M_n = 267\,000\,g\,mol^{-1}$.

Note that removal of the bromo and boron functionality present at the chain ends is done by an end-capping procedure in which corresponding monofunctional reagents are (often) added sequentially to the reaction mixture together with a fresh catalyst prior to workup. For bromo end groups, phenylboronic acid is often used, and for boron end groups, bromobenzene or *para*-fluorobromobenzene is used. Depending on the molar mass, the efficiency of these processes can be determined by NMR spectroscopy. The removal of boron functionality ensures

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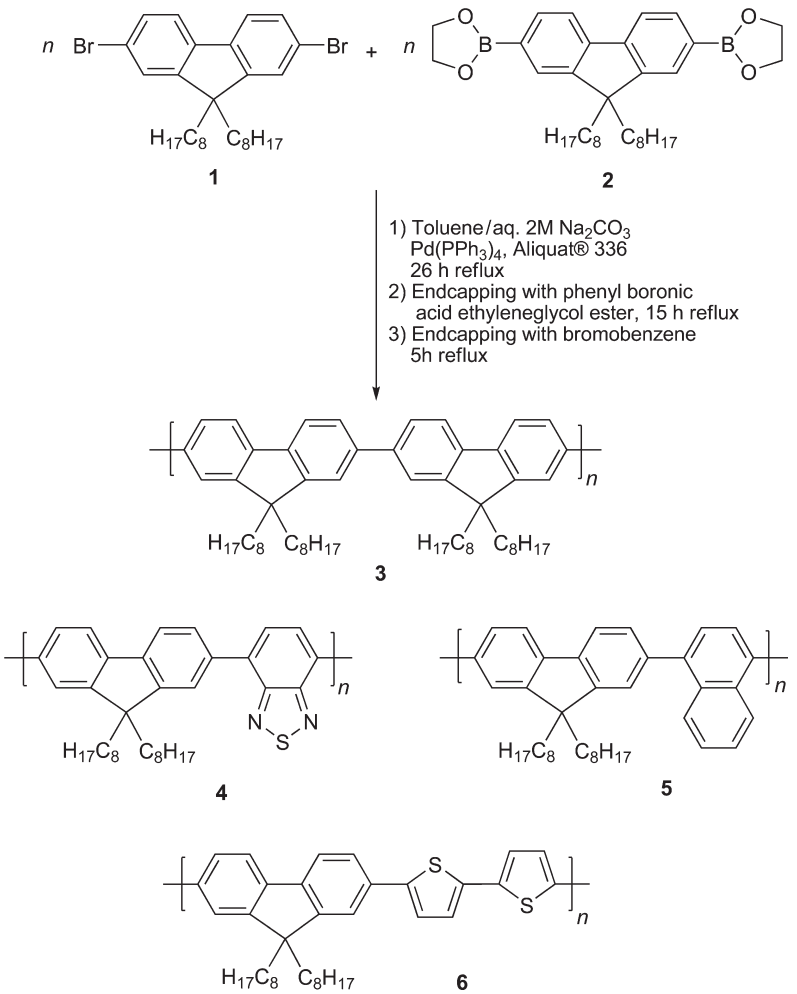
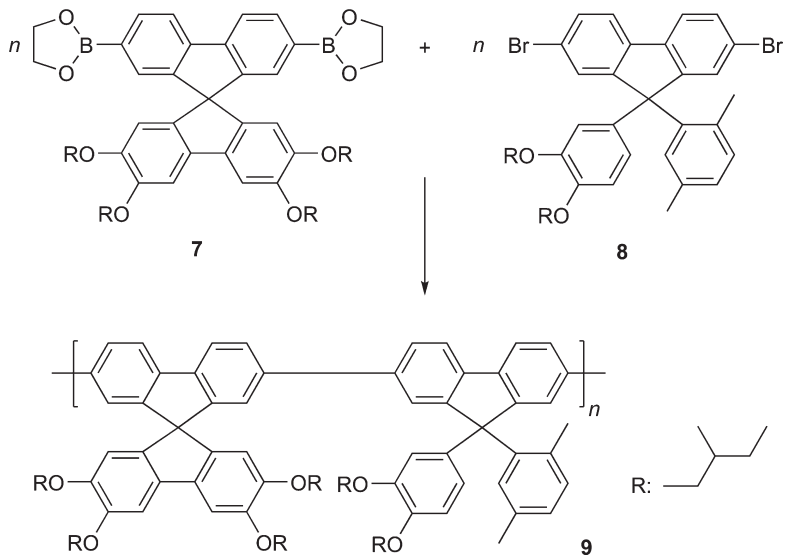


Scheme 5 Synthesis of PF **3** from monomers **1** and **2** and structures of PFs **4**–**6**. These PFs are among those whose synthesis was optimized in industry.



Scheme 6 An especially high-molar-mass case of SPC under optimized conditions: The polymerization of monomers **7** and **8** to give spiro-type PF **9**, with GPC molar masses $M_w = 1\,400\,000$ g mol^{-1} and $M_n = 410\,000$ g mol^{-1}.

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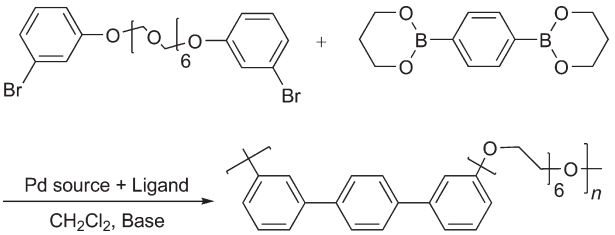

Scheme 7 A fully optimized SPC that furnishes the polymer with molar masses of up to $M_n = 64\,000\,g\,mol^{-1}$ and $M_w = 180\,000\,g\,mol^{-1}$.

complete and time-independent solubility of the product. Boronic acids can condense and hamper molar mass determination.

It should be remarked that when monomers **7** and **8** of an 'extraordinary' purity were treated under the given conditions in the presence of 0.0125 mol.% of Pd catalyst, polymer **9** was isolated in 93% yield and with $M_w = 1\,400\,000\,g\,mol^{-1}$ and $M_n = 410\,000\,g\,mol^{-1}$. The attention of the reader is also drawn to similar work by Towns and co-workers[42] and a recent publication by Liu *et al.*[43] in the open literature.

Murage *et al.*[44] recently reported an excellent optimization study of the SPC shown in **Scheme 7**. This study, which considered solvent, base, and catalyst, is one of the few comprehensive optimizations that appeared in the open literature. While the results naturally only apply to their system, the approach taken provides a valuable road map for others to use.

5.22.3.4 Purification and Side Reactions

Almost all SPCs published to date in the open literature use 1– 3 mol.% of catalyst, whereby $Pd(PPh_3)_4$, $Pd[P(para\text{-tolyl})_3]_3$, or $Pd[P(ortho\text{-tolyl})_3]_2$ are used most often. A few reports used Pd(II) sources. In light of avoiding eventual traces of leftover catalyst in the polymeric product, irrespective of whether this refers to P or Pd (see below), much smaller ratios are desired.[19] For Suzuki–Miyaura cross-coupling, Walker *et al.*[45] and others have shown that catalyst loadings of 0.001 mol.% can still give very good results. Another even more extreme case was recently reported by Arvela *et al.*, who showed that trace amounts of Pd contaminants down to a level of 50 ppb in commercially available sodium carbonate can catalyze the cross-coupling, affording decent yields of biaryl products under microwave (μW) conditions in water at 150 °C.[46] Reduced catalyst amounts were recently applied to SPC. For a poly(*meta-para*-phenylene), high molar masses could be reproducibly obtained if only 0.03 mol.% of $Pd[P(para\text{-tolyl})_3]_3$ were used. Compared to an experiment where 0.3 mol.% of the same catalyst was employed, the molar masses decreased only slightly from $P_w = 390$ to $P_w = 376$ and are, thus, still very high.[47] Residual traces of Pd are of great concern for applications in organic electronics because they interfere with the electronically excited states of the polymers. If present in the active polymer layer of an OLED, for example, Pd traces enhance the rate of nonradiative quenching and intersystem crossing from singlet excitons to long living triplet states with dramatic consequences on the intensity and the spectral properties of the emitted light. It is reasonable to assume that the loadings used in industry are generally much below the ones typically used in academia. It seems that some companies have reached loadings as low as 0.01 mol.%.

Oxygen is another serious concern. Phosphine-based Pd catalysts, which remain the most common, must be prepared freshly and can only be stored for a few days in a high-quality glove box before the first detrimental effects on molar masses are observed. It is essential to do the entire polymerization, which can last for a couple of days, under rigorous exclusion of air (for significantly shorter polymerization times, see Section 5.22.4.3). This exclusion is not only about the sensitivity of phosphine toward oxidation that may result in colloidal precipitation of Pd metal, but also there is evidence that oxygen can give rise to side reactions such as homocouplings of boronic acid/boronate monomers,[48,49] which would lead to a mismatch of the number of functional groups and therefore give lower molar masses. In addition, sequence defects arising from homocoupling cannot be healed. Another side reaction, the oxidative substitution of boronic groups by hydroxyl groups, was reported.[50]

B–C bond cleavage can also take place protolytically (protodeboronation). It is known that this side reaction can be facilitated by the use of strong aqueous bases[51] and can be serious particularly when the boron monomers with *ortho*-substitutions or adjacent heteroatoms are used.[52] Dehalogenation is known as side reaction associated with aryl halogenide that can happen in the presence of Pd catalyst and hydride donors. Specifically, when alcohol serves as the hydride donor, this reaction proceeds through β-hydride elimination of $Ar–Pd–OCH_2R$ giving rise to ArH and RCHO.[52] **Figure 5** shows one example reported by Jayakannan *et al.* describing matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass analysis of SPC products, which underwent such side reactions.[53] It is obvious that a careful optimization of reaction conditions is necessary for SPC in order to minimize all those side reactions, which can terminate chain growth and thus have direct impact on molar masses as well as end functional group pattern.

Once the polymerization is finished, the polymers are typically recovered by drying the crude product, taking the soluble material up in an organic solvent, and precipitating the dissolved polymer into a nonsolvent, often methanol (MeOH) or acetone. The product is collected by filtration and the procedure is repeated until desired quality (color, metal content, etc.) is achieved. Sometimes, products are separated to obtain fractions with higher molar mass, narrower molar mass distribution, and/or less impurities.[54]

Polyarenes used in OLEDs and other devices must have low Pd content. Such polymers synthesized by academia often contain undetermined but large quantities of Pd and other undesired elements. Industrial laboratories have taken pains to prepare polymers with ~1 ppm Pd. Laser ablation inductively coupled plasma mass spectrometry (ICP-MS) is a powerful and useful technique for quantitative trace element analysis. For the aforementioned poly(*meta-para*-phenylene), synthesized with 0.03 mol.% of $Pd[P(para\text{-tolyl})_3]_3$, the lowest Pd content by ICP-MS was 2.8 ppm[55] after only two rounds of careful precipitation. If an even lower Pd content is needed, treatment with aqueous NaCN or Pd scavengers, such as the one advertised by Nielsen *et al.*,[56] can be considered.

The P content has also been quantified by laser ablation ICP-MS and can reach values below 35 ppm.[55] Some P may be

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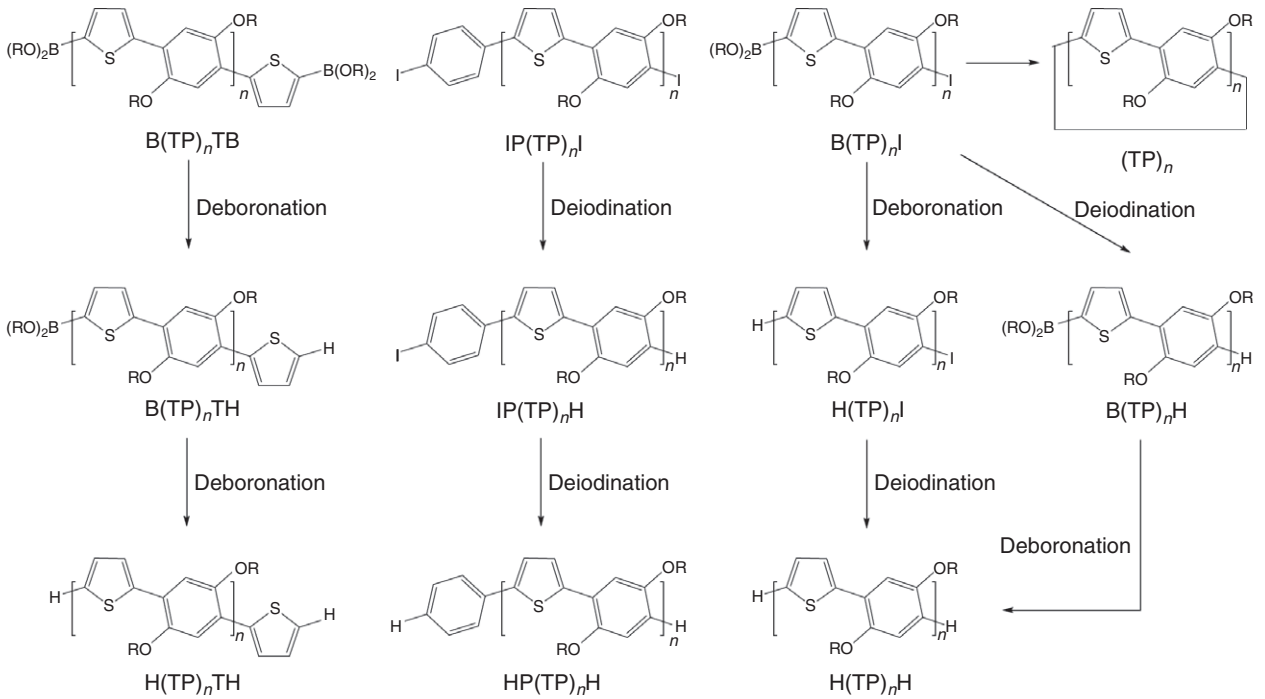

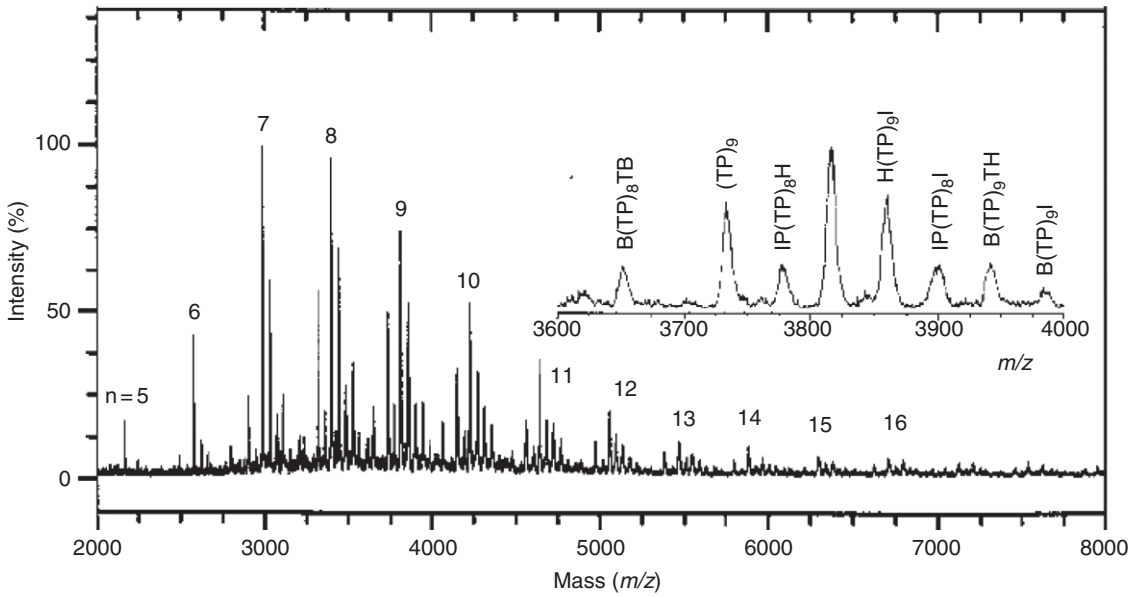

Figure 5 A MALDI-TOF mass spectrometric analysis of SPC products by Janssen *et al.* showing side reactions such as deboronation and deiodination. Reproduced from Jayakannan, M.; van Dongen, J. L. J.; Janssen, R. A. J. *Macromolecules* **2001**, *34*, 5386 with permission by the publisher.[53]

covalently incorporated into the polymer by ligand scrambling,[57–59] where the aryl groups of the aryl phosphine of the catalyst are exchanged with the terminal arylenes of the growing polyarylene chains. The net effect is P incorporation into the resultant polymer structure and chain termination (Scheme 8). Total suppression of this side reaction is difficult, but the use of P-free ligands is a promising solution.

5.22.3.5 Molar Mass Determination

Rigid, rodlike polymers have a larger hydrodynamic volume than flexible ones of the same contour length. For practical reasons, the molar masses and distributions of polymers are commonly determined by GPC, a relative method that separates according to hydrodynamic volume. Absolute methods such as light- and small-angle neutron scattering are applied only in exceptional cases. Narrowly distributed samples of different molar mass standard polymers (e.g., PS or poly(methyl methacrylate) (PMMA)) are used for calibration. A GPC molar mass of a polyarylene derivative of, that is, 50 000 g mol^{-1} means nothing else than that this sample has the same hydrodynamic volume as a sample of the standard polymer used with an actual molar mass of 50 000. With the larger hydrodynamic volume of rodlike polymers, the

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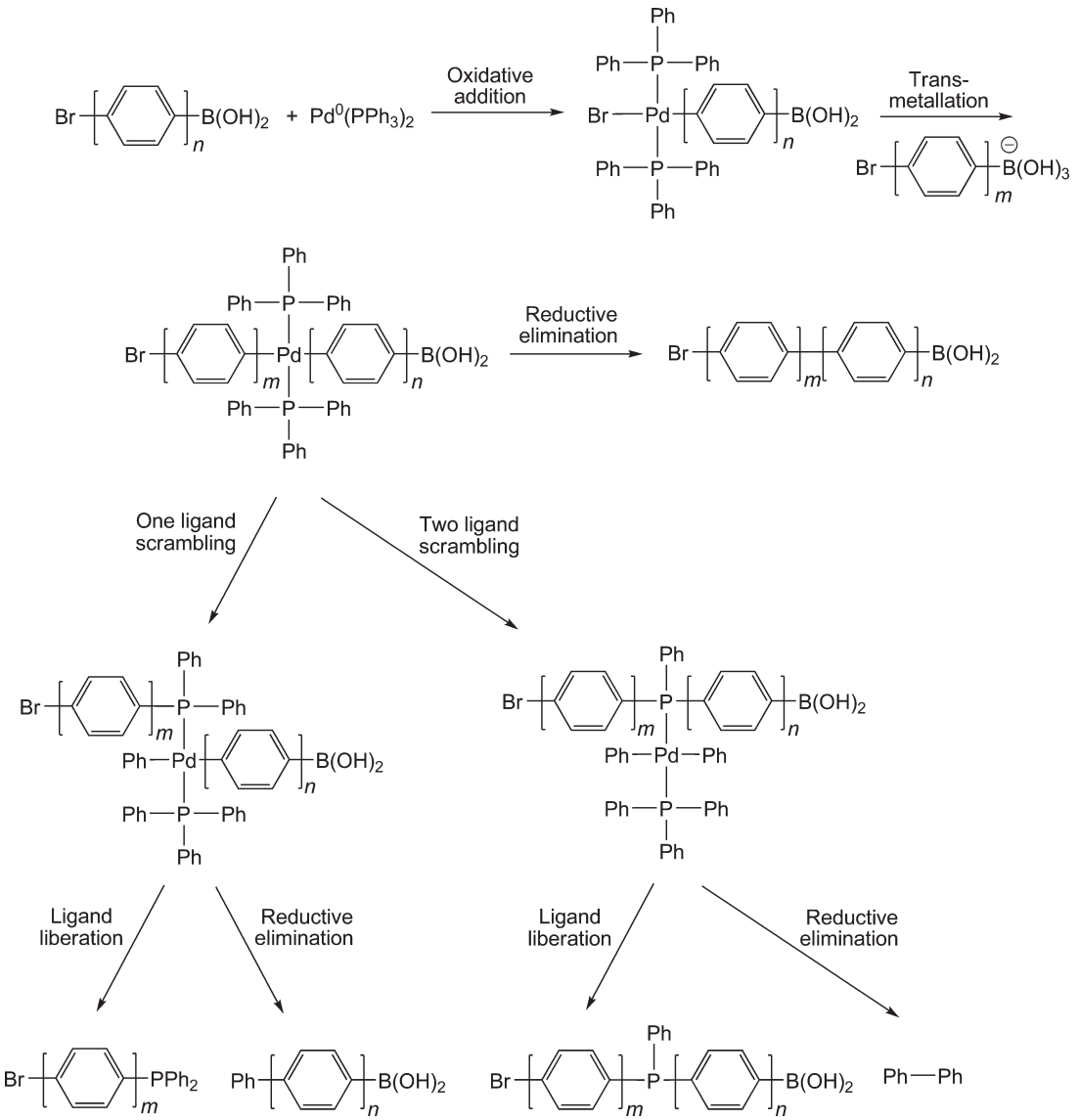

Scheme 8 Rationalization scheme explaining the incorporation of ligand-derived phosphorus into the polymer backbone during SPC. Not all options are shown.

actual molar mass of the polyarylene under consideration must obviously be lower; the number 50 000 represents just an upper limit. With this in mind, many publicized GPC molecular weights of polyarylene derivatives should be considered with care. Further complications may arise caused by the rodlike nature of polyarylenes. This increases their propensity to form aggregates and it needs to be confirmed that the elution curves actually refer to molecularly dissolved polymer.

Fortunately, there is a thorough study available in which the actual molar mass of the PPP **10** in **Figure 6** (R^1 = methyl, R^2 = dodecyl, and R^3 = 3,5-di-*tert*-butylphenyl) was determined by light scattering, osmometry, and GPC using universal calibration and compared with the masses obtained from PS calibration.[60] The universal calibration was done on the basis of the Mark–Houwink–Sakurada equation using nine fractions of PPP **10** with molar masses ranging between $27 < M_w < 189\ \mathrm{kg\,mol^{-1}}$. A calibration based on the wormlike chain model gave very similar results. As can be seen from

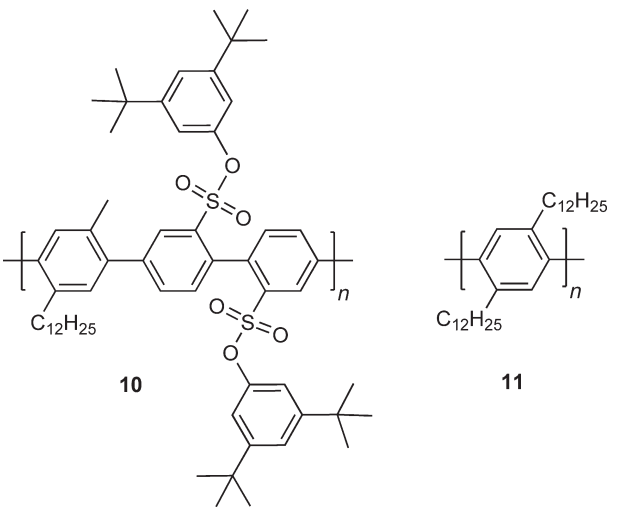

Figure 6 Chemical structures of PPPs **10** and **11**.

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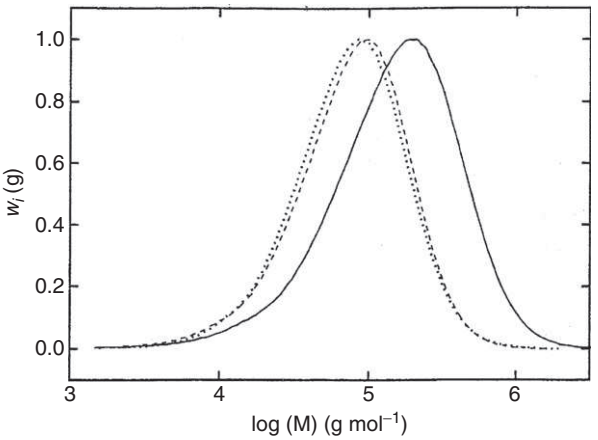


Figure 7 GPC elugrams of polymer **10** (M_w = 113 kg mol^{-1}) in tetrahydrofuran (THF): PS calibration (solid line), universal calibration based on Mark–Houwink–Sakurada equation (dashed line), and universal calibration based on the wormlike chain model (dotted line). Reproduced from Vanhee, S.; Rulkens, R.; Lehmann, U.; *et al. Macromolecules* **1996**, *29*, 5136 with permission by the publisher.

Figure 7, both these calibrations lead to almost superimposable elution curves at much lower molar mass than PS. A quantification of this difference reveals that PS overestimates the real molar mass of PPP 10 by a factor of almost 2. Although substituents certainly have an effect on the stiffness and thus the hydrodynamic volume of a polymer chain, it is reasonable to assume that this effect will normally be small. As a rule of thumb, GPC molar masses of PPP derivatives should, therefore, generally be corrected by this factor of 2 to lower values in order to have a more realistic estimate of the actual molar mass. For PPPs that carry very large substituents such as dendrons, an additional aspect comes into play.[61] If a given polymer's mass per unit length is much larger than the standards', it can happen that GPC calibrated with PS underestimates the real molar mass even for rodlike polymers. It should be noted, however, that this underestimation by GPC is a clear exemption from the rule.

A more recent study by Harre and Wegner[62] highlights the problem of aggregation for molar mass determination even for dilute solutions of PPPs. Freshly prepared solutions of PPP 11 in toluene are metastable at room temperature, regarding the formation of aggregates composed of up to 100 individual macromolecules. This aggregation process has an induction period of more than 10 h at room temperature. The kinetics of aggregation was investigated by making use of a fast capillary membrane osmometer. Aggregation follows an Avrami–Evans-type formalism and suggests that clusters of lyotropic LC phases are formed. The long induction period of aggregate formation in dilute toluene solution allows applying conventional techniques of molar mass determination, such as membrane osmometry and GPC. A relationship $[\eta] = 1.94 \times 10^{-3}\,M^{0.94}$ was found for polymer 11 in toluene at 20 °C and a persistence length of 15.6 nm was derived applying the Bohdanecky formalism. This gives evidence of the wormlike nature of the nonaggregated polymer 11 in dilute solution.

This result also explains why difficulties are frequently encountered if one tries to process solutions of polyarylenes by spin coating, ink-jet printing, roll-to-roll printing, and so on. Unless care is taken of inevitably ongoing aggregation processes in the solutions, irreproducible results will be obtained with regard to the homogeneity or – more general – morphology of the resulting films and patterns. This, in turn, has severe consequences for the reproducibility and control of the photonic and electronic properties of the processed materials.

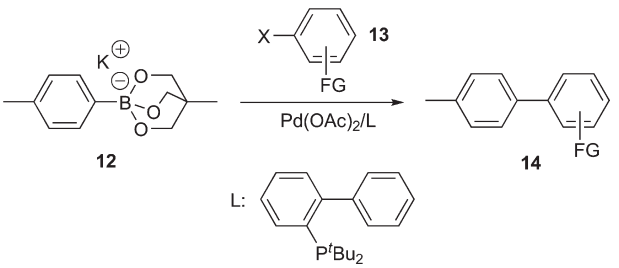
5.22.4 Recent Progress

5.22.4.1 Monomers

There is an increasing demand to design more complex monomers. Recently discovered masking groups for boronic acid such as 1,8-diaminonaphthalene[63] and *N*-methyliminodiacetic acid (MIDA)[64] would be useful because the protected boron functionality can withstand not only purification by silica-gel chromatography but also the synthesis scheme that includes metal-catalyzed cross-coupling steps. (For orthogonal reactivity between organotrifluoro borate and trialkyl borate, see Reference 65.)

Tetracoordinated *ate* complexes of boron have been described in the literature repeated times.[66] It has been known for more than 20 years that they can be employed into cross-coupling reactions without the simultaneous presence of a base, which otherwise is essential to Suzuki–Miyaura cross-coupling and SPC. Though *ate* complexes have the attraction of being isolable in crystalline form (which is of advantage when it comes to realization of a certain stoichiometry; see Section 5.22.3.2) and can even be water and air stable, their coupling efficiencies were so far not in a range making them promising candidates for polymer applications. Very recently, Yamamoto *et al.* disclosed an interesting finding that may actually find its way into polymer synthesis. Their laboratory reported on the novel, stable triolborate 12 that is sufficiently soluble in organic solvents and shows high conversions in model cross-couplings of the sort shown in Scheme 9.[67]

For synthesis of aryl halogenides, placeholder or masking strategies[68] have been studied for a long time and are now available for designing a great variety of potential monomers for SPC. The majority of monomers used in SPC carry bromides. There are a few examples with aryliodides. Some of them seem to furnish better results in terms of molar mass,[69] but there is also a report in which such an improvement was not observed.[44] There is too little information available to draw general conclusions, specifically regarding direct comparisons of dibromo versus diiodo monomers of the exact



Scheme 9 Suzuki–Miyaura cross-coupling (SMC) of the triolborate **12** with the haloaromatic **13** to give biphenyl **14**.

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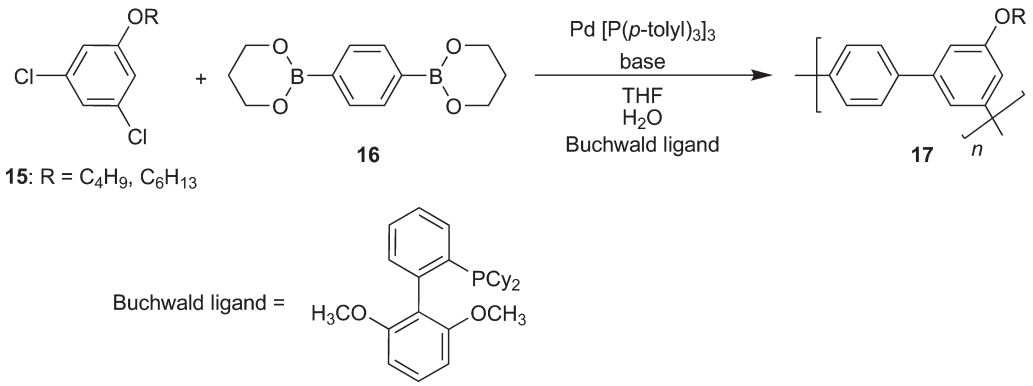

Scheme 10 The first example of an SPC using dichloroaromatic monomers. This success became possible through ligands specifically designed to overcome the relative inertness of the aromatic C–Cl bond toward Pd-mediated cross-coupling reactions.

same structure carried out in the same laboratory. It is, therefore, presently advisable to do case-by-case studies. From the industrial point of view, chloro-functionalized monomers have advantages. They include commercial availability and low cost. Unfortunately, aryl chlorides are still a challenge for all transition metal-mediated cross-coupling reactions. This is due to the considerable stability of the C–Cl bond, though attractive developments have been reported during the past decade (see Section 5.22.4.2). Using a Buchwald ligand, it could very recently be shown that the dichloro monomers **15** (**Scheme 10**) polymerize with boronic ester monomer **16** to poly(*para-meta*--phenylene) **17** in satisfyingly high average molar masses of $M_w = 24\,000\,g\,mol^{-1}$ and in yields of 95% referring to purified and freeze-dried material.[70] This molar mass corresponds to an attractive $P_w = 94$ and will stimulate broader research in this promising direction.

Trifluoromethyl, perfluoroalkyl, and imidazolyl sulfonated aromatics have been subjected to Suzuki–Miyaura cross-couplings[71] but only few to SPC in the open literature.[72–74] The use of sulfonyloxy aromatics is nevertheless an interesting variation because it allows to use the amply available phenols, hydroquinones, resorcines, and related aromatic with phenolic hydroxides as precursors for the corresponding monomers.

5.22.4.2 Catalysts

The recent years have witnessed an enormous development in catalysts for Suzuki–Miyaura cross-coupling[75] aiming at higher turnover numbers, milder conditions, and higher efficiencies, and also allowing the reaction to proceed with enantioselectivity,[76] against high sterical hindrance[77] or via activation of C–Cl, C–O, and C–H bonds.[78,79] Examples of new active ligands specifically addressing C–Cl bond activation include Buchwald's biaryl-based phosphines,[80] Beller's diadamantyl phosphines,[81] Fu's tri-*tert*-butyl and tricyclohexyl phosphines,[82] Hartwig's pentaphenylated ferrocenyl phosphines,[83] and also N-heterocyclic carbenes.[84]

Although the first application of a Buchwald ligand to SPC of a dichloro monomer was mentioned in Section 5.22.4.1, more exploratory work on application of these ligands to SPC would be beneficial to the field.

When biphasic heterogeneous conditions are used, the partitioning of reaction components between organic and aqueous phases needs to be considered. Liu *et al.*[85] describe efficient water-soluble phosphine ligands to be applied to SPC in a mixed solvent of THF and water. The corresponding Pd catalysts not only give improved molar masses when compared with $Pd(PPh_3)_4$, but also lower residual Pd in the final products after extraction with scavengers. Goodson and co-workers recently developed a water-soluble derivative of dibenzylideneacetone (dba). $Pd_2(dba)_3$ is often used as Pd source for *in situ* preparation of active Pd(0) catalysts by ligand exchange. The liberated dba derivative partitions into the water phase, where it does not inhibit SPC taking place in the organic phase.[86]

Phosphine ligands are prone to undergo ligand scrambling and oxidation by inadvertently present traces of air (see Section 5.22.3.4). It has therefore always been a concern of how to avoid P-based ligands in SPC. For example, use of some supported catalysts[87] may be interesting to be considered. Such heterogeneous catalysts can not only be reused in large-scale preparations or flow reactor applications but also may facilitate purification of SPC products.

5.22.4.3 Microwave and Technical Scale Microreactor Applications

There are two engineering-type methodological developments to be mentioned in connection with SPC: the application of μW and of microreactors. Whereas the first is still in its infancy, the latter has reached technical scale maturity. μW technique has led to astounding improvements for numerous chemical reactions. This includes Suzuki–Miyaura cross-coupling for which countless publications have appeared.[88] It has recently also been applied to SPC, so far though met with limited success only. Scherf *et al.* reported the first μW SPC on a rather complex monomer system (**Scheme 11**). They applied two different μW conditions and compared the respective outcome with the result obtained when the same SPC was carried out under conventional conditions. The μW conditions were (1) aqueous K_2CO_3/THF (150 W, 12 min) and (2) solid KOH/dry THF (300 W, 10 min). The polymers were obtained in yields of 60% and 72% and had $M_n = 14\,200$ and $29\,900\,g\,mol^{-1}$, respectively.[89,90] Under conventional, presumably not fully optimized conditions, the yields were about 80% and

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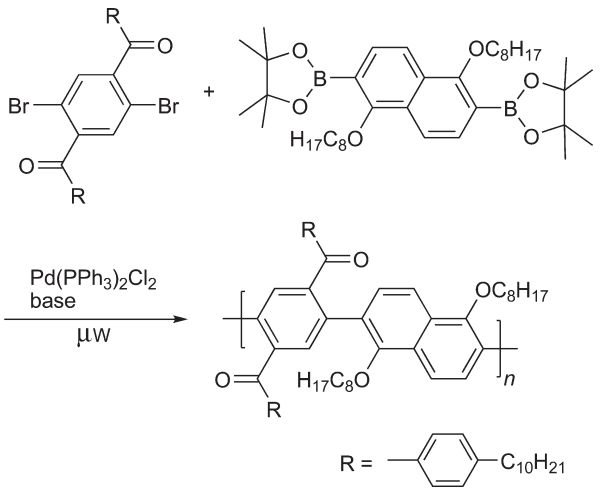

Scheme 11 Microwave-assisted SPC: the first report in the open literature by Scherf *et al.*

$M_n = 4000 - 11\,000\,g\,mol^{-1}$. Thus, μW seems to have had a positive effect on the molar masses, though an unequivocal conclusion is difficult to draw; all products are still more or less in the oligomeric regime. Nevertheless, the drastically shortened overall reaction time (minutes instead of days), which is so often reported on μW applications, would certainly be attractive here as well.

In recent years, microreactors were specifically designed and adjusted to optimally match the commonly biphasic SPC conditions. This aimed at providing a technology that allows a continuous small but nevertheless technical scale production of polyarylenes. Some of these developments took and are still taking place at the Institut für Mikrotechnik, Mainz, Germany (IMM). Sufficient mass transfer in biphasic reactions is an obvious issue and two concepts were developed at IMM to ensure a sufficient interfacial area during SPC. The first is based on the repeated breakage of droplets with the help of a so-called redispersion microreactor consisting of exchangeable redispersion units separated by multichannels and an inspection window. This window allows continuously monitoring and investigating the flow patterns. The second concept uses a metal foam-filled tube reactor as a kind of static mixer. The microstructure of the foam is chosen with a high porosity such that as low as possible pressure decrease is achieved. All details are of course proprietary information, but it seems that the higher conversions in SPC are reached with the second concept. The reader can only be referred to some conference proceedings.[91] There also seems to be a successful development of a fixed-bed column reactor in which SPC can be done in an astoundingly short residence time of 20 min, leading to relatively narrowly distributed, high-molar-mass products.

5.22.4.4 Catalyst-Transfer Polycondensation

In Section 5.22.3.1, SPC was introduced as being of the step-growth kind. Many experimental facts support this view. Rather convincing evidence is the fact that no initiation is needed and series of oligomers are seen at the early stage of polymerization, whose molar masses are continuously shifted to higher values as reaction time passes following step-growth statistics. Also, if a chain mechanism would be operative, it had to be explained how the Pd after each C–C bond formation event should pass toward the chain terminus in order to continue its action on the very same chain. In the AB case, one of the chain ends is always halogenide (or another leaving group such as triflate). Since there is evidence for Pd to be able to rest on π-systems, one could possibly imagine that a Pd(0) fragment, stabilized by a ligand, moves from its last reaction site across the newly added terminal phenylene unit and then adds oxidatively into the there existing C–Br bond. (Preferential twofold oxidative addition of some AA monomers is reported and it supports the sliding hypothesis on conjugated chains, e.g., see Reference 92, it however cannot rationalize a catalyst transfer mechanism to cause chain growth as far as AA/BB monomer systems are concerned.) This would result in continued growth of the same chain. For the AA/BB approach, however, such a picture cannot hold because the nature of the terminal functional group changes from halogenide to boronic acid (or ester) and backward alternating after each addition step.

Initiated by the interesting work of Yokoyama *et al.*[93] there has been quite some activity in regard to this so-called catalyst-transfer polycondensation,[94] which uses AB-type monomers and basically follows the above picture of sliding metals over π-systems[95] whereby the polymerization mechanism can be switched from step to chain growth. Impressive results were obtained mostly for thiophene-based monomers and Kumada-type protocols. For certain cases and low molar masses, it seems that the typical fingerprints for a chain growth can be proven.

Recently, Yokoyama *et al.*[96] reported the first cases in which SPC monomers were polymerized initiated by the Pd complex **18** (**Scheme 12**). Also, here the molar mass linearly depended on conversion, the polydispersity index (PDI) was low, and the phenyl group of the initiator was actually found as end group in each chain of the product. In addition, a monofunctional arylbromide did not get involved into polymerization. Thus, it seems that for AB monomers one has to consider chain mechanisms as an option.[92] Though these findings may have a considerable impact to the field leading to conjugated block polymers[97] and polymer brushes,[98] it is too early to draw any general conclusions at present. One may well ask why in all catalyst-transfer polycondensations the molar masses are rather low. In the above case, number-average molar masses of $M_n = 18\,000\,g\,mol^{-1}$ are reported corresponding to degrees of polymerization of only $P_n \sim 20$. It remains an important open question why the polymerizations were not investigated for higher molar masses. Insufficient solubility cannot be the reason in all cases, though it should be emphasized that the polymerizations are carried out at relatively low temperatures in order not to sacrifice narrow distributions and regioregularity (were applicative). In the end, it may well be that different mechanisms are operating more or less simultaneously. Together with the heterogeneity of the reaction, this could help explain why quite a few high-molar-mass SPC products show rather broad molar mass distributions. PDI values of 4–5 are not uncommon. Further clarification regarding this delicate issue is obviously required. This should include an *in situ* spectroscopic or mass spectrometric proof of the active chain end.[99]

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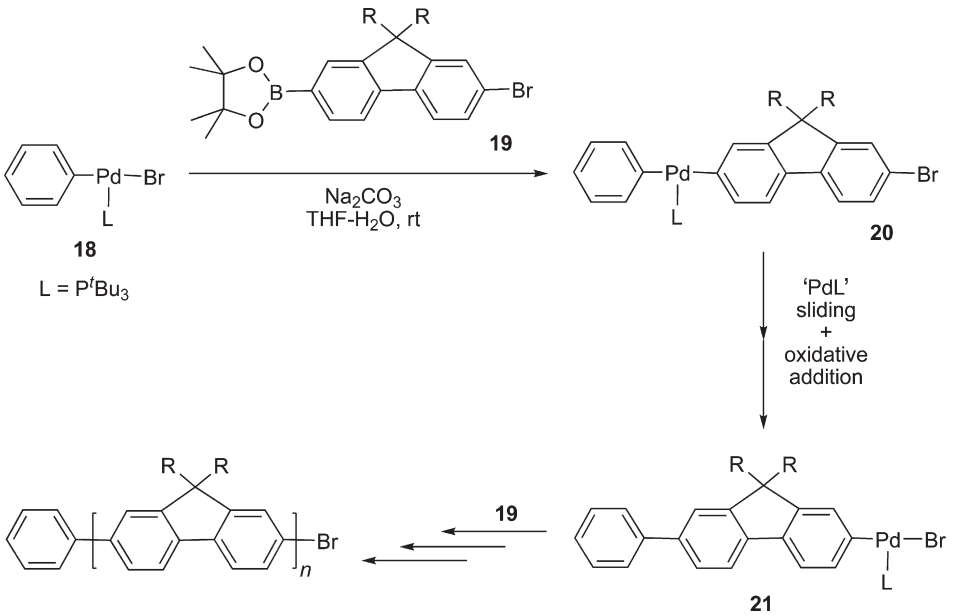

Scheme 12 Mechanism proposed for a catalyst-transfer polycondensation using the Pd complex **18** as initiator and the SPC monomer **19**. After the C–C bond formation in **20**, the Pd residue shifts over the π-part of the fluorene unit to oxidatively add into the terminal C–Br bond, thus creating species **21** prone to undergo transmetallation with the next monomer to collide with the chain end.

5.22.5 Selected Examples

5.22.5.1 Liquid Crystalline and Amphiphilic Polyphenylenes and Polyelectrolytes

For rigid-rod polymers, decorations with flexible side groups such as alkyl, alkyloxy, or oligo(ethylene oxide) chains are generally required in order to gain solubility and processablity (see Section 5.22.1). The substitution pattern can be varied greatly. The nature of the side chains and the way in which they are anchored to the backbone impact properties. This includes aggregation and LC phase formation as was shown for PPPs decorated with both polar and non-polar substituents.[100,101] If charged substituents are installed, the PPPs result that differ from conventional polyelectrolytes by their high backbone rigidity. This rigidity renders them excellent models to study solution properties because the ionic strength of the surrounding medium cannot exert a large effect on polymer conformation. Excluded volume effects have to be taken into consideration only at higher concentration. For an interesting example, the reader is referred to a study on the aggregation behavior of PPPs with sulfonate groups, 22 (Figure 8).[102] In highly dilute aqueous solutions, these polymers self-organize into anisotropic cylindrical micelles. The cross section of these micelles intersects ~15 individual polymer chains, and the length of these micelles is approximately 5 times the contour length of the constituent polymers. These structures can arrange into more ordered motifs such as closed loops and lasso-like structures, a phenomenon most likely driven by entropically motivated avoidance of fringes of dangling chains. The substitution pattern of 22 was designed such that it can segregate lengthwise into hydrophilic and hydrophobic parts: the sulfonic acid groups point toward the side opposite of the dodecyl chains. If this segregation along the backbone is precluded by introducing two short lateral substituents with terminal charges like in 23, the formation of cylindrical aggregates is suppressed. Polymer 23 and a variety of related systems were, therefore, investigated as molecularly dispersed rigid-rod polyelectrolytes and the results were compared with theory.[103]

Eisenbach *et al.*[104] used charged PPP-based rods such as 24 for mixing with countercharged coiled macromolecules for the purpose of molecular reinforcement. The mechanical properties of these ionomeric nanocomposites depend strongly on the molecular parameters of the rod component, that is, on the degree of polymerization and the rod volume fraction.[105]

5.22.5.2 Shielded Polyphenylenes

Sterically demanding substituents, such as dendrons, affixed to each repeat unit of a polymer have been used to separate individual chains from each other and 'insulate' the polymer backbone from the environment (Figure 9(**a**)). Several dendronized PPPs (e.g., 25; Figure 9(**b**)) have been synthesized.[38,106,107] The first experiments that demonstrated shielding[108] were reported by Aida and co-workers,[109] who showed that the collisional quenching of the photoluminescence of poly(*para*-phenylene ethynylene)s can increasingly be suppressed by attaching higher generation dendrons. Shielding can also have impact on the polymers' solvatochromic behavior and conformational effects.[110] Besides dendronization, perhaps the most commonly used shielding concept is to protect the polymer backbones by threading cyclic guests such as cyclodextrins (CDs) onto them. Anderson and co-workers presented a few elegant such cases using a PPP 26 in which threading efficiencies of 1.1 β-CD per repeat unit were achieved (Figure 9(**b**)).[110,111]

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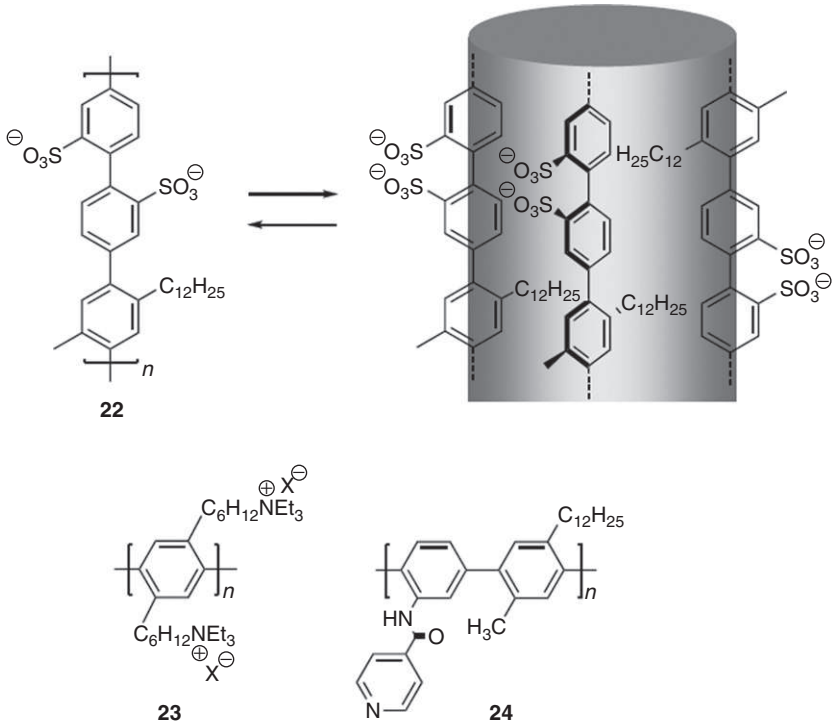

Figure 8 Chemical structures of PPP derivatives **22–24** with lateral substituents, that is, designed so as to induce specific aggregation behavior, test polyelectrolyte theories, and the concept of molecular reinforcement.

5.22.5.3 Bridged and Ladder-Type Polyphenylenes

The concept of bridging consecutive phenylene units to enhance conjugation and to provide a point for incorporation of peripheral substituents has not only been applied to PFs (Section 5.22.2.2) but also to other subclasses of PPs (**Figure 10**).[112–118] The level of coplanarity between two consecutive phenylene units as well as the size of the kink in the backbone can be tuned by choice of the bridges.[112]

Ladder polymers have been studied mostly for their thermal, electrical, and optical properties.[119] One of the possible approaches to this class of polymers uses single-stranded polymer precursor that is designed to allow for an additional strand formation by some follow-up chemistry. Polymers **27**,[120] **28**,[121] **29**,[122] and **30**[118] synthesized by SPC are examples for this (**Scheme 13**). The first three examples carry functional groups that can be used for ring closures between two adjacent phenylenes, leading to formation of the corresponding ladders **32–35**, respectively. The same chemistry used for **53** was also applied to a poly(*meta*-phenylene) precursor, leading to a unique double-stranded, helical structure composed of fused benzothiophene rings.[123] In the context of creating model structures for graphene in Müllen's laboratory,[124] the precursor polymer **31** was designed in order to undergo cyclodehydrogenation among the benzene rings leading to ladder-type polymer **36**.

5.22.5.4 Kinked Polyphenylenes and Foldamers

If *meta*- or *ortho*- instead of *para*-phenylenes are used as monomers, the resultant PPs can adopt many conformations (**Scheme 3**). They range from zigzag to helical, whereby the former is the most extended one and the latter the most compact. Such kinked PPs can provide a basis for designing 'foldamers' with selection of proper substituents.[125] It should be noted though during SPC using *meta*-phenylene monomers cyclic PPs can form in competition with linear products.[126]

The many energetically accessible conformations give such attractive mechanical properties to polymers. For example, Schlüter and co-workers reported SPC synthesis of a poly(*meta-para*-phenylene) decorated with butyloxy chains at every other phenylene unit (**37**) (**Figure 11**).[19] The raw polymer had $M_w = 83\,000\,\mathrm{g\,mol^{-1}}$ ($P_w = 370$) with a relatively broad molar mass distribution and was obtained on the 3.5 g scale. Fractionating precipitation afforded a 1 g fraction with $M_w = 255\,000\,\mathrm{g\,mol^{-1}}$ ($P_w = 1140$), whose NMR spectra are shown in **Figure 12**. Despite the respectable molar mass, narrow signals were obtained, the assignment of which proved integrity of the polymer structure. Melt-compression molded films (thickness ~150 μm) of this polymer were flexible and tough, and could be deformed well beyond the yield point. For comparison, stress–strain curves were also obtained of comparably thick melt-compression molded films of common atactic PS, PMMA, and commercial polycarbonate (PC; MacrolonLQ-2847) (**Figure 12**). Although the films of **37** were of a somewhat lower stiffness, they featured a nominal stress at break similar to the above polymers, but, remarkably, exhibited a macroscopic elongation at break that surpasses those of the brittle bulk polymers a-PS and PMMA, and approaches that of PC, which is reputed of its toughness. Such a film of **37** cast from chloroform and then annealed

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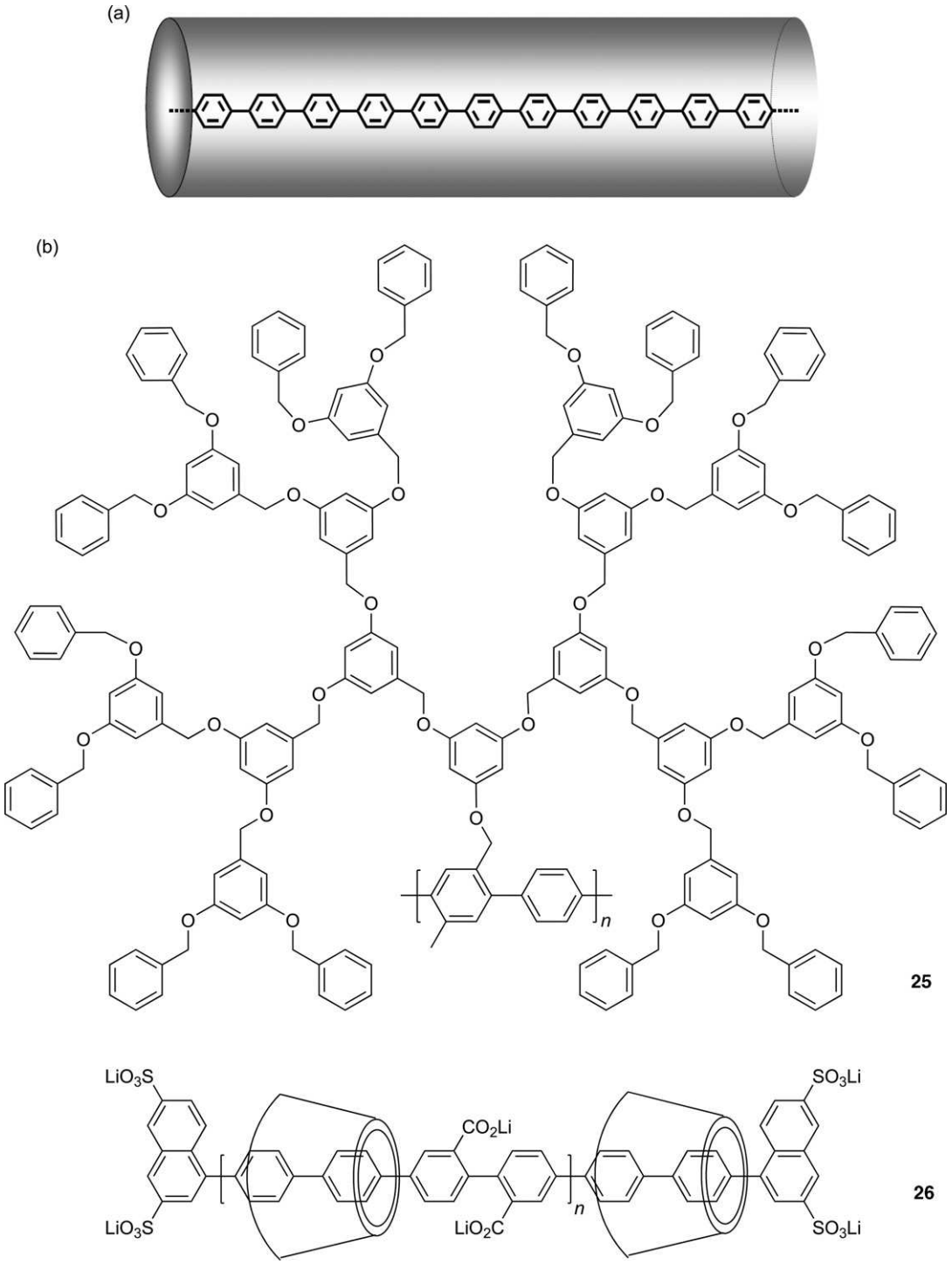

Figure 9 Cartoon of an active PPP backbone surrounded by a shielding shell (a) and concrete examples of PPPs whose main chains are shielded by covalent attachment of dendrons **25** or by threading them through β-cyclodextrines (β-CDs) **26** (b).

in a press at 230 °C for 5 min (well above $T_g = 166$ °C) could be stretched at 180 °C easily by 700–800% (Figure 13).[127] This example shows that SPC is a powerful polymerization protocol that allows entering the domain of high-performance polymers.

The fact that SPC can be used for the gram-scale preparation of such polymers with considerably high molar mass opens another intriguing possibility. Assume a polymer like 37 equipped with substituents such as oligo(ethylene oxide). Under segregating conditions, this polymer should fold up into a helical conformation. Given a very high molar mass, regarding end-to-end distance such a helix would by far overtake everything that is known in the presently vigorously researched area of 'foldamers'. Whereas typical foldamers are

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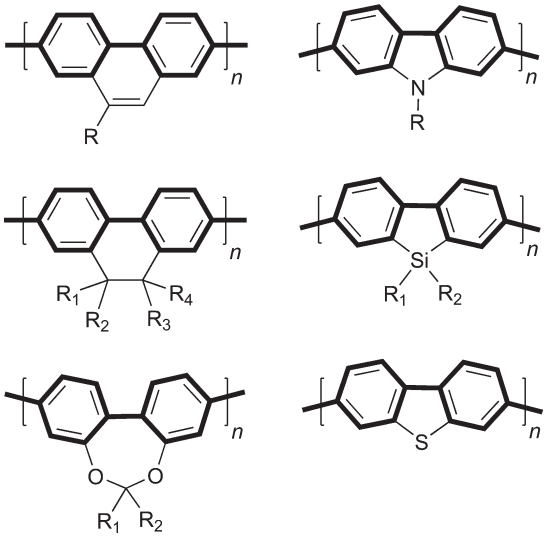

Figure 10 Examples of PPs with pairwise bridged phenylene units.

in the oligomeric regime and, therefore, have end-to-end distances of a few nanometers only in the folded state,[128] for a polymer like **37** with $P_w = 1140$, the helix (**Figure 14**) could reach lengths of 50 nm still maintaining a defined inner pore, large enough to let chemicals pass through, for example, in membrane applications.[129]

5.22.5.5 Hyperbranched and Cross-Linked Polyphenylenes

Hyperbranched polymers based on PP backbones **38** were synthesized early in SPC history (**Scheme 14**(**a**)).[130] Recent examples include those from AB_2 monomers based on terphenylene,[74] oligo(phenylene ethynylene),[131] fluorene,[132] carbazole,[133] oxadiazole,[134] and triphenylamine.[134] The triphenylamine monomer was subjected to SPC with a short oligofluorene core, and the products were tested for their hole-transporting capability in thin layer electrooptical devices. Weber and Thomas reported application of SPC to a network synthesis. They reacted 2,2′,7,7′-tetrabromo-9,9′-spirobifluorene with *para*-phenylene diboronic acid (**Scheme 14**(**b**)) and obtained the expected insoluble product to which structure **39** was assigned. This product was of interest for its presumed microporous nature that was confirmed by nitrogen sorption experiments.[135]

5.22.5.6 Unsubstituted Polyphenylenes

The above sections stressed the importance of flexible chain substitutions whenever dealing with rigid-rod polymers. Despite their extremely beneficial role in regard to synthesis, characterization, and processing, it is important to be aware that the decoration of rods with 'hairs' can also have detrimental effects. We had already addressed that substituents can increase dihedral angles between consecutive aromatics, a consequence that will lead to reduced backbone conjugation. More broadly speaking, substituents 'dilute' main-chain properties particularly in bulk. Given the necessary load with flexible chains to keep rigid rods in solution, the mass fraction of the desired material, the backbone, to the mass fraction of the chains may easily reach 1:1. This means that 50% of the product mass is 'grease'. It has, therefore, always been a wish to reduce the side chain content as much as possible.[16] With this consideration in mind, a 'shaving' approach was developed that would allow synthesis of unsubstituted PPs from a soluble and characterizable precursor polymer.[136] First, the soluble PP **40** was prepared and fully characterized by NMR, MALDI–TOF MS, and GPC. This well-defined 'hairy' PP was then subjected to a 'shaving' process, leading to the corresponding parent PP **41**. The acid-promoted desilylation quantitatively 'shaved' the solubilizing trialkylsilyl groups off (**Scheme 15**).

5.22.6 Poly(phenylene vinylene)s

5.22.6.1 Suzuki polycondensation

The first successful PPV synthesis using SPC was published by Heitz in 1997 (**Scheme 16**):[141–143] benzenediboronic acids **42** and *E*-1,2-dibromoethene **43** were converted into PPVs, **44**. Using silver oxide as a base, the reaction was possible even at room temperature. For 2-ethylhexyloxy-substituted PPVs, **44b**, P_n's ≈ 34 were reported. NMR studies identified biphenyl defects and bromine end groups in these chains. Later, the SPC method was expanded to the synthesis of poly(fluorene vinylene-*co*-phenylene vinylene)s, **47** ($P_n = 20$; **Scheme 17**).[144]

Katayama *et al.*[145,146] showed that appropriate choice of base and solvent allows minimizing the extent of biphenyl defects. Further improvement was achieved by adding phase-transfer catalysts. Under optimized conditions, *Z,Z*-configurated PPVs **49** ($P_n \approx 20$) were obtained (**Scheme 18**). Photoisomerization into their *E,E*-counterparts proceeds essentially quantitatively. As the *Z,Z*-isomer shows much higher solubility than its *E,E*-counterpart, change of solubility can be used for the preparation of structured and multilayer devices: the *Z,Z*-isomer is first processed from solution and then converted into the insoluble *E,E*-isomer, if needed by irradiation through a mask.

SPC can also be used for the preparation of PPV-based polyrotaxanes. These systems represent kind of molecular wires.[147–149] Iodoarenes **51** and **52** were treated with diboronic acid derivatives such as **50** in aqueous solutions containing α-CD (**Scheme 19**).[150] Its molecular coverage by CD causes a pronounced blueshift of the PPVs' photoluminescence while its absorption spectrum remains almost unchanged.

SPC has also been used for the preparation of poly(trypticenylene vinylene-*co*-phenylene vinylene)s (**Scheme 20**).[151] Copolymers **56** were found to be readily soluble despite of minor side-chain substitution (**56b**: $P_n = 18$). Obviously, the rigid conformation of the trypticenylene moieties prevents aggregation efficiently.[152] Moreover, lyotropic mesophases can be observed. Compared to their isotropic solutions, the UV–vis absorption is redshifted in the nematic solutions as the result of additional stretching of the polymer main chains, which induces further increase of the conjugation length.

Li *et al.*[153] used SPC for the preparation of chemosensors[152]: conversion of alkenylboronic esters **59** with mixtures of diiodobenzene **58** and templating diiodobenzene derivative **57** leads to PPVs **60** ($P_n = 28$; **Scheme 21**). If trifunctional monomers were added additionally, branched or even cross-linked products, **60**, were formed. Cavities remain in

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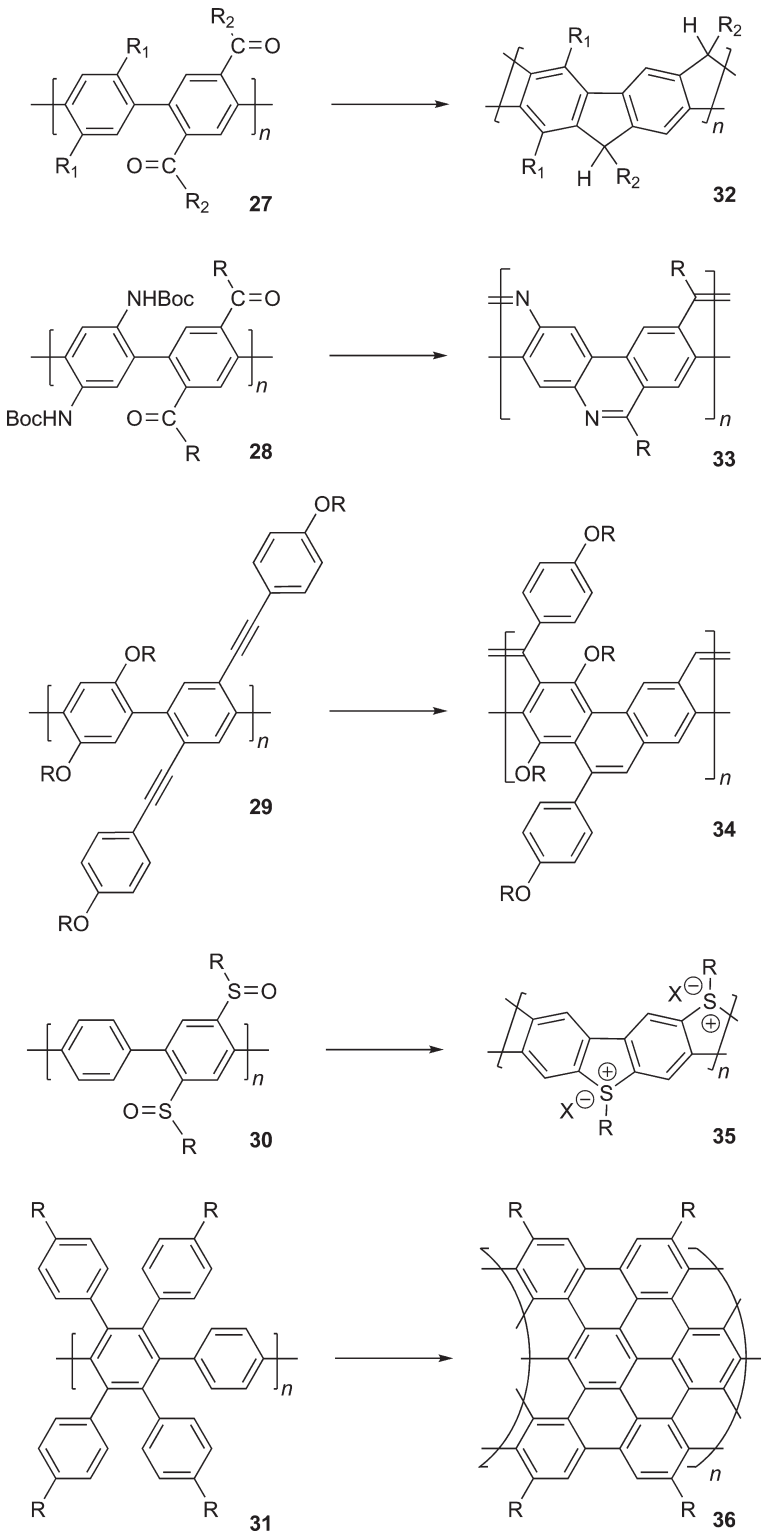

Scheme 13 Precursor PPPs **27–31** synthesized by SPC that were subsequently converted into ladder-type polymers **32–36**, respectively.

the cross-linked material after release of the templating groups, whose shape is similar to that of 2,4,6-trinitrotoluene (TNT). If TNT is incorporated into these cavities in the course of a sensor application, quenching of the polymer's fluorescence is the result.

Preuss used the SPC to synthesize PPV model polymers containing variable amounts of '1,1-defects'. These polymers are of importance in the context of PPVs formed by the Heck reaction (see below).[154] Some of these copolymers **64** and **65** could be obtained with excitingly high degrees of polycondensation ($P_n > 100$; **Scheme 22**). By means of these model PPVs, it could be shown that the 1,1-defects interrupt the π-electron conjugation along the PPV chains very efficiently.

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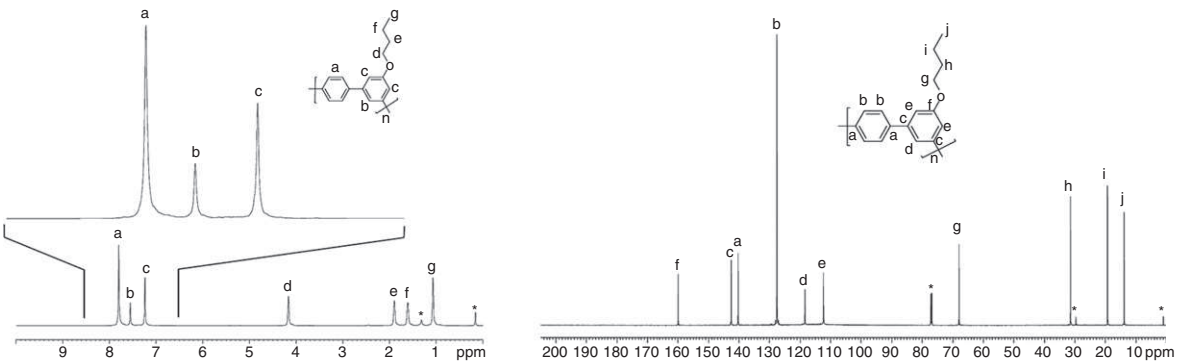

Figure 11 700 MHz ^{1}H (left) and 176 MHz ^{13}C NMR spectra (right) with signal assignment of the fraction of polymer **37** with M_w = 255 000 (P_w = 1140) to show the level of structure perfection achieved. Reproduced from Kandre, R.; Feldman, K.; Meijer, H. E. H.; *et al. Angew. Chem., Int. Ed.* **2007**, *46*, 4956 with permission by the publisher.[19]

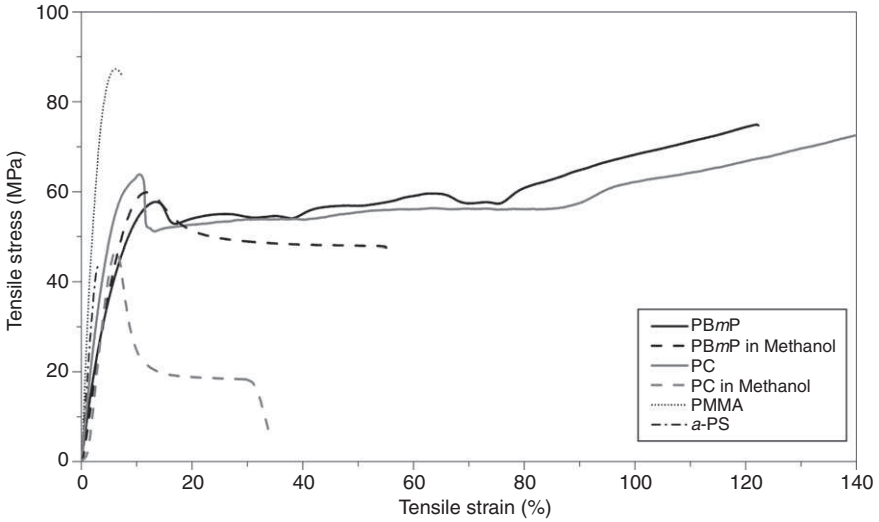

Figure 12 Stress–strain curves, recorded at room temperature of melt-compression molded films of poly(butyloxy-*para*-*meta*-phenylene) (PB*m*P) (**37**) (high-molar-mass part). For reference purposes, corresponding curves of a-PS, PMMA, and PC are also shown, illustrating the excellent mechanical properties of the new polyarylene. In addition, plotted are stress–strain curves of PB*m*P and PC samples, recorded while immersed in MeOH, showing the superior stress-cracking resistance of the former polymer toward this polar organic liquid. Reproduced from Kandre, R.; Feldman, K.; Meijer, H. E. H.; *et al. Angew. Chem., Int. Ed.* **2007**, *46*, 4956 with permission by the publisher.[19]

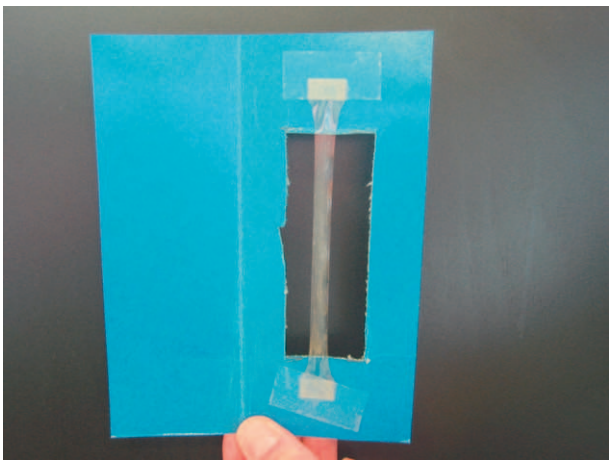

Figure 13 Polymer **37** after stretching at 180 °C by 800%. Reproduced from Sakamoto, J.; Rehahn, M.; Wegner, G.; Schlüter, A. D. *Macromol. Rapid Commun.* **2009**, *30*, 653 with permission by the publisher.[1]

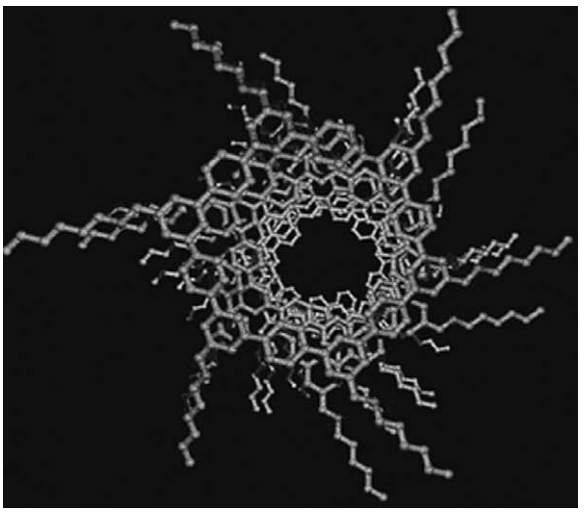

Figure 14 A possible helical conformation of poly(*meta*-*para*-phenylene). Reproduced from Zhang, A.; Sakamoto, J.; Schlüter, A. D. *Chimia* **2008**, *62*, 776 with permission by the publisher.[129]

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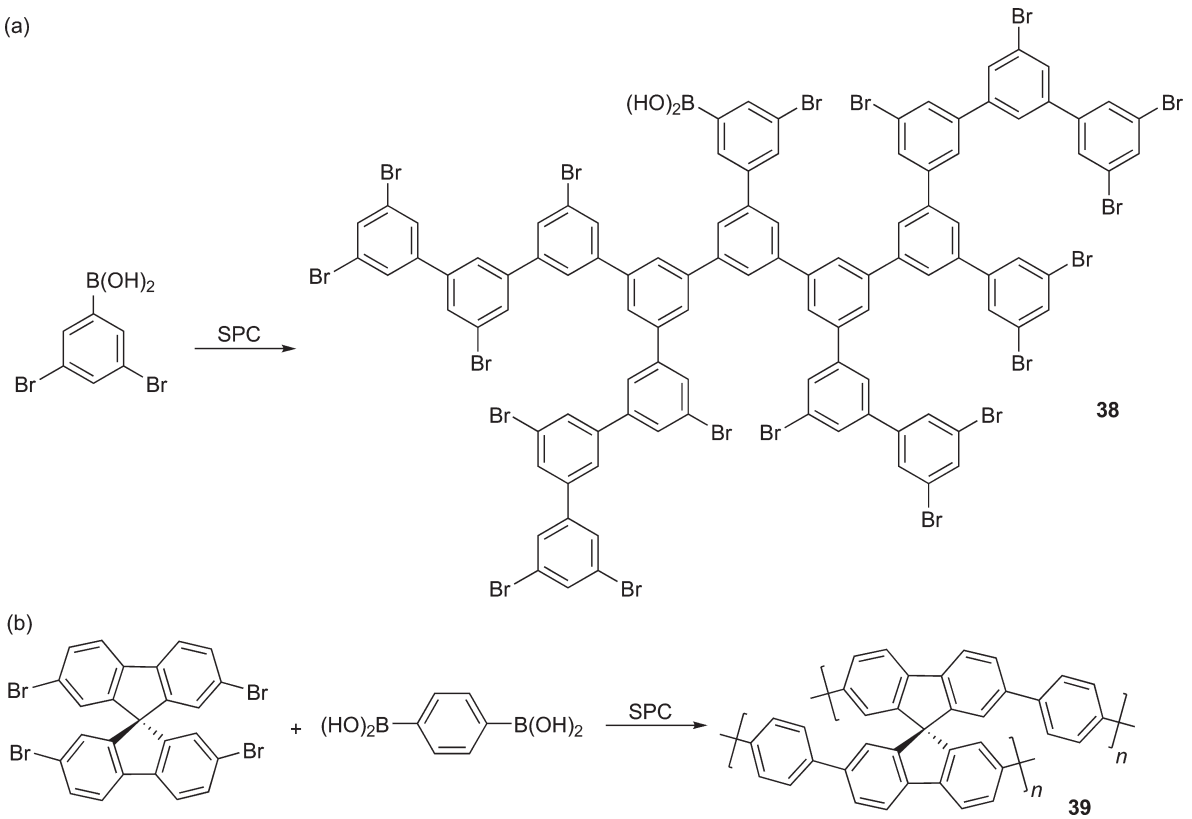
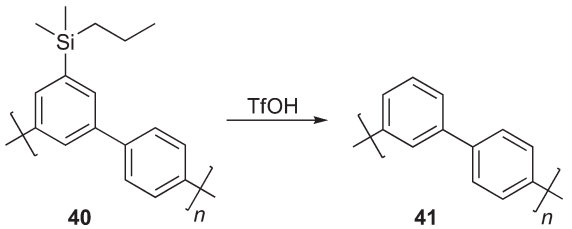
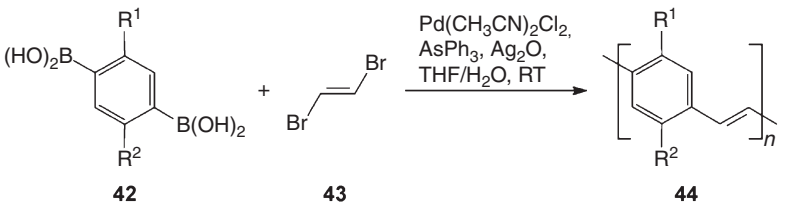


Scheme 14 Two examples of multifunctional monomers applied for the synthesis of hyperbranched and spiro-type PPs **38** and **39**, respectively.



Scheme 15 'Shaving' approach to the unsubstituted PP **41** from its soluble derivative **40**.



a: R^1, $R^2 = OCH_3$, **b**: R^1, R^2 = 2-Ethylhexoxy- **c**: R^1 = Ph, R^2 = H

Scheme 16 SPC leading to PPVs, as tested by Heitz for the first time.

5.22.6.2 Heck Polycondensation

The Heck polycondensation (HPC) is one of the most versatile metal-mediated pathways to PPV: catalyzed by Pd(0) complexes, HX is released in basic media, and C–C bonds are formed between arylene and vinylene carbons (for AB-type monomers 66, see Scheme 23). The bond formation proceeds stereoselectively and leads to *E*-configurated double bonds in the resulting poly(arylene vinylene)s 67.

Not only fully conjugated macromolecules are accessible by HPC, but nonconjugated spacer moieties can be introduced as well – an important tool for improving solubility, to tailor the glass transition, and to adjust the (opto)electronic properties.

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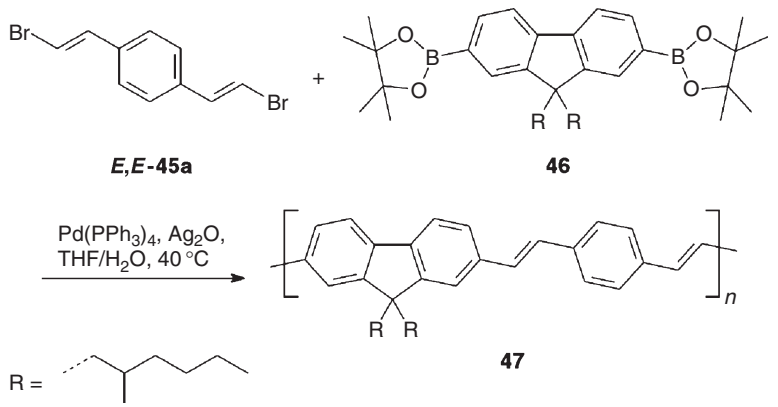
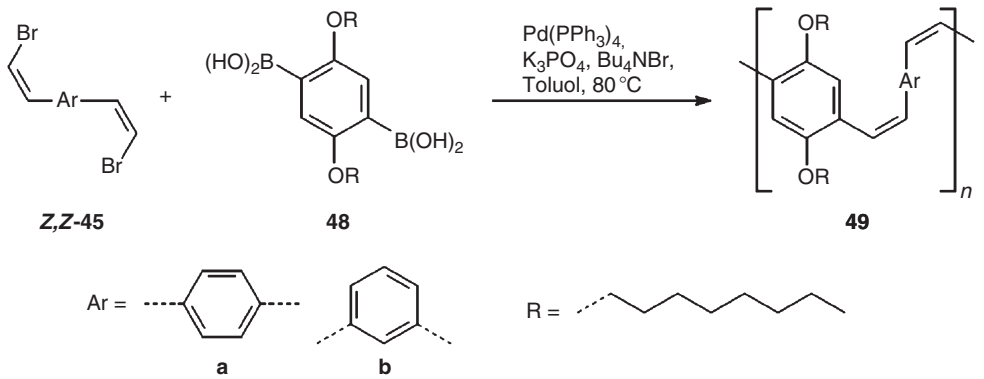
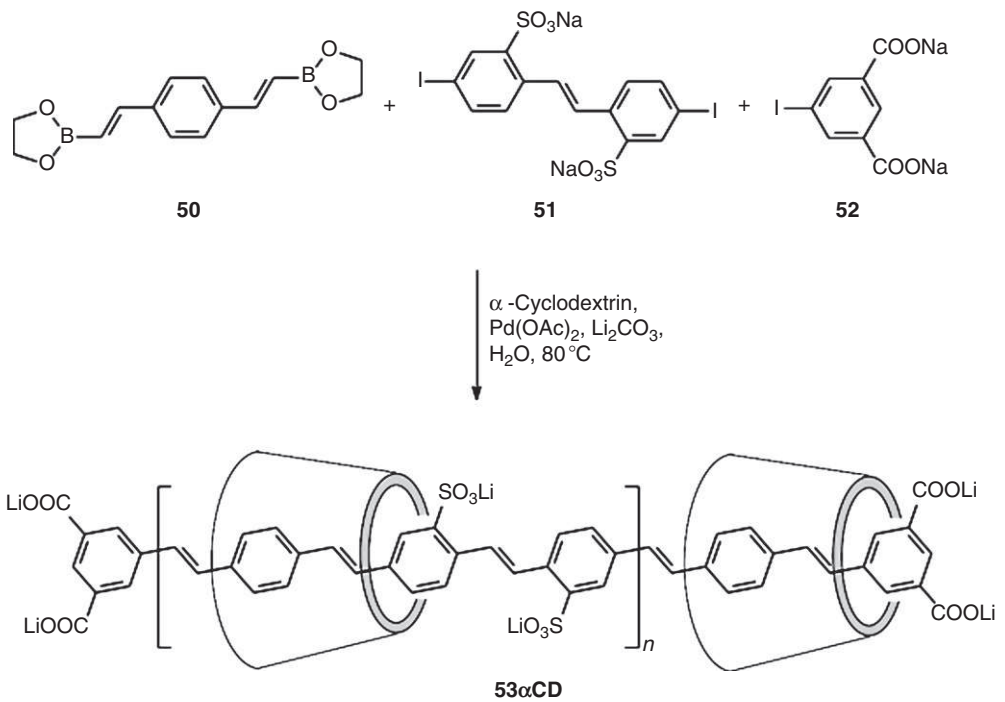


Scheme 17 SPC leading to poly(2,7-fluorene vinylene-*co*-1,4-phenylene vinylene), **47**.



Scheme 18 SPC leading to *Z,Z*-isomeric PPVs **49**.



Scheme 19 SPC leading to PPV-based polyrotaxanes.

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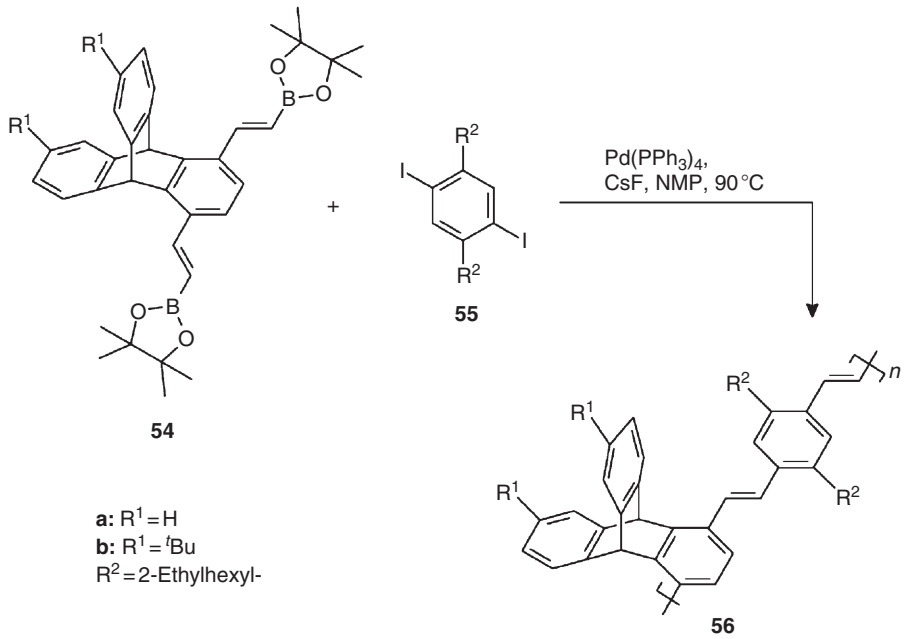
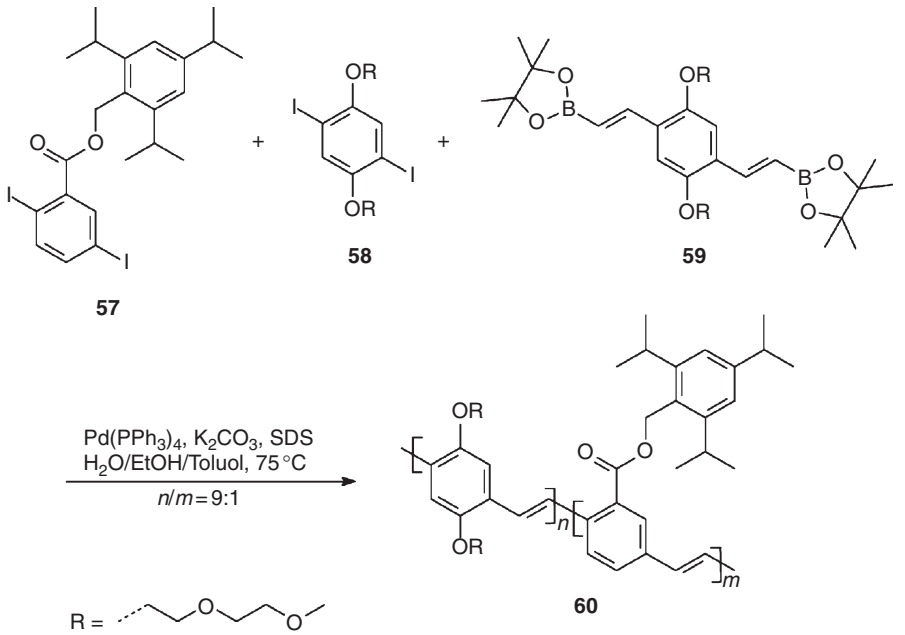


Scheme 20 SPC leading to poly(trypticenylene vinylene-*co*-1,4-phenylene vinylene)s **56**.



Scheme 21 Basic principle of SPC synthesis of a chemosensor material for TNT based on PPV.

Polymers **68** or **69**,[155–158] which contain short conjugated units only, and segmented PPVs such as **70** and **71**[159–162] may serve as representative examples (**Figure 15**).

The specific strengths of HPC are convenient access to the monomers, mild reaction conditions, and tolerance toward additional functional groups present in the monomers. Its most critical drawback, on the other hand, is formation of characteristic defects, which may affect the materials' properties severely.[162–165] Some of these defects are shown in **Figure 16**: it was Heitz who realized that not only *E*-1,2-repeating units (**A**) appear in the Heck-PPVs, but stereoisomeric *Z*-1,2 units (**B**) and 1,1,2-trisubstituted moieties (**C**) as well.[166–168] Moreover, dehalogenation leads to phenyl termini (**D**), and homocoupling of two halide functions results in biphenylene defects (**E**). These defects, however, appear in concentrations below 1%. The really dominant defect is the regioisomeric 1,1-defect (**F**): in the course of the catalytic cycle, the vinyl groups of the monomers add to the Pd catalyst. Usually, this step is guided by steric requirements, leads to Pd–C^{α} bonds, and ends with the desired 1,2-substitution pattern at the vinylene moiety. Sometimes, however, bonds are formed between Pd and C^{β}. In those cases, the 1,1-defect appears finally.

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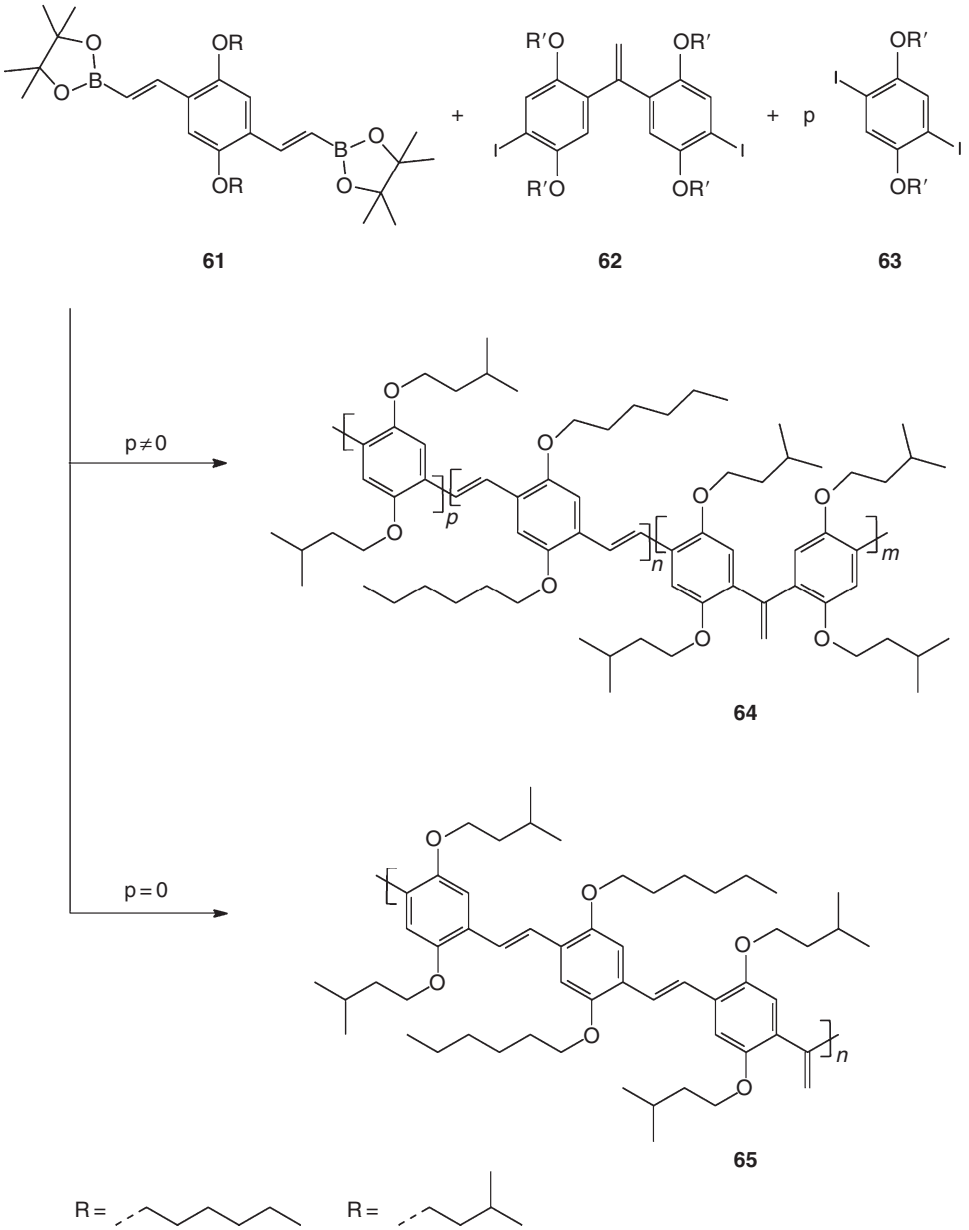
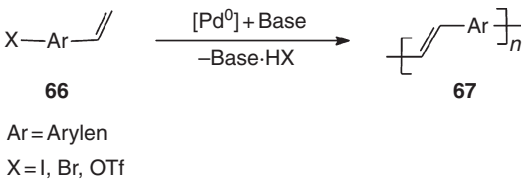


Scheme 22 SPC of model PPV derivatives containing well-defined amounts of 1,1-defects.



Scheme 23 General reaction scheme of the HPC leading to PPVs.

Prediction of the amount of 1,1-defects is a difficult matter as it depends on many parameters in a complex manner, but its extent can be quantified using NMR spectroscopy. For poly (phenyl-1,4-phenylene vinylene), for example,[167,168] increasing blueshifts of UV–vis absorption and photoluminescence were observed with increasing concentration of 1,1-defects.

Another challenge associated with Heck-PPVs is contamination by Pd residues. Krebs *et al.*[169] analyzed photocells and OLEDs from poly(2,5-dioctyl-1,4-phenylene vinylene-*alt*-1,4-phenylene vinylene)s prepared either by HPC or by the metal-free HWE reaction. The devices made of Heck-PPVs showed a 4 orders of magnitude lower electrical resistance. Moreover, higher threshold voltages and much weaker electroluminescence were found for the OLEDs.

Pd nanoparticles seem playing an especially important role in this latter context. Chromatographic purification using phosphane-functionalized stationary phases failed.[170] Later, a powerful method was developed that allows essentially quantitative removal of Pd (**Scheme 24**):[171,172] the azothioformamide chelating ligand **72** coordinates Pd(0) very efficiently and gives an excellently soluble complex **73**. When PPV is

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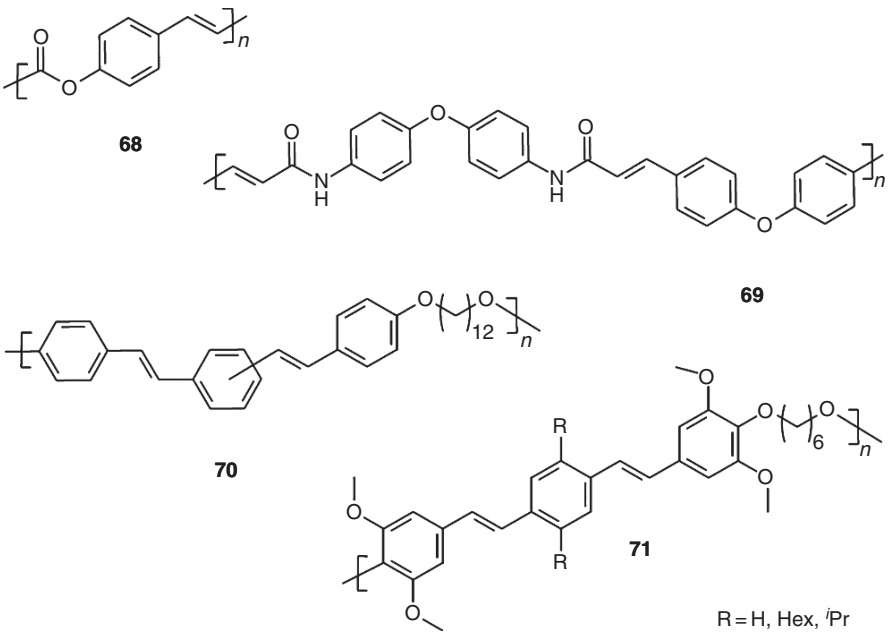


Figure 15 Segmented PPV derivatives as obtained by HPC.

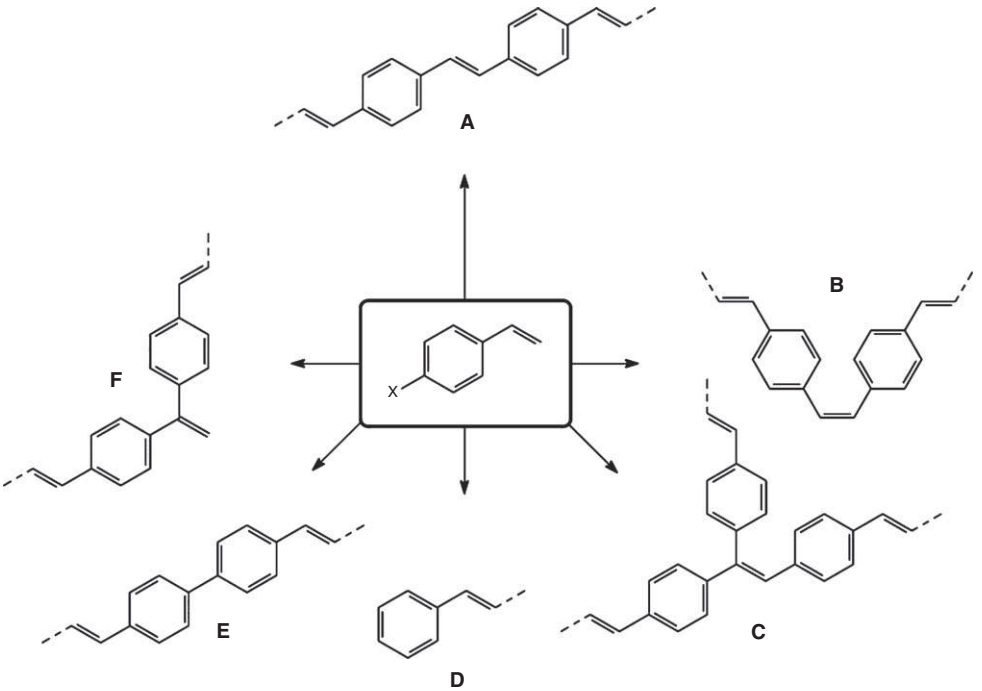
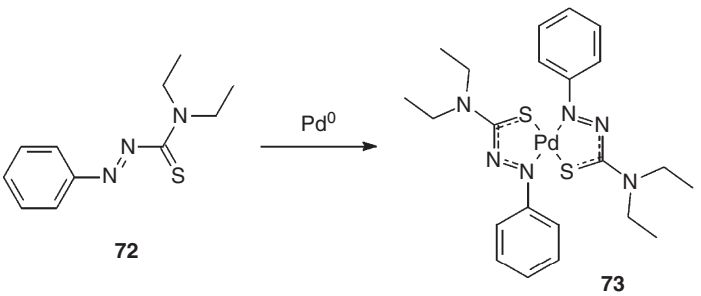


Figure 16 Defect structures observed in PPVs prepared by HPC.



Scheme 24 Complexation of palladium residues, an efficient method for PPV purification.

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precipitated from its solution by adding, for example, MeOH, the complex keeps staying in solution.

In academic literature, HPC-based syntheses of PPV were first described by Greiner and Heitz in 1988.[173,174] Solubility of the obtained unsubstituted PPVs was very low, and profound characterization was impossible. Only when measures were taken that ensure improved solubility, further progress became possible. Initially, small substituents (nitro, fluoro, methyl, phenyl) were introduced into PPVs – with limited success however.[175,176] Only when long, flexible substituents were attached, PPVs with really high molar masses could be realized.[177–181] Poly(2,5-diheptoxy-1,4-phenylene vinylene-*alt*-1′,4′-phenylene vinylene), for example, was shown to be accessible with P_n's up to 40.[177]

Preuss analyzed the constitution of Heck-PPVs in even more detail.[154] Using poly(2,5-dihexoxy-1,4-phenylene vinylene) **76** and its ^{13}C-labeled homologue **77**, he could show that appropriate choice of reaction conditions and catalysts has considerable influence on achievable molar masses, but rather weak influence on the extent of 1,1-defects (**Scheme 25**). In the latter respect, the bulkiness of the lateral substituents is of much larger impact. If optimized conditions were applied, for example, the n-hexyloxy-substituted PPV, **76a**, could be obtained with $P_n = 78$ and 20% 1,1-defects; its 2-ethylhexyloxy-substituted counterpart **76b** was formed with $P_n \approx 42$ and 35% 1,1-defects under identical conditions – result of the bulkiness of the latter substituents.

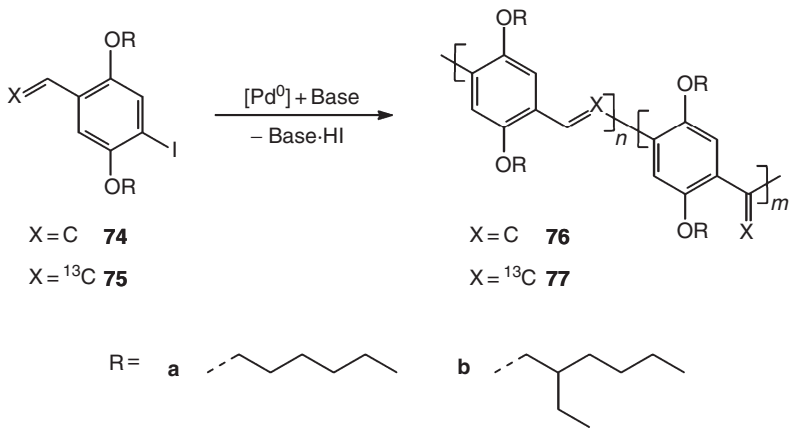
Further studies dealing with substituted PPVs were carried out to suppress aggregation of the polymer backbones in the solid state, a phenomenon that changes the (opto)electronic properties in an undesired way. Attachment of bulky side groups is one option: aromatic substituents (PPV **78a**) and dendrons (PPVs **78b** and **79**) were tested (**Figure 17**). It was shown that HPC ensures acceptable chain lengths even for monomers that bear very bulky substituents: for PPV **78a**, for example, $P_n = 13$ was found,[182] and $P_n = 14$ was determined for PPV **78b**.[183] A critical size of substituents was reached, however, if azomethine-substituted PPVs **79** are addressed.[184,185] In this case, synthesis of homopolymers failed, but copolymerization with unsubstituted comonomers was possible again.

Another example of HPC leading to sterically crowded PPVs are hyperbranched systems (**Figure 18**). Aggregation is prevented efficiently in these readily soluble materials, which moreover show convincing quantum yields of luminescence. Also, they offer pathways for thermal cross-linking, which is a valuable add-on option for creating insoluble polymer layers after processing from solution. Park studied HPC of hyperbranched 1,3,5-PPV derivatives **81** ($P_n \approx 26$). He showed that *meta*-linkages interrupt the π-conjugation efficiently:[186,187] all spectroscopic properties were found to be independent of P_n. For 1,2,4-PPV derivative **80** ($P_n \approx 37$), on the other hand, red-shift of the absorption wavelengths was found with increasing P_n due to the presence of *para*-linkages. Another example of hyperbranched systems is based upon triphenylamines such as **82** ($P_n = 80$).[188,189] These are hole-conducting materials and can be cross-linked thermally as well.

A special benefit of HPC is tolerance toward functional groups. Selected metal-containing systems may serve as examples (**Figure 19**):[190] plenty of polymers have been prepared by HPC, which contain bipyridine-based[191–197] and terpyridine-based[172,195] metal complexes (bipy: **83**, **84a**; terpy: **84b**). Moreover, there are also PPV derivatives known that contain metalloporphyrine moieties such as **85**.[192,198–200]

Changing the predominant hole-conducting characteristics of conventional PPVs into an electron-conducting characteristics is another reason why functional groups should be attached to the PPV. Feasibility of this approach could be proved using, for example, cyano groups and electron-poor heteroaromatics such as pyridine,[199] pyrazine,[101] and condensed ring systems.[202–204] 1,3,4-Oxadiazole-functionalized PPV derivatives were also used as electron-conducting layers.[205] In those cases, the 1,3,4-oxadiazole was introduced as lateral side groups – directly attached to the phenylene rings (PPV **87**),[206,207] connected by spacer groups (PPV **86**), or attached to the vinylene moieties (PPV **88**)[208–210] – as well as incorporated into the polymer main chains (PPV **89**) (**Figure 20**).[205,211–216] Moreover, there have been published some sulfur-containing systems, most of them based on thiophene.[217–221]

PPV has even been used as a backbone of polyradicals (**Figure 21**). Poly(4-diphenylaminium-1,2-phenylene vinylene)s **90**[222–224] and poly[2-(3,5-di-tert-butyl-4-oxyphenyl)-phenylene vinylene]s **91**[225–230] may serve as examples. Polymers such as those show considerable chemical



Scheme 25 HPC of *para*-iodostyrene derivatives, carried out to study the extent of 1,1-defects.

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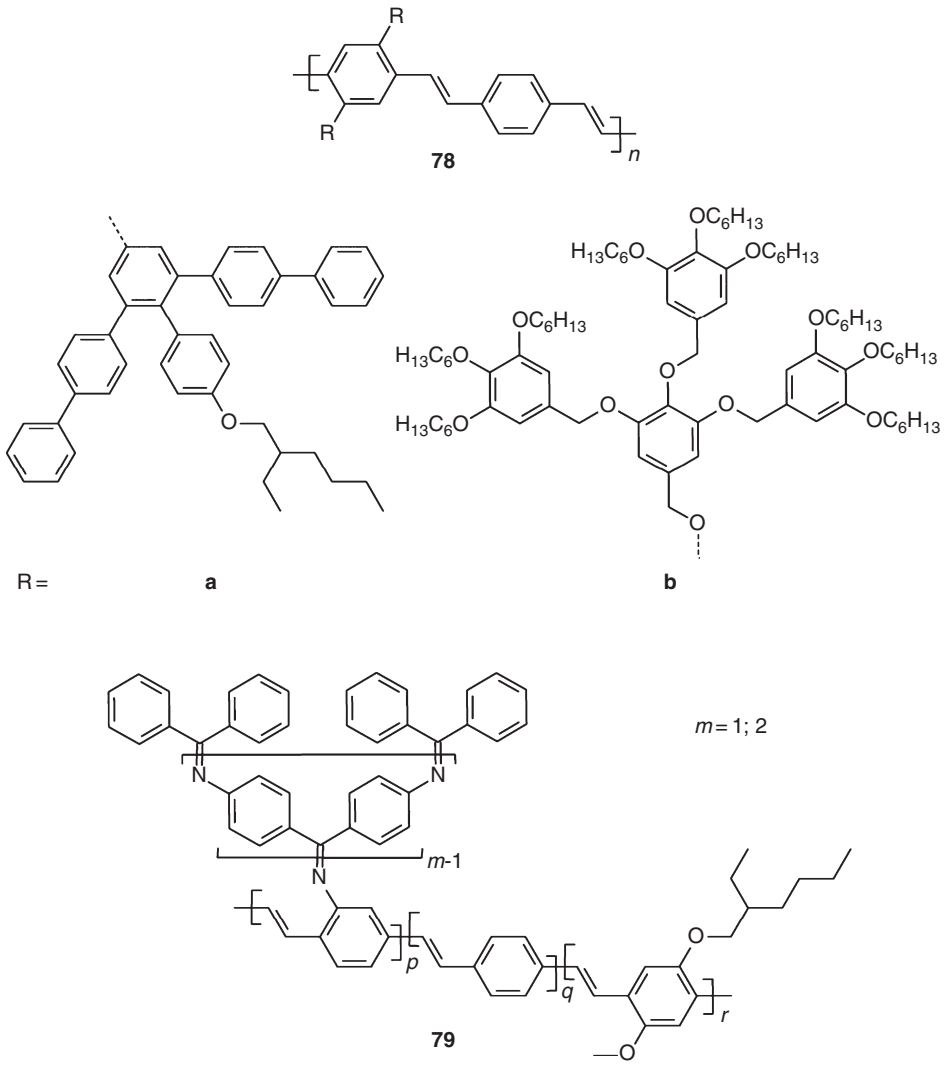

Figure 17 PPV derivatives bearing bulky substituents.

stability, planarity of the backbones, and intramolecular ferromagnetic spin coupling.

5.22.6.3 Stille Polycondensation

First studies dealing with Stille polycondensation were focusing on poly(1,4-phenylene ethynylene)s (PPEs),[231,232] but related investigations dealing with poly(hetarylene vinylene)s followed a little while later (Scheme 26). Poly(thiophene vinylene)s 94 were prepared from diiodothiophenes 92 and bis(tributylstannyl)ethane 93 (94a: $P_n = 13$; 94b: $P_n = 22$).[233–235]

Poly(2,5-pyridyle vinylene) is of interest as a precursor of poly(methylpyridinium vinylene) – which is isoelectronic to PPV – and because it forms different isomers showing different physical properties: appropriate choice of monomers and synthetic conditions allow synthesizing the polymers with exclusively head-tail (HT), head-head (HH), or random monomer placements, respectively.[236–240] Since pyridine is an electron-deficient aromatic, high degrees of polymerization can be reached ($P_n = 60$).[238,239] On the other hand, Stille synthesis of conventional (electron-rich) PPV derivatives is a challenging task, and derivatives bearing electron-donating alkoxy substituents in particular ask for special measures.[241–243] NMR and IR studies verified *E*-configuration of the resulting polymers, but still low degrees of polymerization ($P_n \approx 10$). Dehalogenation and destannylation are side reactions that create most of the chain termini. Moreover, stannyl termini and traces of Pd residues proved to be critical if the materials are applied for (opto) electronic devices.[244–248]

While of minor impact for conventional PPVs so far, the Stille process has gained importance for the preparation of fluorinated PPVs: fluorine induces electron-acceptor characteristics into monomers and PPVs. Thus, the latter are acting as n-conductors – in contrast to their nonfluorinated counterparts, which are hole conductors (p-conductors). The phenylene as well as the vinylene moieties may bear fluorine substituents.[249,250] Naso synthesized poly(2,3,5,6-tetrafluoro-1,4-phenylene vinylene) 98 ($P_n \approx 10$; Scheme 27)[247] and its copolymers 99, which in addition show nonlinear optical properties.[251,252]

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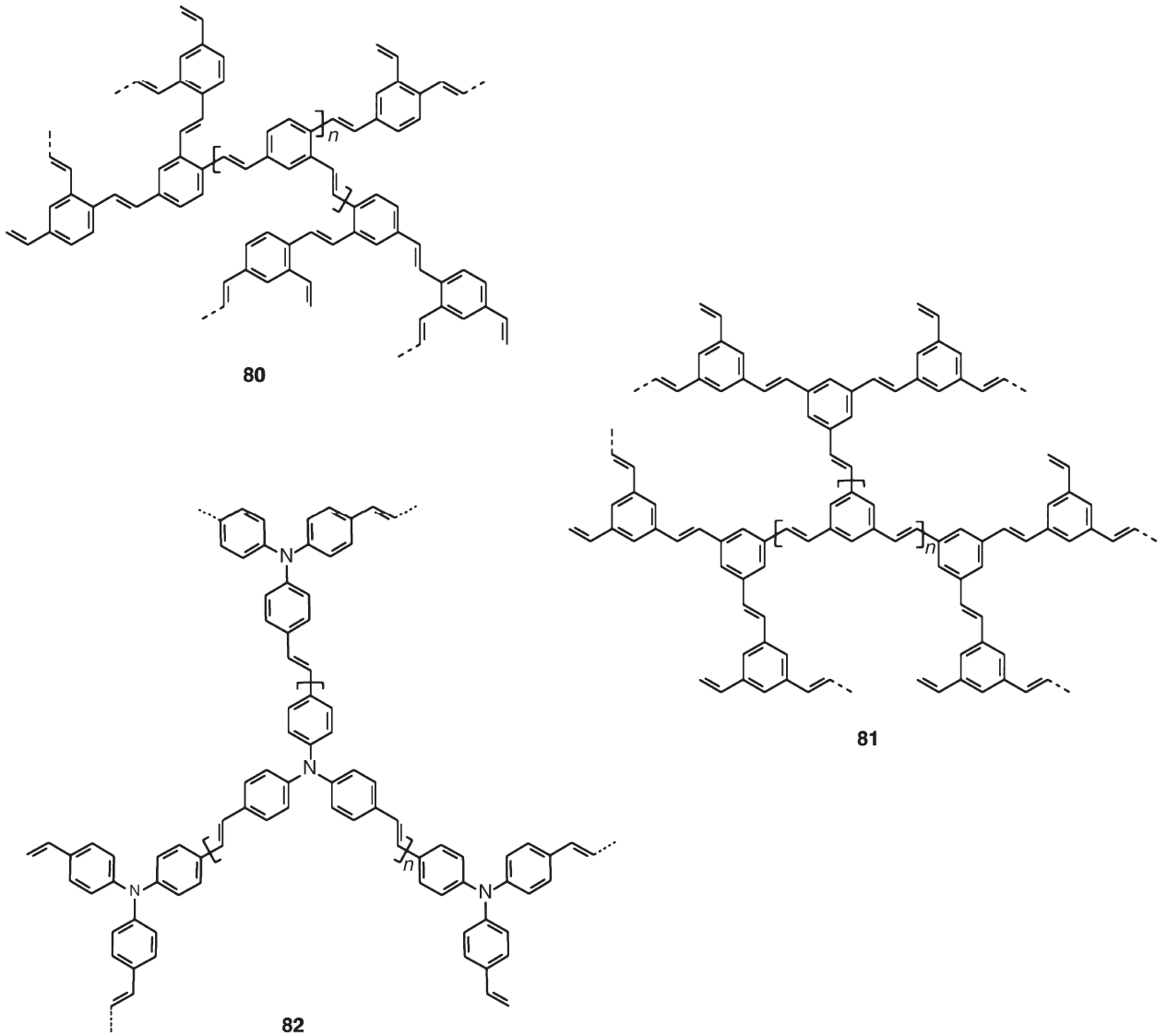

Figure 18 Hyperbranched PPV derivatives.

Using *E*-1,2-bis(tributylstannyl)-1,2-difluoroethene **101** and dihaloaromatics **100**, poly(1,4-phenylene-1,2-difluorovinylene)s **102** were obtained (**Scheme 28**).[241,253] High reactivity of the fluorinated stannane allowed realization of considerable chain lengths (**102b**: $P_n = 94$). The polymers show pronounced blueshifts of photo- and electroluminescence.

5.22.6.4 Hiyama Polycondensation

Organo-silicon compounds have also been tested as metal comonomers in Pd-catalyzed polycondensation reactions (Hiyama protocol). The C–Si bond is slightly polarized, and thus offers low reactivity only. Specific reaction conditions, leaving groups, and substitution patterns are required to build up polymers by this method.[254] Diazonium tetrafluoroborates may be an adequate choice as coupling counterparts. Nevertheless, small PPV oligomers were obtained in first attempts only.[255] Later, somewhat longer polymers could be prepared such as poly(4,4′-biphenylene vinylene-*co*-1,4-phenylene vinylene) **105** (**Scheme 29**).[256] Nevertheless, the reaction is challenging even under optimized conditions due to the intrinsic lability of the diazonium salts: they allow chain growth at moderate temperatures but decompose quickly, thereby causing chain termini that limit the degrees of polymerization (**105**: $P_n = 11$).

Katayama *et al.*[257] tested diiodobenzene derivatives **106** as the coupling counterparts (**Scheme 30**). Highly reactive alkenylsilanes such as **107** together with tetrabutylammonium fluoride (TBAF) were needed in those cases. *E,E*-monomer **107a** leads to stereoregular *E,E*-PPV **108** ($P_n = 14$), but *Z,Z*-monomer **107b** converts into a less stereoregular *Z,Z*-PPV **108** ($P_n = 8$). The lower stereoregularity in the latter case was explained by TBAF-induced desilylation of the alkenylsilane. The formed vinyl end groups undergo Heck reaction subsequently, which is *E*-selective.[258]

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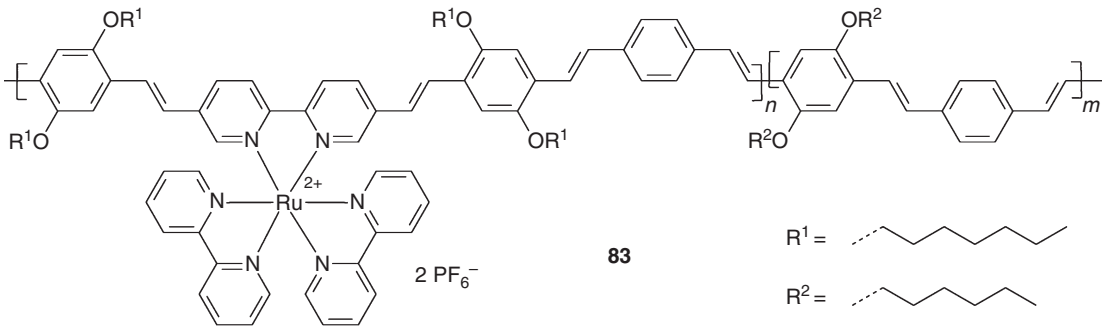

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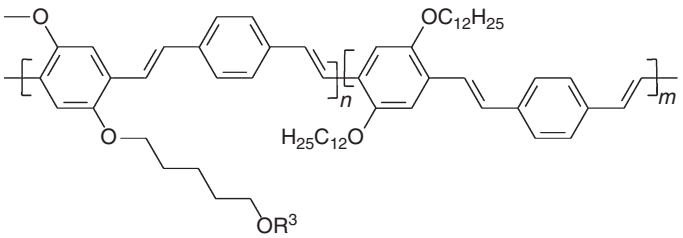

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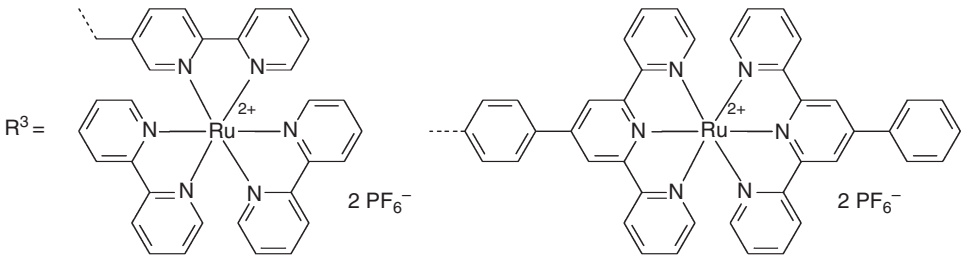

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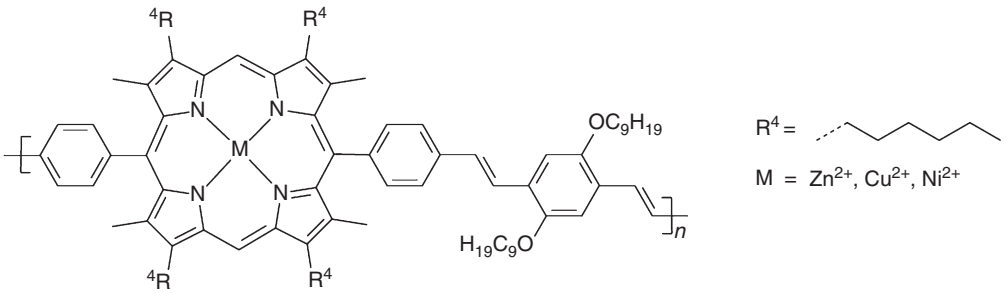

85

Figure 19 Metal-containing PPVs obtained by HPC.

5.22.6.5 Cascade Polycondensation

In some specific cases, AABB-type Heck syntheses using ethene derivatives as the comonomers may offer specific advantages. Appropriately reactive ethene derivatives are needed therefore. Vinyltrisethoxysilane and potassium vinyltrifluoroborate may serve as examples.

The so-called Hiyama-Heck cascade reaction was applied to prepare poly(4,4′-biphenylene vinylene)s **112** using bisdiazoniumtetrafluoroborate **110** as the arylene monomer and vinyltriethoxysilane **111** as its vinyl counterpart (**Scheme 31**).[259] The polymers show very high degrees of polymerization ($P_n = 130$) and low amounts of 1,1-defects.

Itami *et al.*[260] suppressed the cascade reaction intentionally for the synthesis of poly(1,4-phenylene 1,1-vinylene) derivatives (**Scheme 32**): bifunctional vinyldimethyl(2-pyridyl) silanes **113** and diiodobenzene **114** were converted into silyl-substituted poly(1,4-phenylene-1,1-vinylene) **115** by

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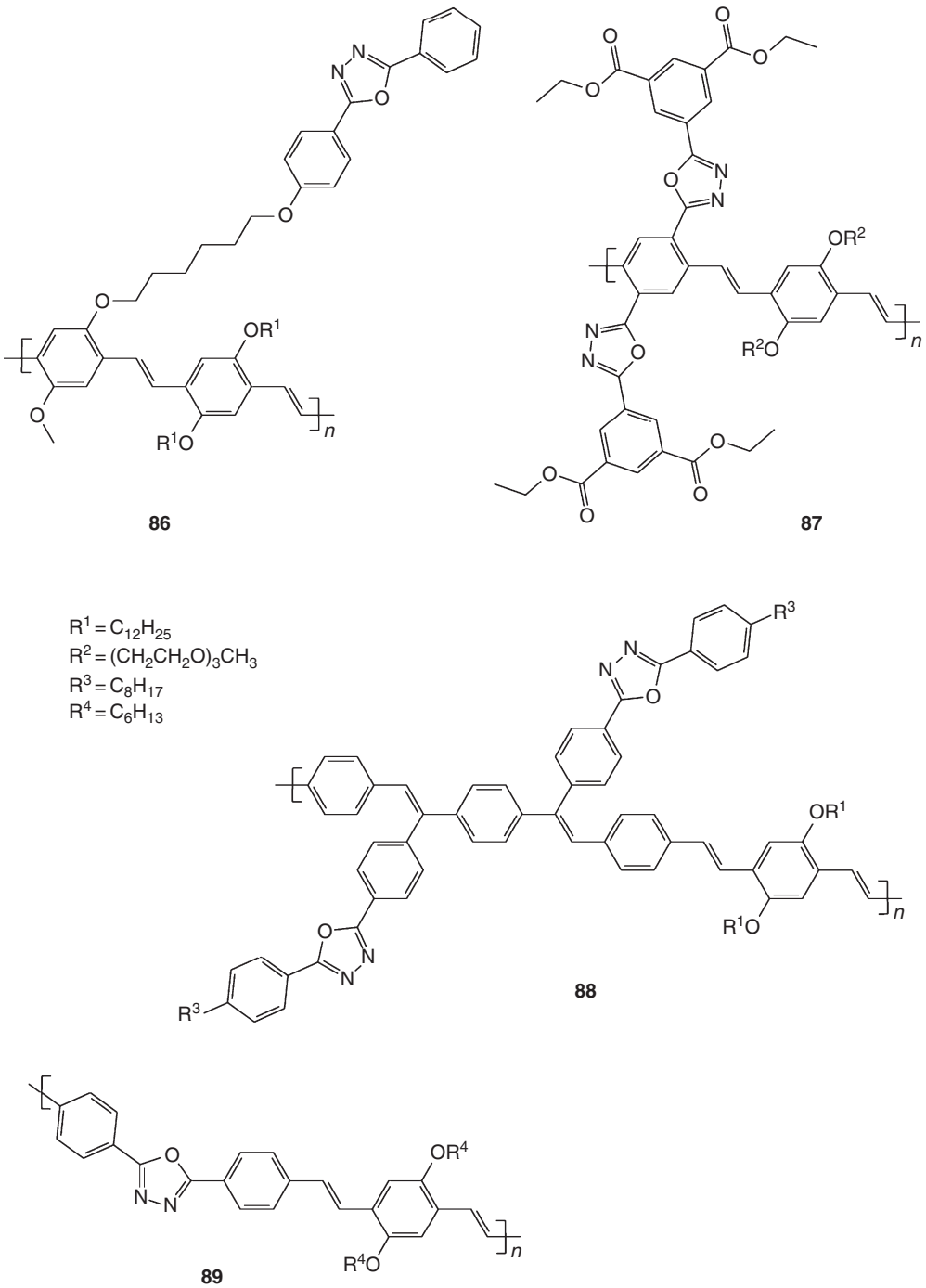

Figure 20 1,3,4-Oxadiazole-containing PPV derivatives obtained by HPC.

HPC using appropriate catalysts. Subsequently, the formed product was arylated by Hiyama reaction, leading to trisubstituted poly(1,4-phenylene-1,1-vinylene)s such as **116** (**116a**: $P_n = 37$; **116b**: $P_n = 31$).

Cascade reactions were also realized by combining SPC and HPC. Here, potassium vinyltrifluoroborate **118** was used as an ethane-type comonomer.[261–273] A representative example is shown in Scheme 33.

5.22.6.6 Multicomponent Polycondensation

HPC even can be carried out as a multicomponent coupling reaction:[274] the Pd(II) complex formed by oxidative insertion of the Pd(0) catalyst into the aryl–halide bond attacks an allene. Transfer reactions finally lead to a π-allyl complex, which reacts further with a nucleophile. If *para*-halogenated phenylallenes **122** are converted accordingly in the presence

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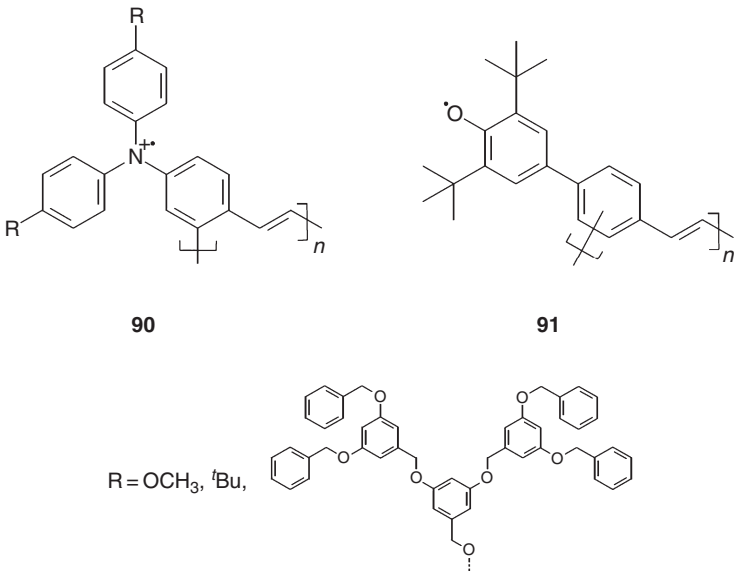
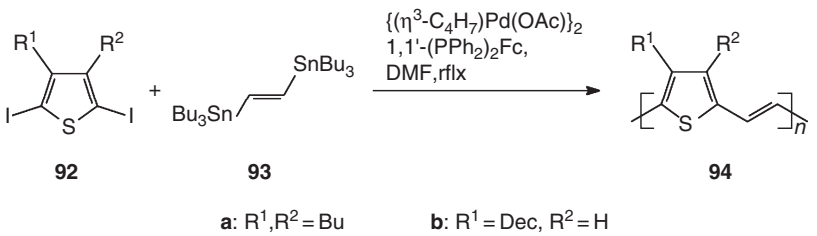
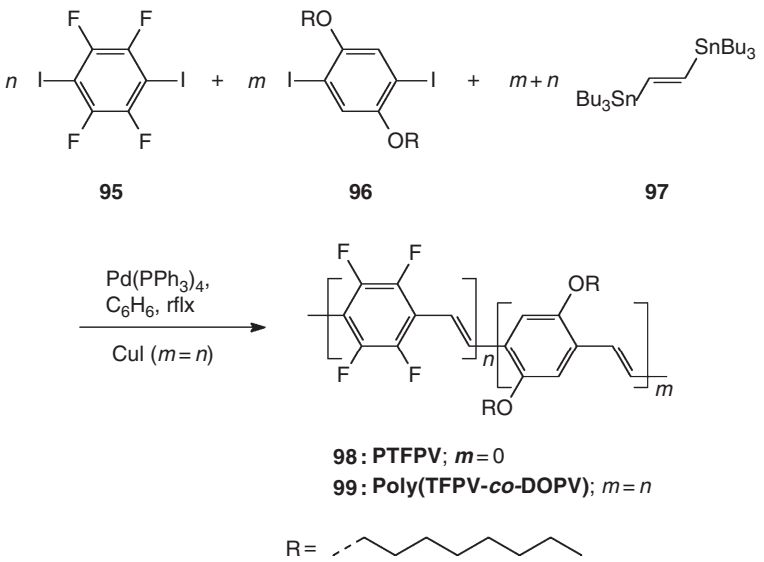


Figure 21 PPV-based polyradicals as obtained by HPC.



Scheme 26 Stille synthesis of poly(thiophene vinylene)s.



Scheme 27 Synthesis of highly fluorinated PPVs by Stille polycondensation.

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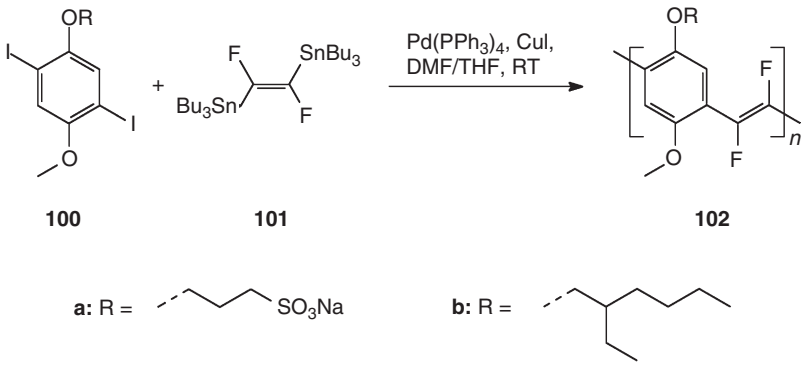
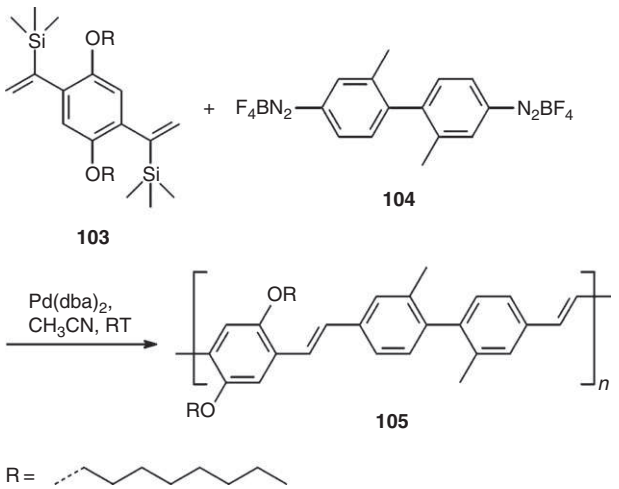


Scheme 28 Synthesis of PPV derivatives bearing fluorinated vinylene moieties by Stille polycondensation.



Scheme 29 PPV synthesis using the Hiyama protocol.

of sodium (dialkyl)methylmalonates **123**, for example, polymers **124** are the result, which have ester-functionalized vinylene moieties (**Scheme 34**).[275–278] These polymers are readily soluble due to their lateral substituents, and the ester groups allow manifold functionalization reactions additionally.

Another multicomponent coupling reaction is three-component SPC.[279] Diiodobenzene derivatives **125**, benzenediboronates **126**, and norbornadiene **127** give precursor polymers **128** (**Scheme 35**).

Polymer **128** releases cyclopentadiene in a Retro–Diels–Alder reaction, and the desired vinylene moieties appear. Unfortunately, the brownish PPVs **129** have low degrees of polymerization ($P_n = 6$), and norbornene defects survive in the material. Therefore, this method is not a true alternative for established coupling protocols. If norbornadiene **127** is replaced by alkynes such as tolane **132**, PPVs **133** ($P_n = 10$) bearing substituted vinylene moieties are formed (**Scheme 36**).[280]

Pd-catalyzed hydroarylation-polycondensation reactions as well may rank among multicomponent reactions.[281] Here, a diiodobenzene derivative such as **134** adds to a dialkinylbenzene derivative **135** in the presence of a hydride donor such as sodium benzylmalonate **136** (**Scheme 37**). The polymeric products **137** contain three isomeric repeating units and show acceptable degrees of polymerization ($P_n = 18$).

5.22.6.7 McMurry Polycondensation

In 1980, the McMurry reaction was applied for the first time to the synthesis of PPVs.[282] Homopolymers as well as copolymers were prepared by treatment of aromatic dialdehydes with low-valent titanium reagents (**Scheme 38**).[283,284] Unsubstituted terephthalic dialdehyde **138a** leads to insoluble and low-molecular-weight PPV **139a** ($P_n \approx 10$).[285] Monomers bearing solubilizing side chains such as **138b** resulted in PPVs **139b** having monomodal molar mass distribution and P_n's > 30.[286] NMR studies indicated high contents of *Z*-configurated repeating units. Limited stereospecificity and large amounts of titanium residues in the isolated material are the main reasons why so far the McMurry route is used in specific cases for PPV synthesis only.[287,288]

5.22.6.8 Acyclic Diene Metathesis Polymerization

Acyclic diene metathesis (ADMET) polymerization is a step-growth polymerization leading to PPVs **142** by conversion

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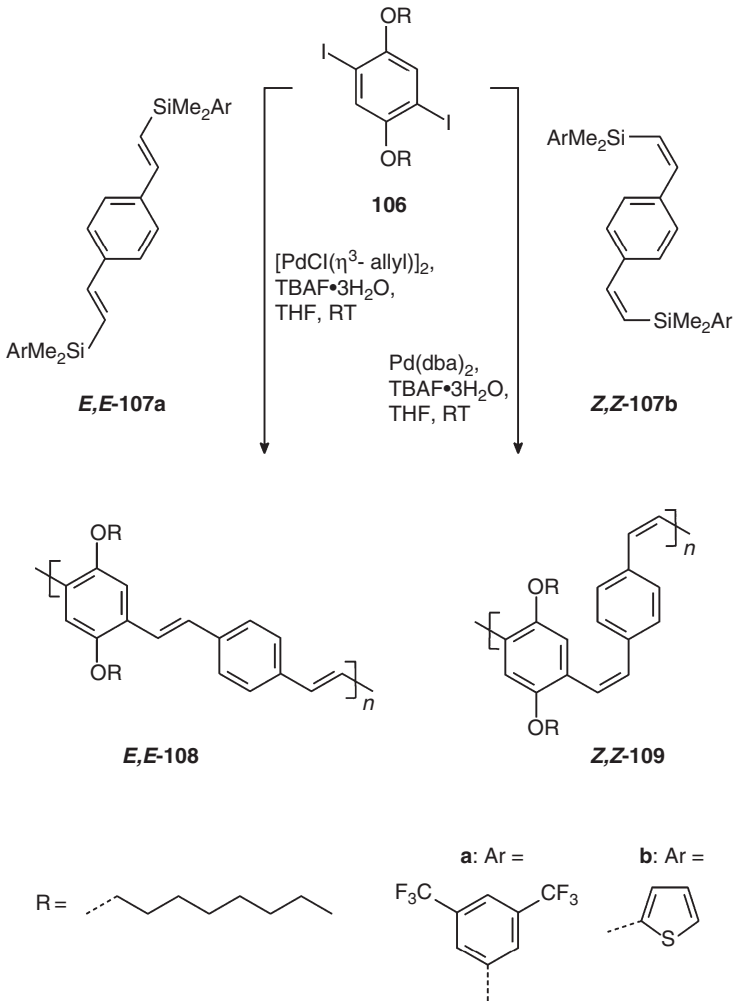
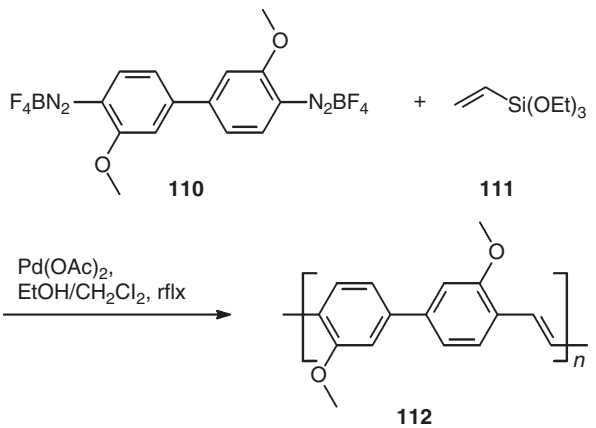


Scheme 30 Hiyama synthesis of PPV as *E,E*- and *Z,Z*-isomers, respectively.



Scheme 31 Hiyama-Heck cascade polycondensation.

of 1,4-divinylbenzenes **140** in the presence of a metathesis catalyst. Ethene **141** is released as condensation product (**Scheme 39**).[289,290] Wolf and Wagener's[291] first attempts to synthesize PPV by ADMET of 1,4-di(1-propenyl)benzene resulted in dimers and trimers only. Thorn-Csányi[292] improved the ADMET-based PPV synthesis ($P_n = 12$) using 1,4-divinylbenzene derivatives. Side-chain-substituted polymers were addressed, and many catalysts were tested in

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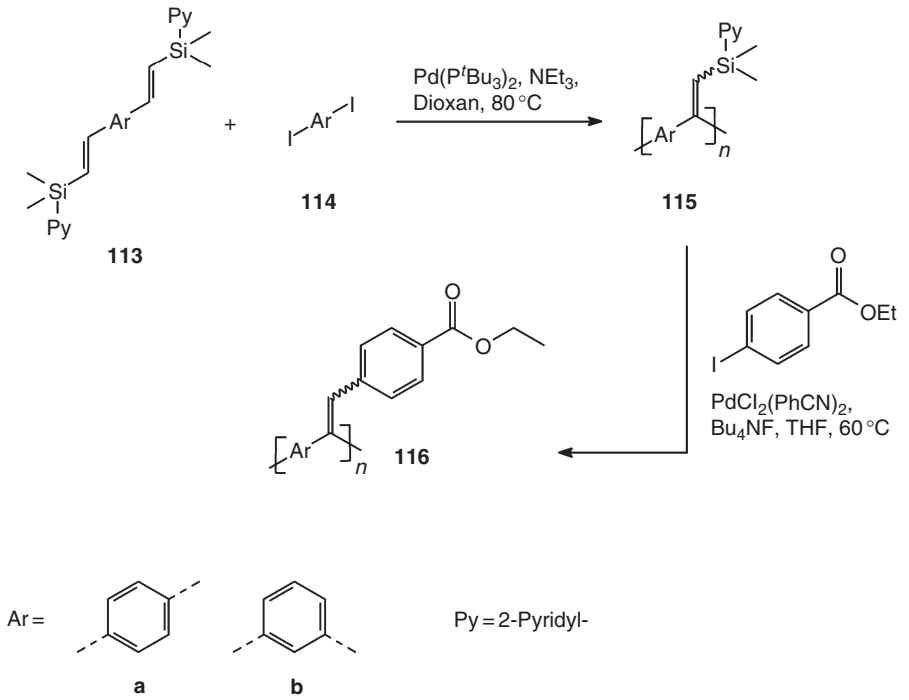
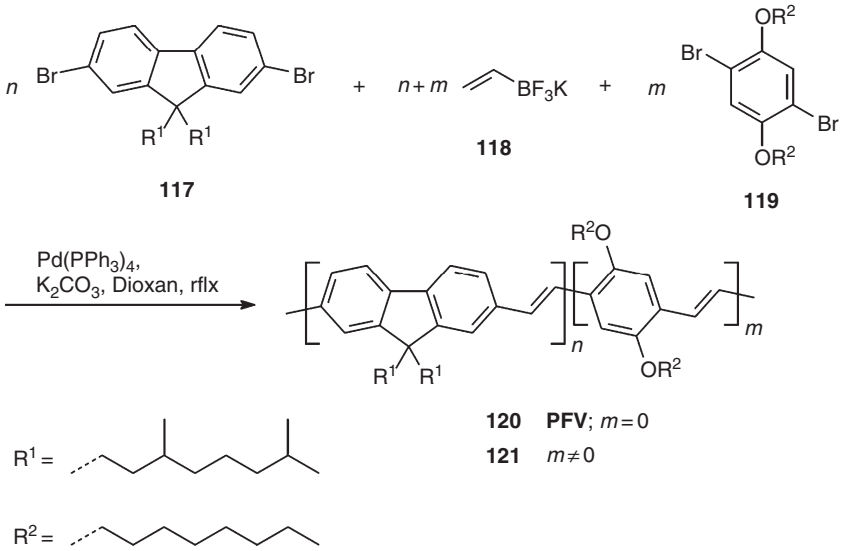


Scheme 32 Two-step synthesis of poly(1,4-phenylene-1,1-vinylene)s.



Scheme 33 Suzuki–Heck cascade polycondensation leading to fluorene-containing poly(arylene vinylene)s.

subsequent time.[293–305] Throughout, the PPVs proved to be *E*-configurated. Recently, Plenio succeeded in increasing the degrees of polymerization significantly by optimizing the reaction conditions further ($P_n = 330$): high-boiling solvents and careful removal of the released ethene proved to be key requirements. If the technically important alkoxy-substituted divinylbenzenes are addressed, however, the limitations of the ADMET protocol become obvious: tremendous loss of the catalysts' performance is the result of interactions with the alkoxy substituents:[299,304,306] coordination of the metal to the oxygen atoms results in chelating complexes, which stabilize the catalytically active centers, slow down the reaction rate, and result in low degrees of polymerization ($P_n \approx 10$).[305]

5.22.7 Conclusions and Outlook

In the past 25 years, SPC has been developed into a powerful synthetic tool that provides access to numerous polyarylenes (particularly PPs, PFs, and PPVs) and related unsaturated

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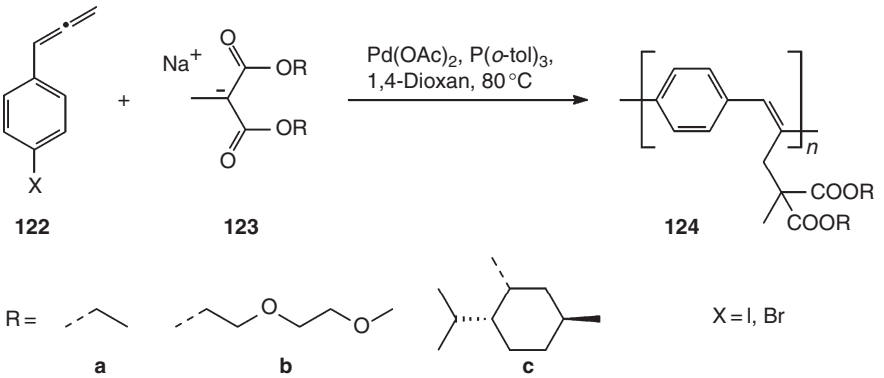
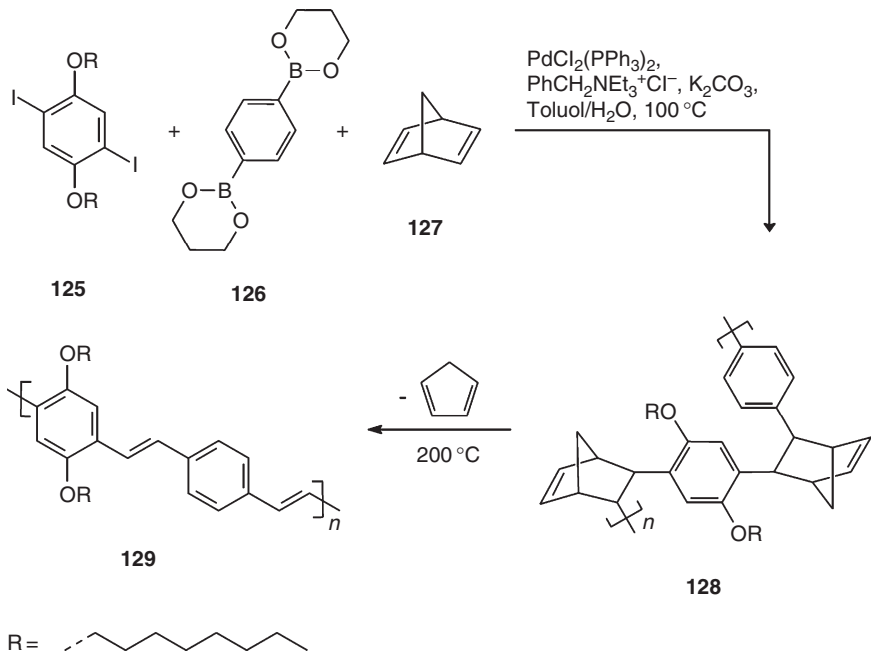
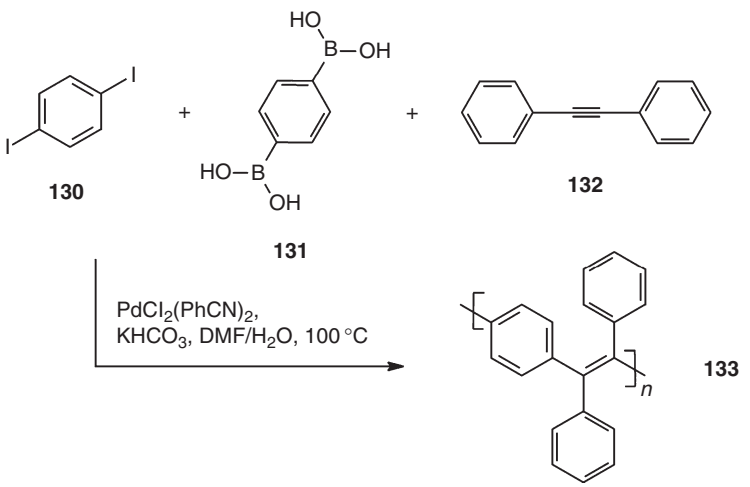


Scheme 34 Multicomponent HPC leading to substituted PPVs.



Scheme 35 Multicomponent SPC leading to PPV derivatives.



Scheme 36 Multicomponent SPC leading to diphenyl-substituted PPV.

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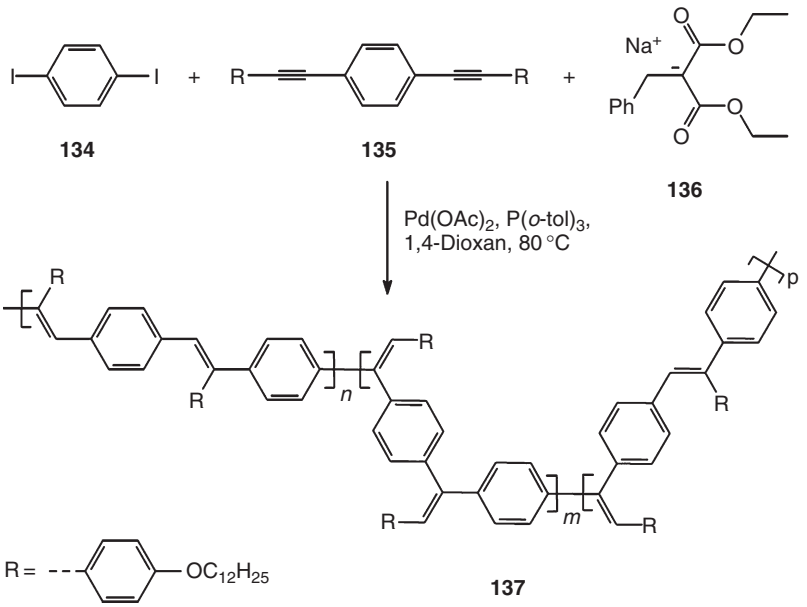
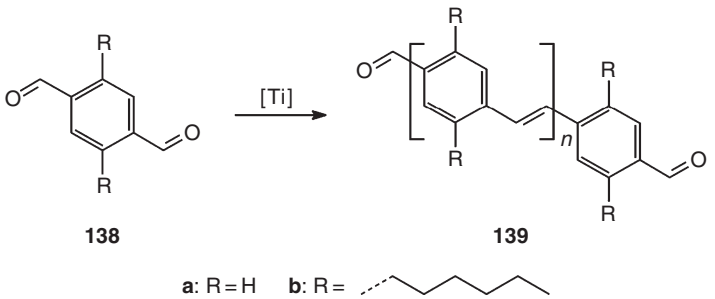
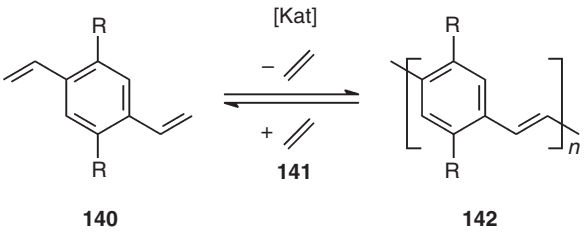


Scheme 37 Pd-catalyzed hydroarylation polycondensation.



Scheme 38 McMurry polycondensation leading to PPV derivatives.



Scheme 39 ADMET synthesis of PPV derivatives.

polymers.[1] Some of these polymers have gained industrial importance that underscores the importance and potential of the method. The key to this success is the Suzuki–Miyaura cross-coupling reaction that regarding conversion is one of the absolutely best chemical reactions known so far. After careful optimization, in SPC degrees of polymerization of 1000 can be achieved; this translates into conversions per bond formation step of 99.9%.

While some directions of SPC have reached maturity, others are still more in their infancy. The use of chloroaromatics as monomers is one of these latter cases.[70] Also regarding the interesting approach to regioregular polythiophene, the authors are not sure whether the optimum has already been reached. It seems that newly developed catalysts considering, that is, the retarded oxidative addition could help improve here. Other aspects where SPC could have considerable impact have practically not been explored at all. This comprises the use of cheap metals such as Fe instead of Pd,[137] the synthesis of high-molar-mass poly(*meta*-arylene)s with the potential to fold-up to helices with defined pores,[129] the synthesis of tactic polyarylenes,[138] and attempts to grow polyarylenes off solid substrates.[98] Also, sp^2/sp^3 coupling[139] and sp^3/sp^3 C–C coupling have not yet been really tried for polymer synthesis, though in low-molar-mass organic chemistry related examples are known.[140] Finally, it will be thrilling to see how attempts to render SPC a chain-growth process will develop.[96,97] This would not only allow to achieve narrow distributions but also to obtain block copolymers with one block being PP or PF. As this short list of important yet unexplored fields shows, we believe that SPC can be developed further and that polymer chemistry and materials chemistry will witness more exciting findings in the years to come.

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Biographical Sketches

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A. Dieter Schlüter was born in Germany. He studied chemistry and geophysics at the University of Munich (LMU) and received a doctorate in organic chemistry in 1984 with Prof. G. Szeimies. After postdoctoral work with Prof. K. P. C. Vollhardt (University of California, Berkeley) and Prof. W. J. Feast (Durham University, England), he joined the Max Planck Institute for Polymer Research in Mainz in 1986, where he concentrated on preparative macromolecular chemistry in the department of Prof. G. Wegner. In 1991, he received his habilitation in organic chemistry at the University of Mainz. Shortly thereafter, he was awarded the Dozentenstipendium of the Fonds der Chemischen Industrie and was briefly an associate professor at the Polymer Institute of the University of Karlsruhe before accepting a chair professorship (succession Prof. G. Manecke) for organic and macromolecular chemistry at the Free University of Berlin in 1992, where he has been until spring 2004. He was on the executive editorial board of Wiley-VCHs *Macromolecular Chemistry and Physics* and *Macromolecular Rapid Communications*, and has been serving on many committees and councils. He has served in several administrative functions. His research focuses on polymer synthesis with a visible component from organic and supramolecular chemistry.

Matthias Rehahn, born in Frankfurt/Main, Germany, studied chemistry at the Johannes Gutenberg Universität Mainz. His PhD thesis was carried out under the supervision of Prof. Schlüter at the Max-Planck-Institut für Polymerforschung, Mainz, in Prof. Wegner's department. After a post-doctoral stay at the ETH Zürich in Prof. Suter's group, he completed his habilitation at the Universität Karlsruhe in Prof. Ballauff's Polymer-Institut. Since 1999, he has been full professor at the Technische Universität Darmstadt and simultaneously head of the German Institute for Polymers (DKI). Current fields of research include living anionic and cationic polymerization methodologies, transition-metal catalyzed polycondensation reactions, semi-conducting oligomers and polymers for optoelectronics, and polyelectrolytes with special focus on basic understanding and fuel-cell applications.

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5.23 Metal-Containing Macromolecules

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5.23.1 Introduction

Interest in the synthesis and characterization of metal-containing polymeric materials has increased dramatically due to their desirable chemical and physical properties.[1] In recent years, polymers containing transition metals have garnered much attention.[2–11] The diversity of metal-containing polymers is a result of the wide range of oxidation states, coordination numbers, and geometries that transition metals can adopt. Oxidation states can differ by changing the nature and/or the number of ligands bound to the metal center. In general, there are two primary classes of metal-containing polymers, those where the metal-containing moiety is a part of the main polymer chain (either as part of the backbone itself or directly coordinated to moieties within the polymer backbone) and those in which the metal is part of the pendant group of the polymer.

Polymers containing metals within their backbones have numerous structural features. They can contain metal–carbon σ or π bonds, or the metal can be coordinated to noncarbon elements. As an example, the nitrogen in a porphyrin or phthalocyanine macrocycle, or the nitrogen and oxygen atoms in a Schiff base moiety, is bonded to their respective metallic moeity. The properties of these polymers are highly dependent on the coordinated ligands, potentially giving rise to polymer metal sites with properties as diverse as those of coordination compounds themselves. Metal–metal bonds can also be used as part of a polymeric backbone. The coordination of metals directly to atoms within the polymer backbone can commonly be observed in sandwich complex-containing polymers or those containing chelating ligands in the main chain, such as pyridyl groups.

The focus of this chapter is on recent developments in coordination and organometallic macromolecules. The extensive area of coordination polymers is divided according to the different macromolecular moieties incorporated into the polymeric materials discussed, including porphyrins, phthalocyanines, Schiff bases, and pyridine-based systems. The organometallic polymers are described with respect to their structural differences, including star-shaped molecules, various metal-containing dendrimers, and a combination of neutral and cationic metal complexes. Herein, the synthetic methodologies of these compounds, as well as their properties and applications, are highlighted.

5.23.2 Coordination Polymers

Coordination polymer chemistry uses metal centers with different coordination geometries and suitable spacer ligands to obtain particular properties in the polymeric material. As an example, Harvey *et al.*[12] studied the photophysical properties of cofacial bismacrocycle dyads, including both intramolecular electron and energy transfers. Bifacial bisporphyrin dyads (**Scheme 1**) were prepared in order to investigate singlet–singlet (S_1) and triplet–triplet (T_1) energy transfer rates through space. The results indicate that these macrocycles closely resemble the through space S_1 energy transfer rates found in light harvesting devices and could, therefore, potentially serve as sensible models for further investigation into such applications.

Two semiflexible models were also studied. The 'calix open' conformer **2** (**Scheme 2**) was produced as a result of the formation of the intramolecular hydrogen bonds between the oxygen atoms on the crown ether unit and the hydroxyl groups on the lower rim. Conversely, replacing the hydroxyl groups with ethoxy groups prevents any hydrogen bonding and results in the formation of the closed conformer **3** ('calix closed'). This conformer allows for fast electron transfer between the two porphyrin chromophores due to their close proximity.

Several tin(IV) polymers containing the polydendate ligand bis(1,2,4-triazoyl)methane (Btm) were designed and characterized by Masciocchi *et al.*[13] The Btm ligands connecting the tin (IV) fragments were determined to be 9.5–11.2 Å apart in one-dimensional (1D) chains grouped in parallel bundles. In contrast to the rigidity of bis(imidazoyl)methane (Bim) ligand **5**, the structure of **4** seems to have greater flexibility and an increased number of coordination sites, thus making it a more suitable ligand for the Sn(IV) 1D polymers.

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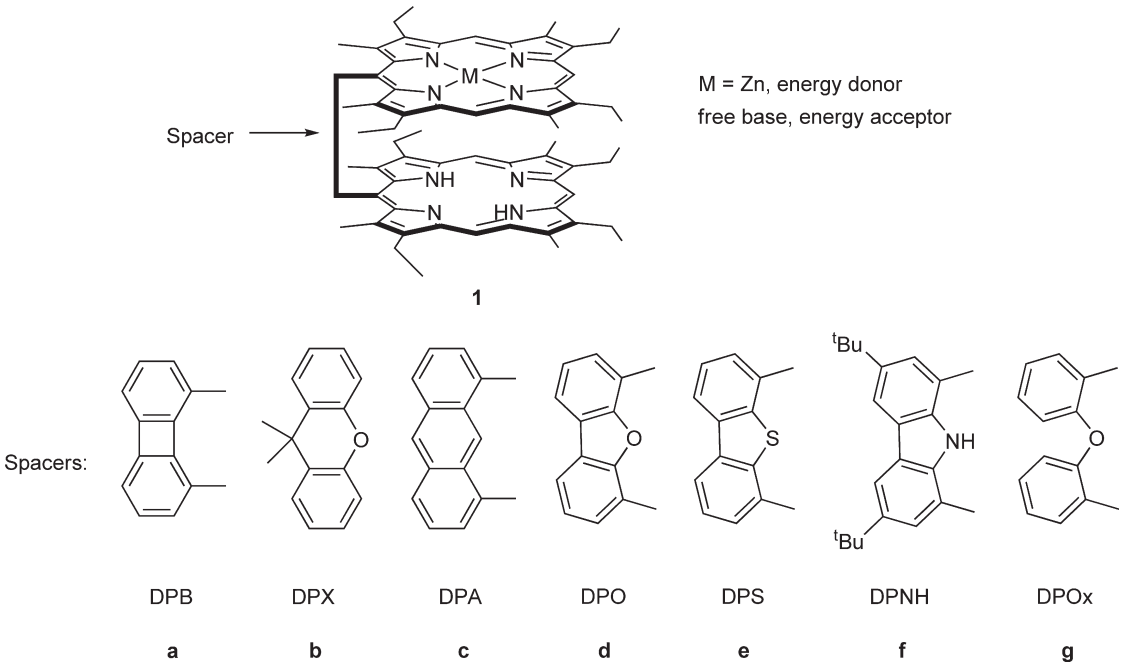
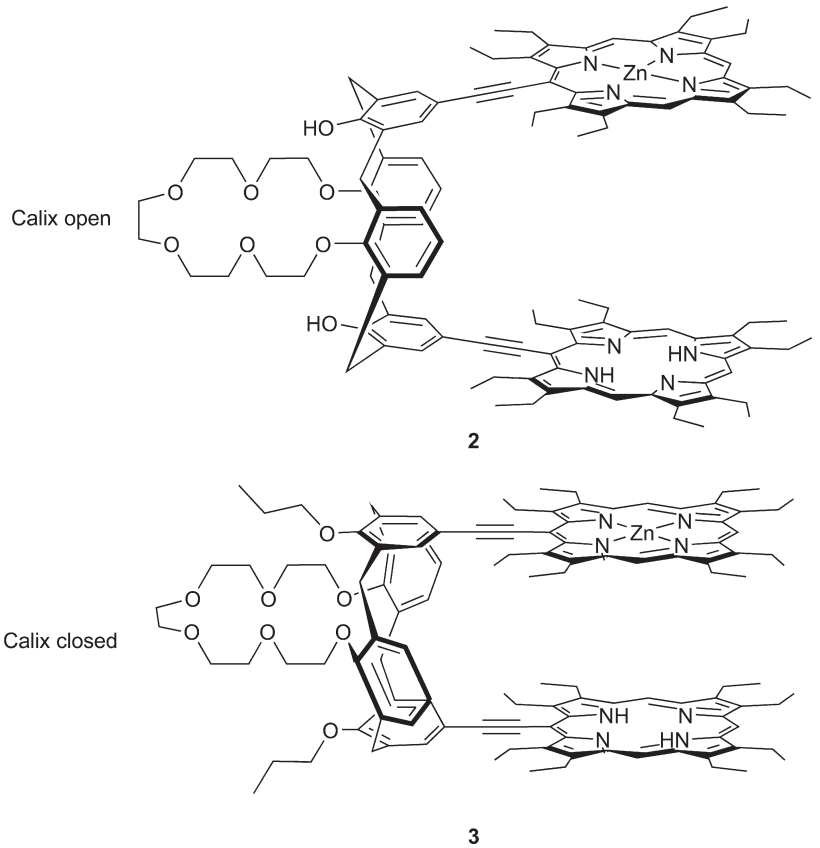
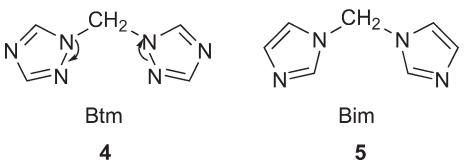


Scheme 1 Example of bifacial bisporphyrin dyads with various spacers.[12]



Scheme 2 'Calix open' **2** and 'calix closed' **3** conformers.[12]



Pombiero and coworkers reported coordination polymer **6** containing (triethanolamine)copper(II) units bridged by pyromellate groups. The peroxidative oxidation of cyclohexene into cyclohexanol and cyclohexanone via H_2O_2 at room temperature resulted in low yields in the polymerization reaction.[14] Polymer **6** is also insoluble in common solvents and has been isolated in 50% yields as a blue crystalline solid.

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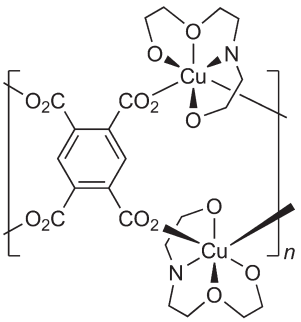

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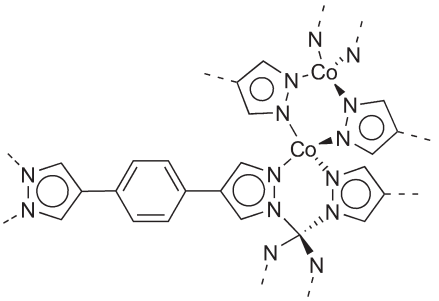
reported.[16] This material is used to catalyze the oxidation of cyclohexene by *tert*-butylperoxide. The reaction of copper(II) salts with either 1,4-bis(benzimidazolyl)butane (8) or 1,4-bis (triazolylmethyl)benzene (9) as linkage groups produces coordination polymers with 1D chains and two-dimensional (2D) grid topologies, respectively.[17]

Gurbuz and coworkers produced palladium(II)-containing siliceous compound 13 as illustrated in Scheme 3.[18] The dispersive structure of the Pd complex promotes the generation of moderately active catalysts for Suzuki cross-coupling of aryl chlorides and phenyl boronic acid under specific conditions.

Nickel(II) complexes containing phthalocyanines can be polymerized when thiophene residues are present on the macrocycle.[19]



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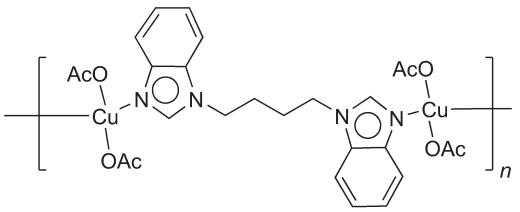

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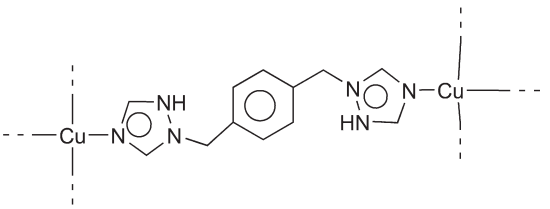

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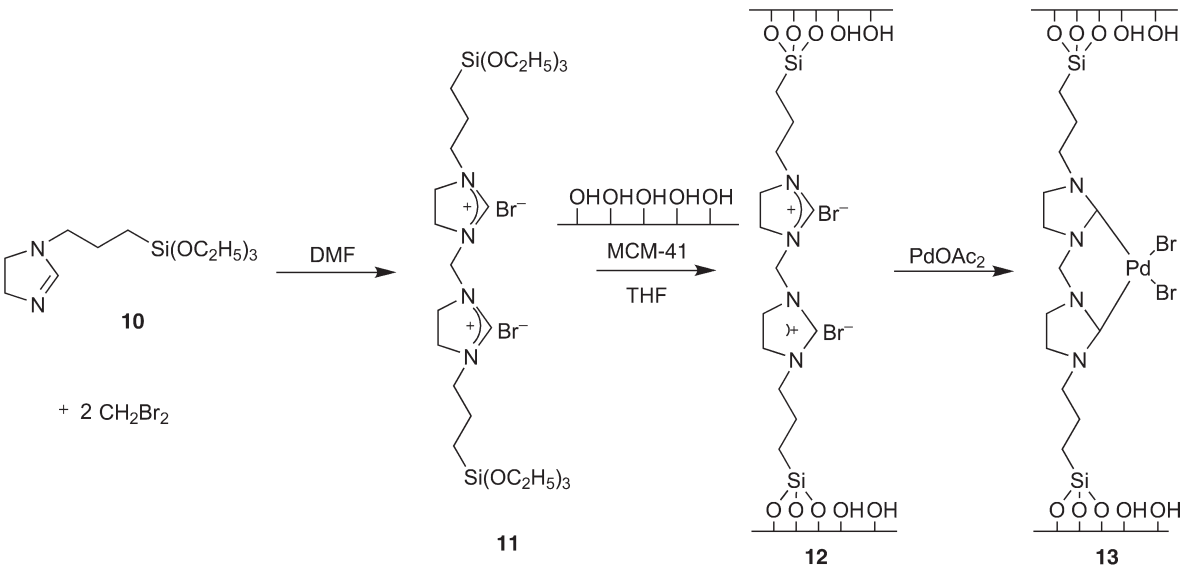
Coordination polymers containing Cu(II) or Co(II) were synthesized, with linking groups 2-hydroxypyrimidinolate or phenylimidazolate, respectively.[15] Cobalt coordination polymer 7, based on bis(pyrazolyl)benzene linkers, was previously

Nickel-containing polymer 14 exhibits two reduction processes at −1.35 and −1.75 V versus Fc/Fc$^+$. The lower redox couple is representative of the Ni^{2+}/Ni^{+} reduction, while the higher redox couple is assigned to a ligand-centered reduction process.



Scheme 3 Synthesis route to palladium(II)-containing siliceous compound.[18]

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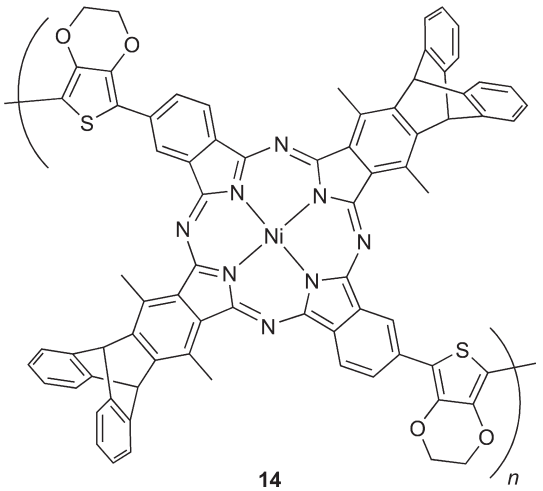

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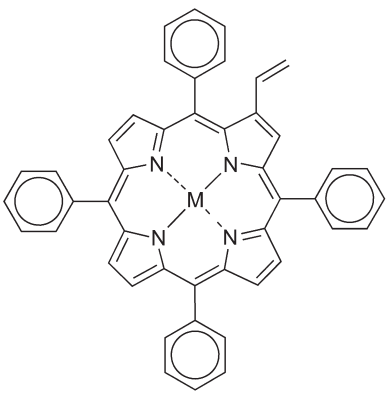
This chapter covers some of the most recent advances in metal coordination polymers and is divided into four subsections based on the nature of the coordination ligands.

5.23.2.1 Porphyrins

Porphyrin-containing coordination polymers can be used in a variety of applications, including optical and electronic devices, enzyme mimics, and solar energy conversion. Pomogailo *et al.*[20] used addition polymerization of porphyryl-coordinated metal monomers to prepare high-molecular-weight metalloporphyrin-containing polymers. Complexes 15 and 16 (M = Cu, Zn) were copolymerized with styrene to make high-molecular-weight products. Characterization of these high-molecular-weight polymers were difficult due to their poor solubility.[20–23]



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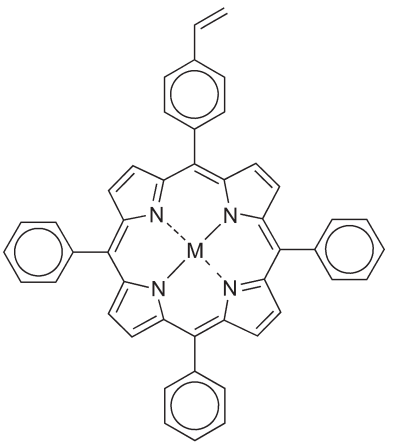

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Metalloporphyrin units can exhibit nonlinear optical (NLO) properties if they are aligned accurately. Anderson *et al.*[22,23] demonstrated that metalloporphyrin-containing polymers display microscopic polarizabilities 3 orders of magnitude greater than their corresponding porphyrin monomers. The results further revealed the largest one-photon, off-resonance, third-order susceptibility for an organic substance, indicating interporphyrin conjugation must occur. An example of a metalloporphyrin-containing polymer (18) is shown in Scheme 4. The solubility of polymer 18 was enhanced by attaching bulky substituents on the meso positions of the porphyrin monomer.

As a result of the luminescent properties of metalloporphyrin coordination polymers, these materials have been used as sensors that can detect dissolved oxygen,[24] furthering the utilization of metalloporphyrin-containing polymers in sensor applications.

The coordination site in the center of a porphyrin ring provides many opportunities for the design of coordination polymers (Scheme 5; X = N, O, S, P).[25–31] The chelated metal can have a six-coordinate geometry, accommodating the porphyrin and two additional ligands in the axial positions, each with one donor atom. Rings can be linked through coordination of ditopic ligands such as 4,4′-bipyridine or pyrazine to form 'shish-kabob'-type coordination polymers (19). The formation of long chains linked by noncovalent interactions was achieved by modification of the substituents on the porphyrin ring to give compound 25, shown in Scheme 6.

Through coordination of ligands such as cyanide, pyrazine, and tetrazine, porphyrin rings can form long polymeric chains. However, the metal center must be able to support an octahedral geometry to form these types of polymers. The coordination of Fe^{2+}, Ru^{2+}, and Os^{2+} to phthalocyanine was demonstrated by Hanack *et al.* (22) in Scheme 6.[25] The coordination polymers have higher conductivity compared to their monomeric species by 7 orders of magnitude for the tetrazine complexes. The tetrazine-linked phthalocyanines were also more conducting than polymers containing 1,4-diazabicyclo[2.2.2]octane (DABCO) and pyrazine without oxidative doping. Porphyrin-containing organic polymer 23 was cross-linked with 4,4′-bipyridine.[26] The addition of a half-equivalent of bipyridine (bpy) to polymer 23 resulted in the formation of ladder polymer 24. Conversely, the addition of one equivalent

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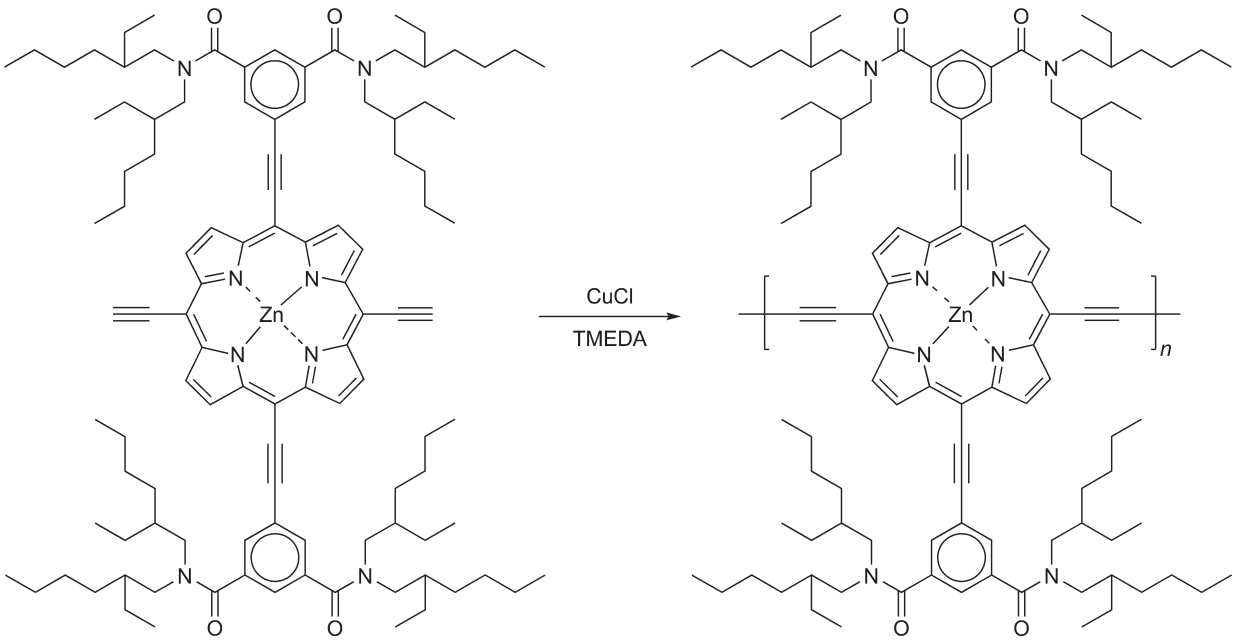
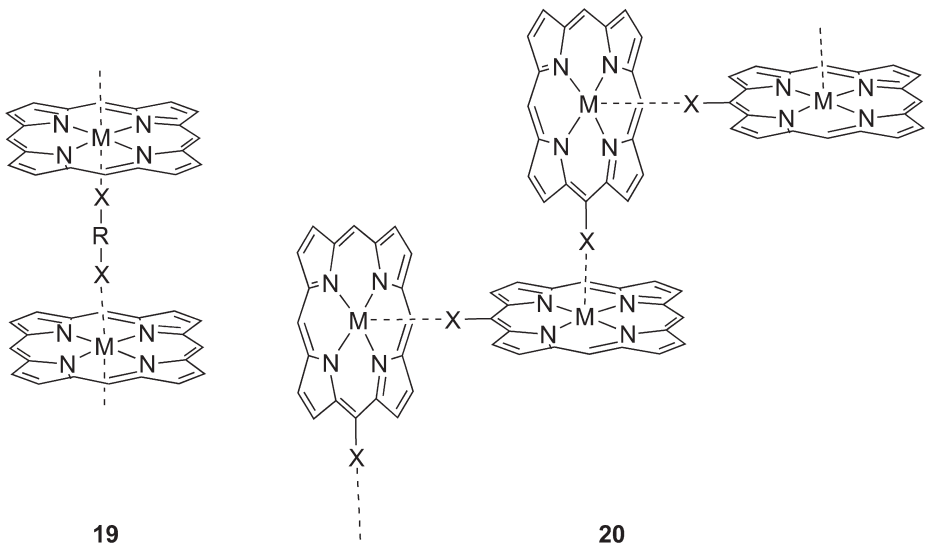
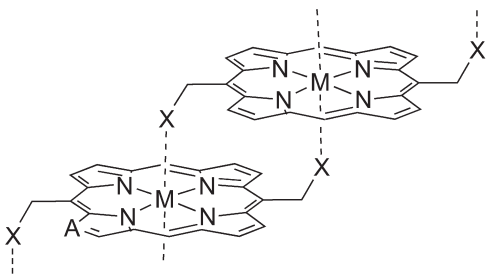


TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine

Scheme 4 Synthesis of metalloporphyrin-containing polymer.[22]





Scheme 5 Coordination possibilities in polymers (X = N, O, S, P).[25–31]

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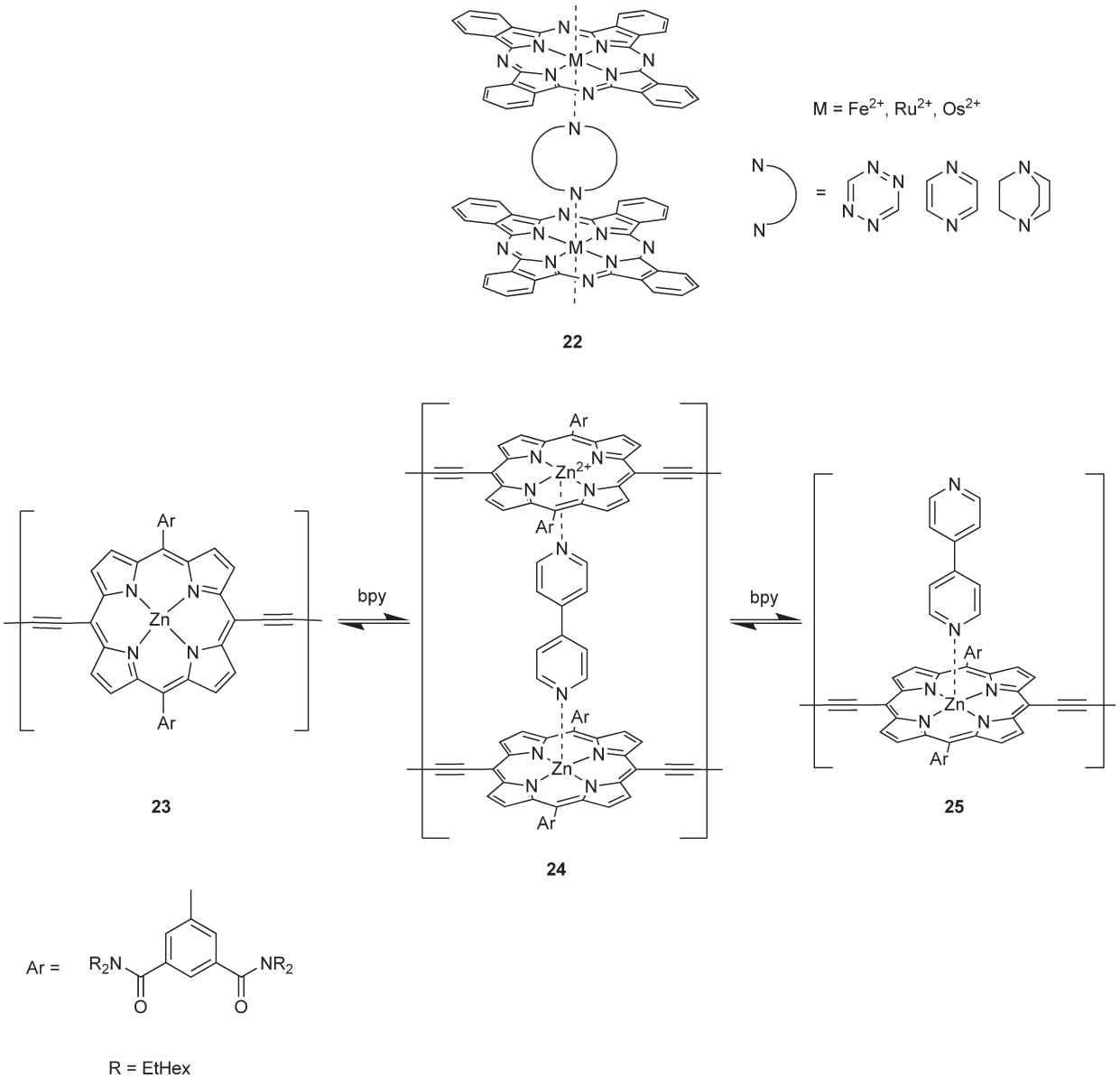

Scheme 6 Examples of porphyrin-containing polymers.[26]

of the bpy ligand resulted in a linear polymer with bipyridyl groups hanging as pendant side chains.

Yamamoto *et al.* synthesized polyphenylene ether (PPE)- or poly(*p*-phenylene) (PPP)-type polymers including bpy or 8-q in the polymer backbone by using palladium-catalyzed cross-coupling reactions.[27,28] As shown in **Scheme 7**, poly (bipyridine) (**26**) was treated with a stoichiometric amount of $Ru(bpy)_2Cl_2$ under reflux to produce the partially soluble solid polymer **27**.

The electrochemistry of **27** has different redox behavior compared to uncoordinated poly(bipyridine) (**26**) and $Ru(bpy)_3Cl_2$. Polymer **27** has a lower potential for the Ru^{2+} to Ru^{3+} redox peak and the potential is significantly broadened due to the interaction between the metal and the polymer chain.

Langecker and Rehahn reported iridium-functionalized polyfluorenes. The results demonstrate that Suzuki or Yamamoto coupling reactions allow for the formation of the organic backbone either before or after coordination (**Scheme 8**).[29] The metal-free polymers **30** and **31** have molecular weights of approximately 23 000 and 30 000 g mol^{-1}, respectively. Polymer **32** has a lower molecular weight compared to polymer **33** due to its low reactivity.

In 1993, Jin *et al.* were the first to report the incorporation of a porphyrin moiety into the center of a poly(benzyl ether) dendrimer, resulting in a porphyrin-containing dendrimer (**34c**) illustrated in **Scheme 9**.[30,31] This research led to further studies of porphyrin dendrimers.[30–41]

Dendrimers can be synthesized via divergent or convergent methods.[30] Dandliker and coworkers synthesized poly (ether-amide) dendrimer **35**, containing a porphyrin core, via the divergent approach and reported its redox properties.[32]

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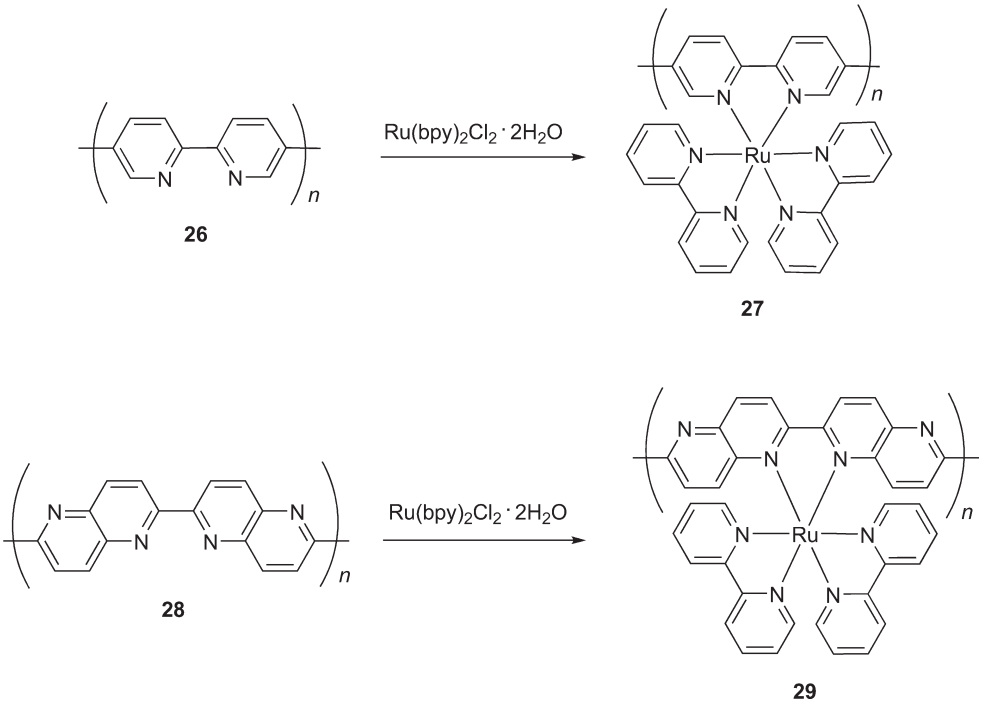
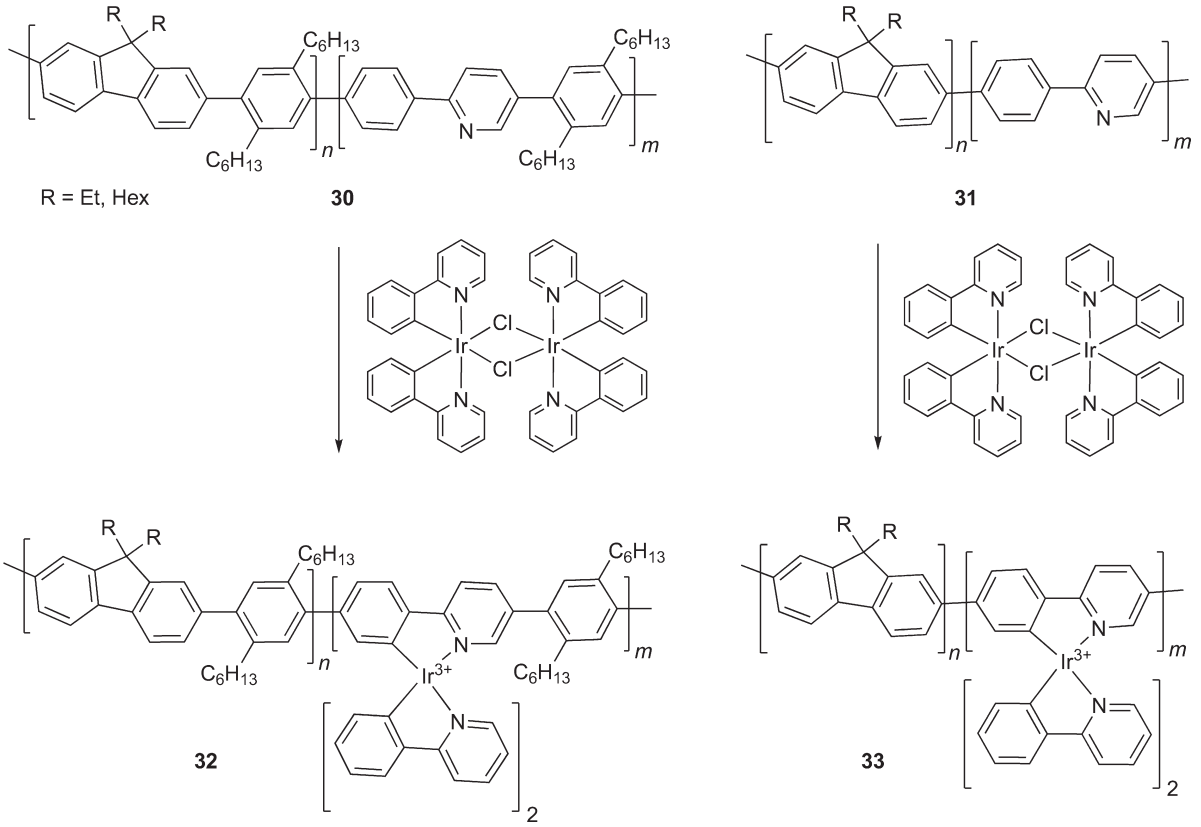


Scheme 7 Ruthenium-containing polymers based on poly(bipyridine) derivatives.[27]



Scheme 8 Polymer analogous reaction to iridium-functionalized polyfluorenes.[29]

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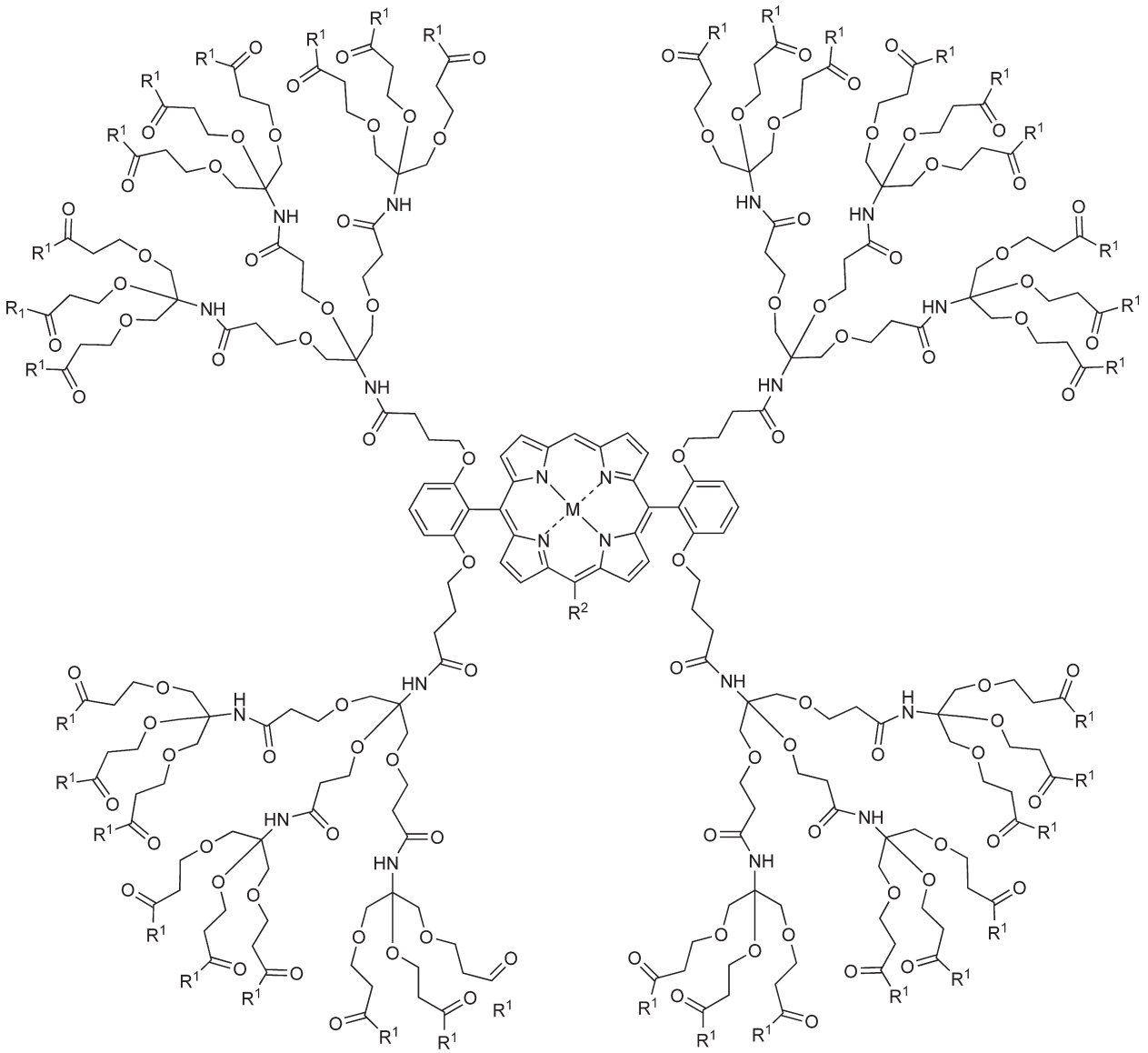
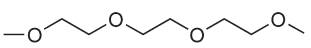


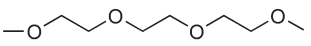
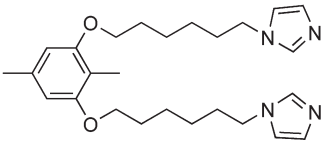
M = Zn, Fe, FeCl, Co

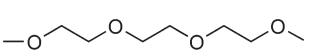
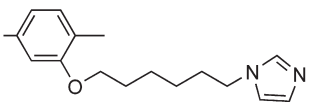
35

a R^1 = OMe, R^2 = H

b R^1 = $NHC(CH_2OCH_2CH_2CO_2CH_3)_3$, R^2 = H

c R^1 =  , R^2 = H

d R^1 =  , R^2 = 

e R^1 =  , R^2 = 

Tsukube and coworkers[42] developed a series of dendrimer porphyrins with an unsymmetrically substituted zinc porphyrin core (Scheme 10). Dendrimer 37, known as a pocket dendrimer, has dendritic wedges on

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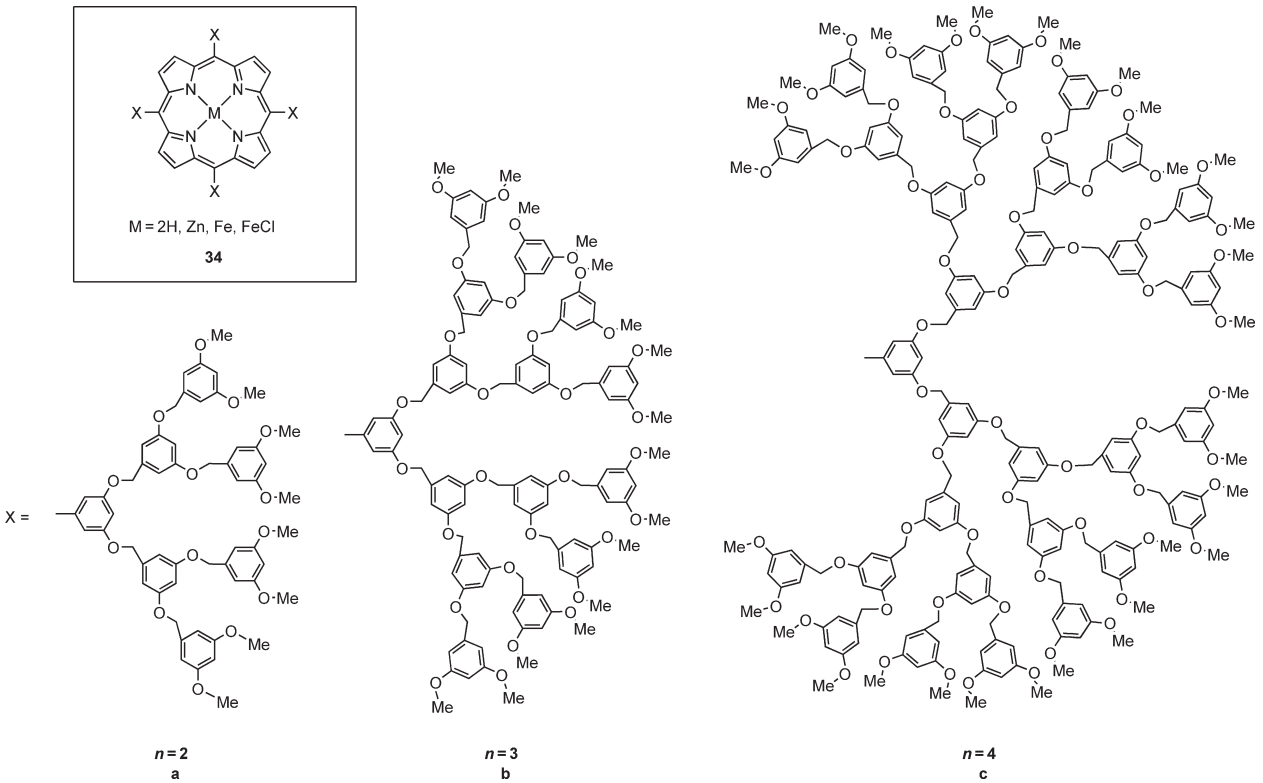
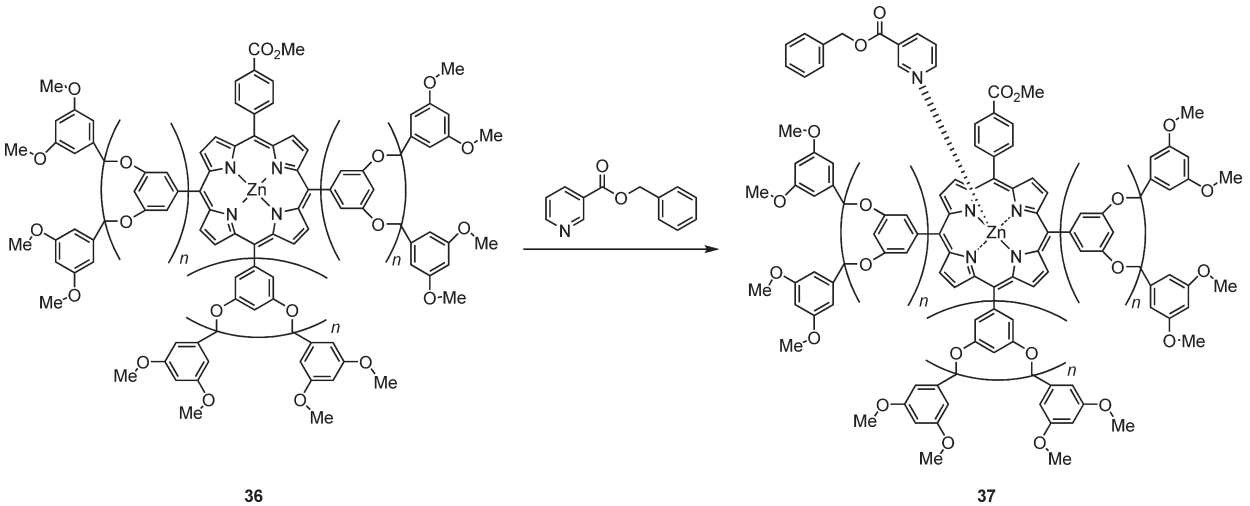


Scheme 9 Examples of porphyrin-containing dendrimers.[31]



Scheme 10 Coordination of guest molecules in pocket dendrimers.[43]

three sides of the metalloporphyrin structure, leaving the fourth side available for the coordination of guest molecules.[43]

Porphyrin dendrimers containing terminal hydrophobic substituents with a sterically protected core function as natural hemoproteins.[44] Bhyrappa *et al.* explored these types of porphyrin dendrimers and synthesized the Fréchet-type poly (phenyl ester) dendrimer **38** using dicyclohexylcarbodiimide (DCC) to promote the coupling reaction of carboxy-terminated dendritic wedges with *tert*-butyl surface groups.[45–47]

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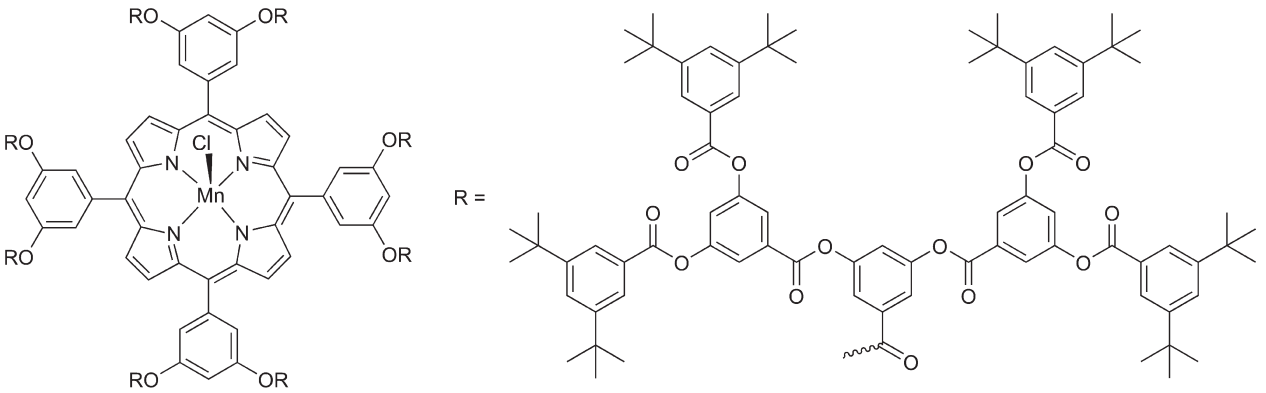
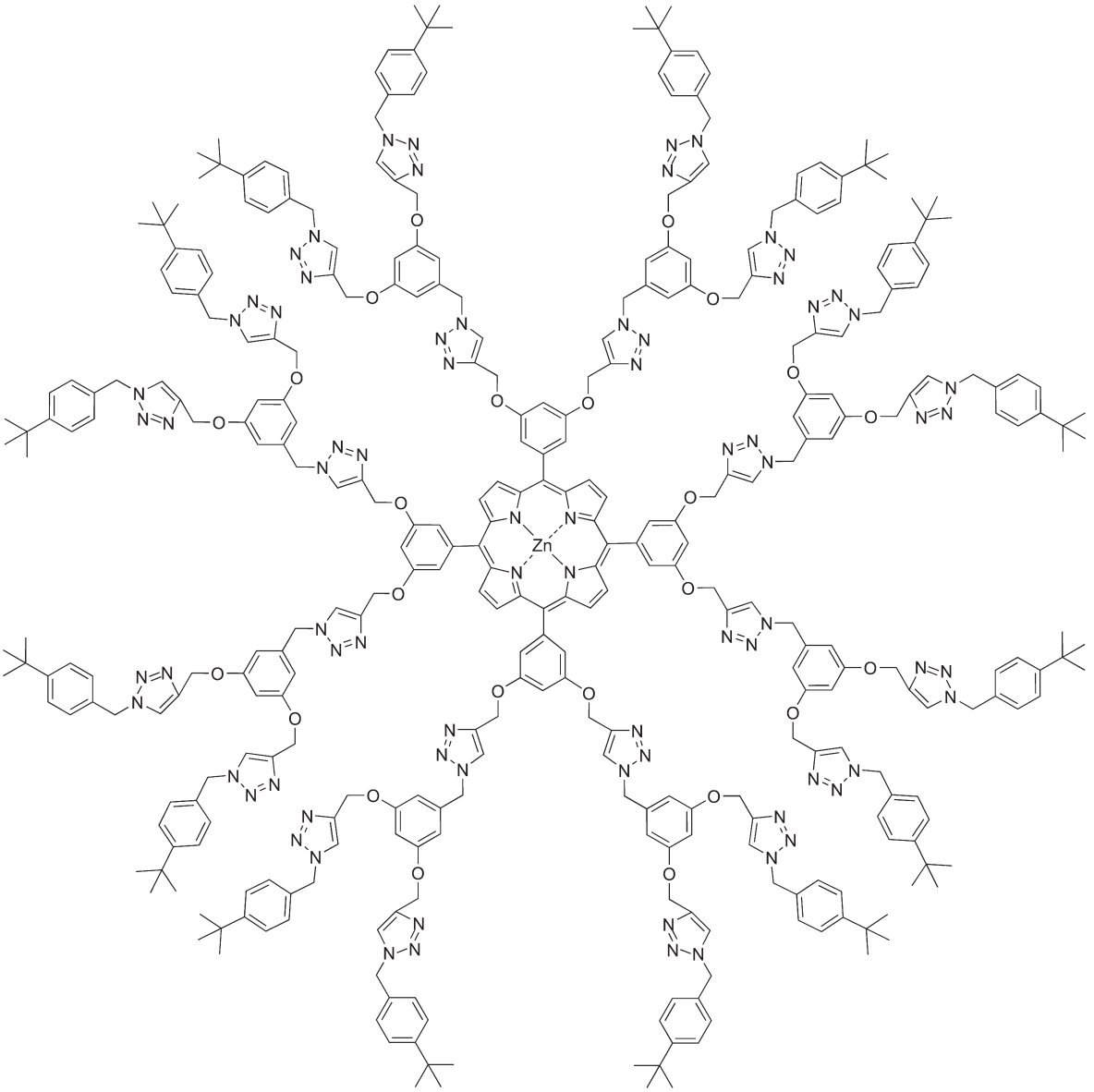


38

In addition, several dendritic porphyrins including benzyl ether dendritic azides (complex 39) were recently reported by Kimura and coworkers.[48] These porphyrin-based dendrimers were 'clicked' to form an acetylene-terminated Zn-porphyrin core. The cyclo-addition reaction used a copper catalyst to afford 1,2,3-triazole links.



39

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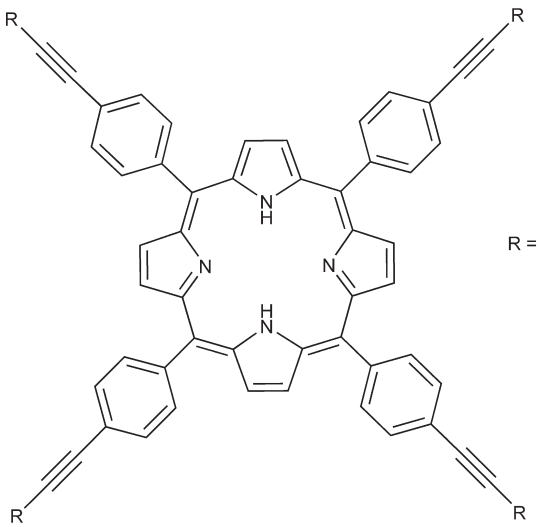
The snowflake-shaped dendrimers with porphyrin cores and multiporphyrin dendritic systems reported by Kozaki *et al.*[49] were synthesized via Sonogashira coupling reactions, resulting in the cross-shaped dendritic porphyrin system **40**. The convergent approach was used to prepare a rigid conjugated phenylethynyl backbone with a porphyrin core, similarly based on the Sonogashira reaction.[50]



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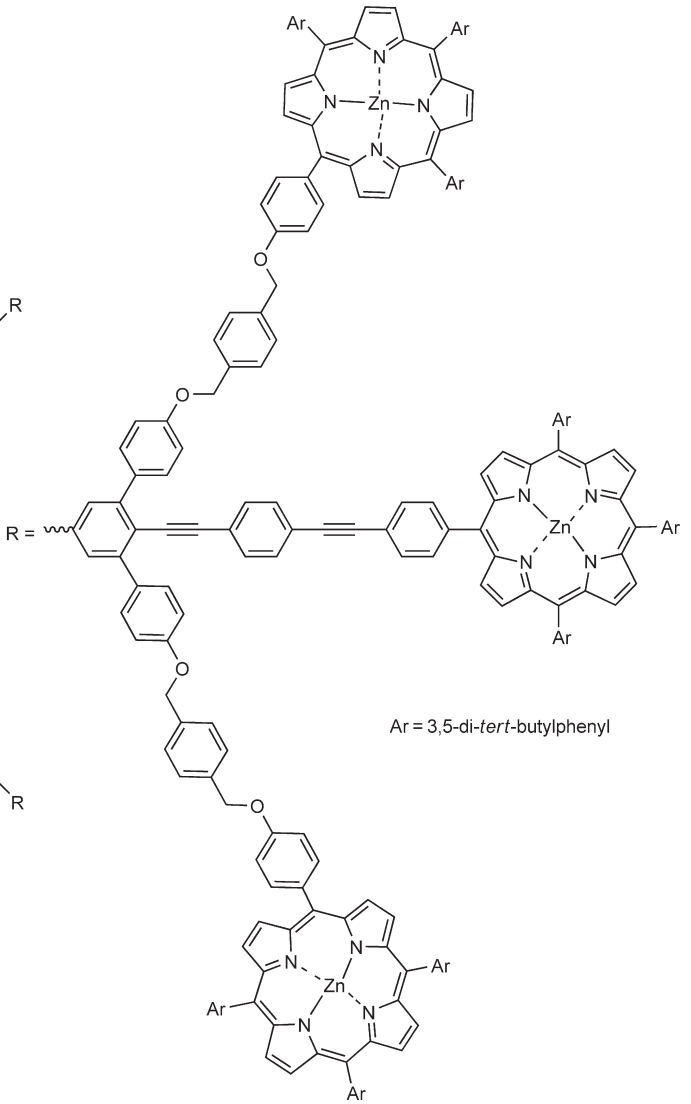

According to recent studies, the ZnP/AuP$^+$ couple was found suitable to perform photoinduced charge separation. A series of octaalkyldiaryl zinc and gold porphyrins were synthesized by Martensson and Albinsson (**Scheme 11**).[51–56]

The covalently linked zinc porphyrin-ferrocene dyads **44–46** recently developed by D'Souza *et al.* are self-assembled via axial coordination to either C60-Py or C60-Im.[57]

5.23.2.2 Schiff Base Polymers

Imines, also known as Schiff bases, are synthesized via condensation reactions of aromatic amines with aldehyde and ketone derivatives. Schiff bases play an extensive role in the preparation of dyes and are often used in the synthesis of coordination polymers as well. Goodwin and Bailor reported the synthesis of coordination polymers containing nickel, copper, and cobalt.[58] **Scheme 12** shows one example of the many coordination polymers prepared. Unfortunately, these materials were difficult to work with due to their poor solubility in organic solvents.

Synthetic methods of synthesis have been discovered enabling the characterization of these coordination polymers. Archer and coworkers were able to prepare coordination polymers by reacting Schiff base ligands that have the ability to complex with two metal ions.[59–63] This method was deemed more effective compared to the approach that Goodwin and Bailor had employed, which involved coordinating metal ions to already existing polymers. Polymers that have the ability to adhere to metal surfaces and glass were also developed.[61–63] One example of this type of polymeric material is represented by zirconium-coordinated Schiff base polymer **49**.

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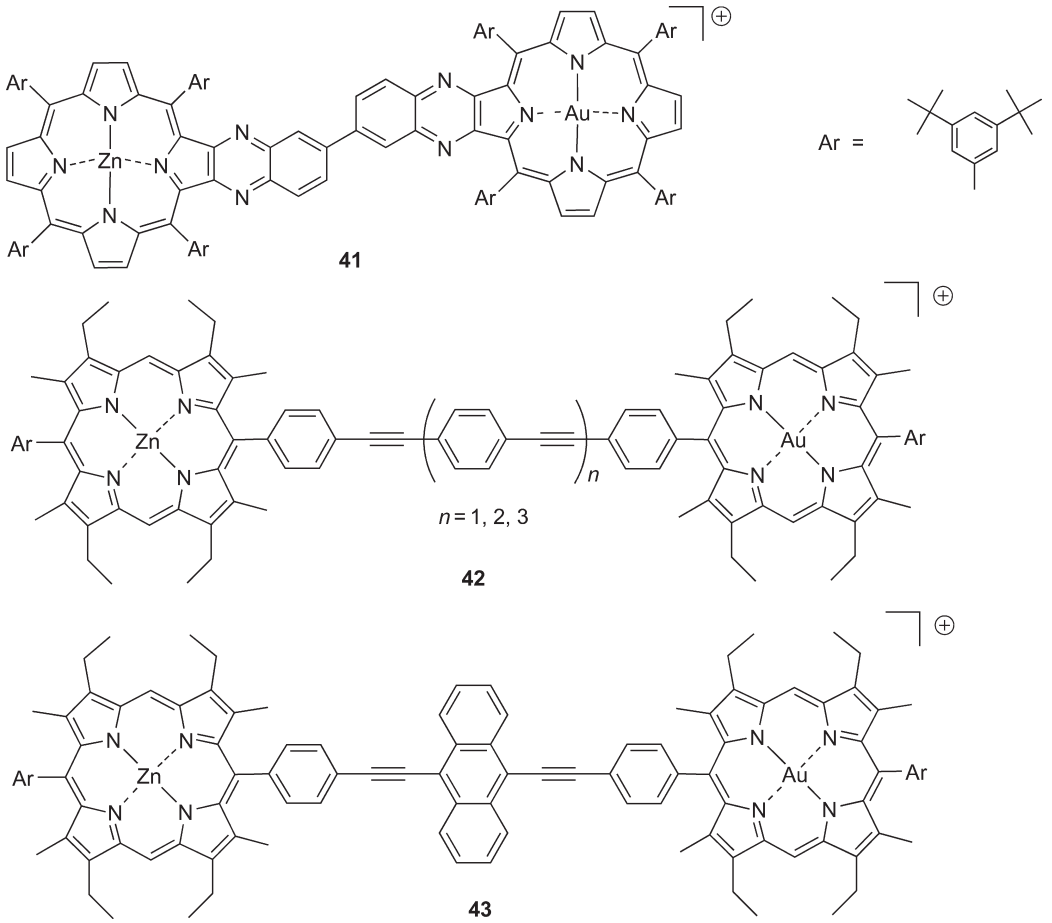
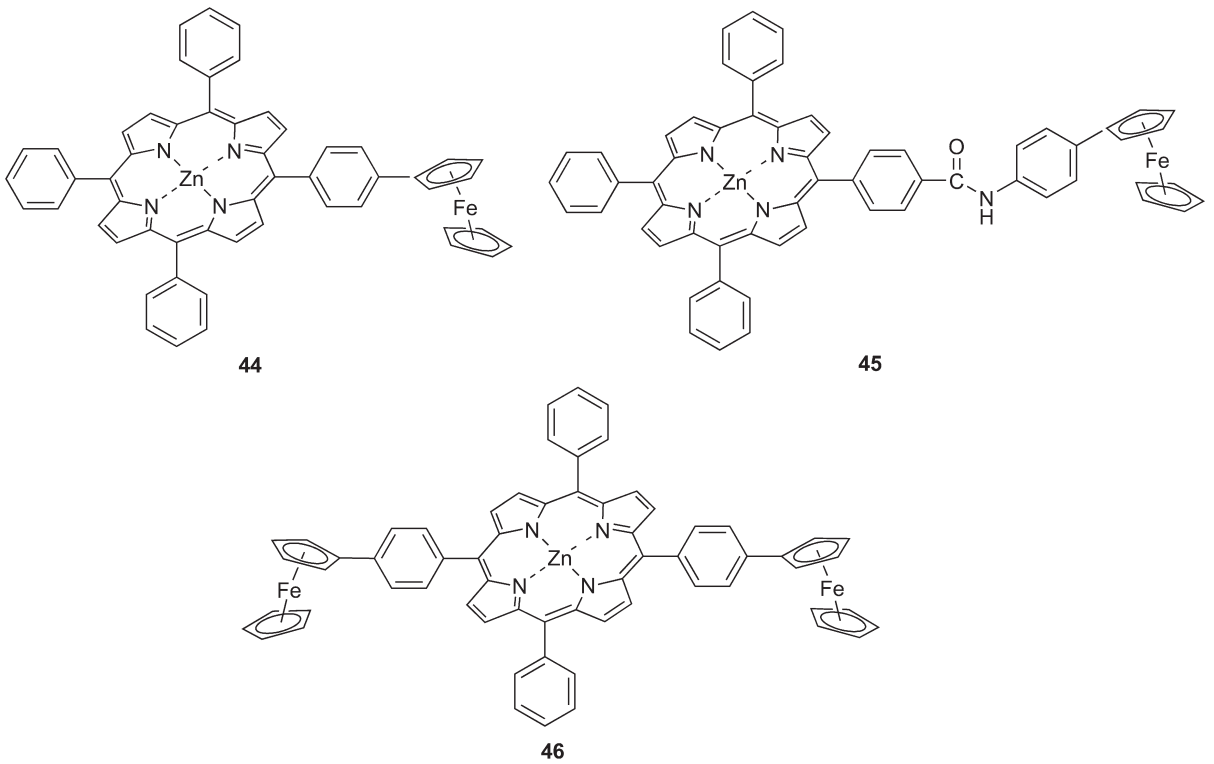


Scheme 11 Series of octaalkyldiaryl zinc and gold porphyrins.[51–56]



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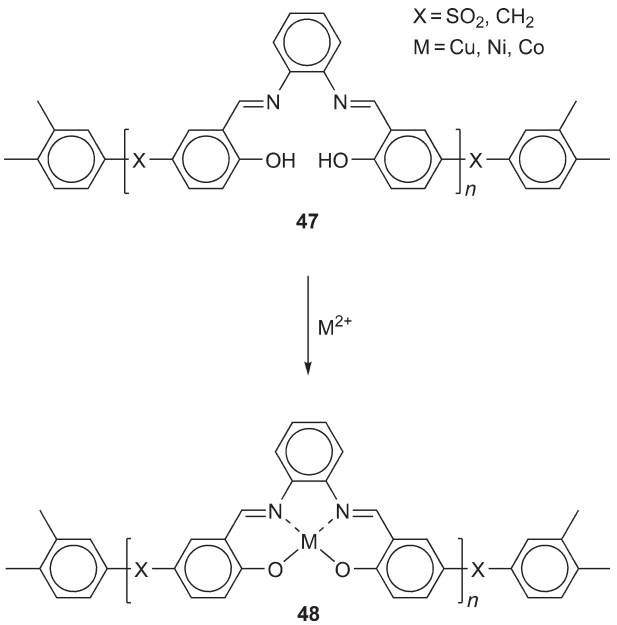
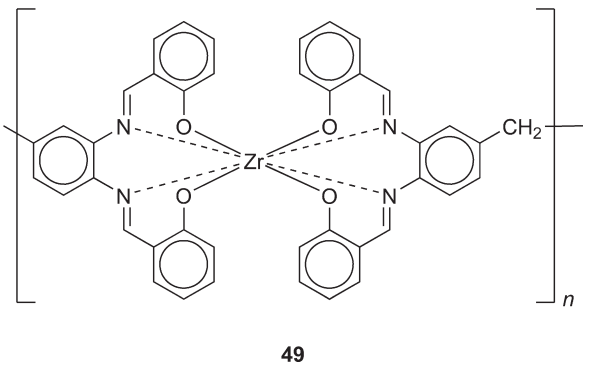
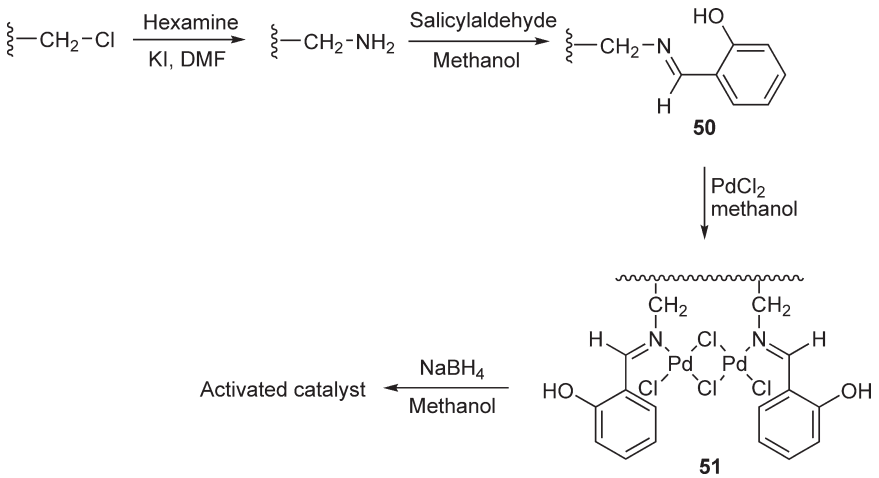


Scheme 12 Examples of metal-coordinated Schiff base polymers.[58]



The polymer-bound palladium(II) Schiff base complex **51** and its catalytic activity toward the hydrogenation of a number of olefins are illustrated in **Scheme 13**. The catalyst is effective in the hydrogenation of various olefins and can be recycled several times without significant loss in its activity.[64] These compounds catalyzed reactions in homogeneous conditions and the recycling of such catalysts was achieved with low-molecular-weight polymers.[65–80] The polymer-supported catalysts were prepared with the copolymerization of metal-containing monomers with styrene and divinylbenzene.[81–83]

The activity of a given polymeric material is greatly dependent on the type and coordination site of the Schiff base ligand, as well as the metal ion used in the formation of polymer-supported Schiff base complexes. The Schiff base ligands **52–54** have been frequently used as catalysts in the formation of metal complexes.[84] The binaphthyl chiral Schiff base ligands **55–57** were also implemented as catalysts for various metal complex reactions.[84,85]



Scheme 13 Synthesis of polymer-bound palladium(II) Schiff base complex **51**.[64]

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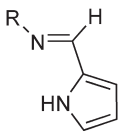

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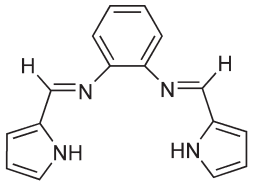

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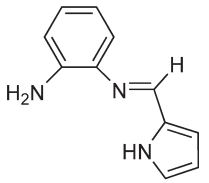

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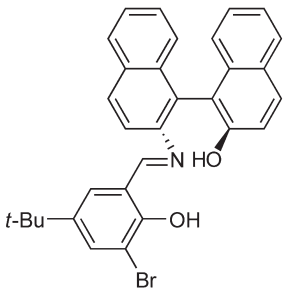

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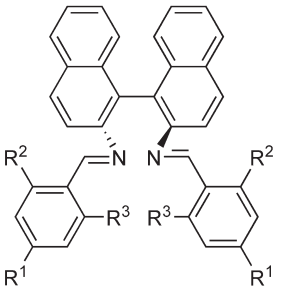

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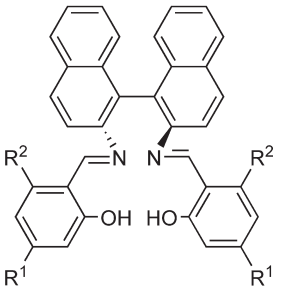
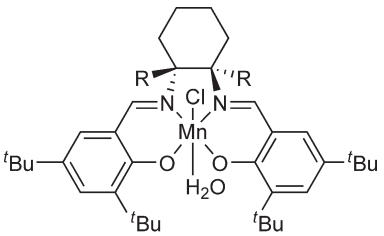


57

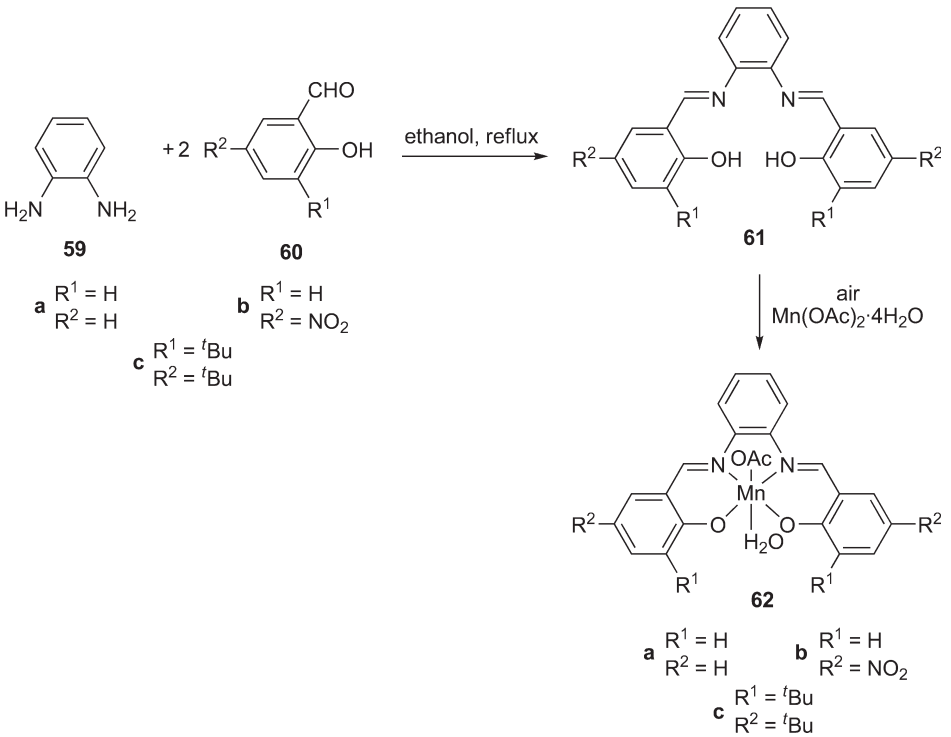
Recently, chirally modified lithium and magnesium *tert*-butyl peroxides were used in the epoxidation of electron-deficient olefins in good yields.[86] Alternatively, chiral manganese Schiff base catalysts (58) have been developed in high enantioselectivity capabilities.[87]



58

The functionalization of chitosan has been studied for several years to provide coordination sites that would support various catalysts and catalytic systems. The synthesis of salophen Mn(III) complexes 62a–c were reported by Tong and coworkers (Scheme 14).[88]

Metal complexes of the Schiff base polymers were synthesized by Tunçel *et al.*[89] The results demonstrate the formation of binuclear complexes 63 and 64 with oxygen and nitrogen donor atoms when the Schiff base polymers and metal ions are present in a 1:1 molar ratio. These complexes have dimeric structures bridged by polymeric ligand units.



Scheme 14 Synthesis of salophen Mn(III) complexes **62a–c**.[88]

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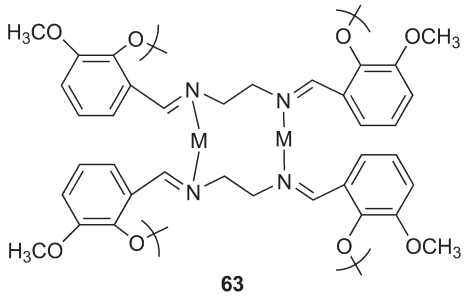
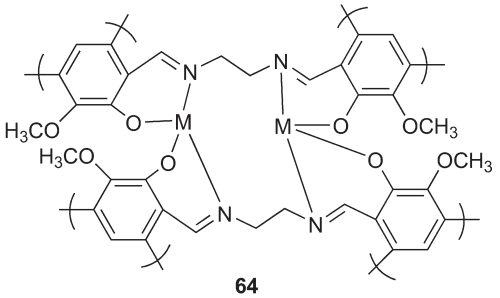


63

Bidentate structure



64

Tetradentate structure

Grivani *et al.* developed a new procedure for preparing catalysts.[90] This method demonstrates the Schiff base molybdenum carbonyl complex **66** attaching via a covalent bond to a pendant chloromethyl group on the surface of polystyrene resin particles, represented as 'R' (**Scheme 15**). Due to its low cost, availability, mechanical robustness, and facial functionalization, chloromethylated polystyrene (2% DVB) was selected as the catalyst.

5.23.2.3 Phthalocyanine Systems

Phthalocyanines are macrocylic molecules that are structurally similar to porphyrins; phthalocyanines contain four extra nitrogen atoms in the inner core and four additional arenes on the exterior. In 1958, the synthesis of copper-coordinated phthalocyanine polymers was reported by Marvel and Rassweiler.[91] The preparation of these materials was achieved by reacting pyromellitic acid, phthalic anhydride, and urea to give blue-green- to blue-black-colored products. As reported by Kimura *et al.*,[92] olefin metathesis polymerizations of copper and zinc phthalocyanine monomers form linear and network polymers. Linear polymer **69**, shown in **Scheme 16**, is an example of metathesis polymerization using copper phthalocyanine monomers.

Phthalocyanine complexes containing iron or other transition metals can mediate several selective oxidation and bleaching reactions, depending on the choice of oxidant. For example, the immobilization of metallophthalocyanines on chitosan aerogel microspheres produce oxidation catalysts containing basic sites.[93,94] These supported catalysts are efficient in the allylic and propargylic oxidation of olefins, alkynes, phenols, and aromatic compounds. The structure of heterogeneous catalyst **70** supported onto SiO_2, TiO_2, and chitosan is illustrated in **Scheme 17**.

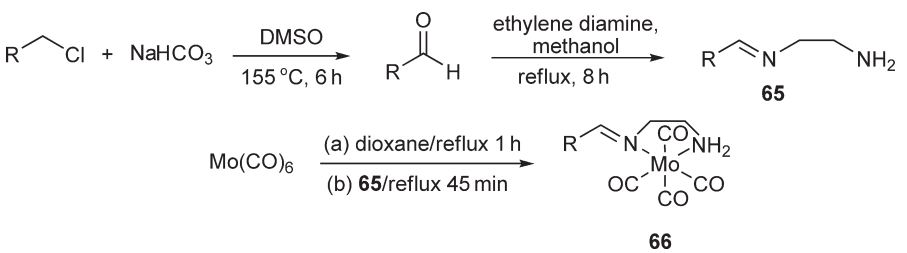
Ribeiro and coworkers suggested a new methodology to obtain stable water solutions of neutral phthalocyanines.[95,96] The preparation of water-soluble 'symmetrically' substituted phthalocyanines with four D-glucose units was reported by Maillard[97] and Cavaleiro.[98] According to such studies, D-glucose units are linked to a different isoindolyl group by the hydroxyl group located on the C-3 or C-1 carbons, respectively (**Scheme 18**).

5.23.2.4 Pyridine and Related Systems

Reactions that involve metal ions and pyridine are well known in inorganic chemistry. Polymerization reactions involving pyridines and metal ions can occur if a pyridine monomer has been chelated to the metal ion prior to polymerization. **Scheme 19** displays an example of both methods of polymerization.

Monomer **74** is reacted with ruthenium chloride to afford a ruthenium-chelated polymeric material. In contrast, polymer **77** was prepared by reacting Ru-coordinated terpyridine monomer **75** via palladium-catalyzed Suzuki coupling reaction.[99] In addition to the two previously mentioned approaches, polymeric products can also form when at least one pyridine unit is attached to a preexisting polymer.

Lee *et al.*[100] have prepared long and flexible bis (pyridine)-type linking ligands (**Scheme 20**). Ligands **78** and **80** are structural isomers because the nitrogen atoms on the terminal pyridine moieties are at different positions. These ligands were used to prepare novel cobalt coordination polymers using either a layer diffusion method or a solvothermal reaction. The N–N separations between the



Scheme 15 Attaching Schiff base molybdenum carbonyl complex onto PS resins.[90]

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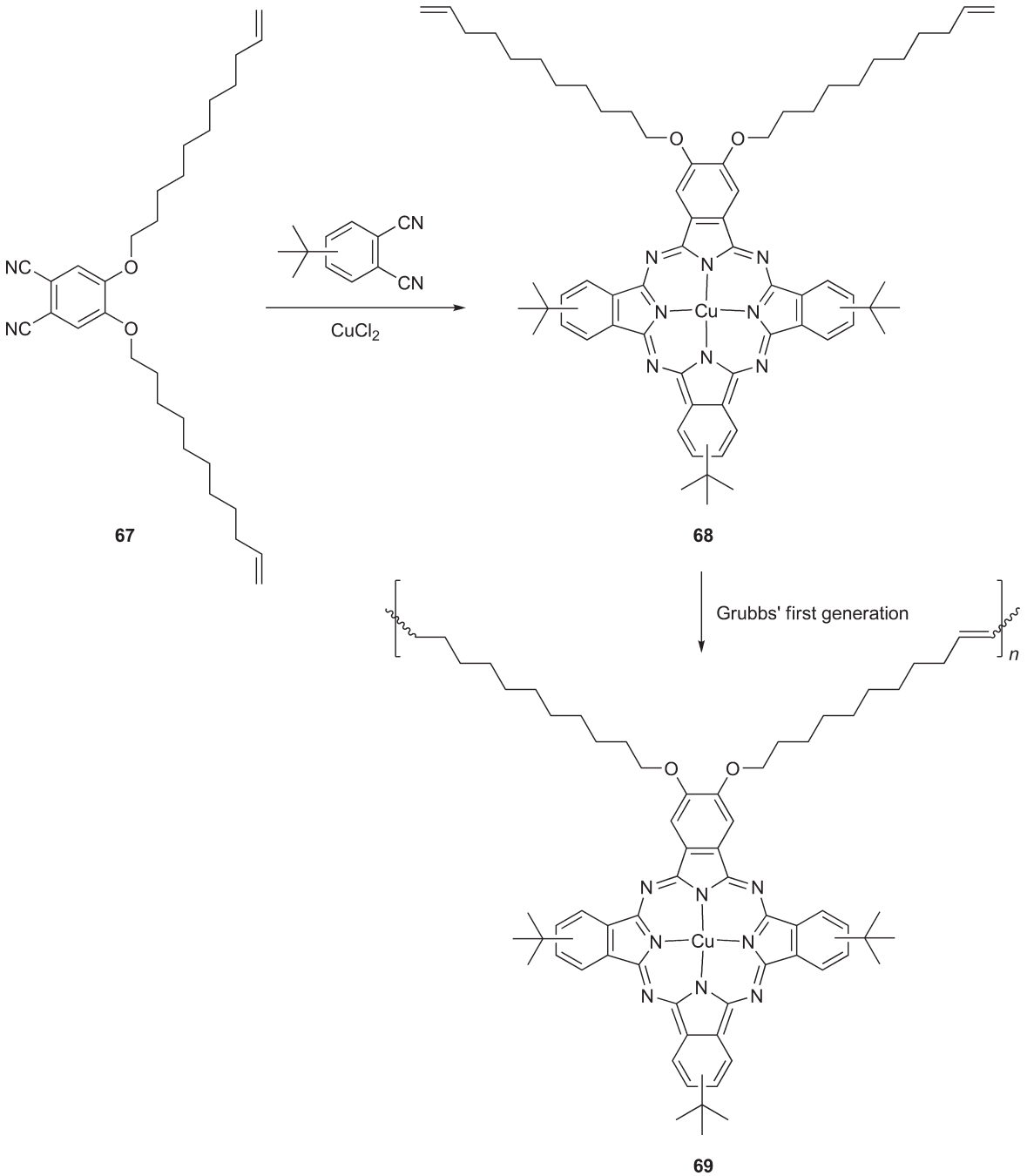
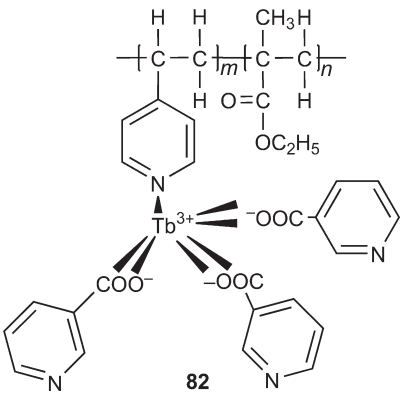


Scheme 16 Metathesis polymerization to linear copper-coordinated phthalocyanine polymers.[92]

two terminal pyridyl groups determined the flexibility of the resulting polymer.

Recently, a convenient synthetic approach to make a series of highly efficient luminescent Tb-containing polymers was reported by Yan and Wang.[101] Three terbium binary complexes with pyridine carboxylic acids were synthesized and then introduced into 4-vinyl pyridine-ethyl methacrylate copolymer matrices using the former as the second ligand. The luminescence properties of copolymers containing terbium were investigated. It was found that the energy transfer mechanism appears standard through these rare earth polymer systems. The predicted structure of copolymer 82 is represented below.[101]



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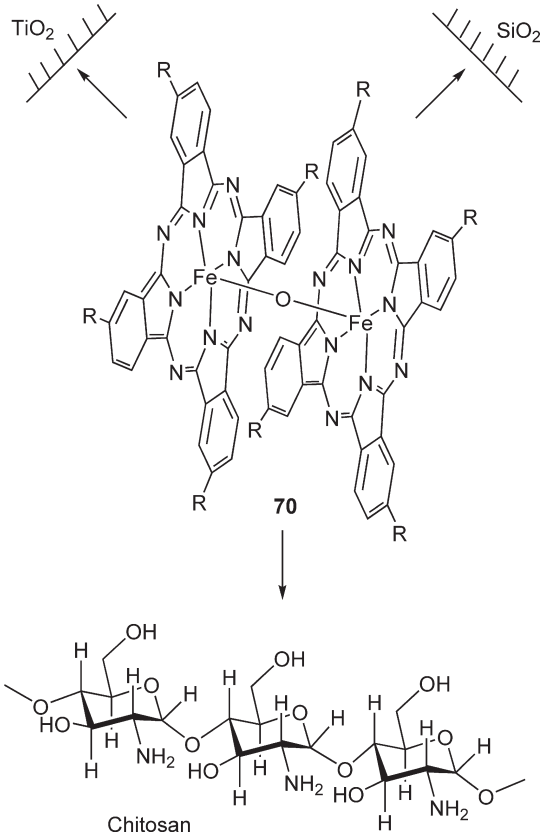
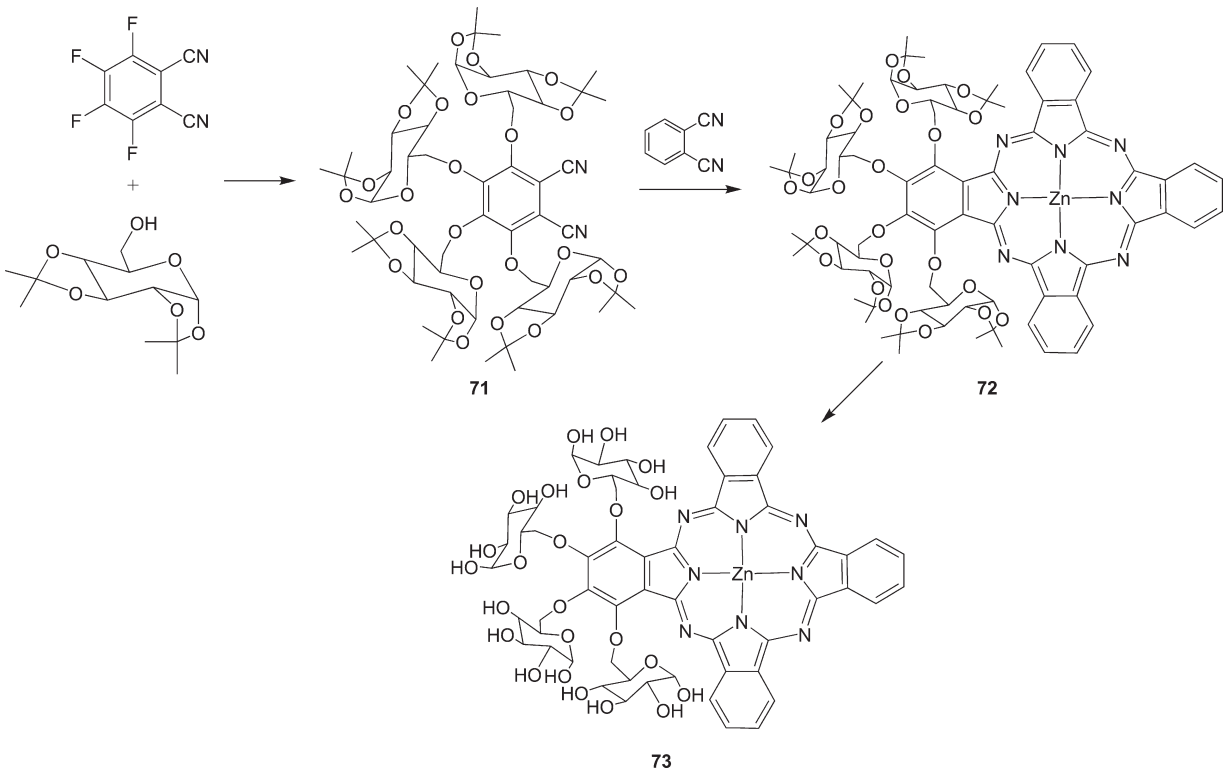


Scheme 17 Immobilization of metallophthalocyanines on chitosan, SiO_2, and TiO_2.[94]



Scheme 18 Preparation of water-soluble substituted phthalocyanines with four D-glucose units.[98]

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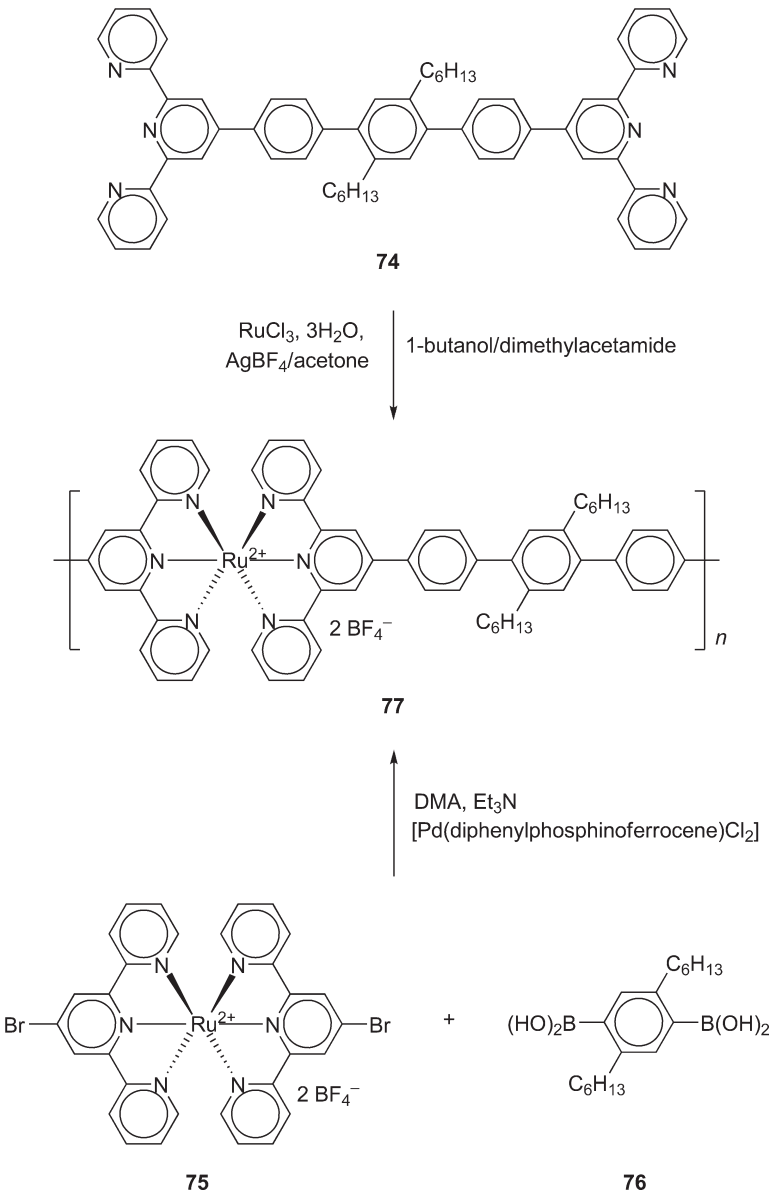
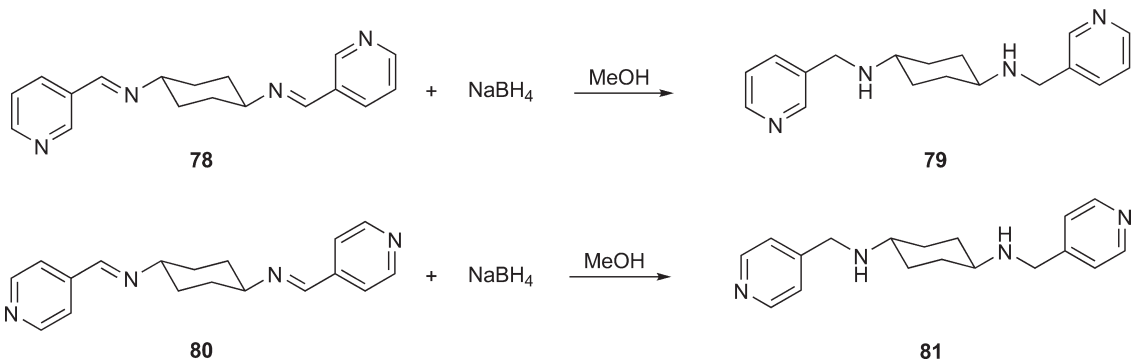


Scheme 19 Example of different methods toward ruthenium-chelated polymers.[99]



Scheme 20 Synthesis of flexible bis(pyridine)-type linking ligands.[100]

Chen and coworkers have synthesized 2,6-disubstituted pyridyl compounds with flanking coordination sites, using molecules like 2,6-bis(imidazol-1-yl)pyridine as the organic tecton to construct coordination polymers of various dimensions.[102,103] The perspective view of the 3D framework of Ag(I) coordination polymer is illustrated as compound 83.

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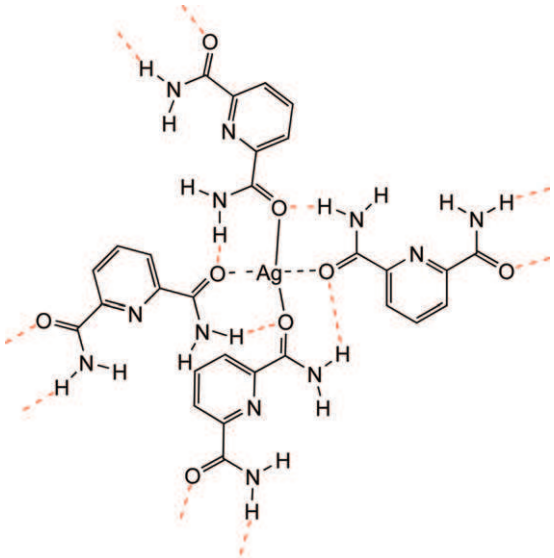


83

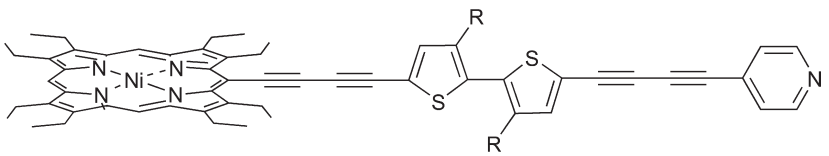
Orientational isomers 84 and 85 of the octaethylporphyrin–dihexylbithiophene–pyridine system (OEP–DHBTh–Py), connected with a diacetylene linkage, were synthesized by Hayashi *et al.*[104] Spectral measurements determined that the orientation of DHBTh affects not only the electronic structures of OEP–DHBTh–Py but also their proton-mediated spectral changes.

Beves *et al.*[105] reported a comparative structural and spectroscopic investigation of complexes 86a–c (M = Fe or Ru). The complexes are thought of as expanded 4,4′-bipyridines, where the distance between the nitrogen atoms is increased from ~7 to ~18 Å. Complex 86c in particular is very reactive toward protons, alkylating agents, and metal ions.

The synthesis of new terpyridine metal complexes such as 87, performed by Schubert and coworkers, reveals a strong relationship between the binding strength of the metal ion and the stability of the terpyridine metal complex.[106–111]

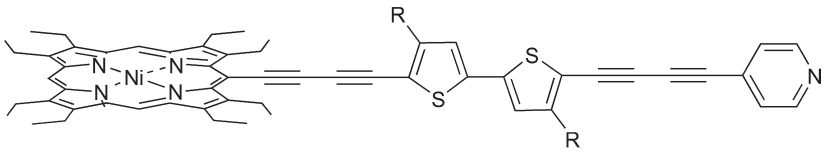
Pd-catalyzed amination reaction of aryl halides was used to convert the macroligand 88 to macroligand 89.[112–114] High conversion of the aryl bromide to triphenylamine unit was achieved with the described method in less than 2 h. The metallation of polymer 89 with Ru-$(bpy)_2Cl_2 \cdot 2H_2O$ was illustrated in Scheme 21 using the activated silver salt method. The amination reaction introduced the charge transport moiety to the polymer, with triphenylamine as pendant groups. The complexation of the bipyridyl unit yielded to a highly soluble bifunctional polymer in which charge transport polymer chains are attached to a tris(bipyridyl) Ru(II) core.[115]

The ligands (92, 94) were used in order to improve solubility of metal complex reagents in atom transfer radical polymerization (ATRP) reaction media. The metallo-reagents are multifunctional additional challenges for attaining 'well-defined' materials by ATRP.[116–123] Bipyridine analogues, $bpy(C_{13}H_{27})_2$, with alkyl chains were used to produce heteroleptic initiators with two and four reactive chloride sites 92 and 94, respectively. The reaction control for the catalyst systems in anisole solution



OEP-(HH)DHBTh-Py

84



OEP-(TT)DHBTh-Py

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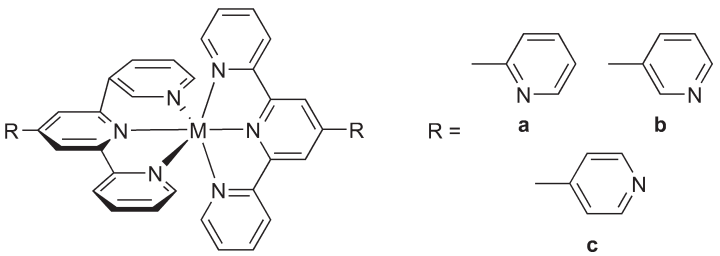

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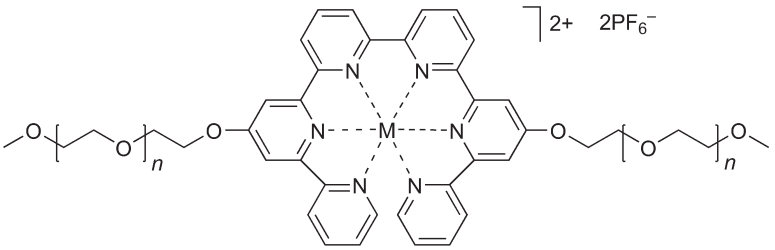

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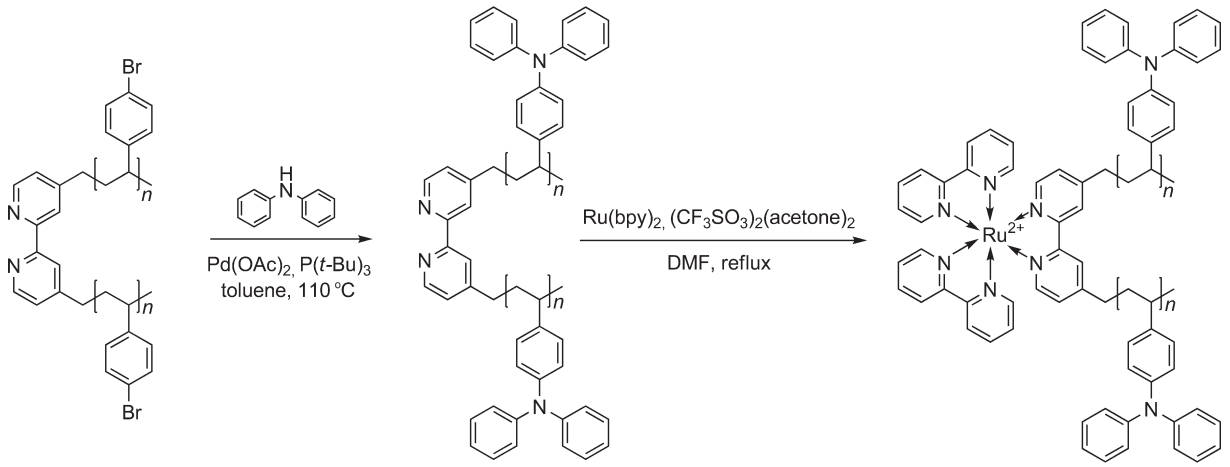

88 89 90

Scheme 21 Amination of polymer **88** with diphenylamine using $Pd(OAc)_2$ and $P(t\text{-}Bu)_3$ as catalytic system and the complexation of the bipyridine unit in polymer **89** with $Ru(bpy)_2Cl_2{\cdot}2H_2O$ using the activated silver salt method in DMF under reflux.[112]

was improved by the use of the difunctional initiator $[Ru\{bpy(C_{13}H_{27})_2\}_2\text{-}\{bpy(CH_2Cl)_2\}](PF_6)_2$ (92). Also polydispersities were low (1.1) and the molecular weight began to increase more dramatically with the use of ligand 94. Similarly, molecular weight control was better for the tetrafunctional initiator $[Ru\{bpy(C_{13}H_{27})_2\}\{bpy(CH_2Cl)_2\}_2](PF_6)_2$ (94).[116]

5.23.3 Polymers Containing Sandwich Complexes

5.23.3.1 Metallocene-Based Polymers

The copolymerization of vinyl ferrocene was reported by Arimoto and Haven after Kealy and Pauson first synthesized ferrocene.[124] Scheme 22 illustrates organometallic polymer 96, synthesized using phosphoric acid, persulfate, or azobisisobutyronitrile (AIBN) as an initiator. Copolymers were synthesized with methyl methacrylate, styrene, and chloroprene, and the homopolymers were cross-linked with formaldehyde. These polymers undergo reversible chemical oxidation with ceric sulfate.[125]

Many ferrocene-functionalized polymers were reported by Pitmann and coworkers in the 1970s.[126–131] The solution and bulk polymerizations of vinyl ferrocene were of great interest due to the potential physical, chemical, and electrical properties of the resulting poly(vinylferrocene).[126–134] The copolymerization of vinyl ferrocene with styrene using living radical initiator 2,2,6,6-tetramethyl-1-piperidine-1-oxyl (TEMPO) was reported in 1999.[135]

Acrylate and methacrylate ferrocene monomers were used to obtain new organoiron polymers through the homopolymerization and copolymerization of acrylate and methacrylate ferrocene monomers.[136–141] These particular polymers show many interesting physical and chemical properties. For instance, polymers with ferrocene units in their side chains exhibit higher glass transition temperatures than those without ferrocene.[136] Furthermore, these polymers have wide applications: one report suggests that halocarbons could be reduced photochemically with modified electrodes containing ferrocene or cobaltocene groups.[141]

The kinetic studies of the polymerization of the organoiron monomers have also been studied. It was found that these polymerizations often did not follow the same rate laws as their corresponding organic monomers. In addition, ferrocene-substituted polymethacrylates indicate NLO properties, as reported by Wright *et al.*[142–144] Scheme 23 shows the copolymerization of ferrocenyl-functionalized monomer 97 (5 mol.%) with methyl methacrylate (98). Polymer 99 displays second-harmonic-generation activity and has a number average molecular weight of 43 000 g mol^{-1}and a glass transition temperature of 100 °C. Polymers with cyano-containing ester groups attached to the other cyclopentadienyl ring indicate NLO properties as well.[144]

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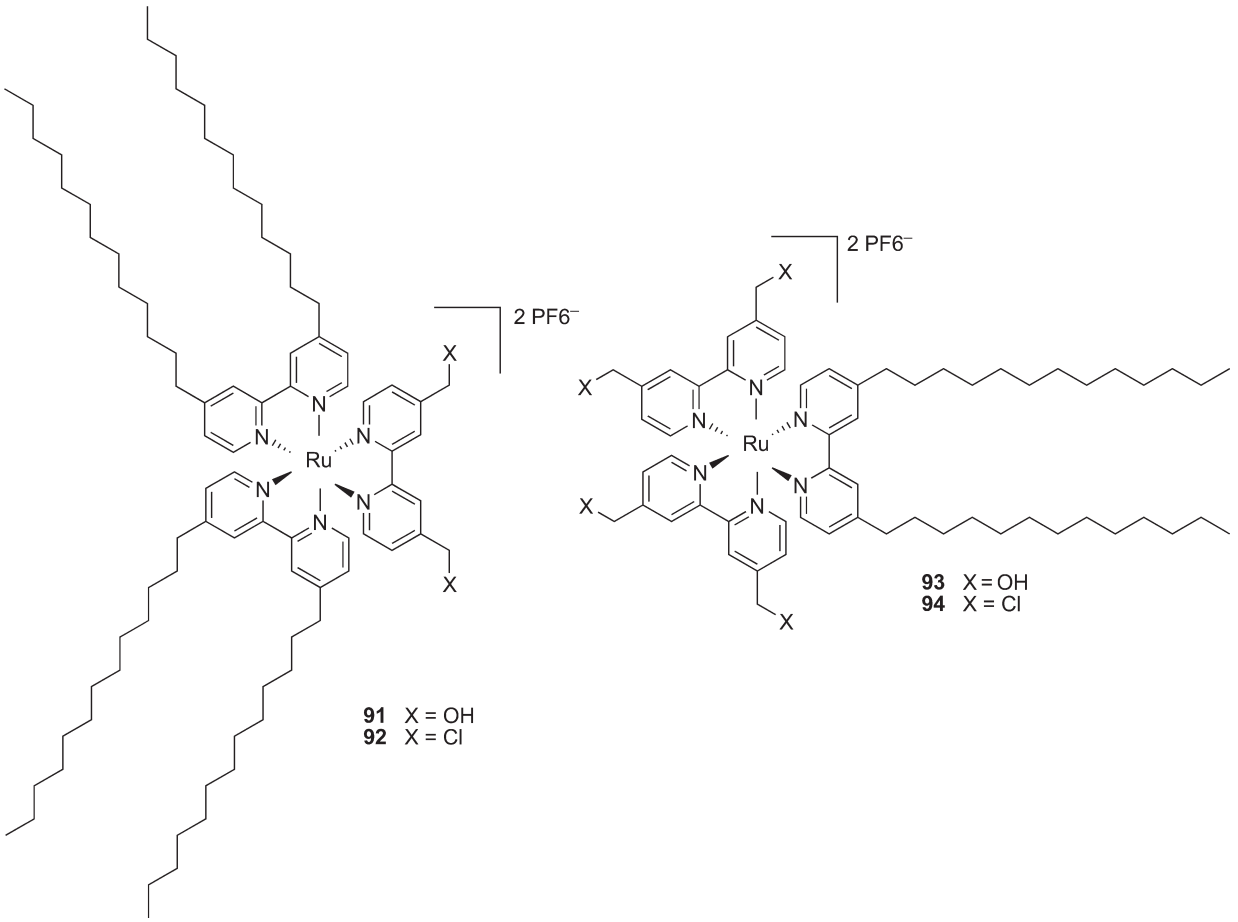
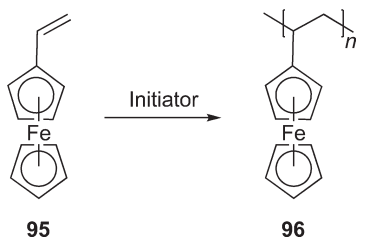
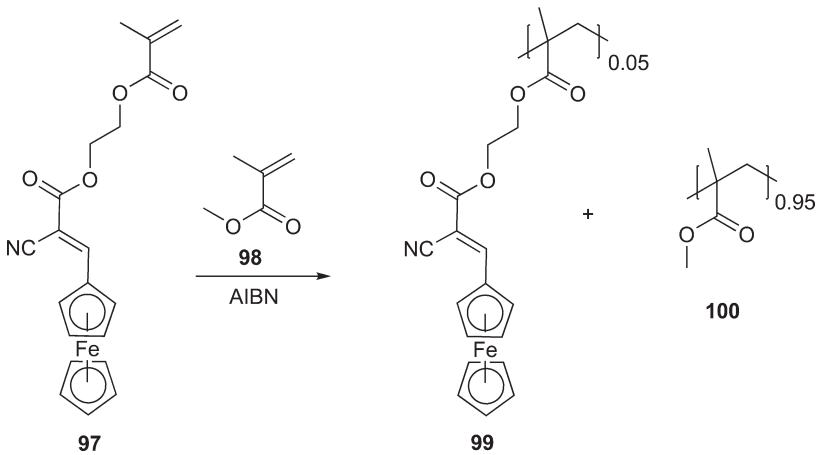




Scheme 22 Synthesis of metallocene-based polymers using phosphoric acid, persulfate, or AIBN as an initiator.[125]

In 2002, the homopolymerization and copolymerization of ferrocene-functionalized acrylates and methacrylates were reported.[145] Polyferrocenylethyl acrylate, methacrylate, acrylamide, and methacrylamide were synthesized using AIBN as initiator, shown in **Scheme 24**.

The organometallic polymers were obtained by the reaction of various diolefins with 1,1-dimercaptoferrocene or 1,1-bis(2-mercaptoethyl)ferrocene. The reaction of 1,1-dimercaptoferrocene (**103**) with **104**, conducted via base-catalyzed polyaddition, is shown in **Scheme 25**.[146]



Scheme 23 Polymerization mixture of ferrocenyl-functionalized acrylates with methyl methacrylate.[144]

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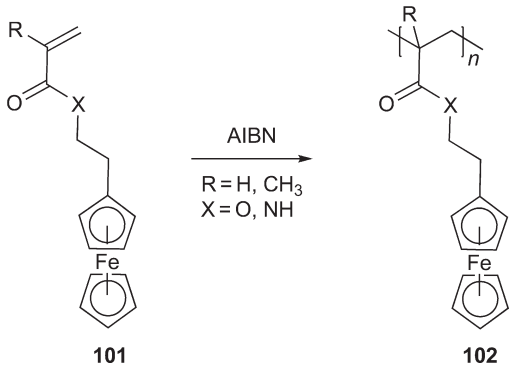
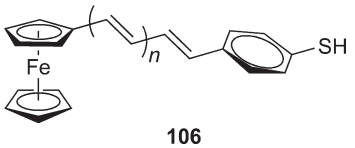


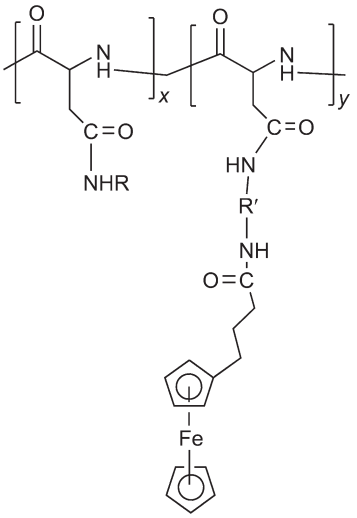
Scheme 24 Homopolymerization of ferrocene-functionalized acrylates and methacrylates.[145]

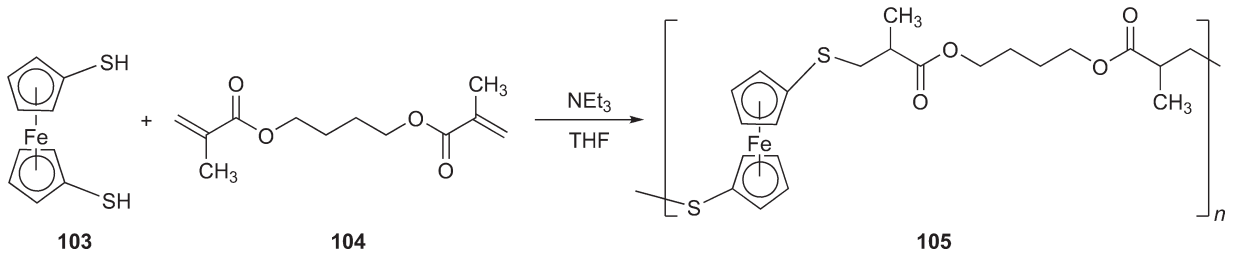
Sachs *et al.*[147] and Smalley *et al.*[148] have reported various ferrocenyl wires. Polymer **106** is another example of self-assembled monolayers of ferrocene-terminated polyalkylthiols. The polymer is covalently connected to an evaporated gold film by a conjugated bond of mercaptooligo (phenyleneethynylene) (OPE).



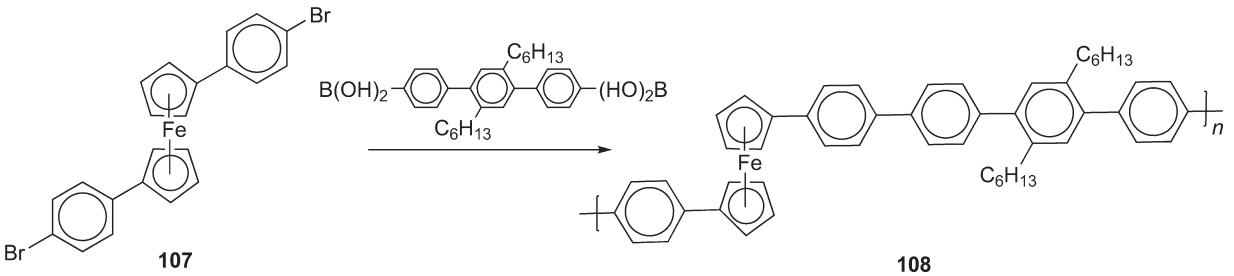
Rehahn and coworkers prepared a new series of poly(1,1′-ferrocenylene-*p*-oligophenylenes) (**108**) via palladium-catalyzed coupling reactions illustrated in Scheme 26.[149] Intrinsic viscosity and light scattering methods were employed to determine the molecular weight of the polymer, which was in the range of 32 000. This polymer has bulk properties due to its excellent solubility. Thermogravimetric analysis indicated that the presence of the ferrocenylene units inhibited the thermal cleavage of the *n*-alkyl side chains, making the material thermally stable up to 400 °C.

Ferrocene-containing polymers were initially researched for potential applications in medical research. Water-soluble ferrocene-containing polymers such as **109** were predominantly studied due to their interesting antiproliferative properties.[150–155] The most important property of these polymers is the ability of the ferrocenyl groups to cleave off easily, allowing the ferrocenium salts to trap free radicals, potentially playing a role in cancer treatment.





Scheme 25 Base-catalyzed polyaddition of 1,1-demercaptoferrocene(**103**) with **104.**



Scheme 26 Palladium-catalyzed coupling reaction of poly(1,1′-ferrocenylene-*p*-oligophenylenes).[149]

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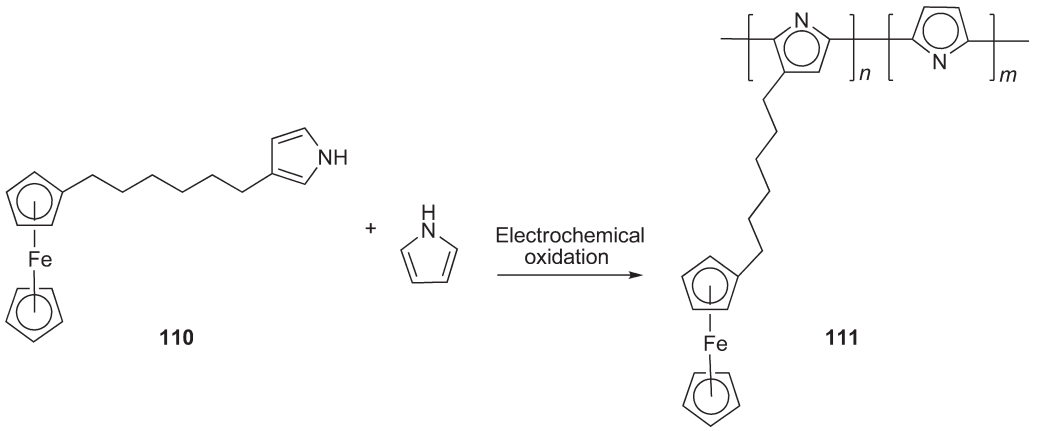
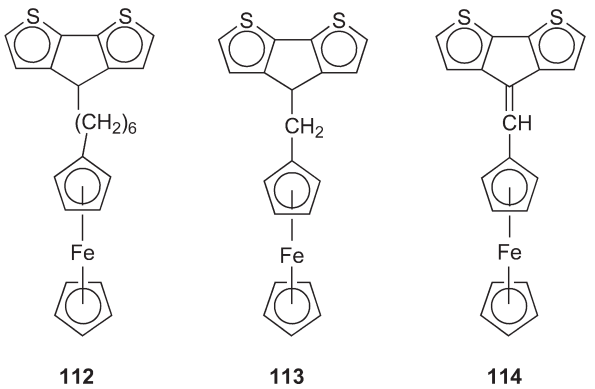


Scheme 27 Electrochemical copolymerization of ferrocene-functionalized pyrrole with pyroll.[158,159]

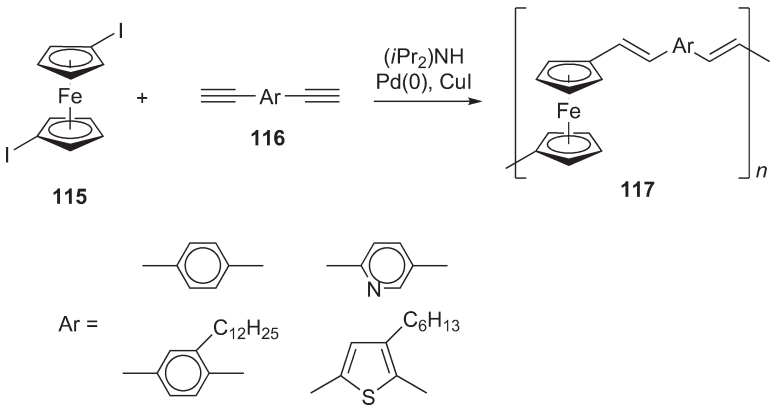
Electropolymerization of metallocene-functionalized pyrrole and thiophene derivatives produces organometallic polypyrroles and polythiophenes.[156,157] Zotti *et al.* studied the electrochemical copolymerization of ferrocene-functionalized pyrrole **110**.[158,159] **Scheme 27** represents the copolymerization of the monomer with pyrrole. The results indicated that polymer **111** has an electrical conductivity of $1.5 \times 10^{-2}\,\mathrm{S\,cm^{-1}}$.

Similarly, polythiophenes containing ferrocene moieties in their side chains were prepared (**112–114**) through the electrochemical polymerization of the monomer. Monomer **112** was polymerized and the polymer obtained had a redox potential equal to that of *n*-hexylferrocene. Polymers of **113** possessed redox potentials of 0.03–0.15 V, and higher oxidation potentials were demonstrated by the third polymer. The increase in the redox energy is attributed to stronger interactions of the ferrocene moieties and polymer backbone. Additionally, the redox potentials decrease as the length between the polymer backbone and the ferrocene moieties increases.[158,159] Monomer **114** was copolymerized with 4-hexylcyclopentadithiophene, producing a polymer with a conductivity of $1\,\mathrm{S\,cm^{-1}}$ and higher oxidation potentials. However, the electrochemical oxidation of **112** gave homopolymers that indicate an *in situ* conductivity of $40\,\mathrm{S\,cm^{-1}}$.



The polycondensation reaction of diiodoferrocene (**Scheme 28**) and diethynyl aromatic compounds **116** via a palladium catalyst resulted in conjugated polyferrocenes **117**.[160,161] As expected, the addition of long alkyl side chains into these macromolecules enhances their solubility in organic solvents. The resulting polymers were converted into semiconducting materials (10^{-7}–$10^{-4}\,\mathrm{S\,cm^{-1}}$) with the addition of iodine.

Interest in the polymerization of cyclic olefins has steadily increased over the last decade, and the development of



Scheme 28 Palladium-catalyzed polycondensation of diiodoferrocene and diethynyl aromatic compounds.[161]

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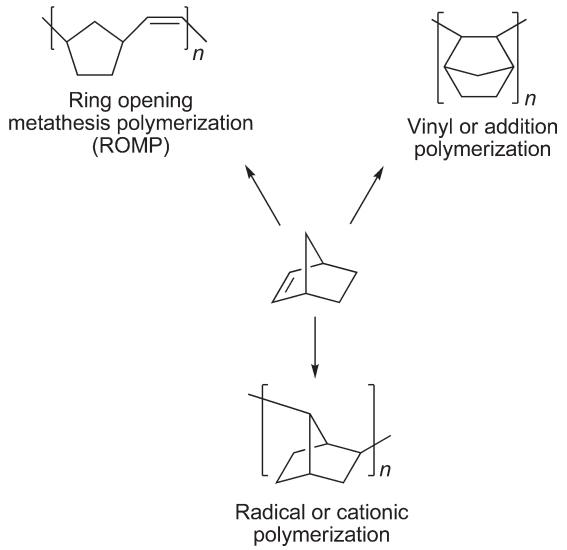


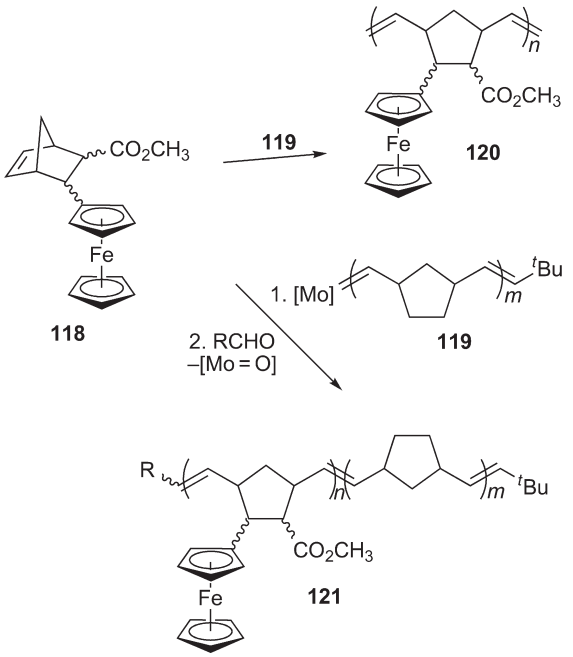
Scheme 29 Polymer structures based on norbornene depending on the polymerization type.[162–180]

well-defined organotransition metal catalysts has improved polymerization processes. Using transition metal-based catalysts, polymerization of strained cyclic olefins is achieved via different techniques: ring-opening metathesis polymerization (ROMP), which retains one double bond in each polymeric repeat unit; addition polymerization, which results in the insertion of the coordinated olefin into a metal–carbon bond; and cationic polymerization, which involves rearrangements in the olefin molecules (Scheme 29).[162–180]

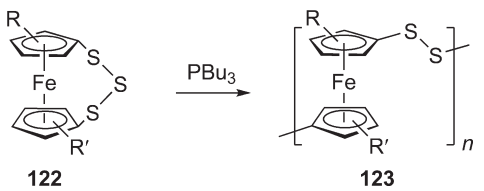
Different studies outline the incorporation of metallic moieties into norbornene homo- and copolymers.[180–185] The ease of functionality and the strong activity of the norbornene units toward ROMP allows for the isolation of macromolecules with high molecular weights and good mechanical properties. Electrochemically active polynorbornenes via living ROMP of norbornene-containing ferrocenyl side groups was first synthesized by Albagli *et al.*[181]

The polymerization reaction was achieved using molybdenum-based catalyst **119**, followed by end-capping with an aldehyde group to cleave off the active catalyst from the polymer chain. The number average molecular weight of the homopolymer was found in range of 5000–9000 g mol^{-1}. The polymerization of norbornene with molybdenum alkylidenes resulted in polynorbornenes end-capped with ferrocenyl groups (Scheme 30). Using end-capping groups, the redox active homo- and copolymers were used in the preparation of modified electrode surfaces.[182]

Rauchfuss and coworkers reported a novel atom abstraction-induced ring opening polymerization of trithiaferrocenophane (**122**), which allowed for the isolation of well-defined poly(ferrocenylene persulfides) (**123**).[186] These complexes are highly soluble in organic solvents due to the alkyl groups substituted on the ferroecene moiety (Scheme 31). The molecular weight range of poly(ferrocenylene persulfides) (where R = ^{n}Bu, R′ = H) was between 12 000 and 359 000 g mol^{-1}. Meanwhile, in polymers where all R groups are hydrogen atoms, the molecular weight was 25 000.[186–188] Polyferrocenes including Se–Se bridges have also been reported using similar methods.[189]



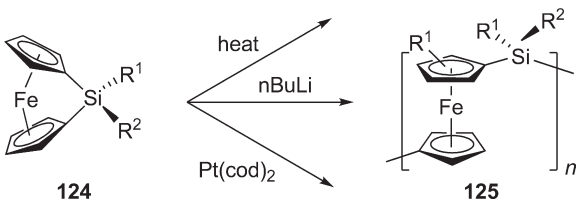
Scheme 30 Synthesis of polynorbornenes with terminal ferrocenyl groups.[182]



Scheme 31 Synthesis of poly(ferrocenylene persulfides) (R = ^{n}Bu, R′ = H)[186–188]

High-molecular-weight poly(ferrocenylsilanes) (PFSs) were synthesized via ring opening polymerization by Manners *et al.* Highly strained, ring-tilted organomonosilyl-bridged ferrocenophanes (**124**) were utilized for thermal ring opening polymerization at 150–220 °C. The glass transition temperature and the solubility of polymer **125** are affected by the substituent on the silicon atom. In addition to the thermal approach, silaferrocenophanes have also been polymerized anionically and with transition metal catalysis (Scheme 32).[190–196]

The electrochemical behavior of these complexes was examined by cyclic voltammetry. Two distinguishable oxidation waves were observed due to the interaction between the iron centers. However, the electrical



Scheme 32 Different approaches to PFSs.[190–196]

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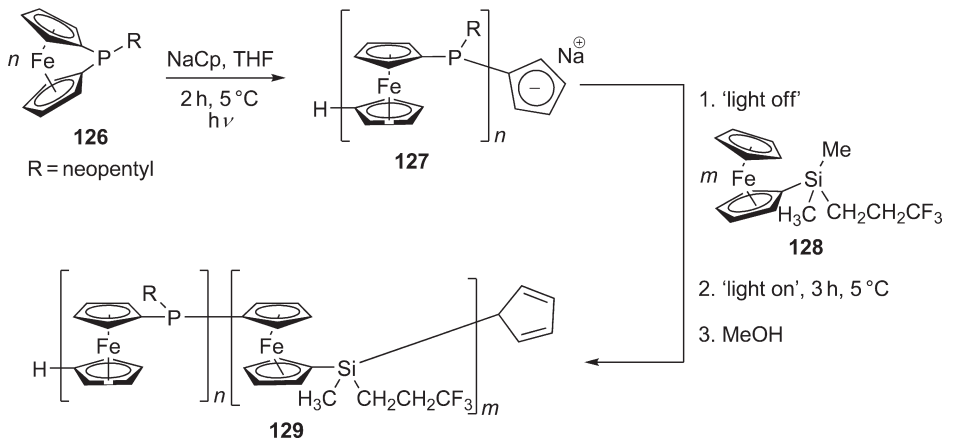


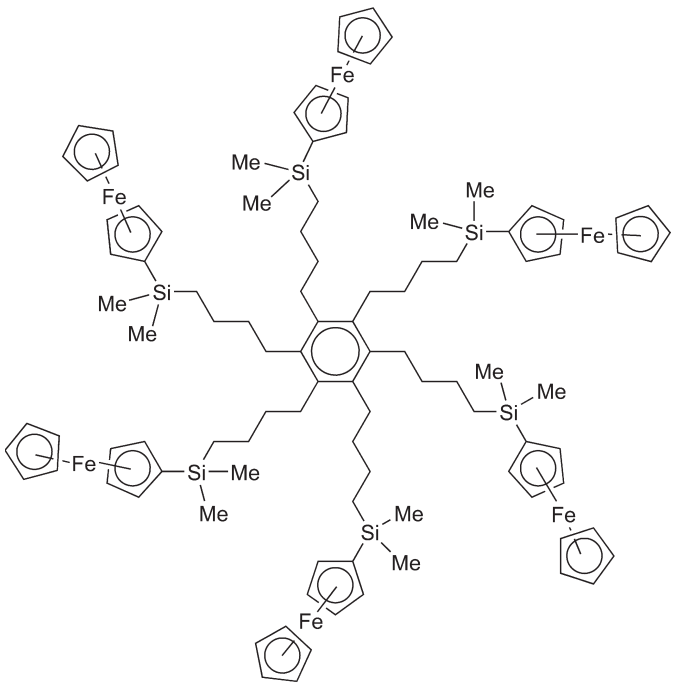
Scheme 33 Synthesis of polyferrocenylneopentylphosphine-*b*-polyferrocenylmethyl(3,3,3-trifluoropropyl)silane block copolymers.[222–226]

conductivity of these complexes remains in the rank of weak semiconductors. These materials have also been established as interesting precursors for producing ceramics with magnetic properties.[190–196]

Manners' group also reported a group of silaferrocenophanes containing a variety of functional groups attached to the silicon atoms.[190] The anionic polymerization of silicon-bridged ferrocenophane allowed for the production of living polymers, which could be polymerized with a number of different monomers.[197–209] In addition, ferrocenophanes containing phosphorus, germanium, tin, and boron bridges have been reported.[210–219] Organometallic nanotubes containing a PFS inner wall covered by a shell of cross-linked polymethylvinylsiloxane (PMVS) chains were also synthesized.[220,221] The resulting shell-cross-linked nanotube displayed redox-active properties due to the presence of the PFS component.

Photopolymerization of strained ferrocenophanes has also been reported by Manners and coworkers.[222–225] Recently, the photocontrolled living anionic polymerization of phosphorus-bridged ferrocenophanes allowed for the synthesis of homo- and copolymers of ferrocenylphosphines containing alkyl substituents on phosphorus.[226] Polyferrocenylneopentylphosphine-*b*-polyferrocenylmethyl(3,3,3-trifluoropropyl)silane block copolymers were prepared via initiating $[Fe\{(\eta\text{-}C_5H_4)_2P\text{-}(CH_2CMe_3)\}]$ with $Na[C_5H_5]$. The polymers were obtained in good yields and possessed narrow molecular weight distribution. Scheme 33 shows the polymerization of compound **126** to produce the synthetic diblock copolymer **129** through photocontrolled anionic ring opening polymerization.

Ruiz and coworkers have also reported silicon-containing star-shaped molecules.[227] Complex **130** was synthesized from a star-shaped hexaolefin core; cyclic voltammetry studies showed the presence of only one Fc/Fc^+ wave at 0.475 V.



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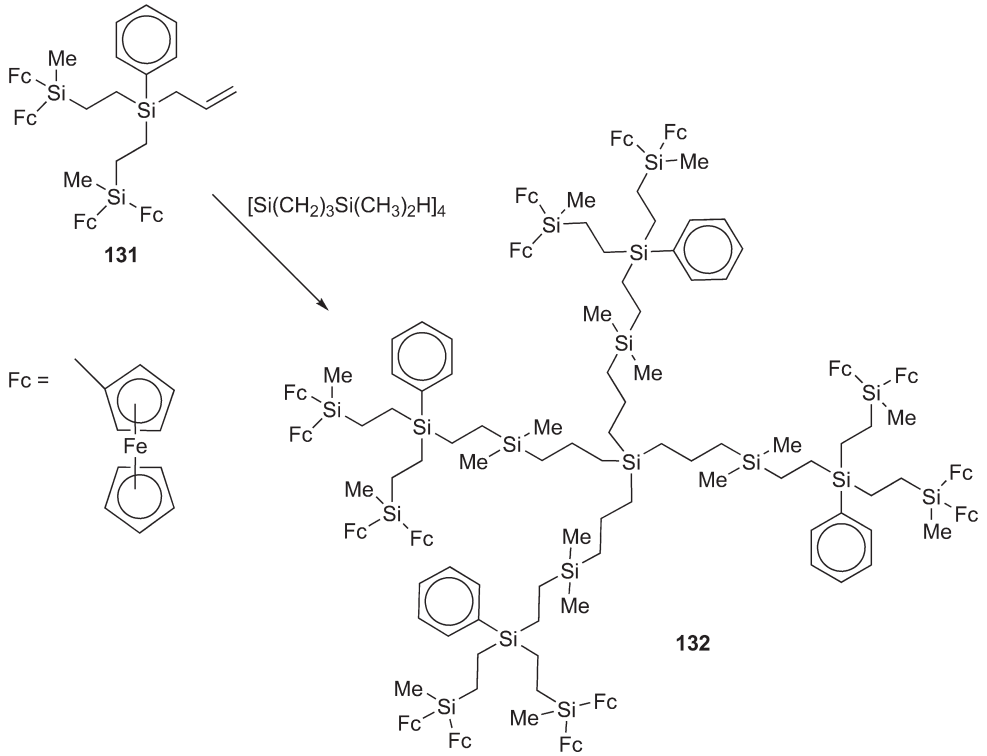

Scheme 34 Synthesis of silicon-based ferrocenyl dendrimers.[228,229]

The synthesis of silicon-based ferrocenyl dendrimers were illustrated in Scheme 34. Electrochemical studies of these dendrimers indicate that there is electrical communication between the iron centers.[228,229]

5.23.3.2 Transition Metal Arene Cyclopentadienyl Complexes

Organometallic complexes containing transition metals coordinated to arene moieties have received much attention due to their chemical and physical properties, as well as their utility in many fields such as organic synthesis, catalysis, and materials chemistry. Arenes coordinated to $Cr(CO)_3$, $Mo(CO)_3$, $Mn(CO)_3$, $CpFe^+$, and $CpRu^+$ are the most commonly studied complexes because of their electron-withdrawing abilities, which can facilitate nucleophilic aromatic substitution and addition reactions.[230–246]

According to the kinetic studies of these *n*-bonded complexes, their degree of electron-withdrawing power decreases in the following order: $Mn(CO)_3 > CpFe^+$ and $CpRu^+ \gg Mo(CO)_3 > Cr(CO)_3$.[230–234] Though $Mn(CO)_3$ has high activation, it has limited applications due to its high degree of toxicity and cost. $Cr(CO)_3$ complexes have been widely used in mediating organic synthesis, as well as in the design of enantiomerically pure compounds.[237–241] The earliest examples of polymers containing arenes coordinated to transition metals were reported by Pittman and coworkers in the early 1970s.[247–249]

The arene complexes with transition metals increase the electrophilicity of the arene rings and improve their susceptibility to nucleophilic attack. This inversion of the ring polarity is attributed to the electron-withdrawing ability of the metallic moieties, allowing for nucleophilic aromatic substitution and addition reactions under mild conditions. The cyclopentadienyliron ($CpFe^+$) complex has more advantages compared to the other coordinated metallic moieties due to its chemical versatility, low cost, and low toxicity.[250,251]

The synthesis of different aromatic ether monomers using metal mediated S_NAr, as reported by Pearson, is illustrated in Scheme 35.[252,253] Taking advantage of the selective substitution of the chlorine atoms of the dichlorobenzene complex 133c allows for the synthesis of organoiron monomers with different functionalities. Photolytic decomplexation of the iron moieties, followed by a polycondensation reaction, resulted in the formation of high-molecular-weight polyester. This polymer demonstrated remarkable stability, whereas some of these materials have also displayed liquid crystallinity.

S_NAr reactions were also used to prepare soluble polyaromatic ethers, thioethers, and amines from dichloroarene cyclopentadienyliron complexes and sulfur-, oxygen-, and nitrogen-containing dinucleophiles, as reported by Abd-El-Aziz *et al.*[254,255] Complex 133c and dinucleophiles 138a–h were reacted in the presence of K_2CO_3 to afford organoiron polymers 139 containing pendant cyclopentadienyliron moieties, which have good solubility in polar organic solvents (Scheme 36).[255]

Exposing the polymers to UV light in acetonitrile results in the photolytic cleavage of the cationic cyclopentadienyliron moieties. However, the organic analogs of the polymers have lower solubilities than their organoiron analogs; the solubility could be increased by the incorporation of aliphatic groups into the backbone of the polymers. The weight average molecular weights of organic polymers 140 were determined to range from 7300 to 21 400 g mol^{-1}.[256]

Organoiron polymers 143 containing azo dyes in their side chains via condensation reactions between azo dye-functionalized bimetallic organoiron complexes 141 and various oxygen- and sulfur-containing dinucleophiles 142 were synthesized (Scheme 37).[257] The isolated polymers were red in

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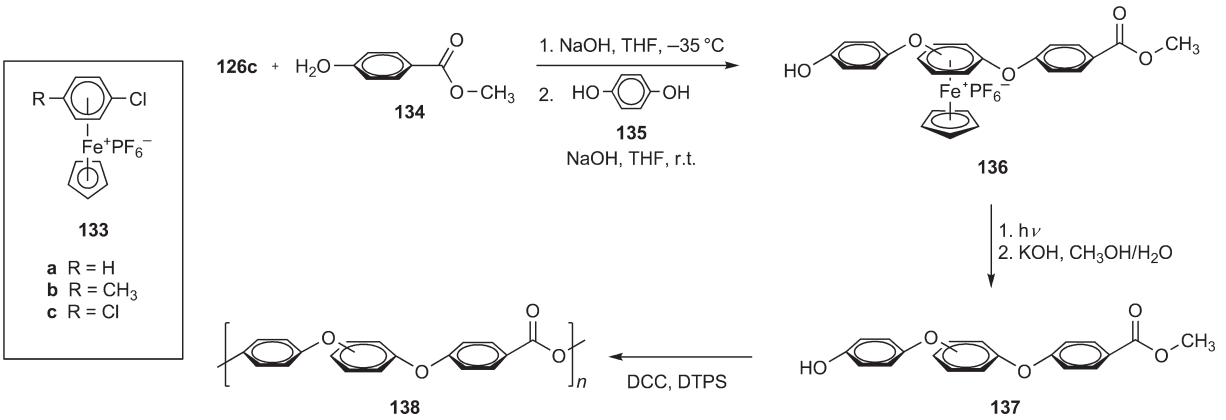
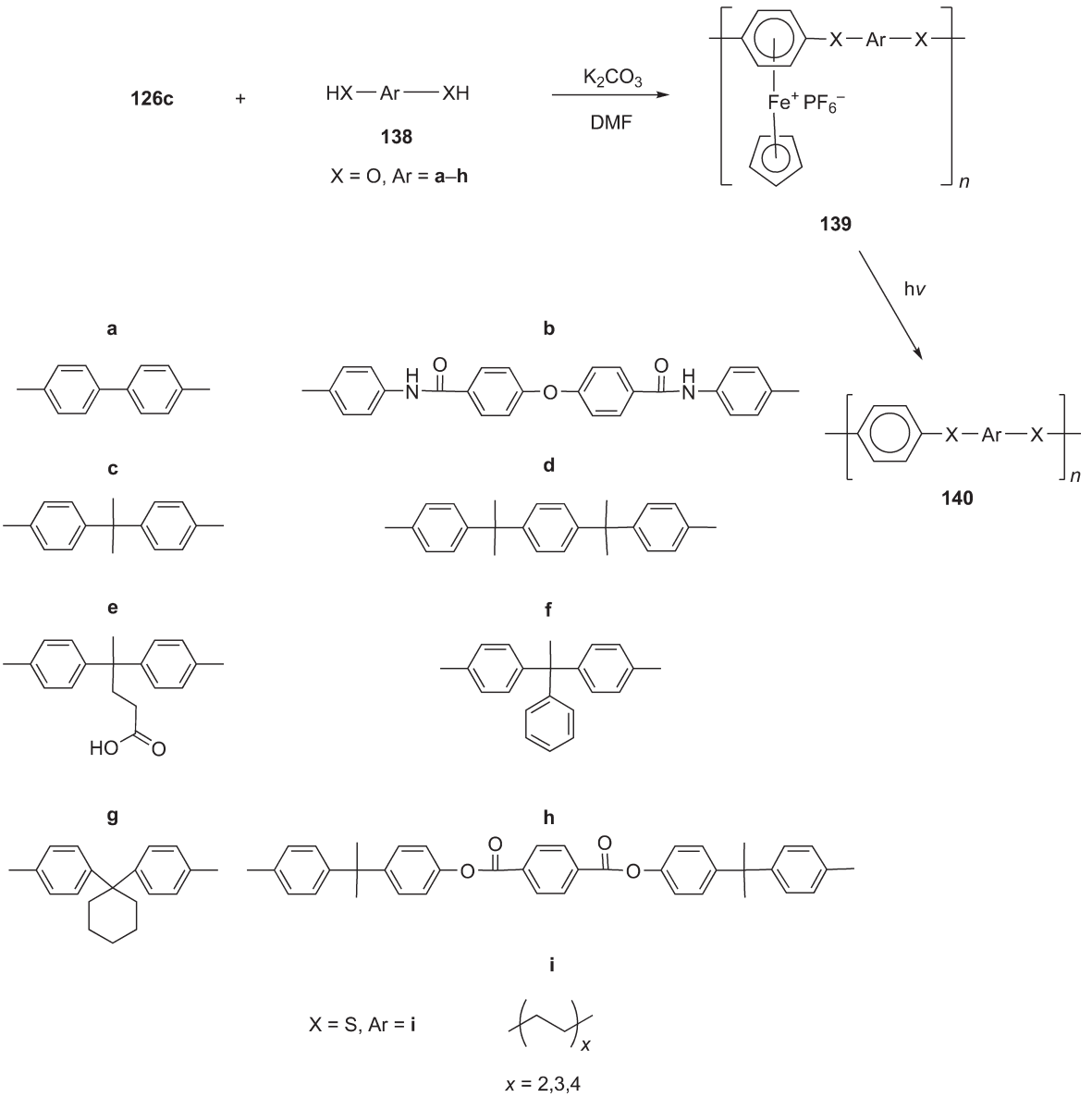


Scheme 35 Synthesis of different aromatic ether monomers using metal-mediated S_NAr.[252,253]



Scheme 36 Examples of different organoiron polymers via S_NAr reactions.[257]

color with λ_{max} values of 417 and 489 nm. Photolysis of the polymers gave their decolored organic analogs when irradiated in the presence of hydrogen peroxide.

During the photolysis process, the polymers were also decolored from the decomposition of the azo dye, when the polymer concentration was 0.025 M or lower.[257] Complexation of the

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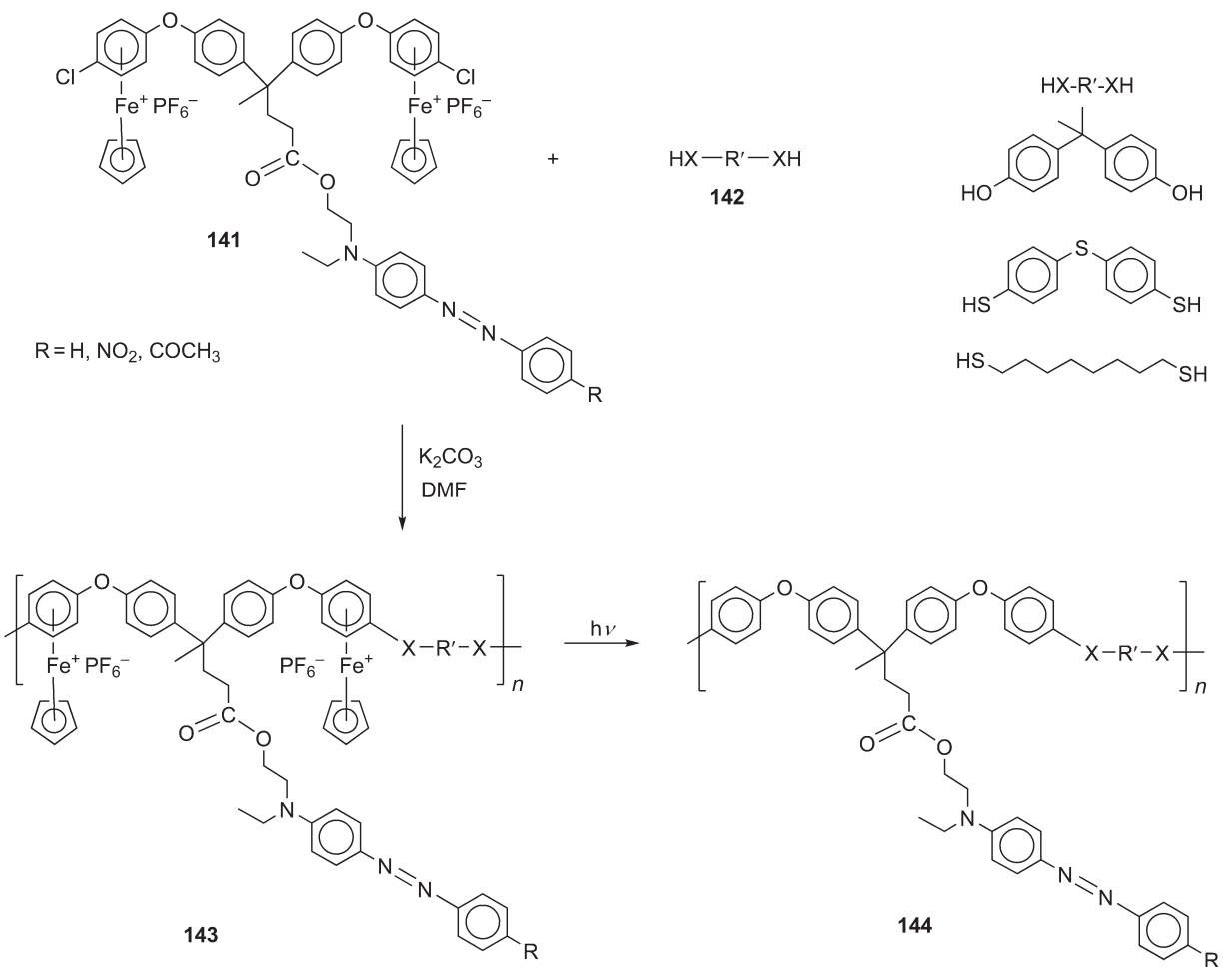
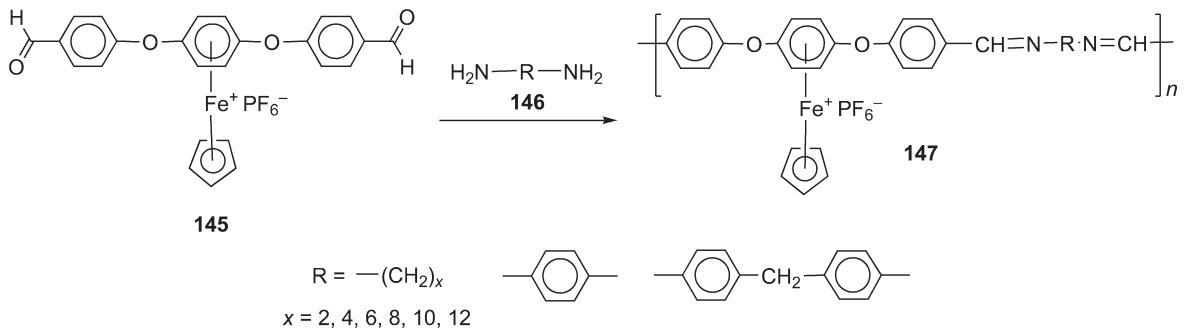


Scheme 37 Synthesis of organoiron polymers containing azo dye side groups.[257]

azo dye and the cleaved cyclopentadienyliron moieties were obtained from the decomposition of the azo chromophores.

Thermal properties and the glass transition temperatures of organoiron polymers can be altered by incorporating different aromatic or aliphatic spacers.[255] In addition, the thermal stability of the polymers is affected by the presence of the cationic cyclopentadienyliron moieties: the loss of the cationic iron groups causes an increase in the thermal stabilities. The cationic cyclopentadienyliron moieties decompose at 245 °C and the polymer backbone degradation begins at 519 °C, whereas the organic analogs decompose at 512 °C. Differential scanning calorimetry indicated that the more rigid polymers with oxygen-containing spacers displayed the highest glass transition temperatures and the polymers with aliphatic sulfur-containing spacers possessed the lowest glass transition temperatures.

Several polyether/imines containing cationic cyclopentadienyliron moieties were synthesized.[256] The condensation reaction of dialdehyde cyclopentadienyliron complex **145** with aliphatic and aromatic diamines **146** forms soluble polymers **147** (**Scheme 38**). These polymeric materials display two thermal decompositions due to the cleavage of the cationic iron moieties and the degradation of the polymer backbone. The temperature at which the cationic cyclopentadienyliron



Scheme 38 Polycondensation of polyether/imines containing cationic cyclopentadienyliron moieties.[256]

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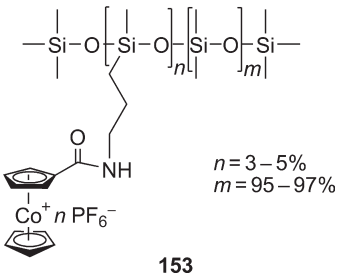
moieties cleave off increases from 250 to 350 °C when the aliphatic spacer is incorporated.[256,258]

Polysiloxanes, often referred to as silicones, are a class of polymeric materials well known for their flexible backbone, thermal stability, durability, resistance to biological degradation, and insulation properties.[228] Due to these useful properties, polysiloxanes have found applications as lubricants, adhesives, mechanical tubing, gaskets, medical tools and implants, and electrical insulators. The low carbon content of polysiloxanes has made them desirable precursors for conducting ceramic materials.

In recent years, siloxane-based redox-active organometallic polymers have been studied frequently. Cuadrado *et al.* reported siloxane polymers containing ferrocene, $[(\eta^5\text{-}C_5R_4)Fe(CO)(\mu\text{-}CO)]_2$ (R = H, Me), as well as $[(\eta^6\text{-arene})Cr(CO)_3]$ moieties, which display interesting redox properties.[156,228,229] Because of its unique electrochemical behavior and resistance to strong oxidizing agents, cobaltocenium is a valuable moiety to incorporate into polymeric backbones. Interest in obtaining cobaltocenium-containing polysiloxane materials is primarily due to their distinct electrochemical and chemical features, combined with the unique and valuable properties of siloxane backbones.

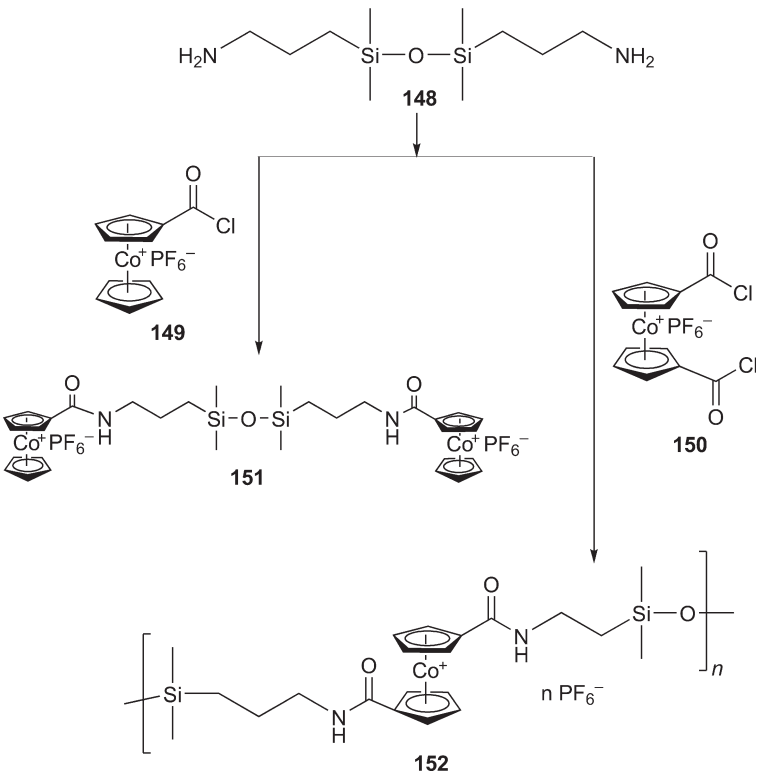
Cuadrado and coworkers have prepared two different types of siloxane-based cobaltocenium-containing polymers. The polycondensation reaction of 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane with 1,1′-bis(chlorocarbonyl)cobaltocenium hexafluorophosphate was performed under the same reaction conditions as those used to prepare the starting materials, and produced polymer **152** with a backbone consisting of alternating dimethylsiloxane segments and cobaltocenium moieties bonded through amide linkages (**Scheme 39**). The polymer, isolated as a greenish solid, was essentially insoluble in most common organic solvents, thus preventing a complete characterization.

Conversely, the reaction of $[(\eta^5\text{-}C_5H_5)Co(\eta^5\text{-}C_5H_4C(O)Cl)]^+PF_6^-$ with (aminopropyl)methylsiloxane (3–5%)-dimethylsiloxane (95–97%) copolymer, complete with NH_2 functionality, allows facile access to the block copolymer. Polymeric material **153** is composed of a poly (dimethylsiloxane) chain, in which pendant amide-linked cobaltocenium moieties are randomly distributed along the methylsiloxane backbone.



153

New cobaltocenium complexes have been synthesized, including chemically and electrochemically polymerizable pyrrole and allyl substituents, by Cuadrado *et al.*[156,228,229] Electrode surfaces were coated with stable and electroactive cobaltocenium polymeric films upon oxidative electrochemical polymerization of the new pyrrole-functionalized monomers, resulting in detectable electroactive material. Additionally, redox-active siloxane-based cobaltocenium polymers and block copolymers were prepared.



Scheme 39 Polycondensation of 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane (**148**) with 1,1′-bis(chlorocarbonyl)cobaltocenium hexafluorophosphate (**150**).[228]

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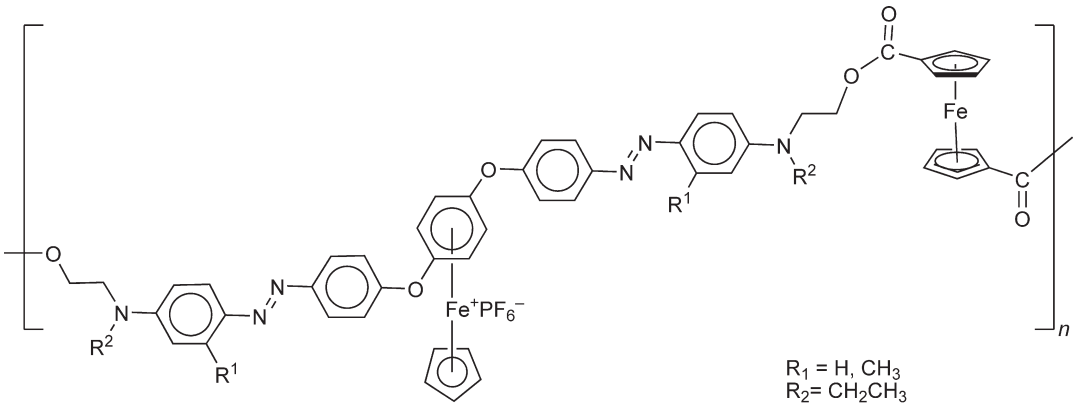
Electrodes coated with films of the hydrophobic siloxane-based copolymer exhibit redox activity in acetonitrile and in aqueous solution, when an ionic surface-active agent is added to the film.

There are two different methods to prepare polymers that include both neutral and cationic cyclopentadienyliron complexes within their structures. The first method incorporates the ferrocene units into the polymeric backbones (Scheme 40). Monomers 154a and 154b were each reacted with 4,4′-thiobisbenzenethiol (155) to obtain mixed-charge organoiron polymers 156. These polymers have unique properties, in that they have both neutral ferrocenyl units in their backbones and cationic cyclopentadienyliron moieties in their side chains. The resulting polymers have good solubility in polar solvents such as dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), and were obtained as orange-brown solids in the range of 85–90% yields.[259]

The second class of mixed-charge organoiron polymers have ferrocenyl moieties in their side chains instead of the polymer backbone. Having ferrocenyl moieties as side chains makes controlling the polymer structure and increasing its molecular weight less difficult.

Three different monomers were prepared with three different diols to examine mixed-charge organoiron polymers.[259] Scheme 41 displays the condensation reaction of carboxylic acid-functionalized diiron complex 157 with different diols to give complexes 159 with terminal alcohols. Subsequently, these complexes underwent coupling reactions with ferrocene carboxylic acid to produce monomers 161.

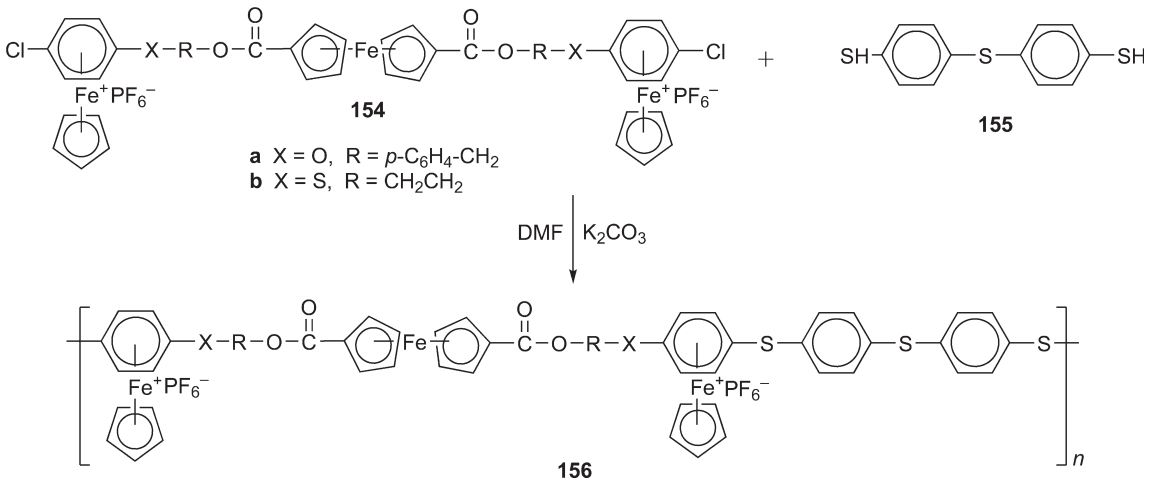
Cationic arene complexes with azo dyes in their backbones were synthesized and found to be soluble in polar organic solvents.[260] In electrochemical studies, polymers 162 showed two redox couples corresponding to the two different iron centers: the oxidation of the ferrocene unit at $E_{1/2} = 0.89$ V versus Ag/AgCl, and the reduction of the cationic cyclopentadienyliron complex at $E_{1/2} = -1.42$ V. The neutral polyferrocene analogues were produced via photolytic cleavage of the cationic cyclopentadienyliron moieties.



162

Cyclopentadienyliron complexes containing cyclopentadienylruthenium moieties give polymers with pendant mixed-metal moieties (Scheme 42).[261,262] The number average molecular weight (M_w) of the organic analog of the resulting polymer was 12 600, with a PDI of 1.9, corresponding to an M_w of 19 000 for the organometallic polymer.

Star-shaped polymers are branched macromolecules consisting of polymeric chains attached to a multifunctional core. These compounds can be synthesized via divergent or convergent methods. The divergent method involves the



Scheme 40 Synthesis of ferrocene main chain polymers.[259]

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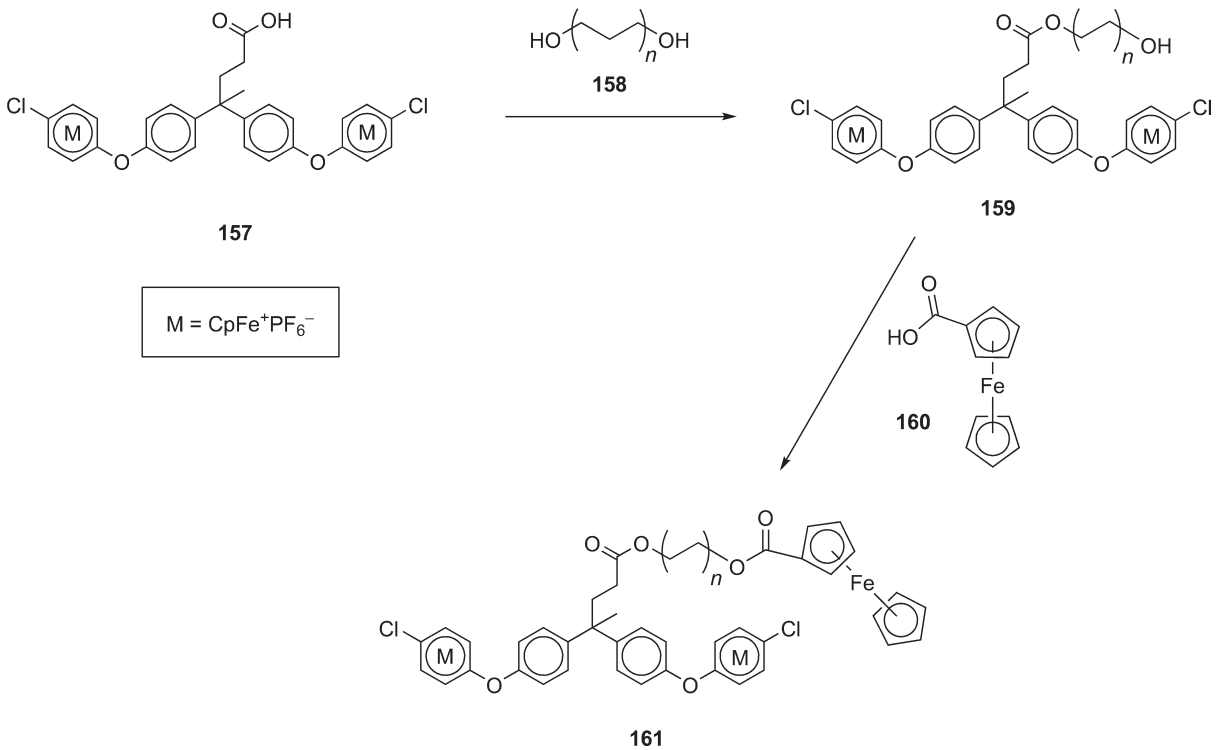
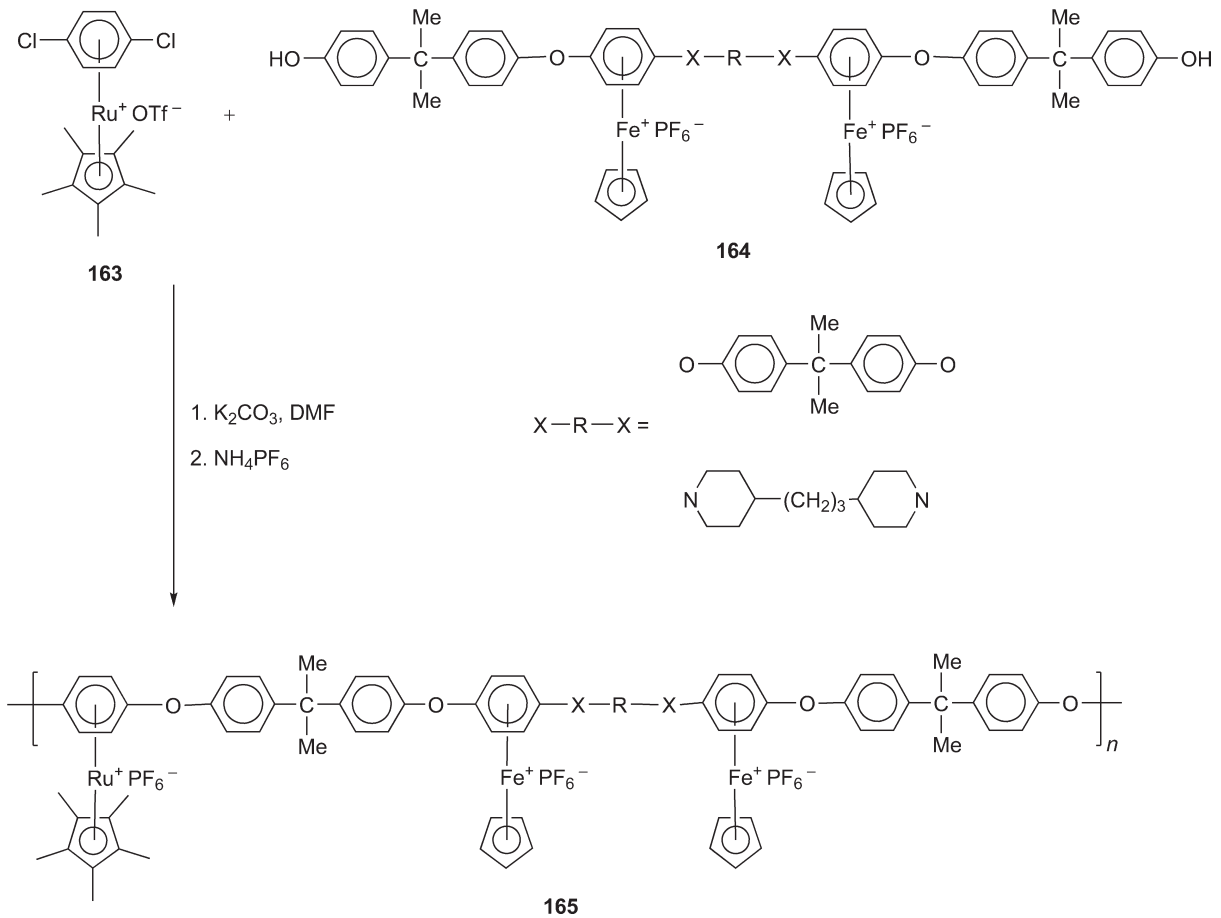


Scheme 41 Synthesis of ferrocene side chain polymers.[259]



Scheme 42 Synthesis of polymers with pendant mixed-metal moieties.[261,262]

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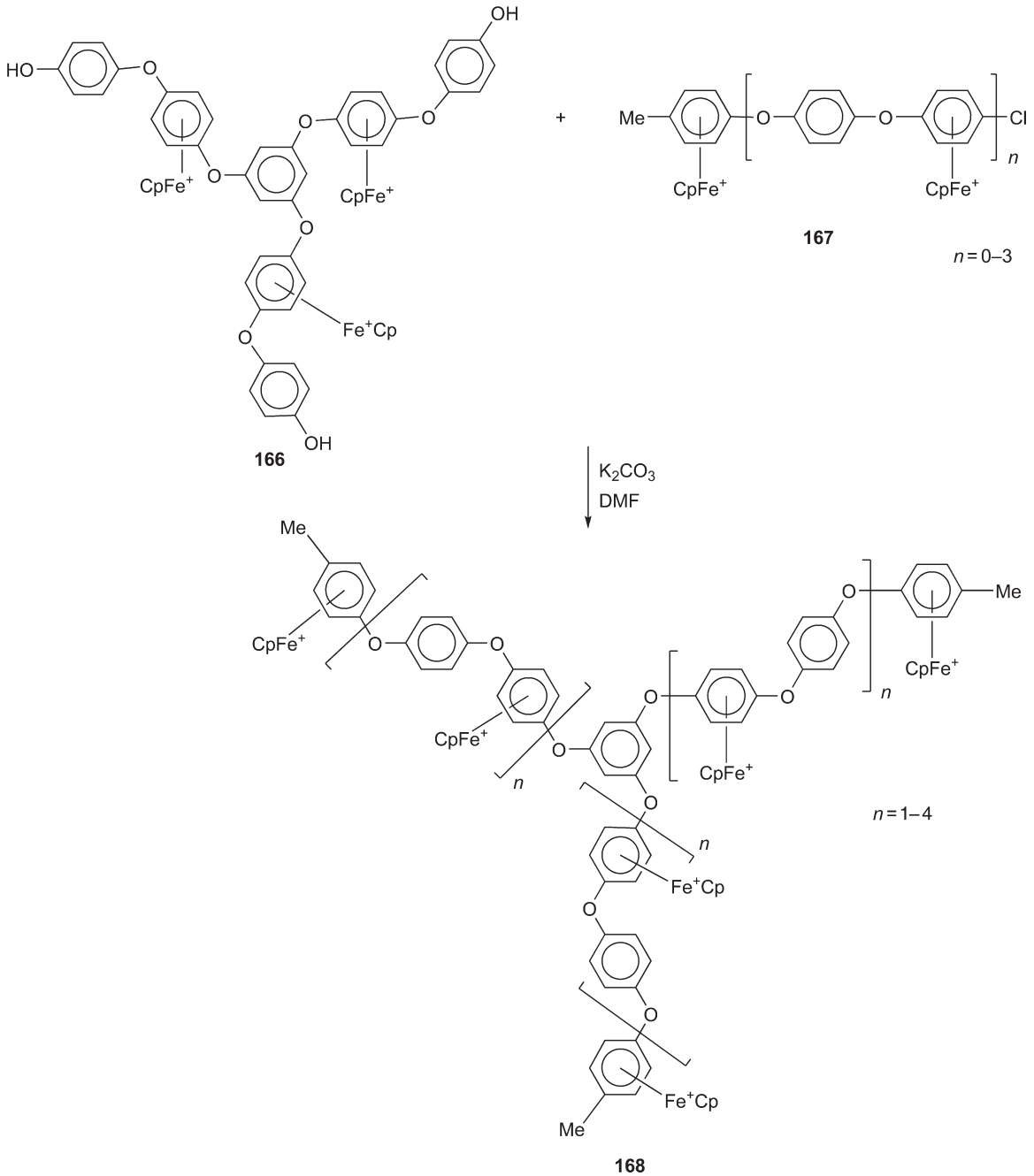
reaction of a linear chain with a multifunctional core through a reactive group placed at the terminal end of each chain. The convergent approach includes the use of a multifunctional core as an initiator for the attachment of monomers.[263] Abd-El-Aziz *et al.* prepared cationic star-shaped molecules containing cyclopentadienyliron complexes (**Scheme 43**).[264,265] Electrochemical studies of these materials indicate reversible reductions in the iron centers (**Figure 1**). The star-shaped molecule containing six metal centers ($n = 1$) showed two redox potentials at $E_{1/2} = -1.20$ and -1.30 V.

Organoiron-containing cationic polyelectrolyte three-arm stars were reported by Abd-El-Aziz and coworkers.[264,265] The nucleophilic aromatic substitution of chloro-substituted arenes coordinated to cyclopentadienyliron complexes gave various first-generation dendrimers and star-shaped molecules containing either ether (**134**) or ester (**172**) bridges (**Schemes 44** and **45**).



Scheme 43 Synthesis of cationic star-shaped molecules containing cyclopentadienyliron complexes.[264,265]

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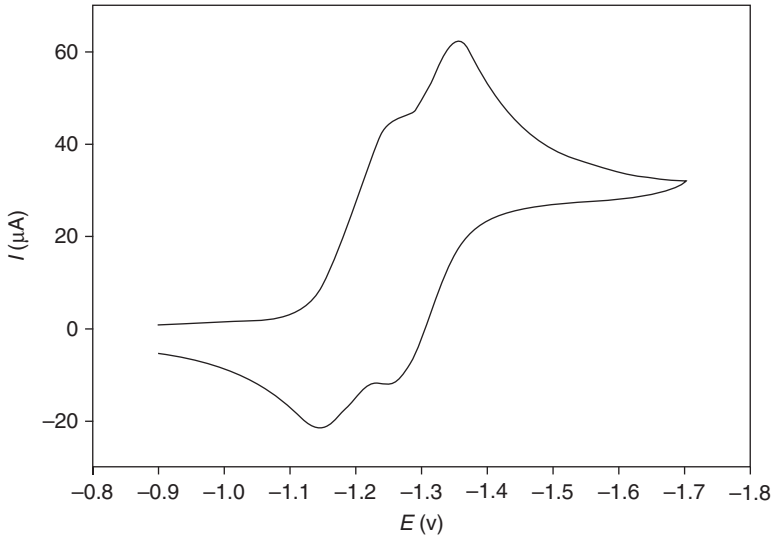
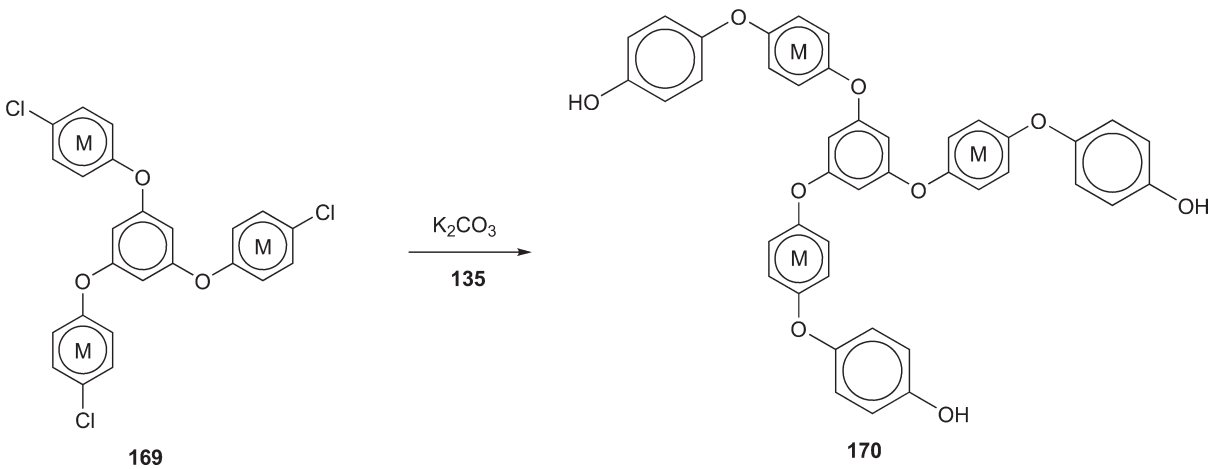


Figure 1 Cyclic voltammogram of **168** at glassy carbon in 0.1 m TBAP in DMF, m = 0.1 V s^{-1} at –40 °C.



Scheme 44 Synthesis of first-generation dendrimers and star-shaped molecules based on ether bridges.[264,265]

The solubility of star-shaped molecules is increased with ether bridges because the size of the molecule increases. However, the incorporation of ester bridges decreases the solubility of a star-shaped molecule. Thermal studies of these polymers show that the ester-containing stars have glass transition temperature (T_g) values between 150 and 195 °C, while the ether-containing stars display T_g values between 120 and 200 °C.

As studied by Abd-El-Aziz and coworkers, iron-containing hyperbranched polymers were prepared by the reaction of a number of different diols, dithiols, or organoiron complexes with star-shaped molecules (**Scheme 46**) with low viscosities, ranging from 0.175 to 0.300 dl g^{-1}.[265] The cationic cyclopentadienyliron moieties cleave from the main molecules between 230 and 280 °C and the polymeric backbone degrades between 390 and 567 °C. The resulting polymers have glass transition temperatures between 60 and 134 °C, and the melting points in the range of 155–190 °C.

The synthesis of several star-shaped molecules and dendrimers containing ferrocenyl or arene cyclopentadienyliron moieties has been reported.[266–282] Many of these multifunctional dendrimers were prepared via cyclopentadienyliron-mediated per-alkylation, -benzylation, and -allylation reactions of cationic tri-, tetra-, and hexamethylbenzene complexes as a precursor to branched organic and organometallic polymers. **Scheme 47** represents the reaction of star-shaped core **173** with a cationic iron complex, producing octametallic star-shaped molecule **174** containing cyclopentadienyliron arene complexes at the peripheries.

Organosilane dendrimers containing transition metal moieties, such as **175** and **176**, were prepared by Kriesel and coworkers.[283] Mass spectroscopy confirmed the successful synthesis of the complex with 72 metallic moieties.

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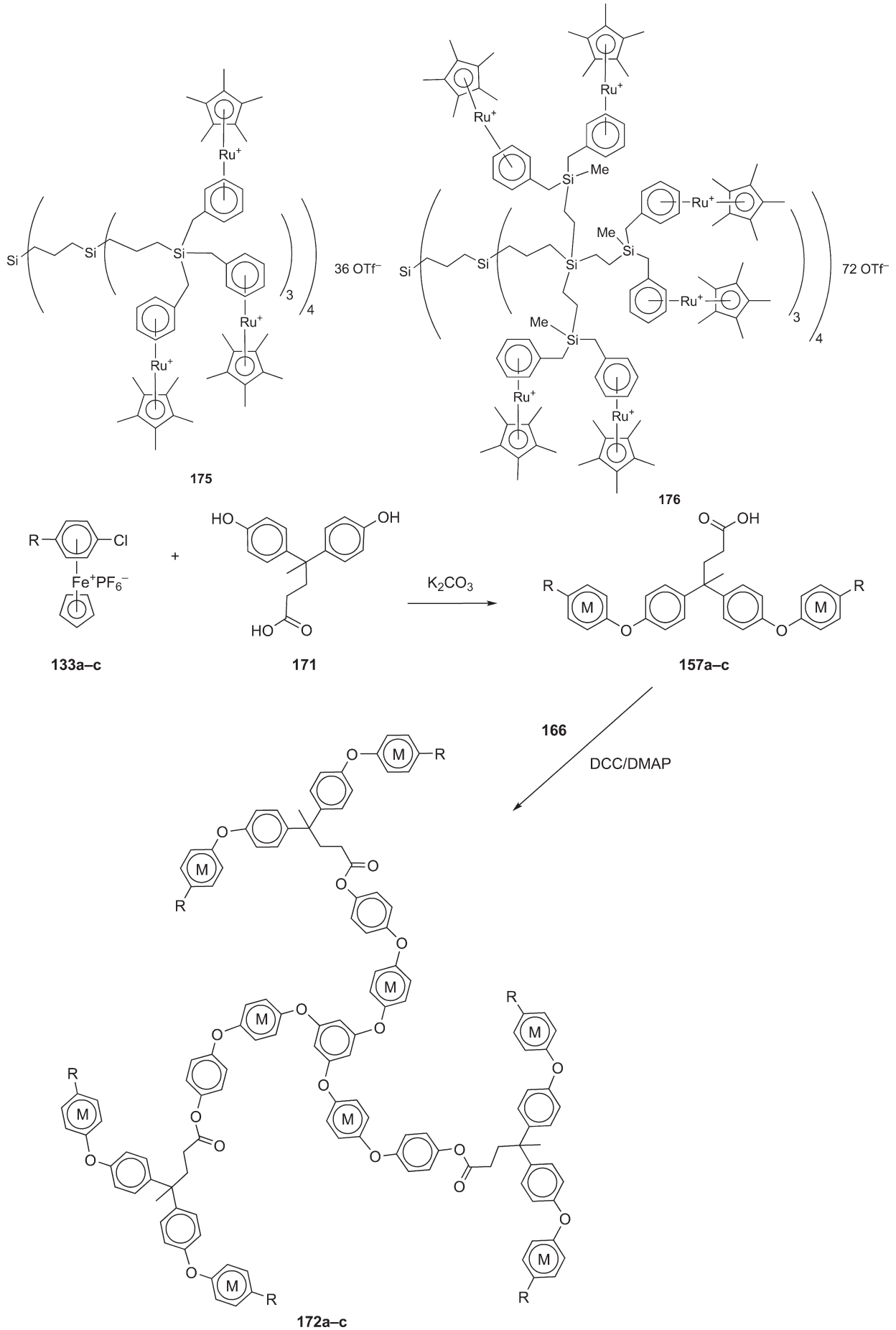

Scheme 45 Synthesis of first-generation dendrimers and star-shaped molecules based on ester bridges.[264,265]

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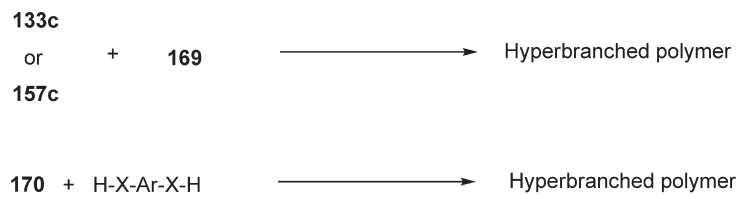
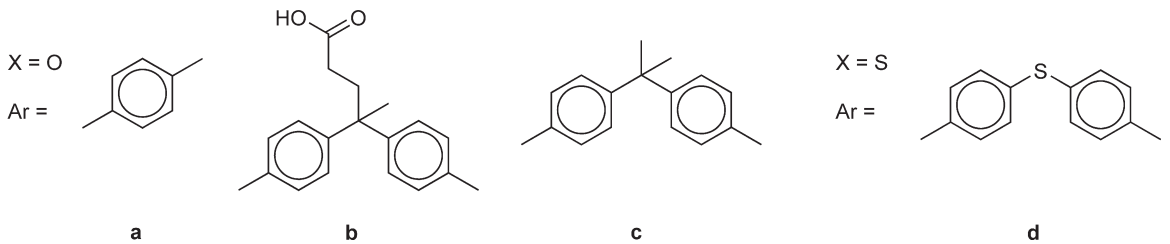
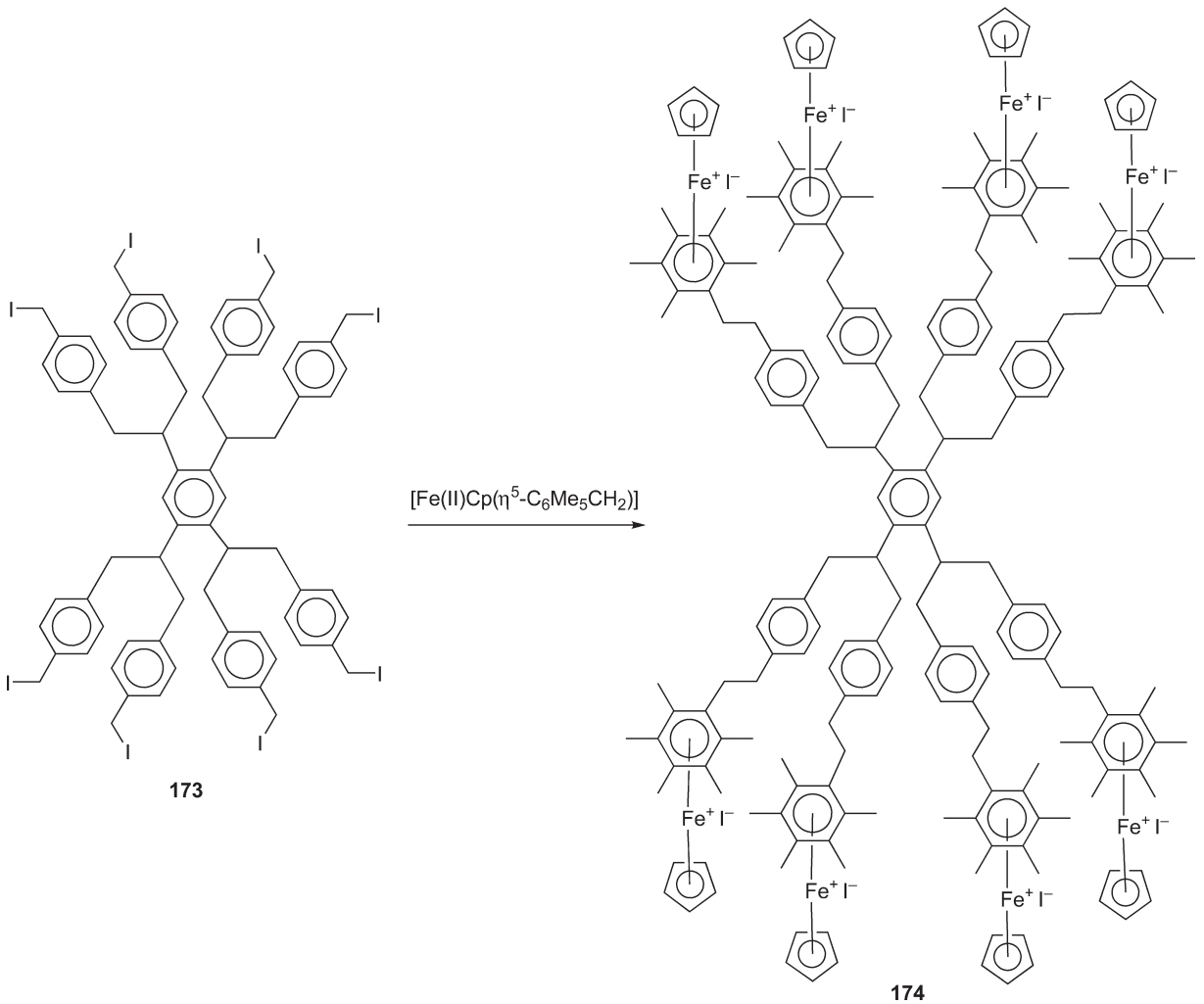




Scheme 46 Examples of iron-containing hyperbranched polymers.[265]



Scheme 47 Synthesis of octametallic star-shaped molecule **174** containing cyclopentadienyliron arene complexes at the peripheries.[268]

Cuadrado also reported silicon-containing dendrimers, such as 177, which incorporates $Cr(CO)_3$ moieties into an organosilicon dendritic core. These macromolecules demonstrate how some aromatic rings on the dendrimer could not be complexed to metals due to steric hindrance at higher generations.[284]

Star-shaped molecules containing cationic arene complexes of iron (179) and ruthenium (181 and 183) (Scheme 48) were reported by Alonso and Blais.[285]

Abd-El-Aziz *et al.* recently synthesized various azo dye and organoiron-containing branches with multifunctional cores via metal-mediated nucleophilic

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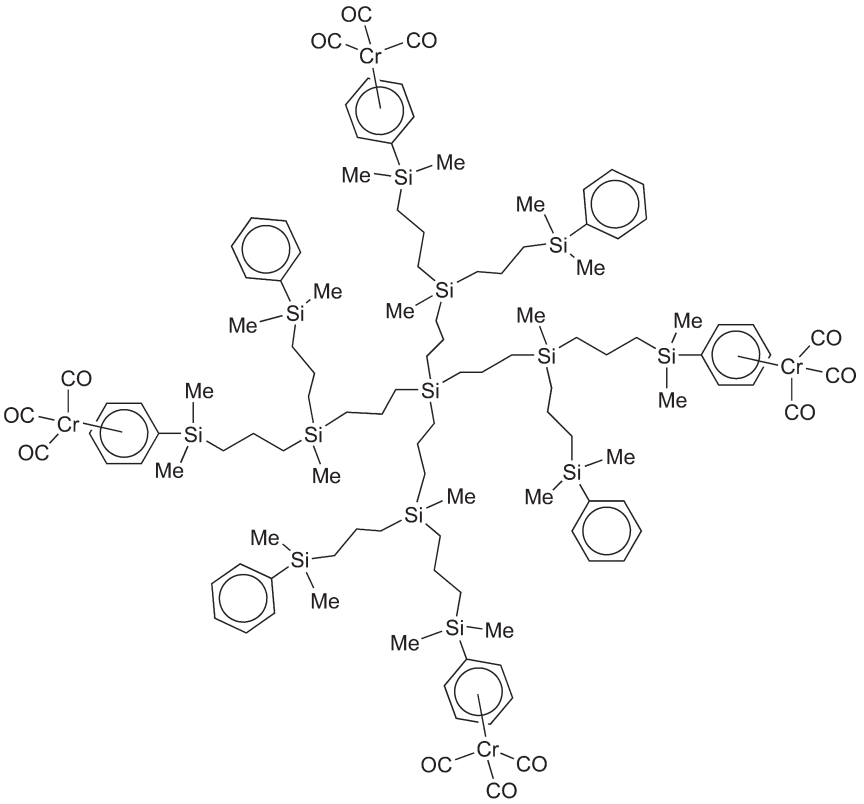

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aromatic substitution and ester condensation reactions (Scheme 49).[263]

Metallocalixarenes, reacted with azo dyes, were prepared by Abd-El-Aziz and coworkers; one example is shown in Scheme 50.[286] The cyclic voltammograms of azo dye 188, metallocalix[4]arene 187, and the azo dye-containing metallocalix[4]arene 189 are shown in Figure 2. The free azo dye displayed two redox couples: one at $E_{1/2} = 0.27$ V and another at $E_{1/2} = 0.89$ V, corresponding to the oxidation of the aniline and the azo group, respectively.[287,288] The metallocalix[4]arenes displayed an $E_{1/2} = -1.49$ V for the reversible reduction of the cationic iron moieties to the 19-electron complex.

Azo dye-containing metallocalix[4]arene 190 showed excellent solubility in polar organic solvents. The azo dye-containing metallocalix[4]arenes reversibly changed color in the presence of acid and base, indicating their potential use as acid sensors in the solid state and in solution. The iron centers of the metallocalix[4]arenes were reversibly reduced at $E_{1/2} = -1.49$ V in the solid state and in solution. Polymers containing calix[4]arenes in either their side chains or main chains were obtained by reacting nonbranching organoiron-based calix[4]arenes with dithiols. The polymers had weight average molecular weights between 35 000 and 53 000, and were found to be thermally stable with backbone decomposition occurring above 500 °C.[286]

Cationic cyclopentadienyliron-functionalized norbornene monomers 191 undergo ROMP in the presence of Grubbs' catalyst to give new organoiron polynorbornenes 192 (Scheme 51).[289–294] Electrochemical studies indicate that the organometallic polymers were reduced between $E_{1/2} = +1.2$ and $E_{1/2} = -1.4$ V versus Ag/AgCl. Photolysis of the organometallic polymers yielded organic analogs 193 with weight average molecular weights ranging between 10 600 and 18 600 (PDI = 1.3–1.6).

Abd-El-Aziz and coworkers have synthesized organometallic norbornene complexes containing cationic cyclopentadienyliron coordinated to arenes.[291,292] The formation of polynorbornenes with aromatic side chains using Grubbs' catalyst (or ruthenium chloride in 1:1 EtOH:H_2O) with norbornene monomers obtained from the photolytic demetallation of organoiron norbornene complexes is shown in Scheme 52.

Higher glass transition temperatures and thermal stabilities are obtained by increasing the number of aromatic ether linkages in the polymer side chains.[291] Similarly, aliphatic ether spacers have also been incorporated into the side chains of polynorbornenes.[290] These polymers have high molecular weights ($M_w = 397\,000$) and good thermal stability.

Several polynorbornenes containing cationic iron moieties within their side chains were synthesized via ROMP by a ruthenium-based catalyst. The iron-containing polymers have excellent solubility in polar organic solvents. These polymeric materials have weight average molecular weights in the range of 18 000–48 000 g mol^{-1}.

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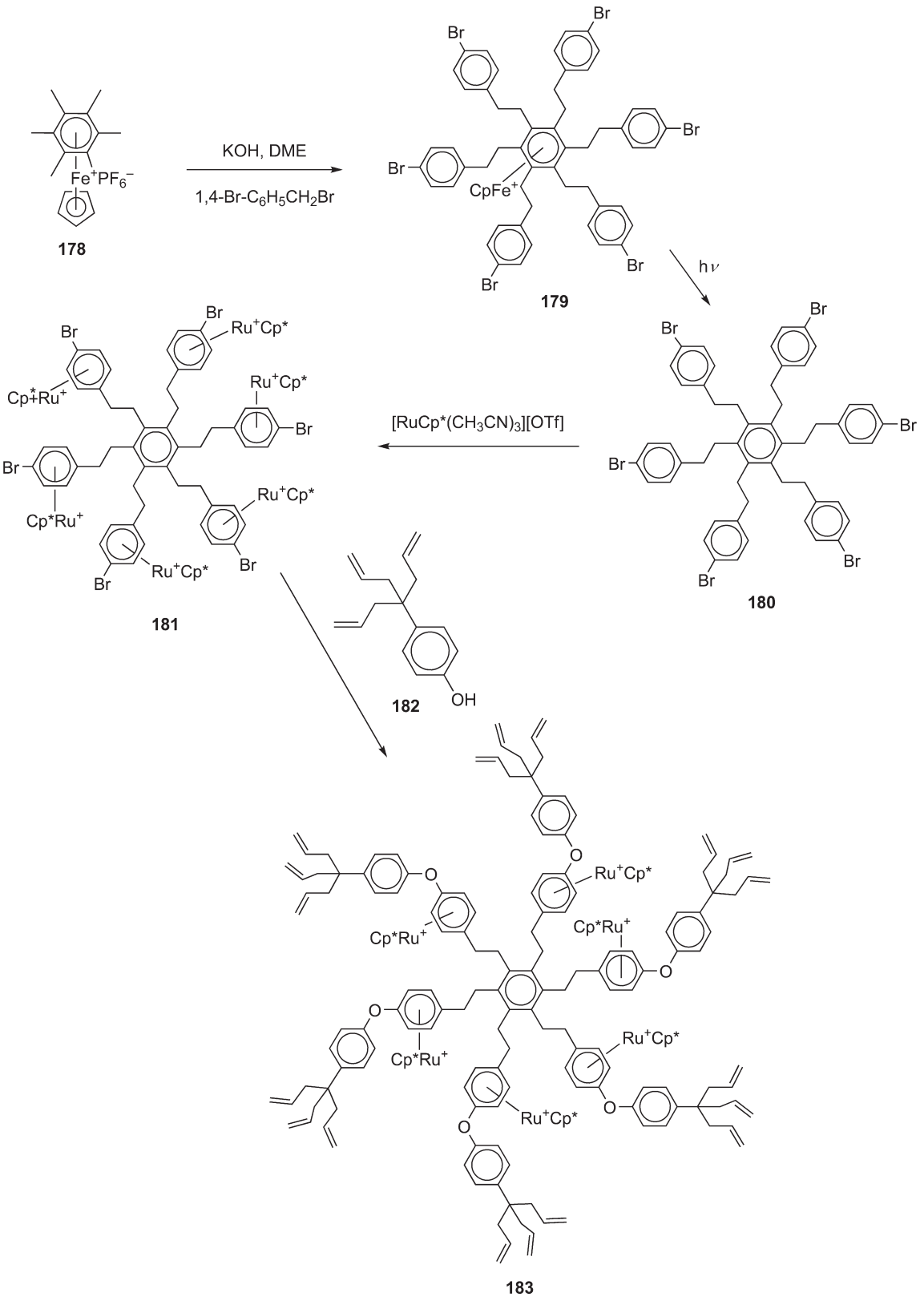

Scheme 48 Synthesis of star-shaped molecules containing cationic arene complexes of ruthenium.[285]

Thermogravimetric analysis of these polymers showed two distinct weight losses: the first, in the range of 204–260 °C, was due to the loss of the metallic moieties, while the degradation of the polymer backbones was observed between 368 and 512 °C as the second weight loss. Photolysis of the metallated polymers gave very good yields for the isolation of the norbornene polymers. Differential scanning calorimetry studies showed a sharp increase in the glass transition temperatures,

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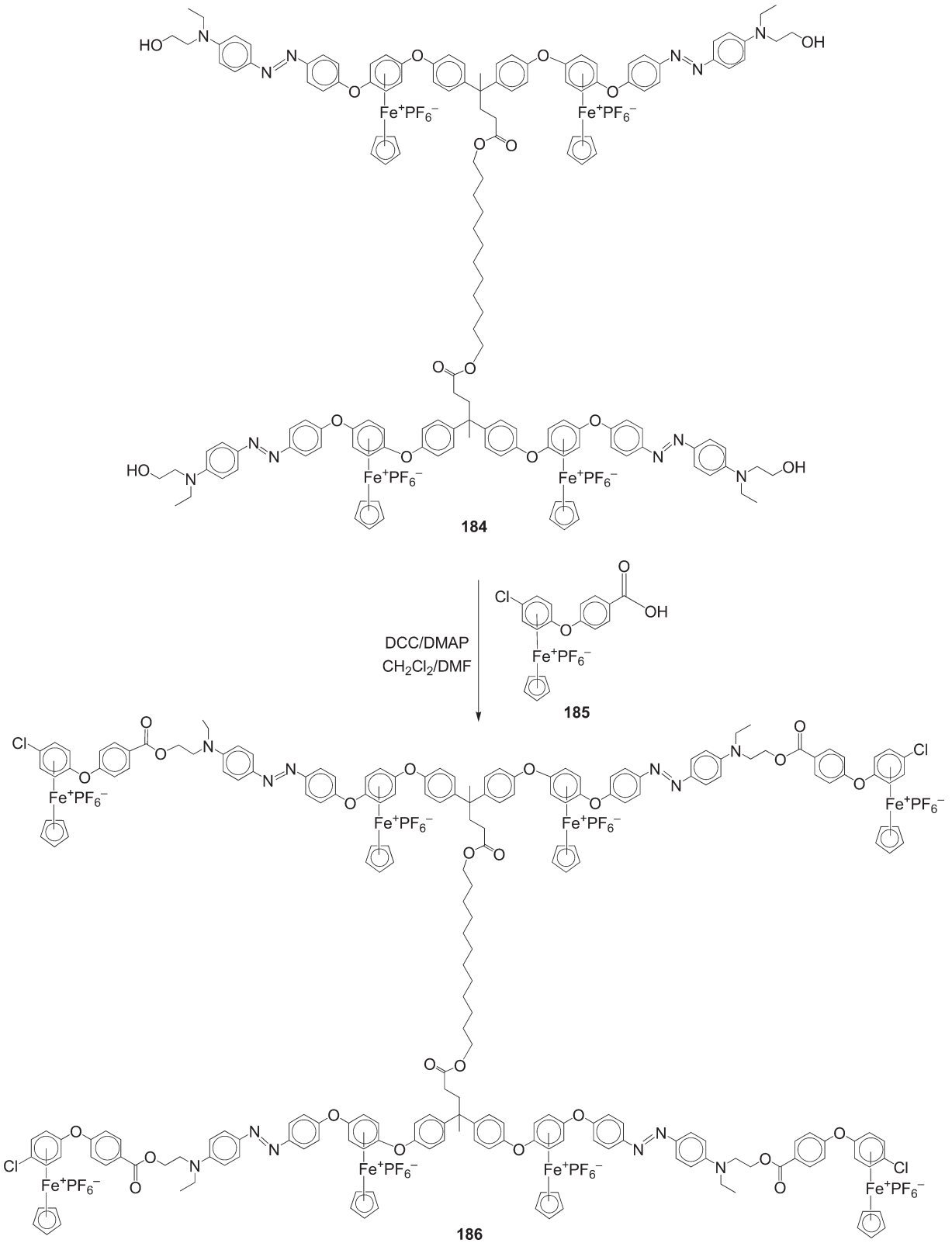

Scheme 49 Ester condensation to azo dye and organoiron-containing branched molecules.[263]

up to 91 °C, when rigid aromatic side chains were incorporated into the norbornene polymers (Scheme 53).[294]

The addition of azo dye chromophores into organoiron polynorbornenes has also been studied.[295] The ROMP of azo dye-functionalized organoiron norbornene-containing monomers 203a and 203b via Grubbs' catalyst gives colored polynorbornenes 204 that undergo a reversible reduction between −1.2 and −1.4 V versus Ag/AgCl (Scheme 54). The polymers are dark orange in

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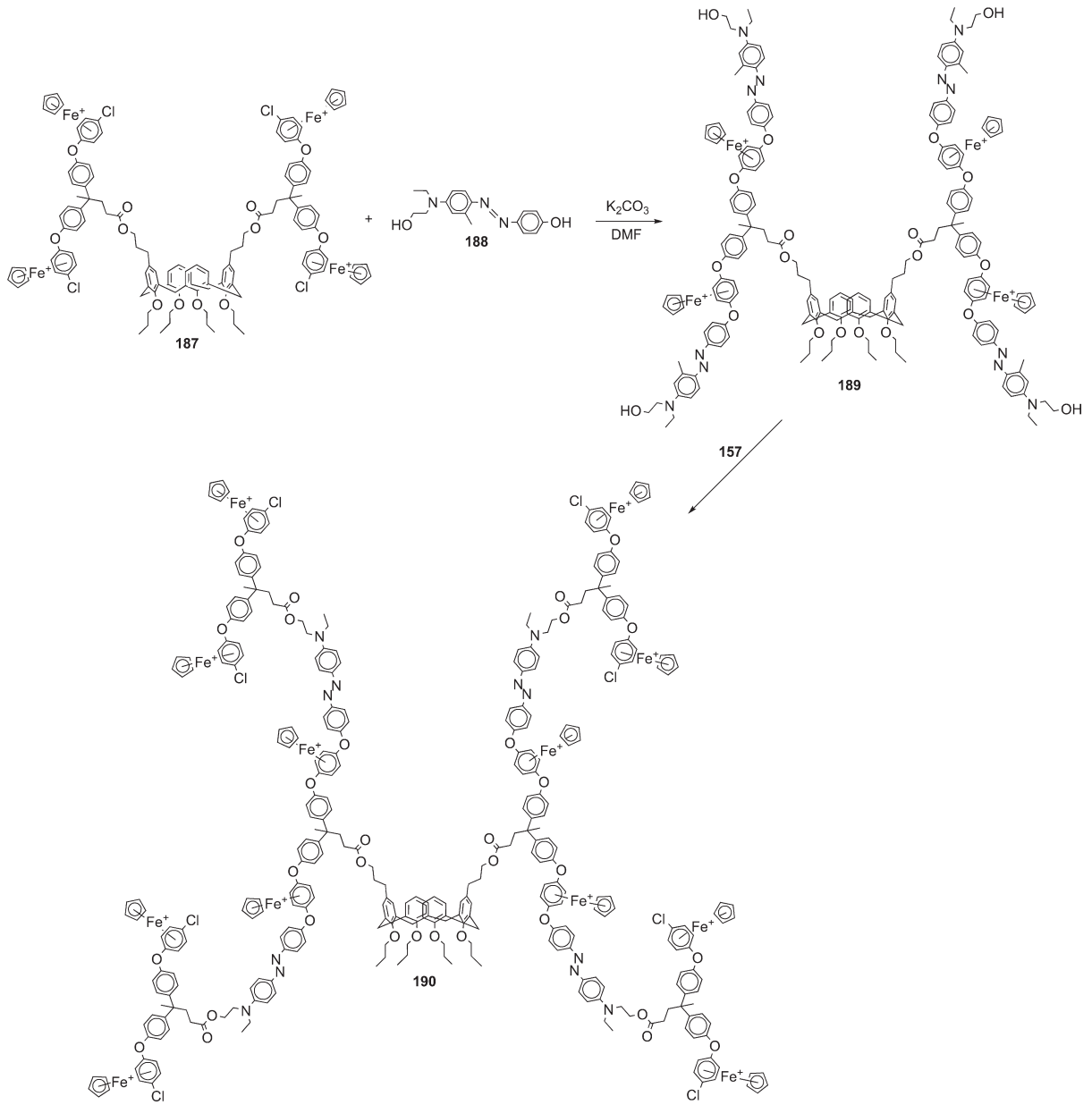
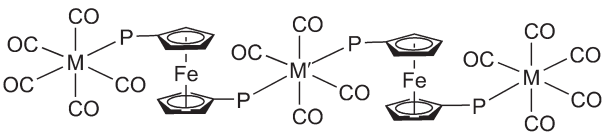


Scheme 50 Synthesis of azo dyes containing metallocalixarenes.[286]

color, with λ_{max} values between 420 and 430 nm in DMF. The addition of HCl to the polymer solution leads to a bathochromic shift in λ_{max} values in the range of 510–520 nm.[295]

5.23.4 Macromolecules Containing Metal Carbonyl Complexes

The oxidation process of ferrocene to ferrocenium is well known; therefore, compounds **206a–g** are suitable to study the electronic communication between the inner and outer metallic units. Similar materials were prepared by Phang and coworkers by reacting dppe (**207**) and dppp analogs (**208**) with **206b** (P = PPh_2).[296] Larger oligomers and polymers could be prepared using similar metallic units and the same strategy, or by reacting them with an alternate bridging ligand before reaction with another metallic moiety.



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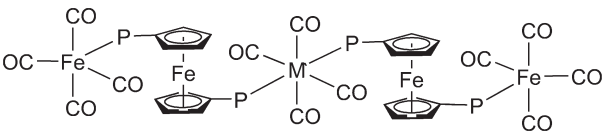
	a	b	c	d	e	f	g
M	Cr	Mo	W	Mo	Cr	Cr	W
M′	Cr	Cr	Cr	Mo	Mo	W	W
M	Cr	Mo	W	Mo	Cr	Cr	W



h (M′ = Cr), **i** (M′ = Mo)

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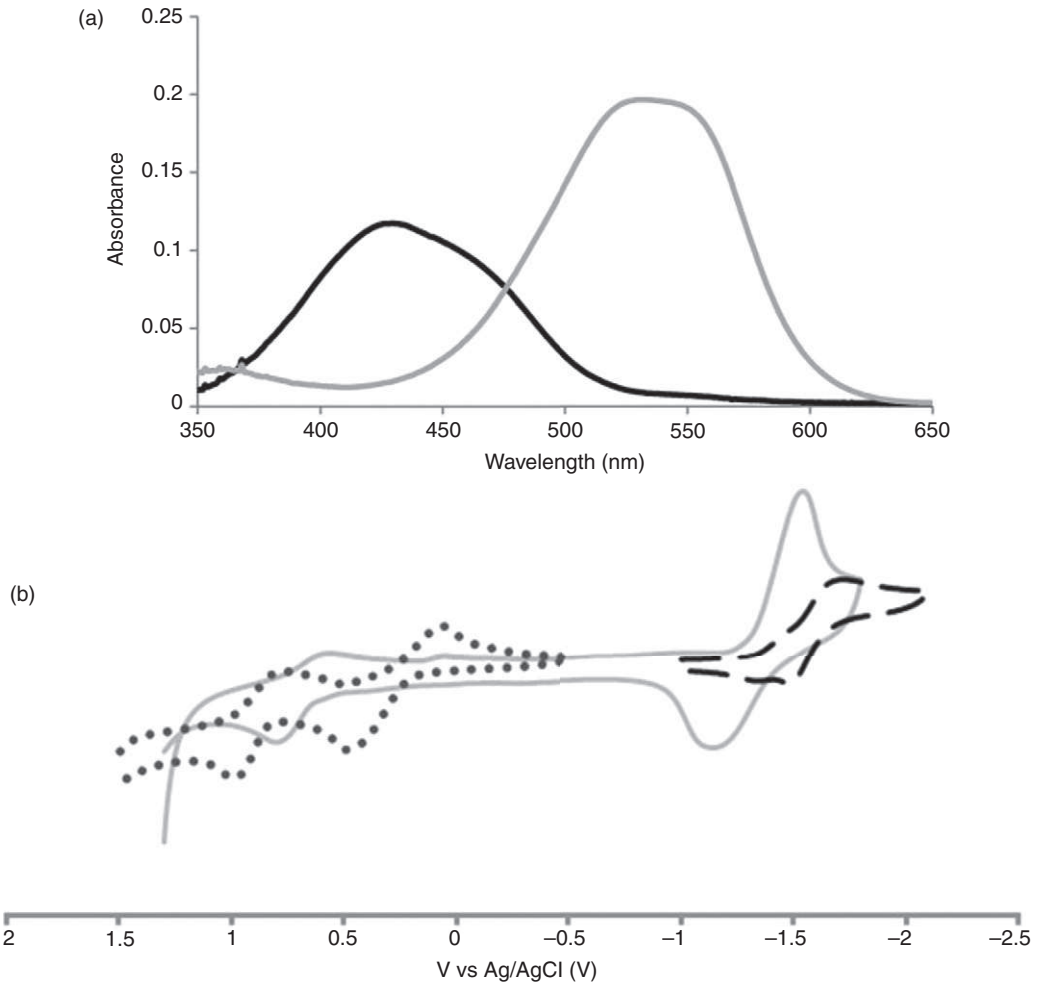
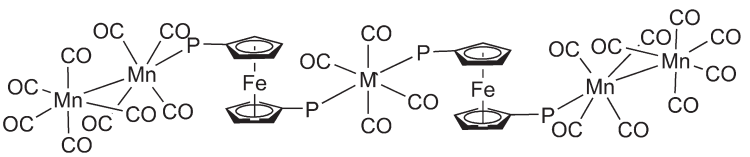
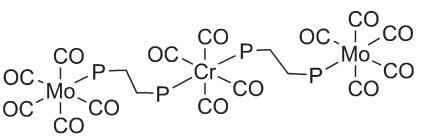


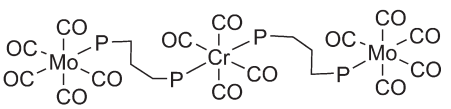
Figure 2 (a) Absorption spectrum of complex **190** in DCM (black) and in DCM after exposure to HCl(g) (gray); (b) cyclic voltammogram of **188** (…..), **187** (- - -), and **190** (gray), using glassy carbon electrode, Ag/AgCl reference electrode, and 0.002 M (analyte) in 0.1 M TBAP in propylene carbonate.



j (M′ = Cr), **k** (M′ = Mo)



207



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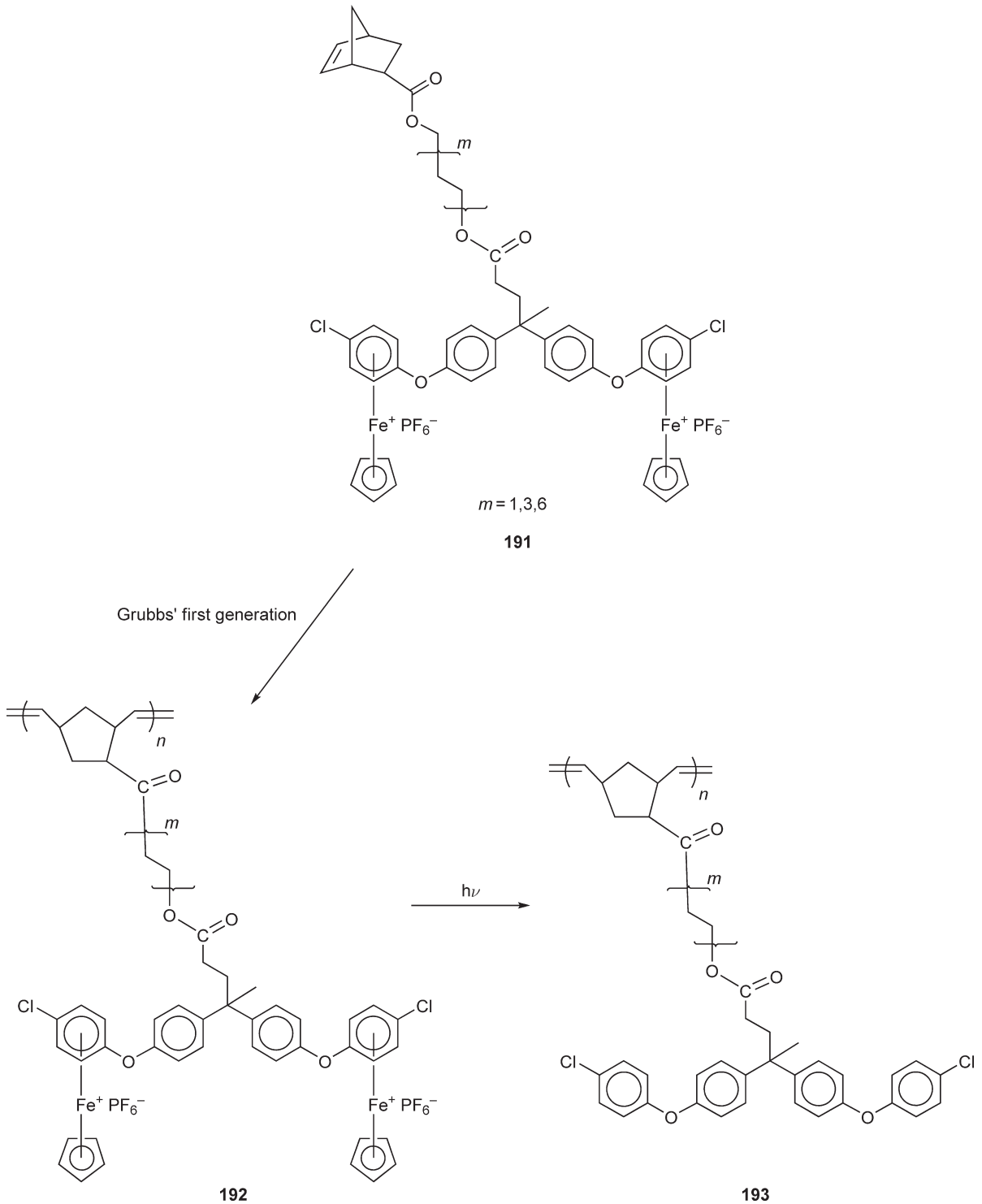
The convergent method was employed by Moss *et al.* to prepare dendrimers containing cyclopentadienylruthenium complex **209** by Moss, giving the fourth-generation dendrimer containing 48 organometallic moieties.[297]



Scheme 51 ROMP of cationic cyclopentadienyliron-functionalized norbornene monomers to new organoiron polynorbornenes (**192**).[289–294]

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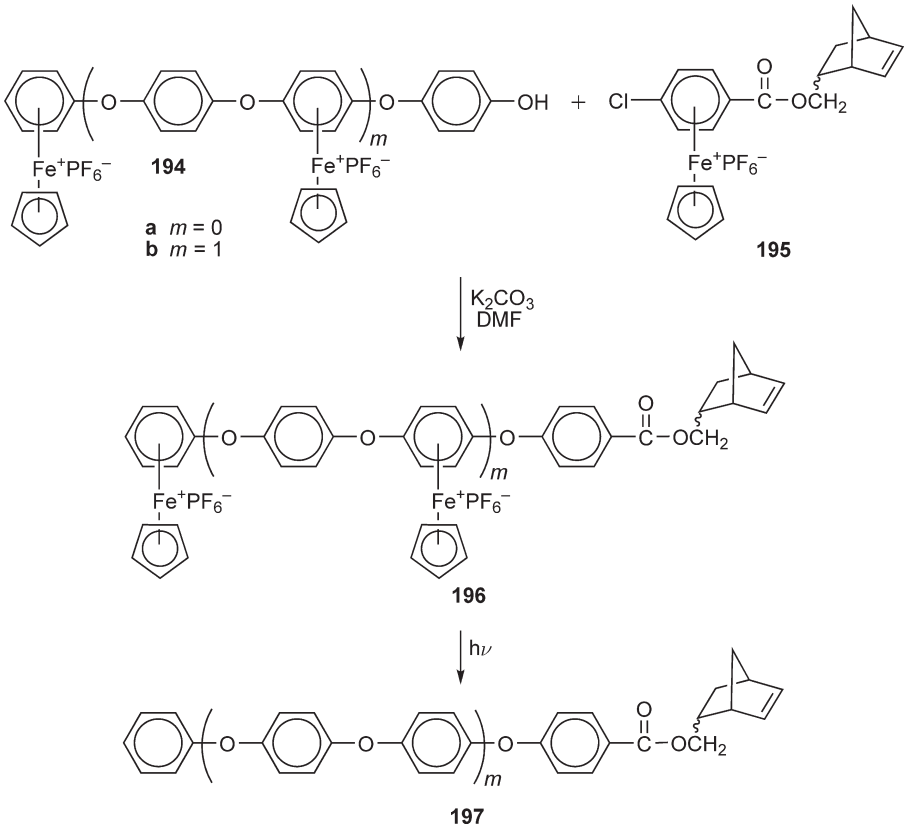
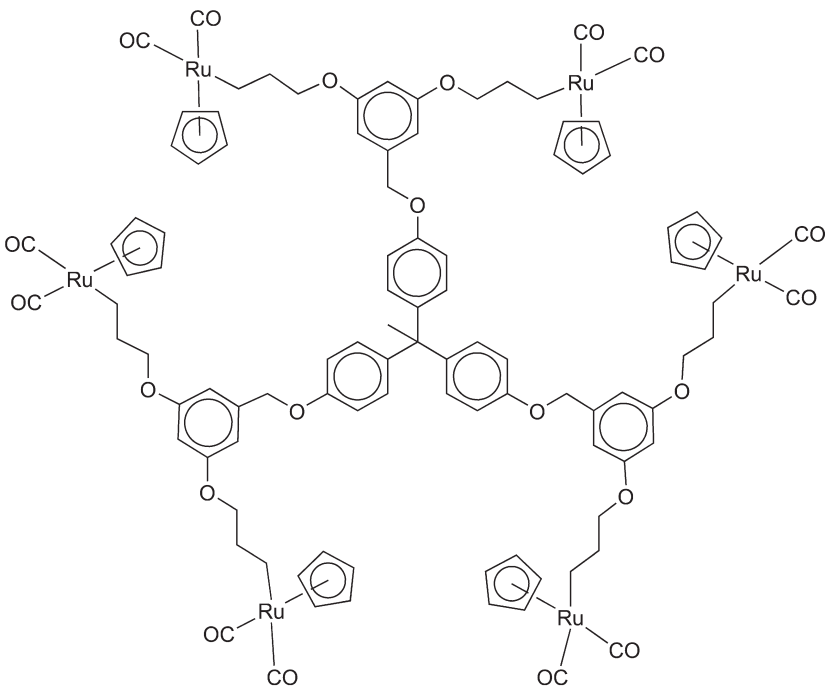


Scheme 52 Photolytic demetallation of organoiron norbornene complexes.[291]



209

An iron tricarbonyl-containing polymer was synthesized from the irradiation of polymer 213 in an excess of iron pentacarbonyl (Scheme 55).[298] Polymer 211 possessed a 2:1 ratio of coordinated to noncoordinated silole rings. Conductivity studies on polymers with $FeCl_3$ vapor showed that 210 had a conductivity of 10^{-8} S cm^{-1}, while 211 had a conductivity of 10^{-5} S cm^{-1}.

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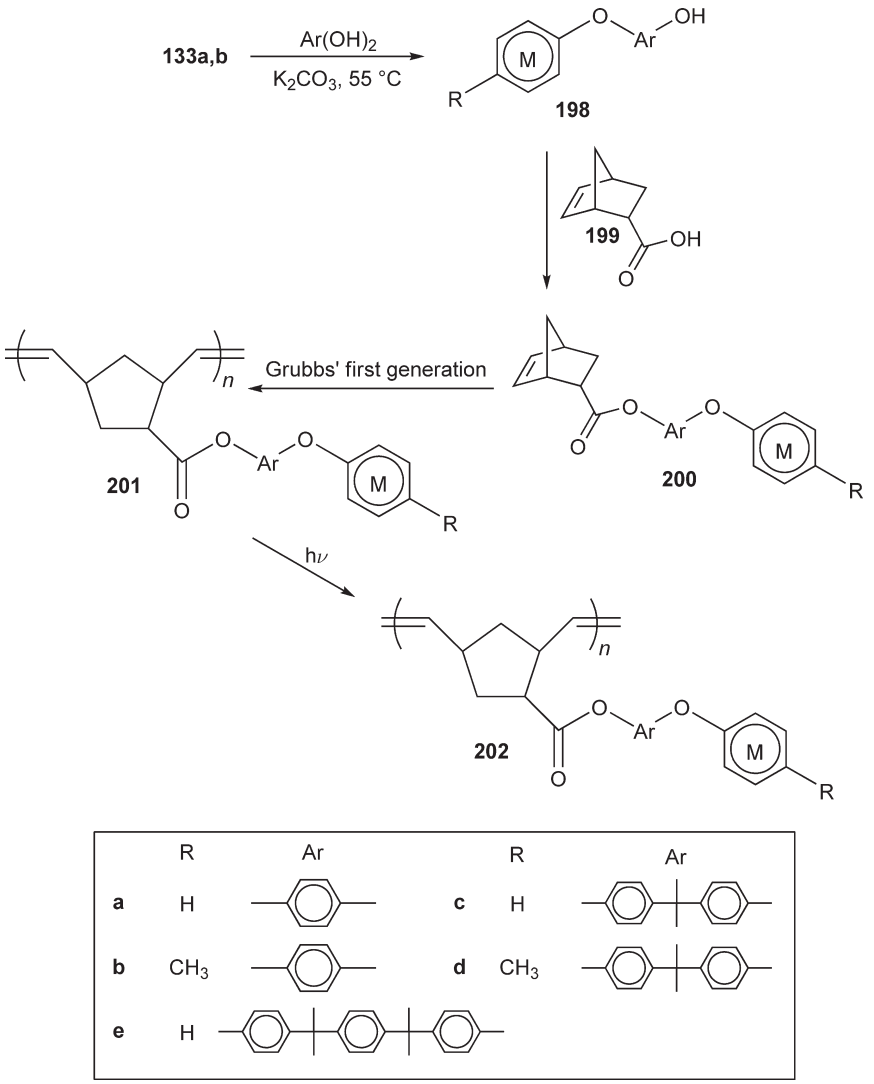
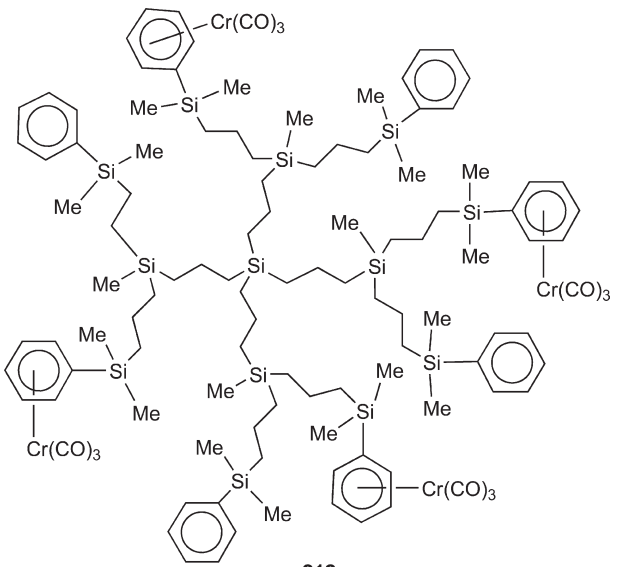


Scheme 53 Examples of polynorbornenes containing cationic iron moieties within their side chains as synthesized via ROMP.[294]

Chromium-containing organosilicon dendrimer **212**, reported by Cuadrado and coworkers, have chromium tricarbonyl units incorporated pendant to the terminal aromatic rings.[284] Complete complexation was not possible due to steric hindrance at higher generations of the silane dendrimer with chromium hexacarbonyl moieties.



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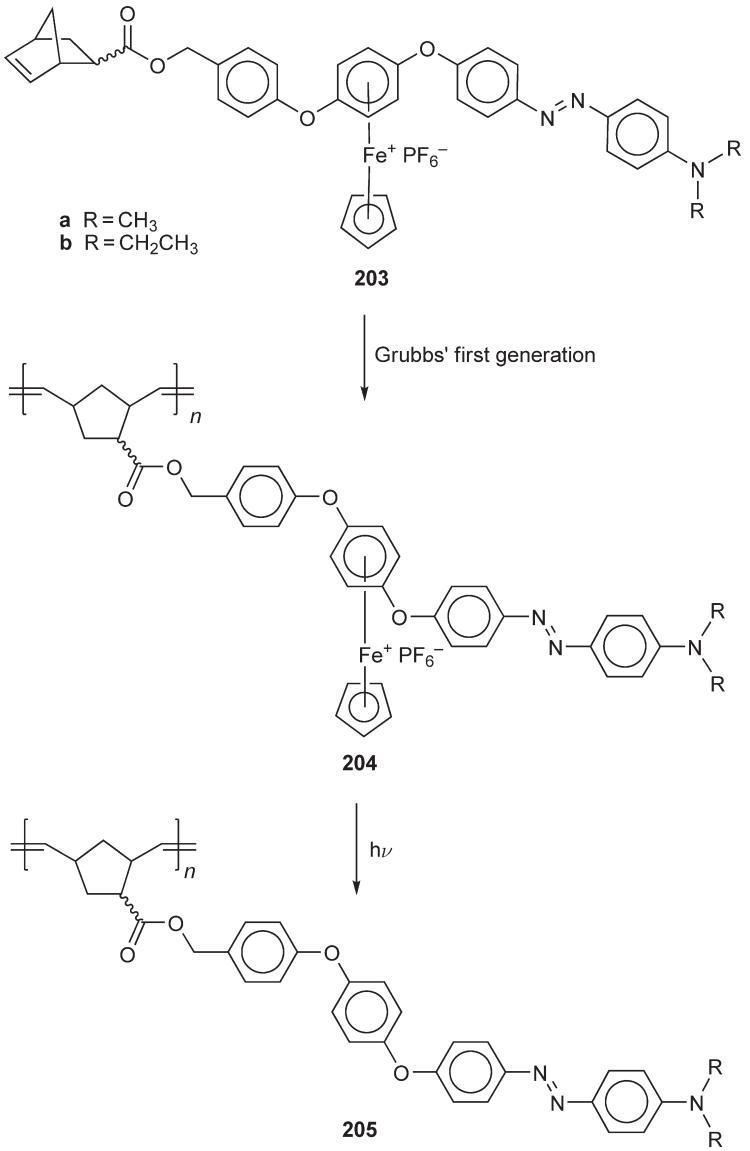
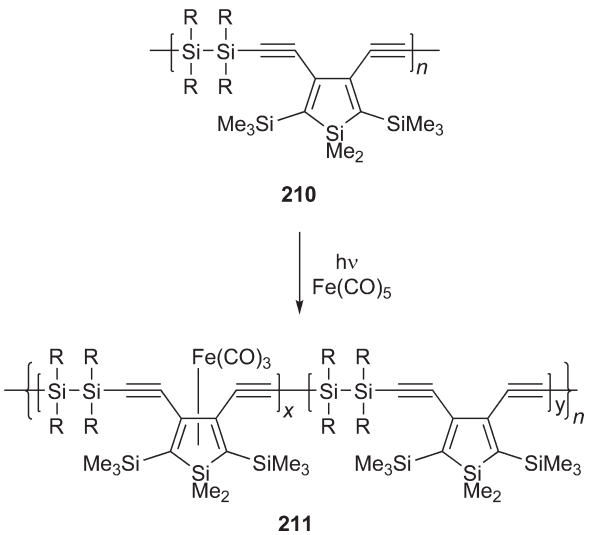


Scheme 54 ROMP of azo dye-functionalized organoiron norbornene-containing monomers to polynorbornenes.[295]



Scheme 55

5.23.5 Transition Metal Polyynes

The polymerization reaction of 1-iodo-2-methoxymethyl-3-ethynylferrocene and 1-iodo-2-(*N*,*N*-dimethylamino methyl)-3-ethynylferrocene gave 1,3-linked ferrocene-acetylene polymers using Sonogashira coupling, resulting in polymers that have optical activity or functionalized side chains.[299,300] The palladium-catalyzed reaction of diiodoferrocene with diethynyl monomers **213** gave polymers **214** with semiconducting behavior when doped with iodine (**Scheme 56**).[160,299–301] Polymer **214a** has electrical conductivity when oxidized with the iodine polymer; however, polymer **214b** is resistant to oxidation.

Several ferrocene-containing hyperbranched polymers were created from the copolymerization of yne-containing ferrocene monomers **216** with bis(aroylacetylenes) (**215**; **Scheme 57**).[302] The molecular weights of polymers **217** were between 7600 and 23 000. When the concentration of

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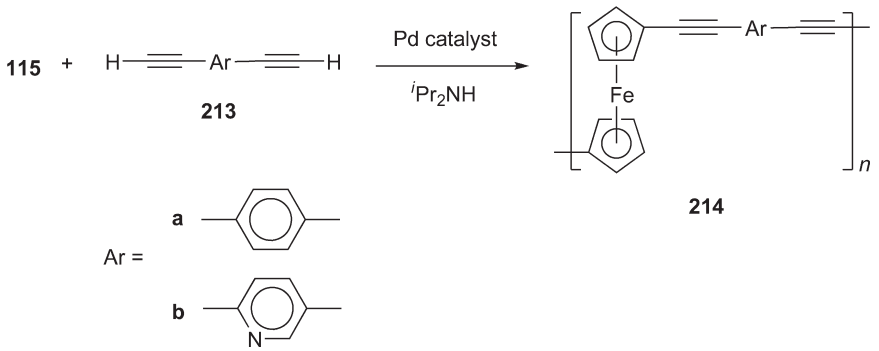
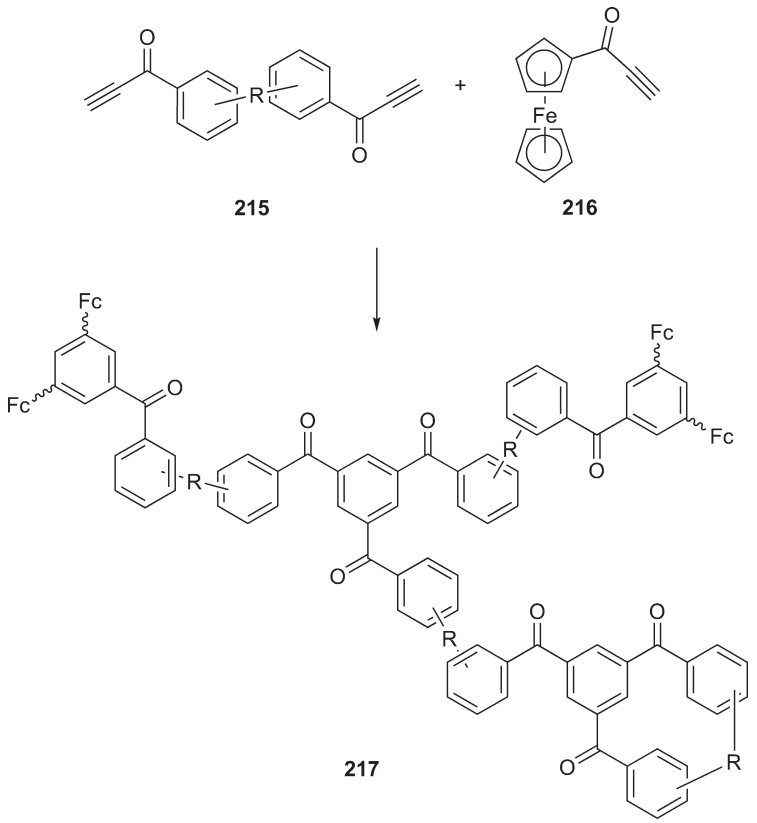


Scheme 56 Sonogashira coupling of 1-iodo-2-methoxymethyl-3-ethynylferrocene and 1-iodo-2-(*N,N*-dimethylamino methyl)-3-ethynylferrocene yielding 1,3-linked ferrocene-acetylene polymers.[160]



Scheme 57 Copolymerization of yne-containing ferrocene monomers **216** with bis(aroylacetylenes) **215** to ferrocene-containing hyperbranched polymers.[302]

the ferrocene monomer increases, the corresponding polymer has a low molecular weight due to the ferrocene acting as a capping agent in the polymerization. The thermal characterization proposed that polymer degradation starts at 340 °C.

Humphrey, Hor, and coworkers used Ru-alkynyl complexes to make di- and trimetallic heteronuclear organometallics with NLO properties (**Scheme 58**).[303–305] While product **220** has low nonlinearity, the extension of the systems through complexation to Pd/Pt significantly increases the NLO response of the materials.

Similar results were observed when the Ru-alkynyl species was combined with an appropriate Re-complex building block (**221** or **222**). The improved NLO properties were assigned to the Ru(donor)–Re(acceptor) character of the resulting bimetallic material.

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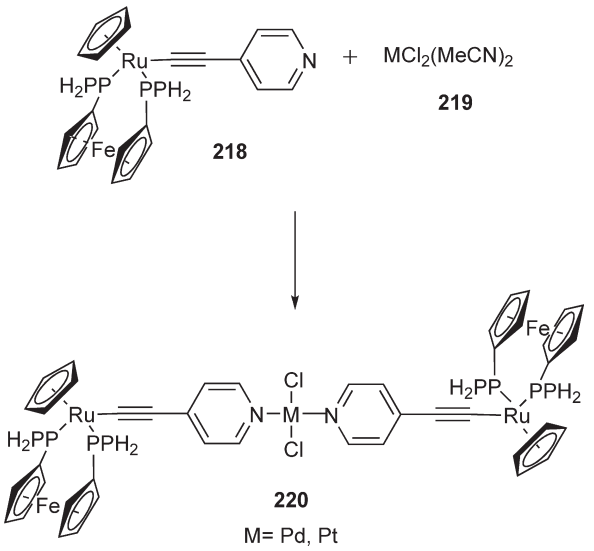
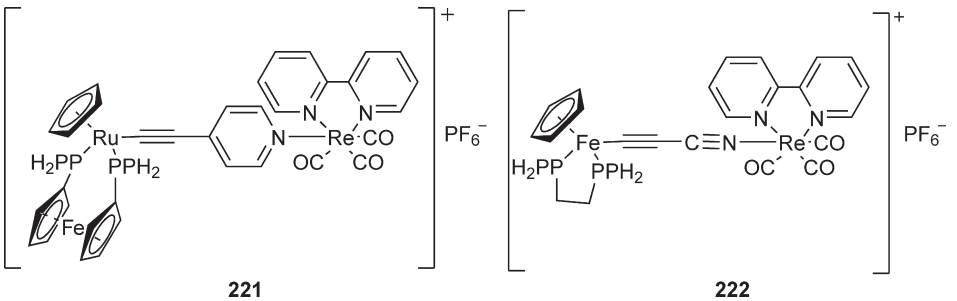


Scheme 58 Complexation to heteronuclear organometallics.[303–305]



5.23.6 Metal–Metal Bonded Systems

Polymers comprised of photochemically reactive metal–metal bonds were reported by Tyler and coworkers.[306–309] Shown in Scheme 59, exposure of 223 to light in the presence of carbon tetrachloride results in the photolysis of the Mo–Mo bonds to give 224, whereas metal–metal triple bonds form to yield polymer 225 when exposed to light.[307] Due to the cleavage of the metal–metal bonds, similar polymers start to degrade in the presence of light.[310,311] Recent studies show that the quantum yields of the photochemical degradation of the polymers decrease over a period of 30 days.[312]

Electrochemical reduction of *trans*-$[M^{II}(Cl)_2(bipy)(CO)_2]$ (226; M = Ru, Os) from M^{II} to M^0 causes polymerization with the loss of the chloride ligands.[313,314] Polymers 227 (Scheme 60) have backbones consisting of metal–metal bonds. Both polymers were selective for the catalytic reduction of carbon dioxide to carbon monoxide.

A number of photodegradable organometallic polymers containing metal–metal bonds were recently prepared by Shultz *et al.*[315] Similarly, photodegradable organometallic oligomers including metal–metal bonds were synthesized via acyclic diene metathesis polymerization (ADMET). Scheme 61 shows the reaction between $Cp_2Mo_2(CO)_4$ and phosphine ligand 229 with a terminal alkene group. The polymerization of resulting monomer 230 was unsuccessful with various catalysts, attributed to steric effects rather than electronic effects of the C=C of the phosphine ligand, based on previously successful ADMET polymerization of *cis*-$Mo(CO)_4(Ph_2P(CH_2)_6CH{=}CH_2)$.

5.23.7 Conclusion

This chapter is designed to provide a comprehensive representation of recent developments in the field of metal-containing polymers. The combination of transition metals with macromolecules such as porphyrins, phthalocyanines, and pyridine-based systems has furthered the field of coordination and other metal-containing polymers. Organometallic complexes containing transition metals coordinated to cyclopentadienyl or arene moieties have produced polymers containing both neutral and cationic organometallic complexes. These polymeric materials have received much attention due to their chemical and physical properties, as well as their utility in many fields such as organic synthesis, catalysis, and materials chemistry. This is a rapidly growing field of polymer research, as new synthetic approaches are developed to create valuable transition metal-containing macromolecules and polymers with applications as new magnetic, photoactive, and electroactive materials as well as potential drug delivery systems.

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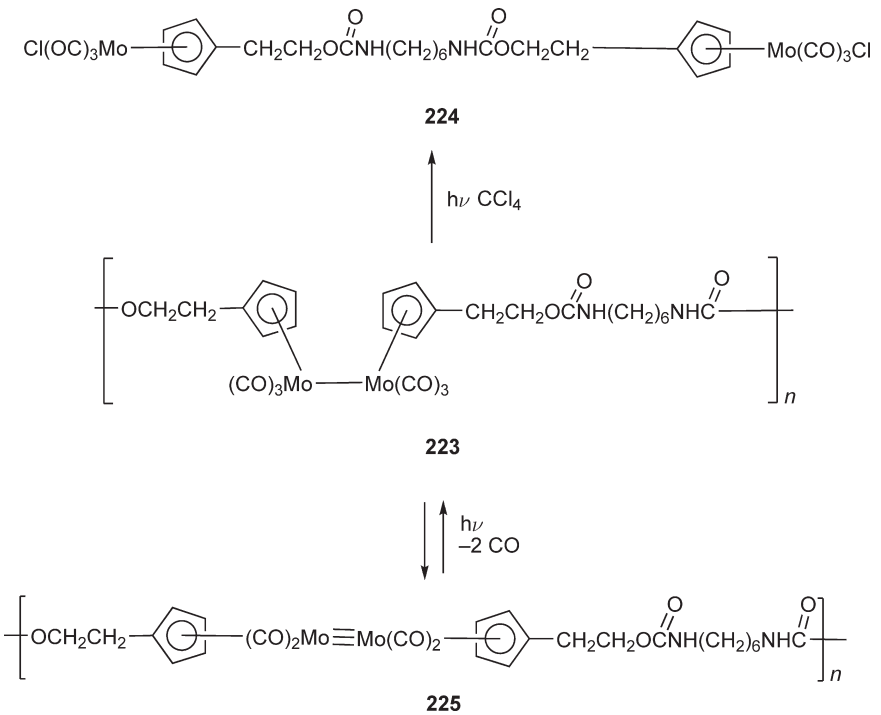
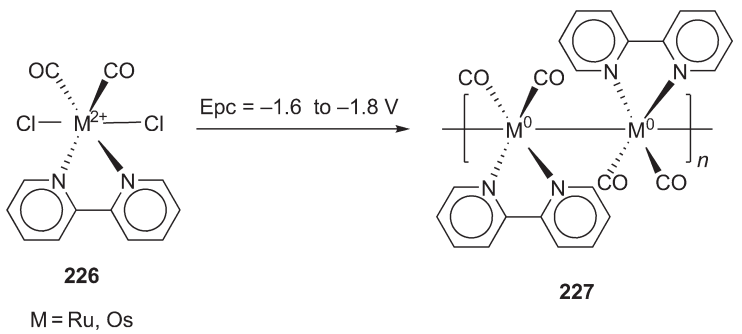
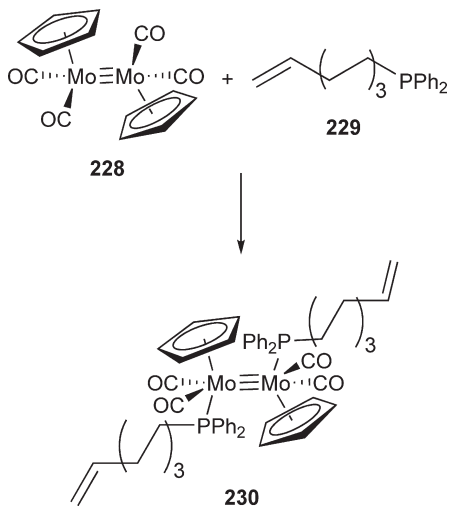


Scheme 59 Photolysis of the Mo–Mo bonds.[307]



Scheme 60 Electrochemical reduction of *trans*-[$M^{II}(Cl)_2(bipy)(CO)_2$].[313,314]



Scheme 61 Reaction of $Cp_2Mo_2(CO)_4$ with phosphine ligand **229** with a terminal alkene group.[315]

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Acknowledgments

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Dr. Abd-El-Aziz is a prolific researcher with 132 publications, 14 conference proceedings, three patents, nine book chapters, and 136 national and international conference presentations to his credit. He has authored and edited 14 books and has given 47 invited lectures at national and international universities. Dr. Abd-El-Aziz is one of two editors of the Journal of Inorganic and Organometallic Polymers and Materials and he has served on nine editorial boards.

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5.24 Phosphorus-Containing Dendritic Architectures

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5.24.1 Introduction

Dendrimers are hyperbranched macromolecules having a perfectly defined and highly functionalized repetitive structure.[1–3] In contrast to all the other types of polymers, they are not synthesized by polymerization reactions but step by step ('layer after layer'), which allows a perfect control of their structure. The structure of dendrimers is fundamentally different from that of hyperbranched polymers, which are irregularly branched by multifunctional polymerization reactions. The presence of many terminal functions, easily accessible and thus easily modifiable, constitutes the principal attractiveness of dendrimers. **Figure 1** displays the various types of branched polymeric architectures, compared with that of dendrimers.

Dendrimers have gained growing interest since more than 20 years; the number of patents in the field increases currently more quickly than the number of publications, with more than 1300 publications and 350 patents per years since four years. If these beautiful objects initially induced fundamental curiosity in research laboratories, they now may find real uses in various fields that will be emphasized in the Conclusions of this chapter (section 5.24.5). In most cases, the synthesis of dendrimers is carried out using a divergent process. The synthetic process starts from a multifunctional core, to which successive layers of monomers are progressively grafted, most generally using the repetition of two quantitative steps. Each time the number of terminal functions is multiplied, a new generation is created (see **Figure 2(a)** for the various elements constituting a dendrimer, and a dendron, also called dendritic wedge). The divergent processes allow high generations of dendrimers to be obtained, and afford a periphery that is highly reactive, facilitating further functionalizations to modify and adapt the properties of dendrimers (**Figure 2(b)**). The main problem of the divergent processes is the possibility to have relatively imperfect structures for high generations, due to the necessity to react an increasing number of small molecules, and to the impossibility to remove slightly imperfect structures from the perfect structure. A less used method is the convergent process, in which the growing of the dendritic architecture is carried out from the surface toward the core. Such convergent synthesis creates dendrons (dendritic entity having one function at the core different from the functions on the surface) which can be associated to a multifunctional core in the last step, thus creating a real dendrimer (**Figure 2(c)**). The convergent process should give purer dendrimers than the divergent process, but the number of generations obtainable is lower, due to the steric hindrance occurring when grafting large dendrons to a core.

Our first publication about dendrimers dates back to 1994;[4] we proposed a particularly powerful method of synthesis of dendrimers since it enabled us to obtain the generation 12,[5] which is still today the highest generation of any type of dendrimers with precisely defined structure. The type of dendrimers that we synthesized possessed one phosphorus atom at each branching point. This chapter will focus on the methods of synthesis of phosphorus-containing dendritic architectures, mainly coming from our group, but also from other laboratories. A comprehensive survey of the field will be given, displaying the synthesis not only of regular dendrimers, but also of dendrimers with layered architectures, of dendrons (dendritic wedges) and of various types of less-symmetrical dendritic architectures, emphasizing the extraordinary versatility of the chemistry of phosphorus.

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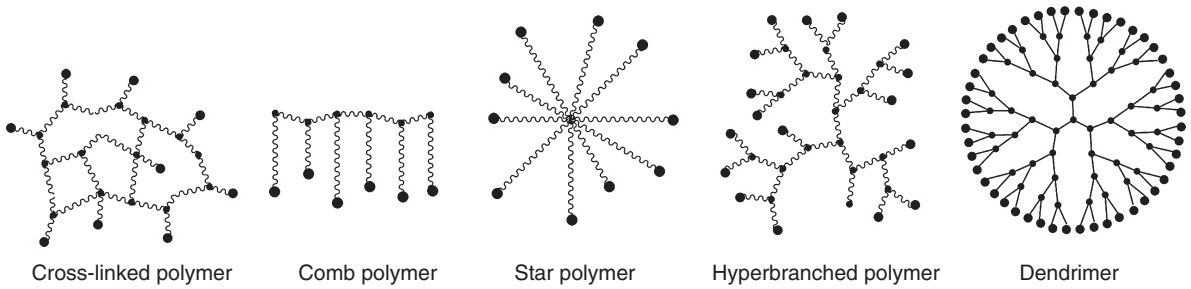

Figure 1 Branched polymeric architectures, synthesized by polymeric reactions, except the dendrimer.

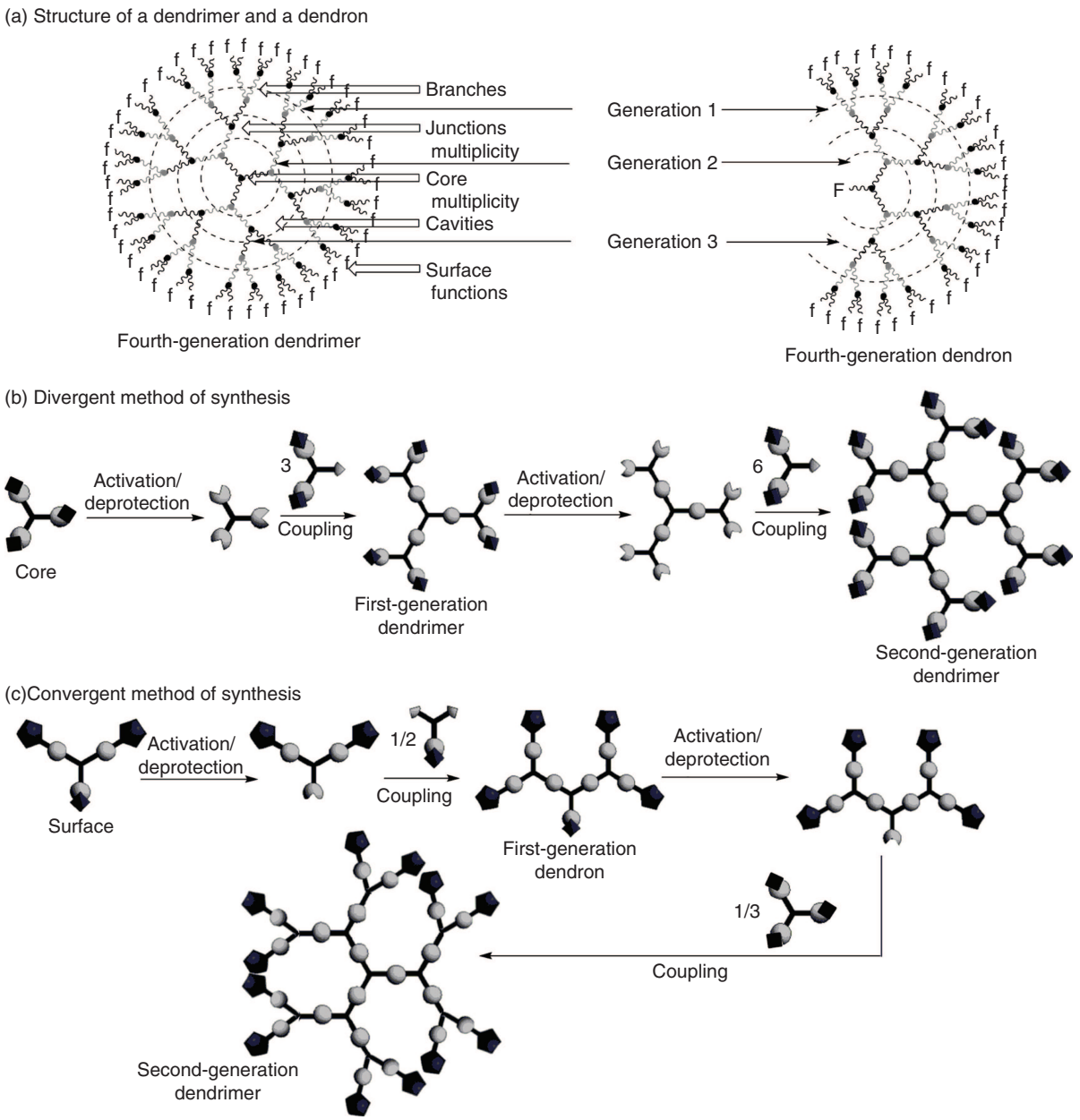

Figure 2 (a) Structure of dendrimers and dendrons; (b) principle of divergent process; and (c) principle of convergent process.

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5.24.2 Syntheses of Phosphorus-Containing Dendrimers

5.24.2.1 Syntheses of Dendrimers by Simple Repetitive Multistep Processes

5.24.2.1.1 Dendrimers having exclusively P–C bonds at the branching points

The first method of synthesis of any type of phosphorus-containing dendrimers was described by Rengan and Engel in 1991, using a divergent process.[6] This first two-step method consisted of the cleavage of ether linkages by Me_3SiI to afford alkyliodide terminations to the dendrimers, which were used in the second step for alkylating a phosphine possessing three ether groups. This process was applied up to the third generation **1-G$_3$**, and it allowed multiplying by 3 the number of terminal groups at each generation (instead of 2 in most cases, as will be seen later) (**Figure 3**). Other cores such as phosphonium[7] or phosphine oxide[8] were also used applying the same synthetic process.

After this pioneering work, two methods of synthesis of two very different families of phosphorus dendrimers were described at the same time in 1994, one by DuBois *et al.*,[9] and the other one by us;[4] we will emphasize later our own work, because our dendrimers have no P–C bonds within their structure. DuBois *et al.* obtained a small dendrimer constituted of phosphines at each branching points, by a radical addition of primary phosphines to the vinyl group of phosphonates. Reduction of the phosphonates by lithium aluminum hydride afforded again primary phosphines. This synthesis was carried out up to the second generation **2-G$_2$**[9] (**Figure 4**).

Larger dendrimers possessing phosphines at each branching point were described later on by Kakkar *et al.* in 1999.[10] The first step of the synthesis consisted of the aminosilanization of alcohol end groups; the second step was a controlled acid-based hydrolysis of the aminosilanes by a single OH function of $P[(CH_2)_3OH]_3$. The synthesis was carried out up to the third generation. Despite the possibility of multiple reactions on

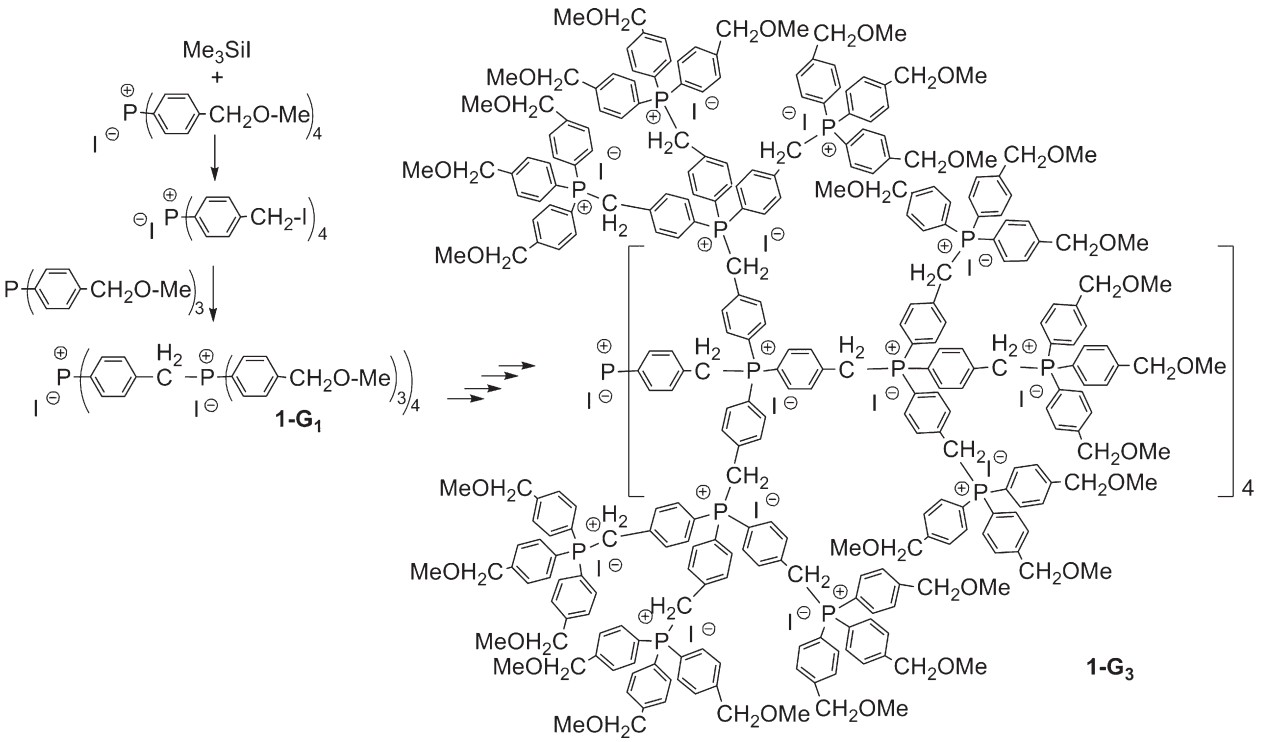

Figure 3 The very first example of synthesis of phosphorus-containing dendrimers.

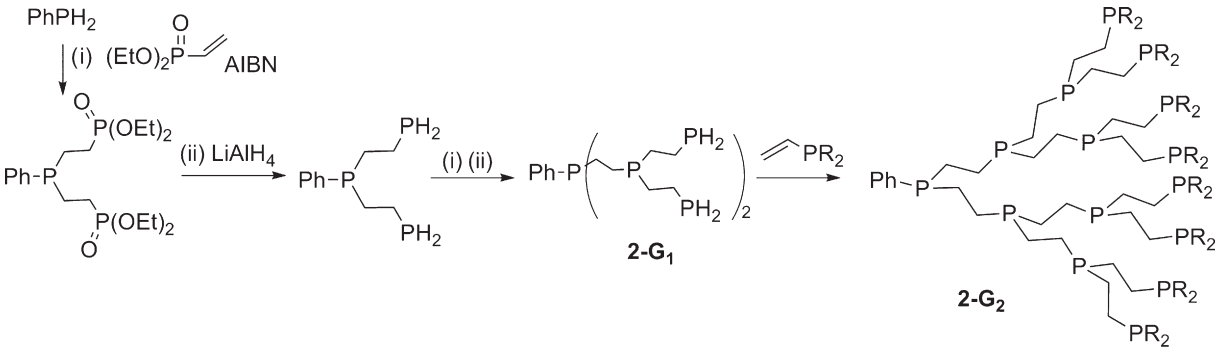

Figure 4 First synthesis of phosphine-containing dendrimers.

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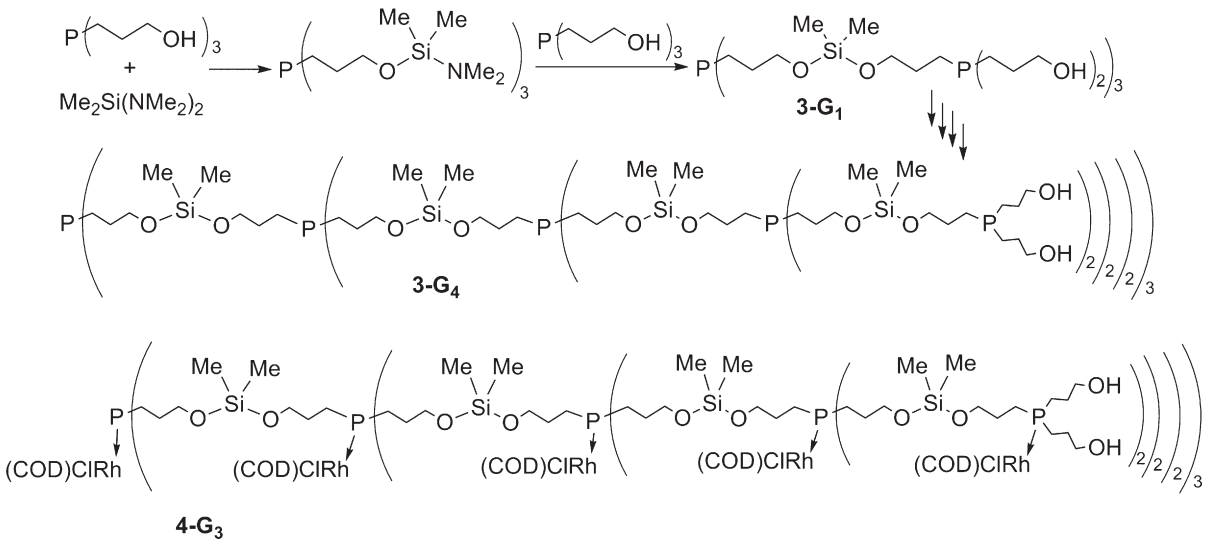

Figure 5 Synthesis of large phosphine-containing dendrimers and structure of the corresponding complex.

$P[(CH_2)_3OH]_3$, characterization of these compounds indicated dendrimer rather than hyperbranched growth. The corresponding rhodium complexes **4-G$_n$** were obtained either by complexation of the free phosphine dendrimers **3-G$_n$** or using the complex $[RhCl(COD)]P[(CH_2)_3OH]_3$ (COD = cyclooctadiene) instead of the free phosphine for the synthesis of the dendrimer (**Figure 5**).

5.24.2.1.2 Dendrimers having exclusively P–O bonds at the branching points

The first method of synthesis of dendrimers possessing phosphate groups as branching points was reported by Damha *et al.* in 1993;[11] it is also the unique convergent synthesis of phosphorus-containing dendrimers known to date. Using an automated DNA synthesizer for chain extension in the solid phase, adenosine phosphoramidate was added for creating the branching points by coupling two adjacent polymer-bound nucleotide chains. Various dendrimers based on thymidine and adenosine building blocks were synthesized by repetition of chain elongation and branching steps.[12] The dendrimers were isolated after cleavage from the solid phase (**Figure 6**).

The use of phosphoramidites as building blocks in solution was developed by Roy *et al.* in 1997.[13] It consisted of coupling a phosphoramidite bearing siloxane groups with alcohol end groups, followed by oxidation. The second step of this method was the deprotection of the siloxane. Repeating twice both steps afforded the second generation, which was functionalized by *N*-acetylgalactosamine (**Figure 7**). However, no experimental details were given.

Another method of synthesis of phosphate dendrimers is related to the previous one. It was proposed by Salamonczyk *et al.* in 2000.[14] This series of thiophosphate dendrimers was obtained first by the reaction of a triol with a phosphoramidite possessing acetate groups, followed by oxidation with elemental sulfur. The second step was the deprotection of the acetates to afford the polyols of the next generation. The repetition of both steps was carried out up to the fifth generation **6-G$_5$**. All experimental details were given in this case. The same method is also used for the synthesis of dendrimers possessing selenium, oxygen,[15] or boron hydride[16] instead of sulfur linked to phosphorus. It is even possible to build original dendrimers possessing a different type of phosphate at each generation, chosen between P = S, P = Se, and P = O, affording layered dendrimers[17] (**Figure 8**).

5.24.2.1.3 Dendrimers having one P–N bond at the branching points

The most generally used method of synthesis of phosphorus dendrimers was described by us in 1994.[4] It consists in applying a two-step reiterative process using 4-hydroxybenzaldehyde in basic conditions and $H_2NNMeP(S)Cl_2$ successively (**Figure 9**). Both steps generate only NaCl and H_2O as byproducts and are quantitative. They afford hydrazido thiophosphates as branching points. This process was carried out first up to generation 4,[4] then up to generation 7,[18] and generation 10,[19] and finally gave rise to the highest generation well characterized obtained up to now for any type of dendrimers (generation 12, **7-G$_{12}$**).[5] It is also the highest generation obtainable from a practical point of view (the twelfth generation is the last one soluble) and from a theoretical point of view, due to the fact that the number of end groups increases more rapidly than the free space available for them for very high generations, preventing full substitutions. These reactions can be applied starting from various cores, in particular from $N_3P_3Cl_6$ instead of $P(S)Cl_3$ (compounds **7-G$_n$**, **Figure 8**). In this case, the reactions were first carried out up to generation 5,[19] then up to generation 8;[20] the highest generation obtainable from this core is unknown.

This method of synthesis was also applied to various types of cores having P–Cl functions such as $(O)PCl_3$[21] and $N_4P_4Cl_8$,[22] and to a series of aldehyde derivatives possessing one aldehyde and an ester,[23] two aldehydes and a pyridine,[24] or a ferrocene,[25] or a vinyl,[26] or a chloromethyl,[24] or a phosphonate group,[27] three aldehydes and one ammonium,[28] four aldehydes and two P = N–P = S linkages connected to an alkyl chain[29] or a ferrocene,[30] or even eight aldehydes linked to a phthalocyanine[31] (**Figure 10**).

In addition to these examples, we have also developed the specific reactivity of the hexachlorocyclotriphosphazene ($N_3P_3Cl_6$), in particular for linking one fluorophore to the core, using the remaining five Cl or aldehydes to grow the

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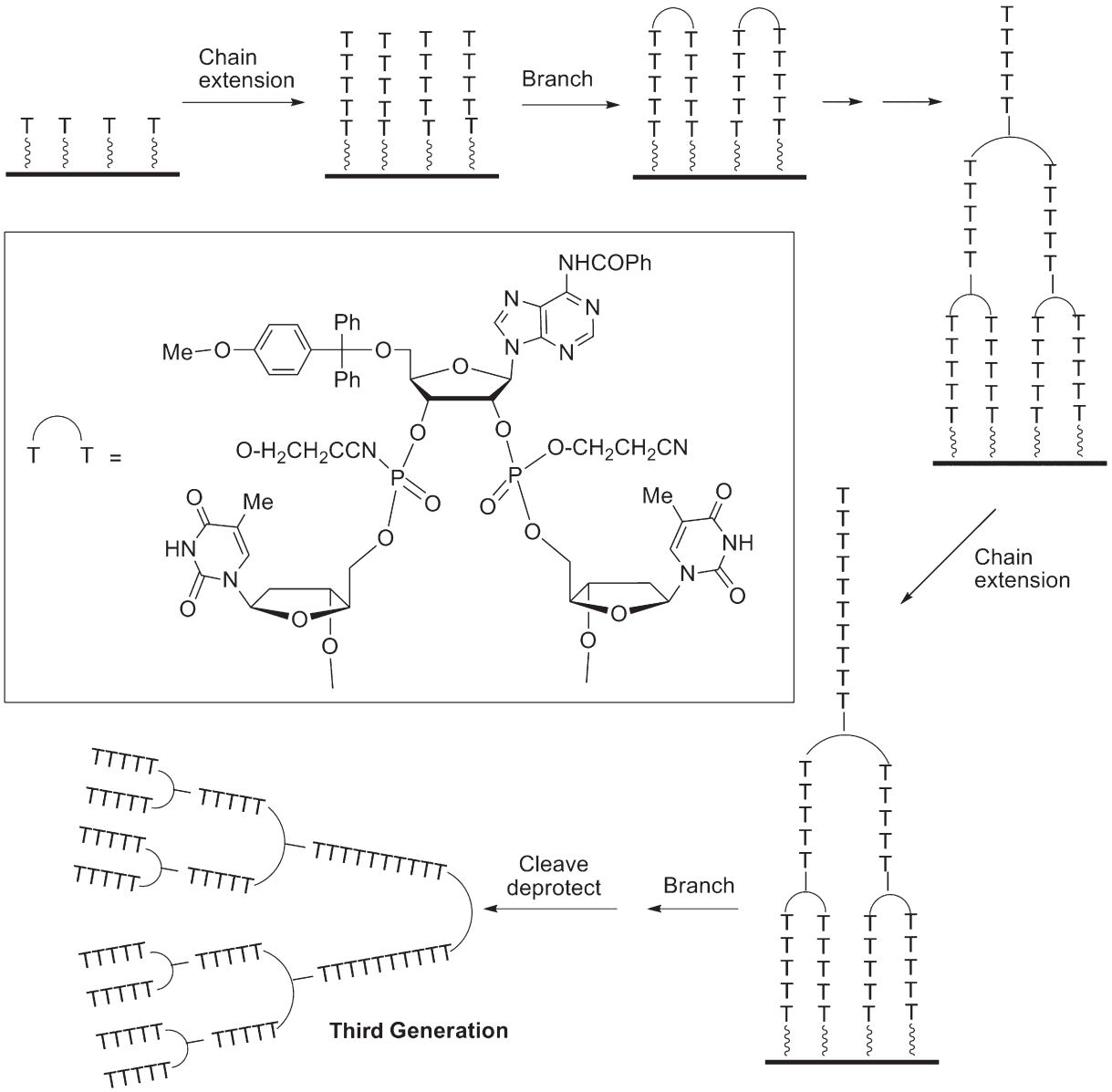

Figure 6 Synthesis of phosphate based dendrimers by a convergent process in the solid phase.

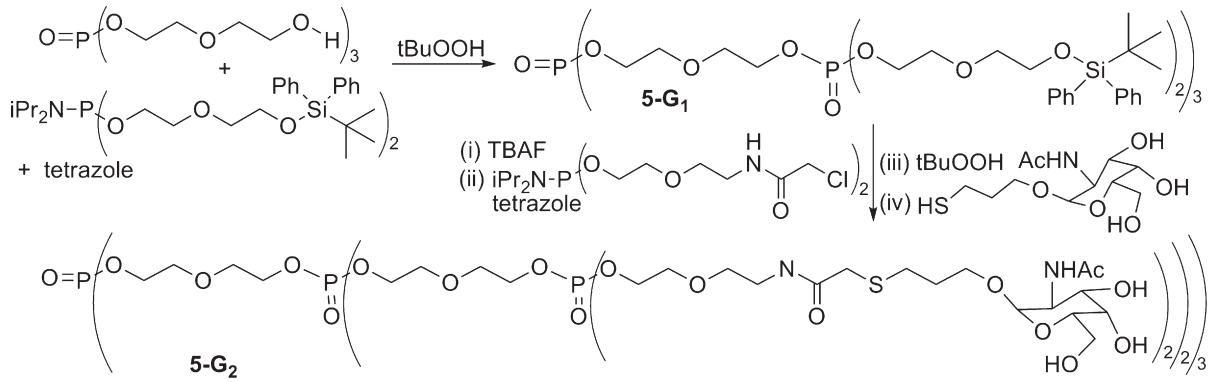

Figure 7 The first method of synthesis of phosphate dendrimers.

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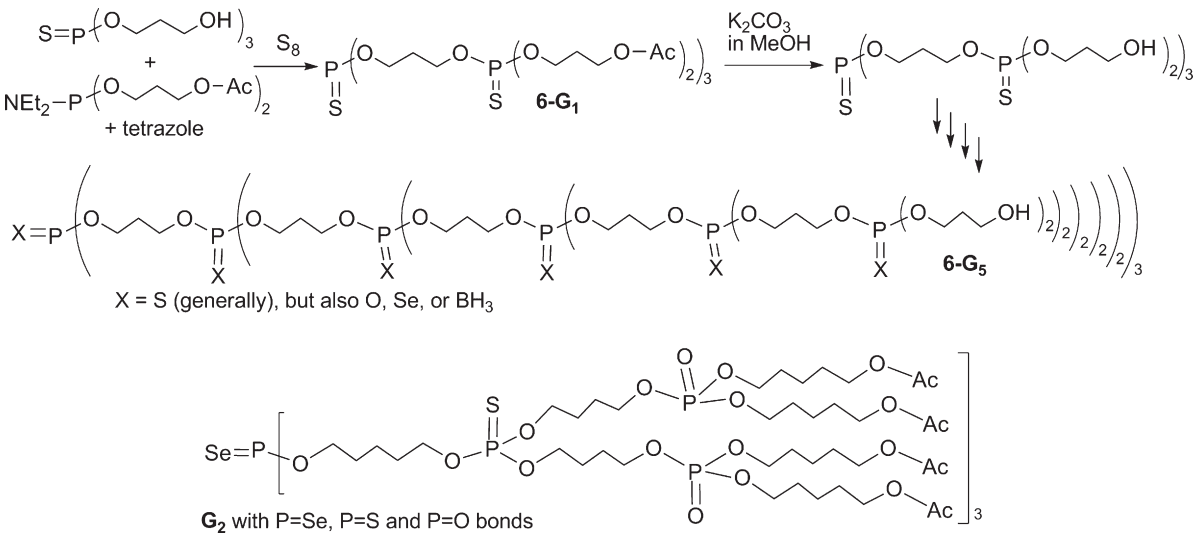

Figure 8 Synthesis of thiophosphate dendrimers and related compounds.

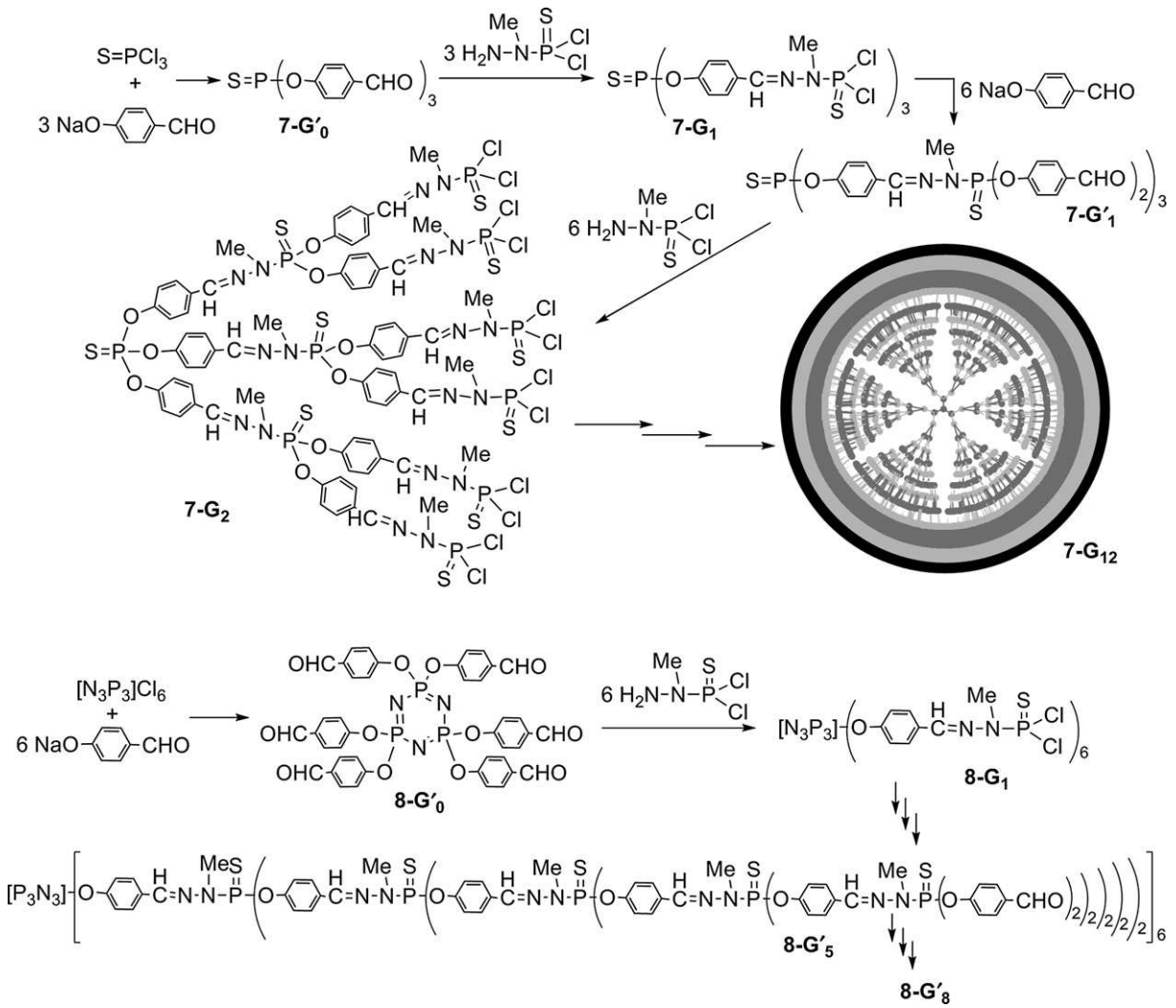

Figure 9 Synthesis of hydrazido thiophosphate dendrimers starting from a tri-($PSCl_3$) or hexa-functional ($N_3P_3Cl_6$) core.

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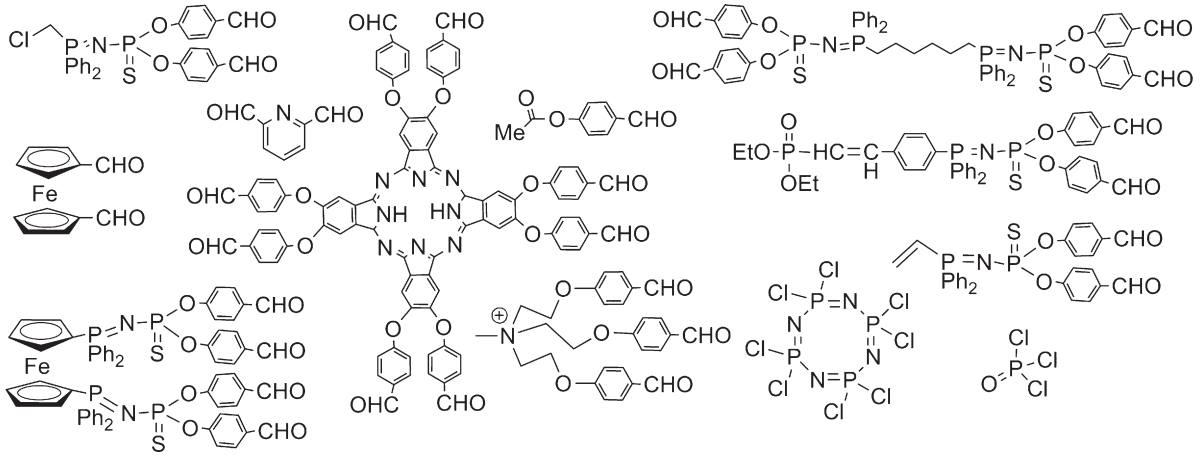

Figure 10 Various compounds used as cores of phosphorus dendrimers, applying the method of synthesis shown in **Figure 9**.

dendrimer. Examples with 1,4-diphenylmaleimide and five Cl[32] or five aldehydes,[33] a julolidine derivative and five aldehydes,[22] are reported in **Figure 3**, as well as examples of two-photon absorbing fluorophores built with double bonds[34] or triple bonds[35] and linked to two cyclotriphosphazenes. In all these cases, five (or 10) Cl or aldehydes remain available for synthesizing the dendrimer. In addition, it is possible to play with the number of these remaining functional groups, as shown in the lower part of **Figure 11**, in which four, three, or two Cl, or one aldehyde remain.[22]

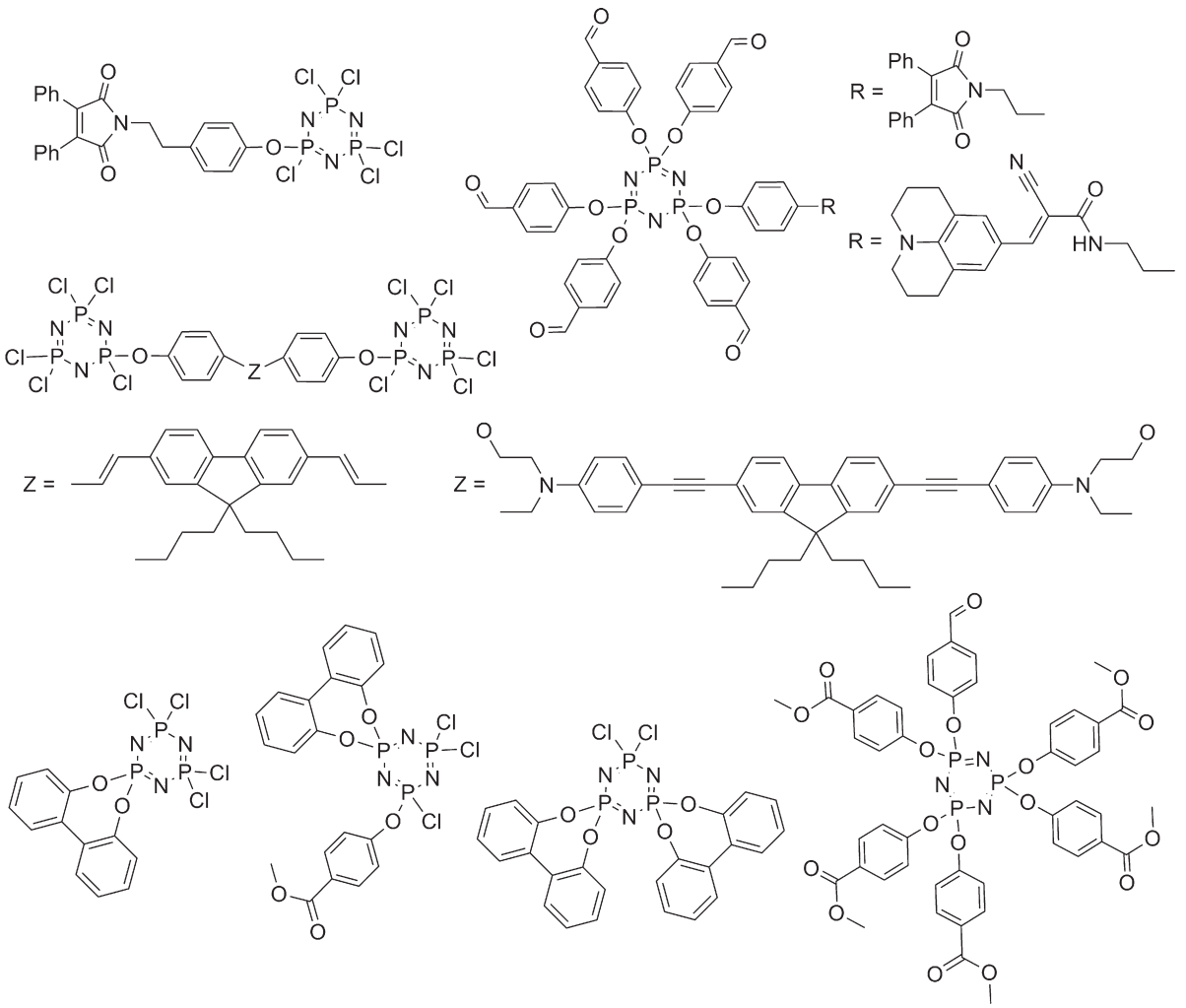

Figure 11 Various types of cores elaborated by modifications of $N_3P_3Cl_6$.

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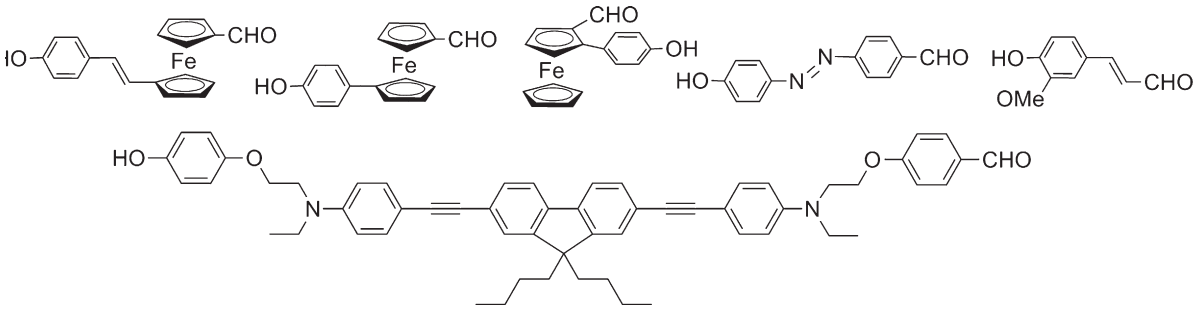

Figure 12 Various types of functionalized hydroxybenzaldehyde derivatives, used as branches of phosphorus-containing dendrimers.

Besides the modification of the core shown on the previous page, the method shown in Figure 9 also allows many modifications at the level of the branches, such as using $H_2NNMeP(O)Cl_2$ instead of $H_2NNMeP(S)Cl_2$, at each generation[21] or at selected generations, affording in the latter case the first regularly layered phosphorus dendrimers.[36] Several functionalized hydroxyaldehydes have been used instead of 4-hydroxybenzaldehyde. In particular, various types of ferrocene derivatives including an alkene bond[37] (or not[25]) or possessing a planar chirality[38] were used as constituents of the branches of phosphorus dendrimers. Organic derivatives such as azobenzene[39] and methoxycinnamaldehyde[40] were also used to lengthen the branches, but the longest branches include two-photon absorbing fluorophores[41] (Figure 12).

5.24.2.1.4 Dendrimers having two P–N bonds at the branching points

The method of synthesis shown in Figure 9 creates O–Z–CH = NN(Me)P = X linkages (where X = S, O, and Z = is generally C_6H_4) from the core toward the surface groups. We have also attempted creating the same linkage in a reversed order, that is, N(Me)N = CH–C_6H_4–OP = S, from the core toward the surface groups. In this case, the branching point (the phosphorus atom) will be linked to one oxygen and two nitrogen atoms, instead of one nitrogen atom and two oxygen atoms in the previous case. In the first step of this reversed method, only the HNMe side of methylhydrazine should react with P–Cl functions; however, it is difficult to avoid the reaction of a small amount of the NH_2 side. The second step is a condensation of NH_2 with a dichlorophosphoraldehyde. This method was stopped at the second generation **9-G$_2$**, due to the impossibility to purify the dendrimer at the step of the substitution with methylhydrazine for higher generations (Figure 13).[42]

5.24.2.1.5 Dendrimers having P = N–P = S linkages at the branching points

We have also proposed several methods of synthesis of phosphorus dendrimers including in their structure P = N–P = S linkages at one, several, or all generations. These linkages are easily obtained by Staudinger reactions[43] between phosphines and thiophosphorus azides. These reactions are quantitative and generate N_2 as single byproducts, thus they are particularly attractive for the synthesis of dendrimers. The first two series of phosphorus dendrimers including these linkages necessitated three steps to build one generation, starting from aldehyde groups: (1) condensation of methylhydrazine, (2) reaction with Ph_2PCl in basic conditions, and (3) Staudinger reaction between the phosphine end groups and an azido dialdehyde, to have again aldehydes as terminal groups. The repetition of these three steps was carried out up to the third generation **10-G$_3$**.[44] A modification of this method used Ph_2PCH_2OH instead of Ph_2PCl, for creating CH_2–P = N–P = S linkages[29] (Figure 14). It must be emphasized that these three-step methods are fully compatible with the two-step method shown in Figure 9, because they afford aldehyde groups, which are used in both types of processes. It means that the P = N–P = S linkages can be introduced at one or several generations, where desired when applying the two-step process.

Later on, in 2000, we described another method of synthesis of dendrimers possessing P = N–P = S linkages at each generation. It is a two-step process, which consists of condensation reactions between terminal NH_2 issued from methylhydrazine, and a monoaldehyde derived from triphenylphosphine. The

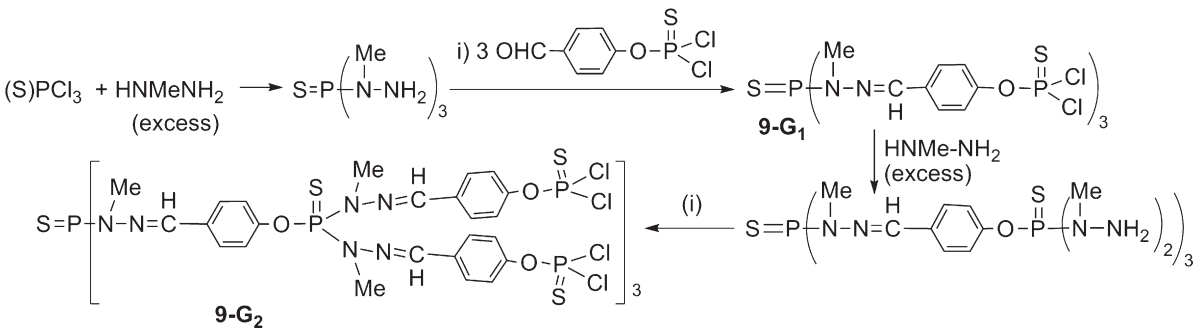

Figure 13 Synthesis of small dendrimers having the N(Me)N = CH–C_6H_4–OP = S linkages in a reverse order, compared to the method shown in Figure 9.

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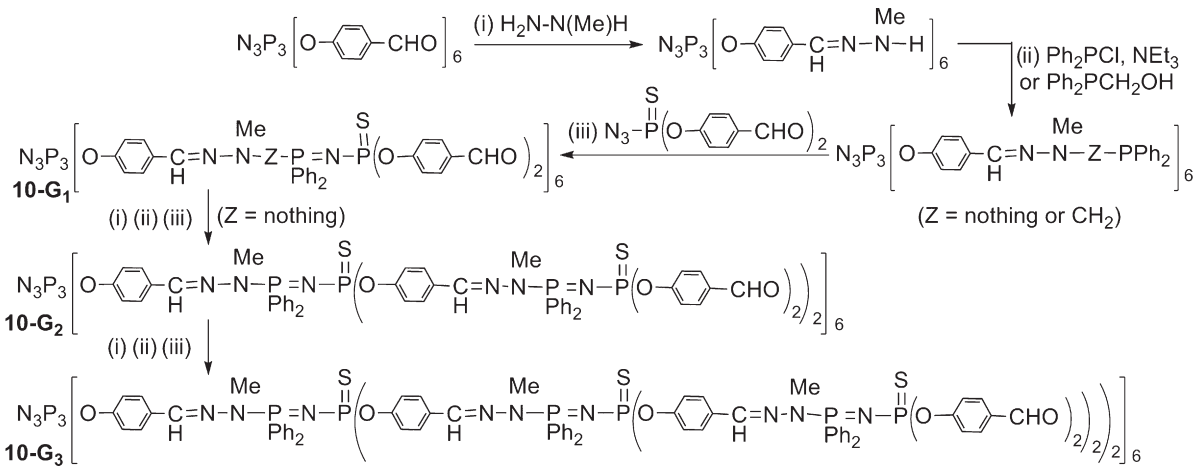

Figure 14 Three-step method of synthesis of dendrimers incorporating P = N–P = S linkages.

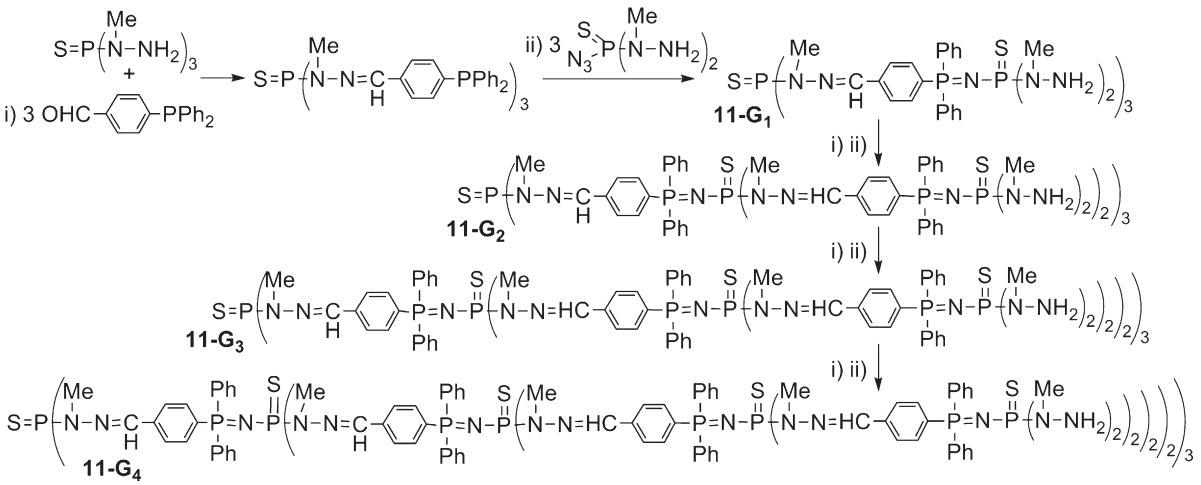

Figure 15 Two-step method of synthesis of dendrimers incorporating P = N–P = S linkages.

second step was a Staudinger reaction between the phosphine and a phosphorus azide linked to two methylhydrazine. The repetition of both steps was carried out up to the fourth generation **11-G$_4$**.[45] These compounds have three nitrogen atoms around the phosphorus of the branching points (**Figure 15**).

5.24.2.2 Accelerated Syntheses of Dendrimers

Despite the numerous interesting and often unique properties of dendrimers, they suffer from a main drawback, that is, their cumbersome and tedious stepwise synthesis. Thus, any method allowing a more rapid increase of the number of end groups is particularly welcome. Hyperbranched polymers appear as an attractive alternative to dendrimers, due to their simple one-pot synthesis. Thus, we designed a protected branched monomer having two types of functions in a 1:2 ratio. The deprotected functions should react readily intermolecularly. The Staudinger reaction was chosen, due to the absence of byproducts and to its high yield. The monomer had one azide and two protected phosphines, which were deprotected by bases. Various hyperbranched polymers were obtained, with different molar masses and mass distributions, depending on the temperature, the reaction time, the solvent, the concentration, and the type of amine for the deprotection. However, the degree of branching was found very high and practically identical (0.83–0.85), irrespective of the conditions used, and all these polymers possess P = N–P = S linkages in their structure (**Figure 16**).[46]

The polydispersity was very high for these hyperbranched polymers (from 1.5 to 8, depending on the sample), and the properties, for instance, the intrinsic viscosity that slowly increased with the molecular weight, were different from those expected for dendrimers. In order to relate these differences eventually to the topological structure or to the chemical structure, dendrimers issued from the same monomer were also synthesized by a stepwise process. The time needed to synthesize these dendrimers was shorter than for to classical dendrimers, because the deprotection of the phosphine and the Staudinger reaction were performed by a one-pot process (**Figure 17**). The series of compounds **12-G$_n$** have the normal behavior expected for dendrimers, in particular concerning the very low polydispersity (the highest value is 1.029 for **12-G$_5$**), and the variation of intrinsic viscosity with molecular weight was a bell-shaped curve. It can be concluded from these results that the replacement of dendrimers by hyperbranched

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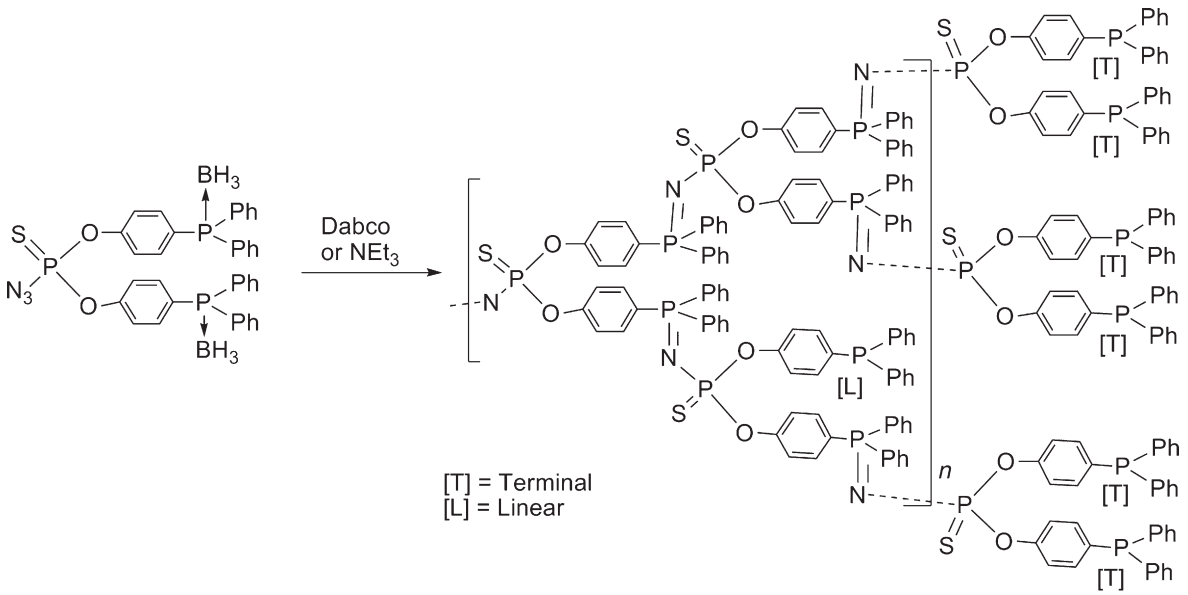

Figure 16 Hyperbranched polymers built by Staudinger reactions.

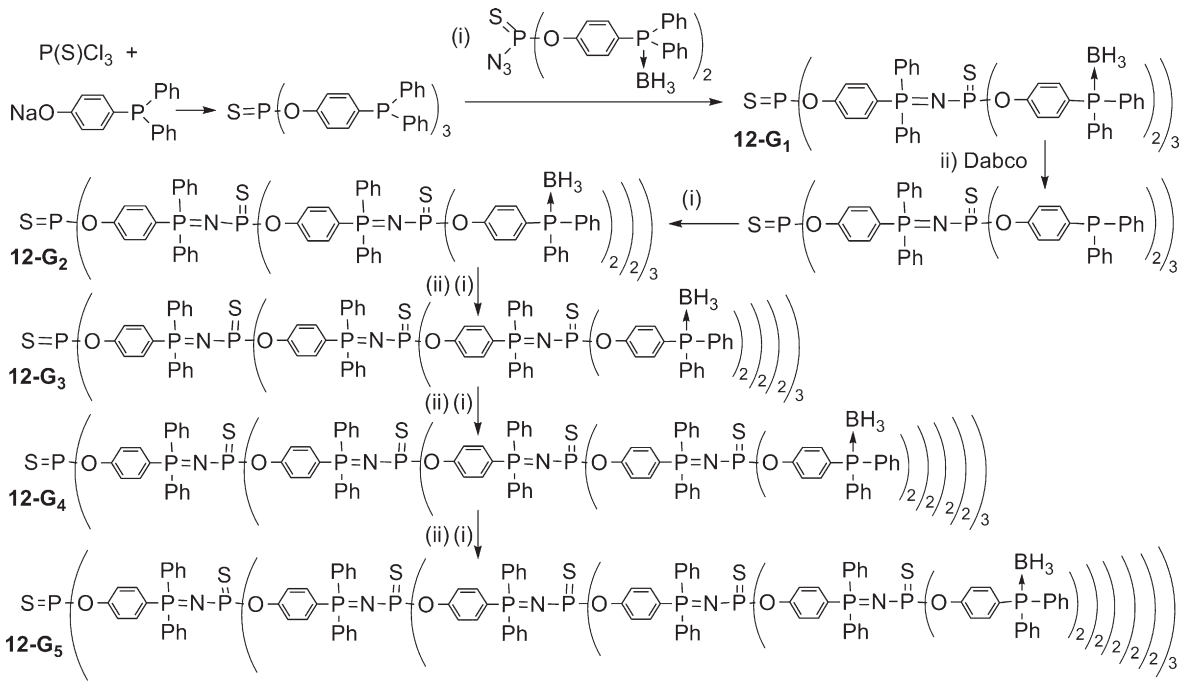

Figure 17 Two-step method of synthesis of dendrimers incorporating P = N–P = S linkages having the same branches as the hyperbranched polymer shown in **Figure 16**.

polymers having the same chemical composition might not be a good solution, the physicochemical properties being really different.[46]

5.24.2.2.1 Accelerated syntheses using branched monomers at each step

In fact, the most powerful recent strategy to grow rapidly dendrimers is the 'orthogonal coupling strategy',[47] which consists in using two types of branched units (AB_n and $CD_{n'}$ monomers, where n and n' are generally equal to 2). This method gives at each step a new generation of layered dendrimers, but it has been mainly used with a set of completely independent classes of protecting groups. To avoid the inconvenience of using protection/deprotection strategies, we have modified our main method of synthesis, by using a 5-hydroxyisophthaldehyde (two CHO groups) instead of 4-hydroxybenzaldehyde. In this way, each reaction step allowed multiplying by two the number of terminal groups, instead every two steps by our classical method (**Figure 18**).[48] The expanded structure of the largest compound obtained in

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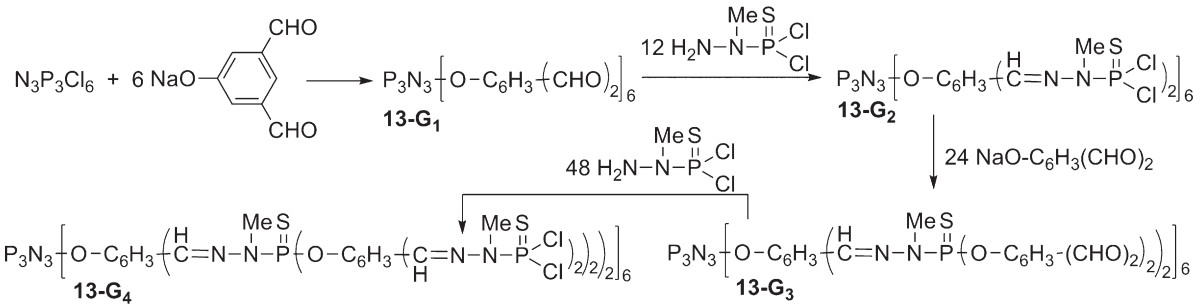

Figure 18 Synthesis of layered dendrimers using two types of branched monomers by a method derived from the one shown in **Figure 9**.

this series (**13-G$_4$**) is shown in **Figure 19**, together with the second generation obtained after the same number of steps with the method shown in **Figure 9**. A clear increase of the density is easily seen.

We have also elaborated a number of branched monomers based on **A, B, C**, and **D** functions in which **A** reacts only with **D**, and **B** reacts only with **C**, without needing any type of protection. The functions were chosen taking advantage of two quantitative reactions shown in the previous parts of this chapter, that are the condensation reaction of hydrazine with aldehyde, and the Staudinger reaction of phosphine with azide. Thus, the goal was to synthesize compounds in which **A** is NH_2, **B** is PPh_2, **C** is N_3, and **D** is CHO. This goal was first achieved by designing compounds $H_2NNMeP(S)(OC_6H_4PPh_2)_2$ (**AB$_2$**) and $N_3P(S)(OC_6H_4CHO)_2$ (**CD$_2$**). Starting from a trialdehyde core (**D$_3$** type), the reaction of the **AB$_2$** monomer afforded the first generation; then, the reaction with the **CD$_2$** monomer afforded directly the second generation. Using again the **AB$_2$**, then the **CD$_2$** monomers gave finally the fourth generation of the layered dendrimers **14-G$_4$**. In this series, the dendrimers have either aldehydes or phosphines as end groups. This method is very powerful and generates only N_2 and H_2O as byproducts, thus it was even possible to synthesize the fourth generation in a one-pot (but multistep) process, adding periodically strictly stoichiometric amounts of reagents. The purity of the fourth generation obtained by this one-pot process was found very close to that of the same generation **14-G$_4$** obtained by the stepwise process, with purifications at each step (**Figure 20**).[49]

A real 'Lego' chemistry was developed using the same orthogonal concept. In particular, **CA$_2$** and **DB$_2$** monomers were designed in which the **A, B, C**, and **D** functions are the same as previously mentioned. The reaction was carried out also up to the fourth generation, affording another type of layered phosphorus dendrimers. In this series, the dendrimers **15-G$_n$** have either NH_2 or phosphines as terminal groups (**Figure 21**).[50]

5.24.2.2.2 Accelerated syntheses using highly branched monomers

The same concept was extended to monomers having a larger number of functional groups, in order to multiply more rapidly the number of terminal groups. In particular, $N_3P_3Cl_6$ offers the opportunity to differentiate the reactivity of one chlorine atom among six, in order to graft specifically either one or five functions, as we have previously shown in **Figure 3**. **AB$_5$** and **CD$_5$** monomers based on the cyclotriphosphazene scaffold were synthesized in this way. These highly branched monomers may rapidly induce problems of steric hindrance, thus they were used first in combination with the **AB$_2$** and **CD$_2$** monomers shown previously. The successive reaction of **AB$_2$** and **CD$_5$** monomers was carried out up to the fourth generation **16-G$_4$** without any particular problem (**Figure 22**).[51]

Another attempt was made using **AB$_5$** and **CD$_2$**. In this case, an important steric hindrance was expected at the first generation; indeed the condensation reaction was abnormally slow and needed 4 days at 100 °C to go to completion, whereas a few hours at room temperature are generally sufficient for such condensations. However, the next steps occurred without any problem; thus the synthesis was carried out also up to the fourth generation **17-G$_4$** (**Figure 23**).[51] A comparison of the crowding of the second generations dendrimers **16-G$_2$** and **17-G$_2$** shows that the interior of the latter is more dense, despite the fact that they have exactly the same number of aldehyde terminal groups (60) (see **Figure 24** for a graphical comparison).

Despite the crowding observed for compound **17-G$_1$**, the synthesis using both **AB$_5$** and **CD$_5$** monomers was attempted. Each step needed several days to go to completion, and the synthesis was stopped at the third generation **18-G$_3$**; no attempt was made to synthesize the next generation, due to the steric hindrance of the third-generation outer shell (**Figure 25**).[51]

Dendrimer **18-G$_3$** was synthesized in only three steps from the core and it had 750 phosphine end groups. A comparison of the number of end groups obtained at each step (not at each generation) starting in all cases from the hexafunctional N_3P_3 core, and using the methods described in **Figure 9** and **Figures 20–23** and **25** shows a dramatic acceleration of the increase of the number of end groups when the **AB$_5$** and **CD$_5$** monomers are used (**Figure 26**).

Very recently, we have elaborated another series of dendrimers built with a highly branched monomer, but using the 'click' reaction of organic azides with alkynes, which affords triazole rings.[52] The first layer of triazoles was obtained by reaction of the hexaazide **19-G$_0$** built from $N_3P_3Cl_6$ and highly branched monomer possessing one alkyne and five alcohol groups, also elaborated from $N_3P_3Cl_6$. Successive reactions of the alcohols with $SOCl_2$ and NaN_3 afforded the first-generation dendrimer **19-G$_1$** possessing 30 azide terminal groups. At this step, the click reactions could have been performed again with the highly branched monomer, but it was with an alkyne

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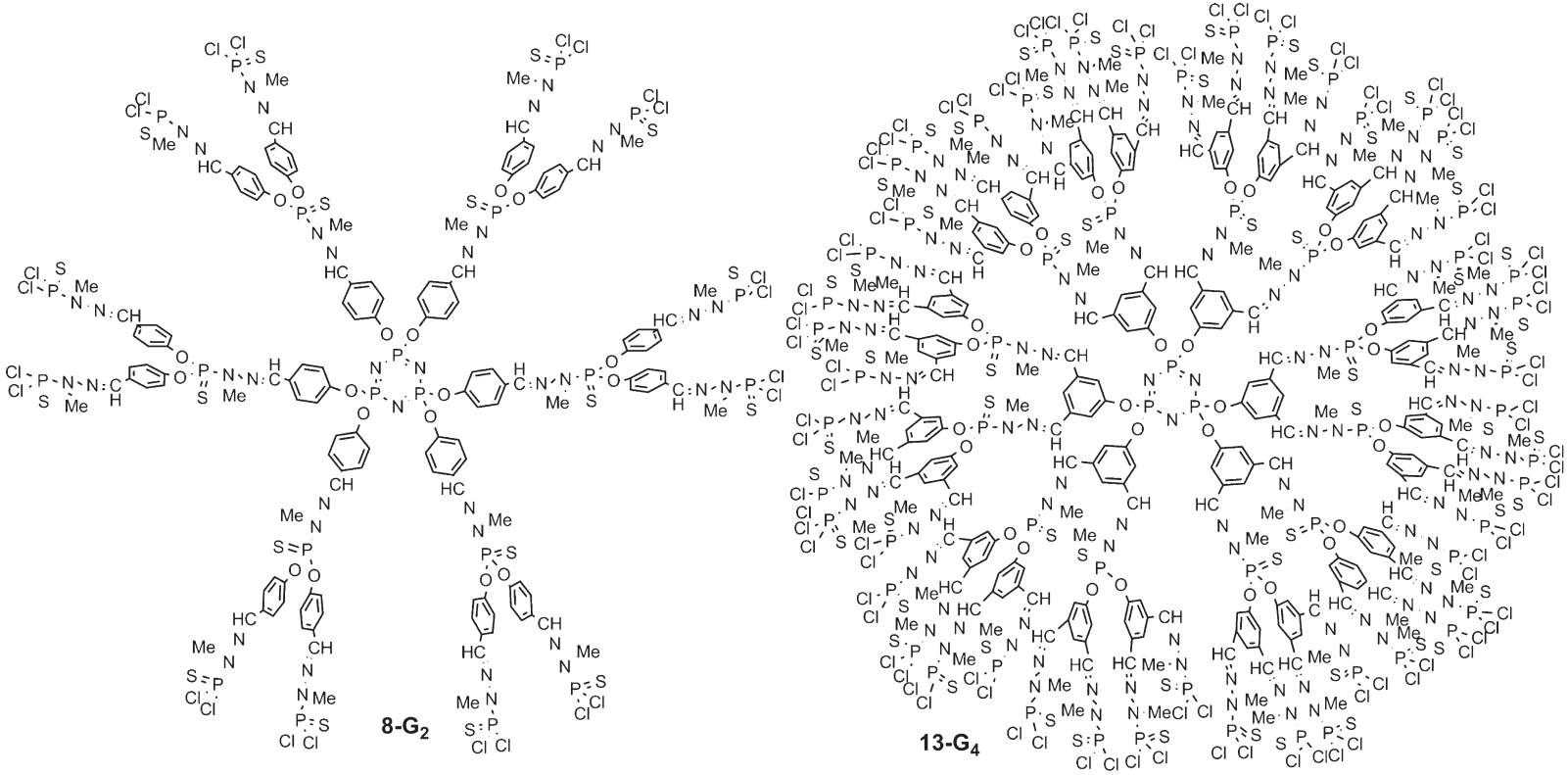

Figure 19 Comparison of the structure of the dendrimers obtained after 4 steps using the method shown in **Figure 9** (**8-G$_2$**) and the method shown in **Figure 18** (**13-G$_4$**).

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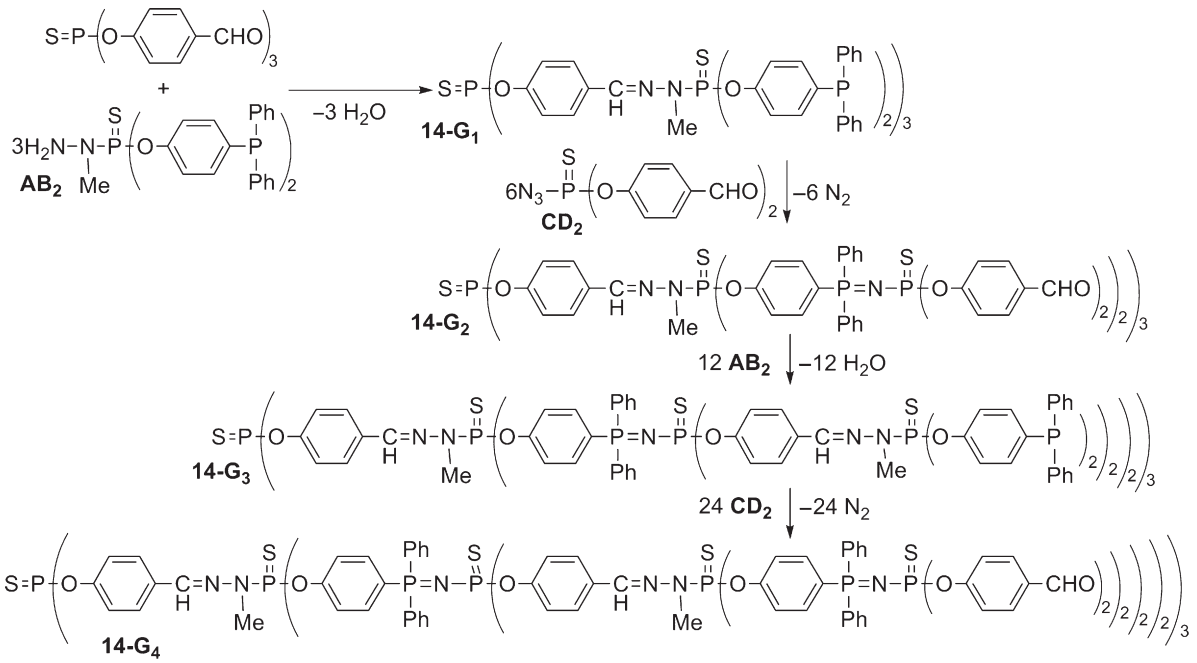

Figure 20 Synthesis of layered dendrimers using condensation reactions and Staudinger reactions with **AB$_2$** and **CD$_2$** branched monomers.

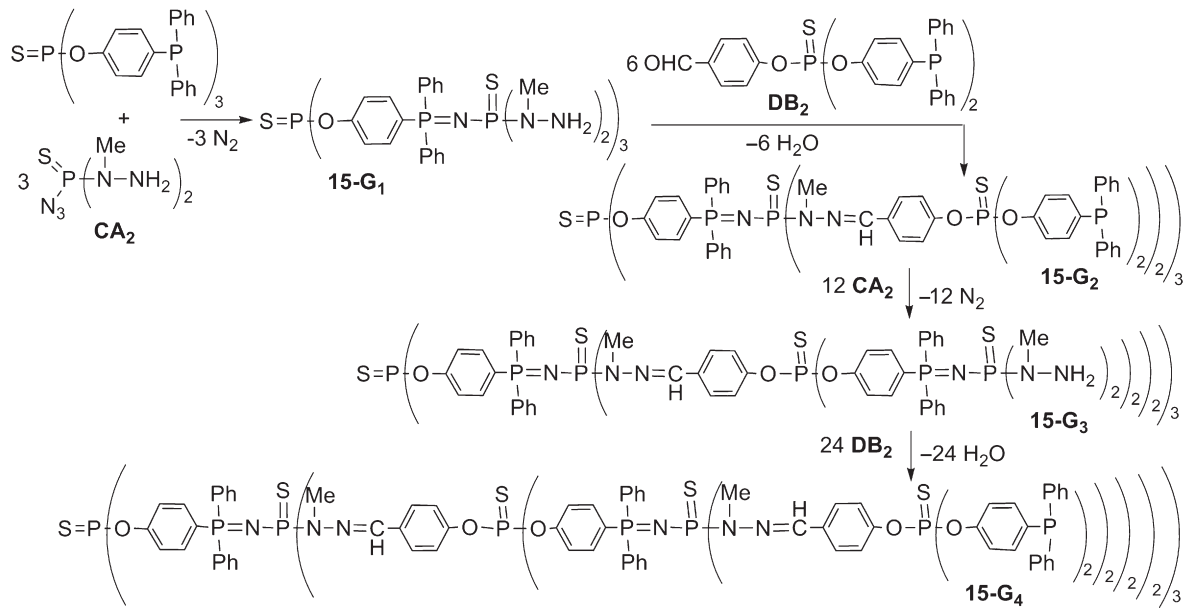

Figure 21 Synthesis of layered dendrimers using condensation reactions and Staudinger reactions with **CA$_2$** and **DB$_2$** branched monomers.

diphosphonate, which allowed decorating the surface of this dendrimer with phosphonate groups (Figure 27).[53]

5.24.3 Syntheses of Phosphorus-Containing Dendrons

We have published in 2006 a review about phosphorus-containing dendrons.[54] In some cases, these dendrons can be used as building blocks to elaborate more sophisticated dendritic architectures, as will be emphasized later. One may note that, contrary to what is shown in Figure 2, the phosphorus dendrons are not synthesized by a convergent process, but by a divergent process, as for most dendrimers.

5.24.3.1 Synthesis of Dendrons from Phosphines

In most cases, we have elaborated dendrons starting from a functionalized phosphine reacted by the Staudinger reaction with the **CD$_2$** monomer, then the dendron was grown using the

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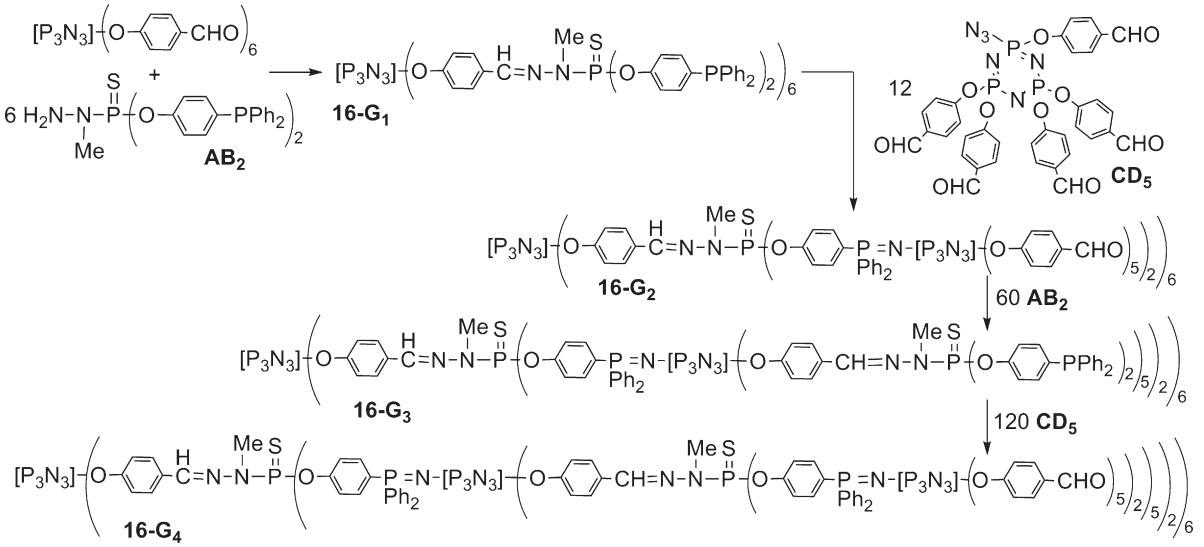

Figure 22 Synthesis of layered dendrimers using condensation reactions and Staudinger reactions with **AB$_2$** and the highly branched monomer **CD$_5$**.

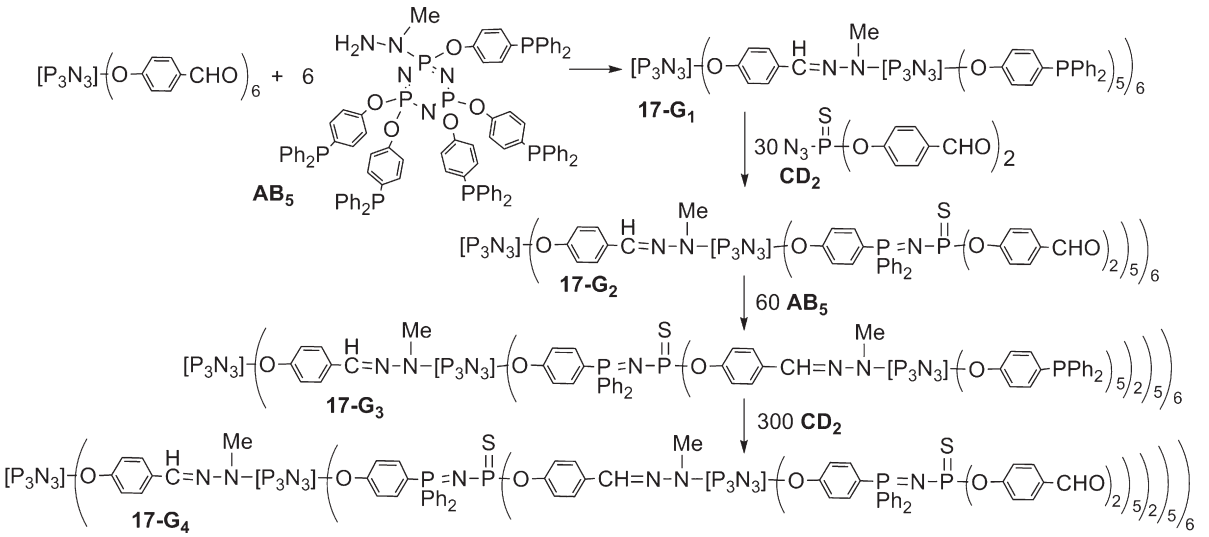

Figure 23 Synthesis of layered dendrimers using condensation reactions and Staudinger reactions with **CD$_2$** and the highly branched monomer **AB$_5$**.

same method than in Figure 9. The use of Staudinger reactions allowed us to synthesize various types of dendrons possessing a R–PPh$_2$=N–P=S group at the core. The most often used R substituent was the vinyl group **20**,[26] but an allyl **21**,[24] a styryl **22**,[24] a methyl **23**,[55] a protected benzaldehyde **24**,[55] a triethoxysilane **25**,[56] a diethoxyphosphonate **26**,[27] and a cage derivative **27** (tris(1,2-dimethylhydrazino)diphosphane) and its *p*-cymene ruthenium complex **28**[57] were also used as cores of these dendrons (Figure 28). In most cases, the synthesis of the corresponding dendrons was carried out up to generation 3. Obviously, the growing of the dendrons could have been performed up to higher generations. However, it was already stopped at the third generation in order to follow the reactions at the core when some of these dendrons were used as building block for more complex structures. The synthetic process leads directly to the end groups P(S)Cl$_2$ (case a) and CHO (case b). Various functionalized end groups have also been grafted starting from these functions. Most widely, the substitution reaction of Cl in the last step of the synthetic process was used, by phenols (case e)[58] generally functionalized, in particular by nitrile (case c),[26] dimethylamine (case d),[26] diphenylphosphine (case f),[56,58] or its ruthenium complex (case g), trifluoromethane (case h),[59] iminophosphine free or complexed (cases m, n),[27] monophosphine and diphosphine (cases o, p), and Ru complex (case q).[60] The reaction of a diamine was also used (case j).[55] In a few cases, condensation reactions of hydrazines with the aldehyde end groups allowed the grafting of other functional groups, such as Girard T (case i),[61] hydrazine (case k), and diphosphine (case l).[55] All compounds obtained by this method are gathered in Table 1.

The method of synthesis shown above is not compatible with some kinds of functional groups; in particular, for those sensitive to water, the condensation step must be avoided. In consequence, we designed other ways of synthesis. For

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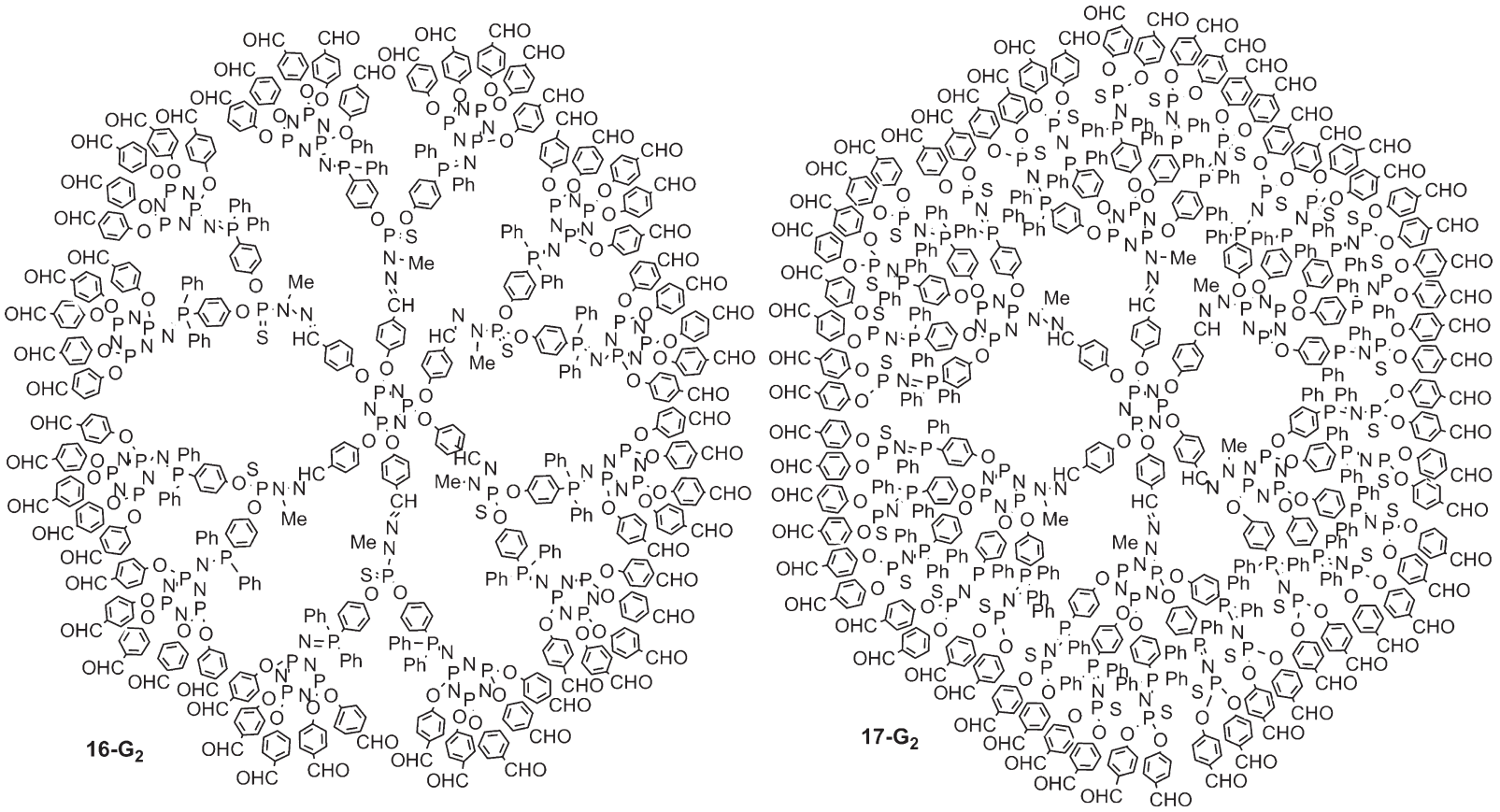

Figure 24 Comparison of the chemical structure of dendrimers **16-G$_2$** and **17-G$_2$**, both having 60 aldehyde terminal groups.

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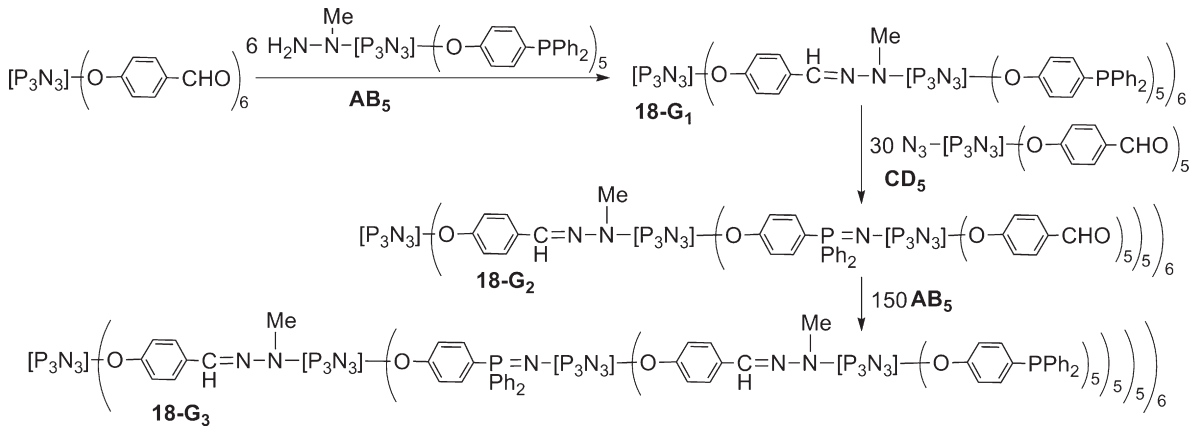

Figure 25 Synthesis of layered dendrimers using condensation reactions and Staudinger reactions with two highly branched monomers **AB$_5$** and **CD$_5$**.

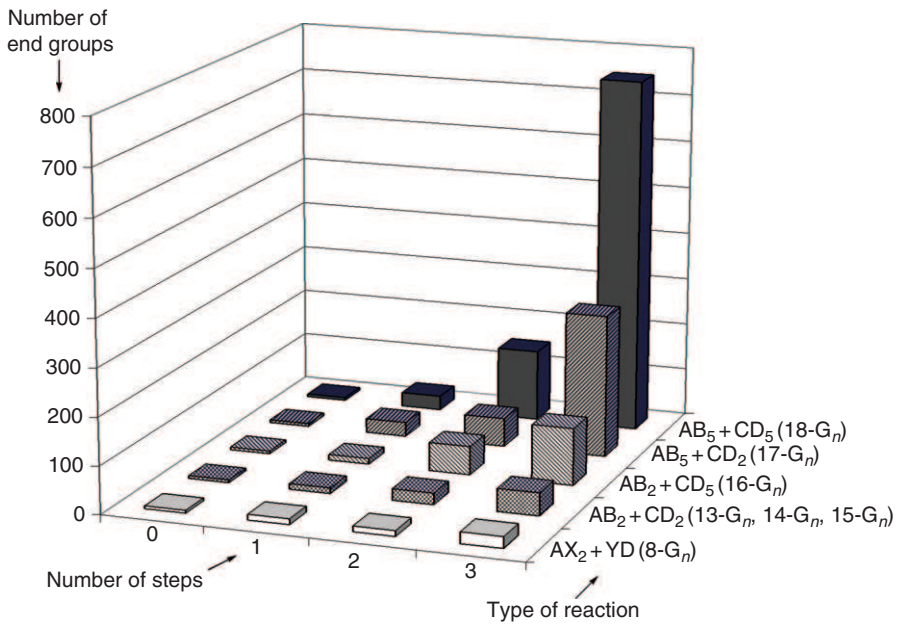

Figure 26 Comparison of the theoretical number of end groups, depending on the type of method used to build a dendrimer, and number of the corresponding series of dendrimers.

instance, the $Si(OEt)_3$ group is readily hydrolyzed by traces of moisture, and the dendron **30a-G$_n$** could be synthesized by our traditional method. Thus, the sodium salt $NaOC_6H_4PPh_2$ was used instead of $NaOC_6H_4CHO$, then the azide **29** was reacted via a Staudinger reaction, affording directly the third generation **30a-G$_3$** with $P(S)Cl_2$ end groups. Aldehydes were grafted in the last step using $NaOC_6H_4CHO$ (**Figure 29**). This method was also found useful for the grafting of other functional groups, such as a pyrene derivative (see, for instance, dendron **31-G$_2$** in **Figure 29**).[56]

5.24.3.2 Synthesis of Dendrons from Other Cores

The presence of chlorine at the core of a dendron is incompatible both with our traditional method of synthesis, in particular with the use of the strong nucleophile $NaOC_6H_4CHO$, and with the method shown in **Figure 29**, due to the use of the salt $NaOC_6H_4PPh_2$. Thus, the dendron grown from the chloromethyl phosphine oxide derivative **32b-G$_0$** was built using the repetition of three steps. The first one was the condensation reaction of methylhydrazine with aldehydes; the second one was another condensation reaction, between Ph_2PCH_2OH and the secondary NH of hydrazone. The third and last step before the repetition of the three steps was the Staudinger reaction of the phosphine end groups with the azide **CD$_2$**, which afforded again aldehyde end groups. This dendron was grown up to the fourth generation **32b-G$_4$** (**Figure 30**).[24]

The type of function located at the core of a dendron is of crucial importance for its properties, in particular for using it as building block for complex structures. In particular, the presence of a NH_2 function at the core should open large perspectives. We synthesized the second-generation dendron **33-G$_2$**,[62] obtained by a convergent process using a Staudinger

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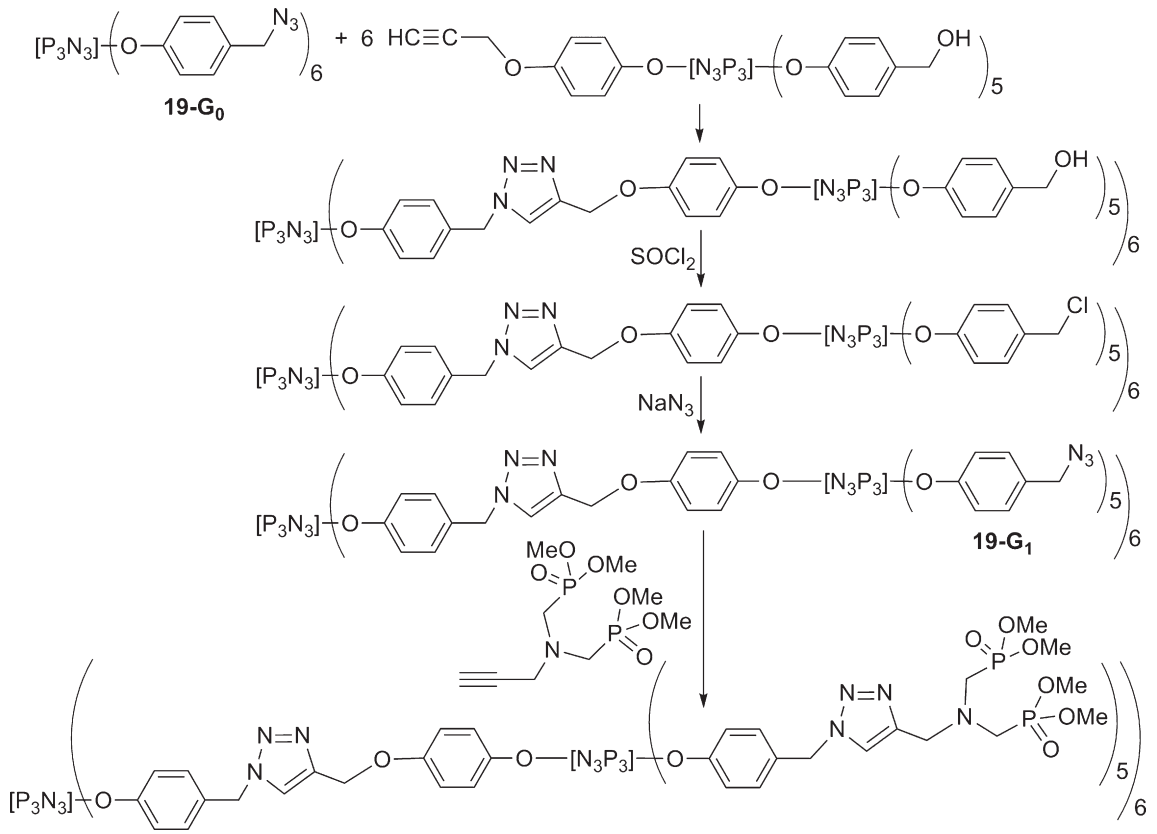

Figure 27 Synthesis of phosphorus dendrimers incorporating triazole units at each generation and using a highly branched monomer at the branching points.

reaction between $H_2NNMeP(S)(OC_6H_4PPh_2)_2$[49] and $N_3P(S)(OC_6H_4CO_2Me)_2$, synthesized according to a method we reported previously[59] (Figure 31).

5.24.3.3 Reactivity of Dendrons

The best way to graft NH_2 function at the core of a phosphorus-containing dendron consists in using the reactivity of the vinyl groups located at the core of dendrons **20-G$_n$**. Indeed, the P = N–P = S linkage induces an electro withdrawing effect on the functional group linked to the phosphazene (P = N). Though we also performed Diels–Alder additions on this vinyl group,[23] most of the reactions we carried out were Michael-type additions of primary and secondary amines. They were first tested with small compounds possessing one $CH_2 = CH–PPh_2 = N–PR_2 = X$ (X = O, S) linkage,[63] then applied to dendrons. In all cases, we used functionalized amines. The reaction worked nicely with primary amines (compounds **34–37**) and gave at the core a secondary amine together with an alkyne,[62] a triethoxysilyl group,[56,63] or even a phenol[58] (Figure 32 and Table 2). In the later case, the reaction of the amine was specific, no addition of the phenol was observed. Analogous reactions were obtained with secondary amines, such as diallylamine **38** and thiomorpholine **39**.[58] The reactions were carried out either at room temperature or by heating, depending on the rate of the addition, and using either a stoichiometric amount or a slight excess of reagent. The reactions were easily monitored by ^{31}P NMR, with a deshielding effect on the signal of the P = N group from δ = 10–12 ppm for **20-G$_n$** to δ = 17–18 ppm after addition.

A large excess of reagents must be used with diamines. Two cases can be distinguished: either the diamine possesses two identical primary amino groups, or it possesses one primary and one secondary amino group. In the former case, the use of several hundreds of equivalents prevented the coupling of two dendrons (cases **40** and **41** in Figure 32 and Table 2), as shown by the loss of symmetry of the diamine, evidenced by ^1H and ^{13}C NMR.[26,58] The reaction was expected to be more complicated when using nonsymmetrical diamines having two types of amino groups (primary and secondary). Indeed, besides avoiding the association of two dendrons as for symmetrical diamines, a regiospecific reaction of only one type of amine must be obtained. Such specificity was expected with methylhydrazine (considered as a special nonsymmetrical diamine), in which the most substituted nitrogen is generally more reactive. The reaction proceeded rapidly at room temperature with an excess of methylhydrazine (30 equiv.) leading to a single product, **42-G$_n$**, corresponding to the exclusive addition of the NMeH group.[26,58,59] The same specificity for the secondary amine was observed with the diamine **43**.[63]

A particular case of the reactions shown in Figure 32 was afforded by dendrons possessing as end groups functions able to react with amines, because both the core and the periphery reacted. An example of such compound was provided by the dendrons **20b-G$_n$**, in which the vinyl group at the core reacted in a Michael-type addition, whereas the aldehyde end groups

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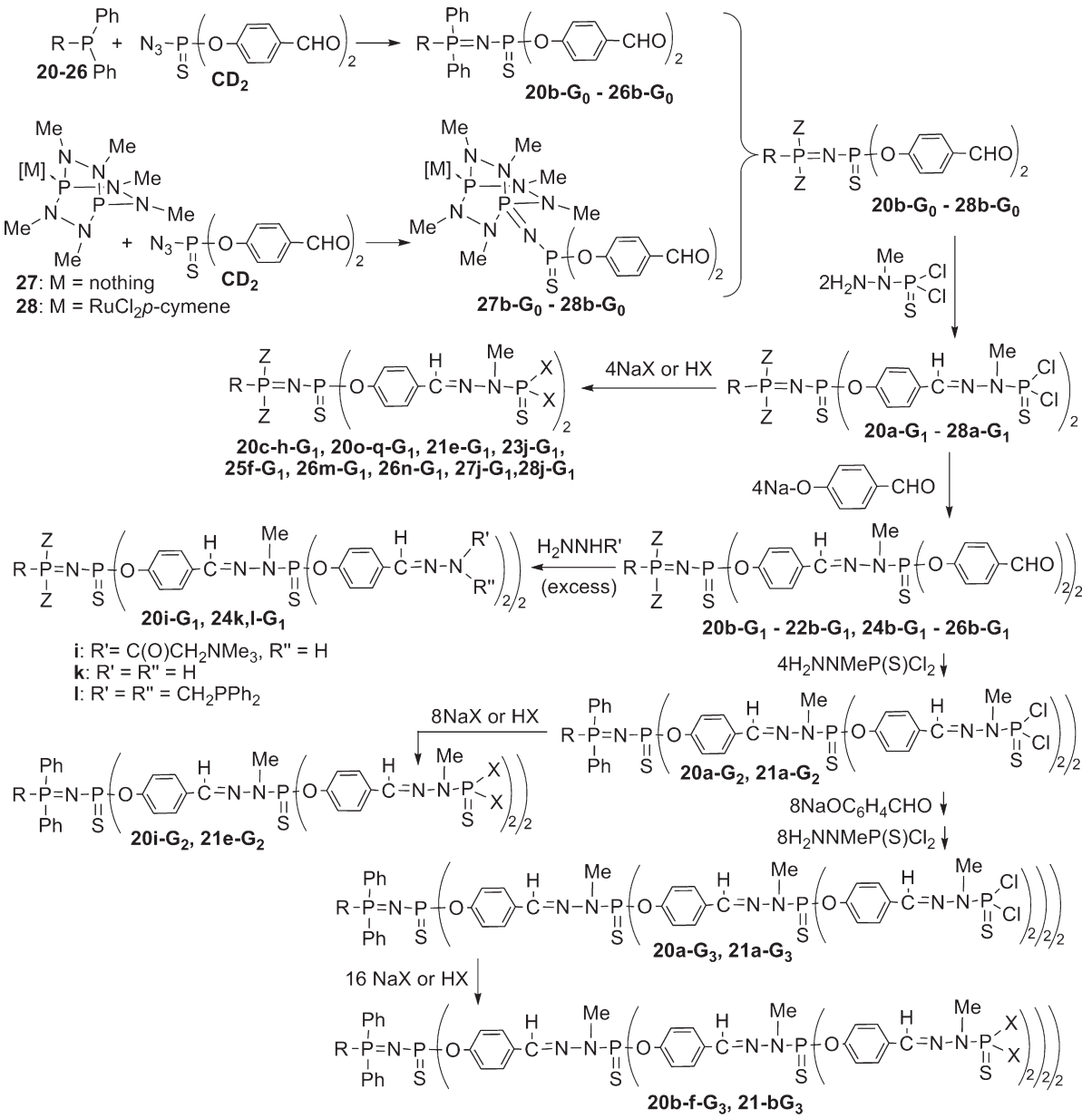

Figure 28 Synthesis and functionalization of dendrons built from phosphines. See **Table 1** for the definition of RPZ_2 and X.

Table 1 Functional groups located at the core (R and Z) and on the periphery to the most external PS group (X) of dendrons shown in **Figure 28**

Number	*RPZ_2*	*X*	*Highest G_n*	*References*
20a	$CH_2=CH\text{-}PPh_2$	Cl	3	26
20b	$CH_2=CH\text{-}PPh_2$	OC_6H_4 *p*-CHO	3	26
20c	$CH_2=CH\text{-}PPh_2$	OC_6H_4 *p*-CN	3	26
20d	$CH_2=CH\text{-}PPh_2$	OC_6H_4 *m*-NMe_2	3	26
20e	$CH_2=CH\text{-}PPh_2$	OC_6H_5	3	62
20f	$CH_2=CH\text{-}PPh_2$	OC_6H_4 *p*-PPh_2	3	62
20g	$CH_2=CH\text{-}PPh_2$	OC_6H_4 *p*-PPh_2RuCl_2*p*-cymene	1	64
20h	$CH_2=CH\text{-}PPh_2$	OC_6H_4 *p*-CF_3	1	63
20i	$CH_2=CH\text{-}PPh_2$	OC_6H_4*p*-$CH=NNHC(O)CH_2NMe_3^+$	2	65
20o	$CH_2=CH\text{-}PPh_2$	OC_6H_4*p*-$CH=NNMeCH_2PPh_2$	1	64
20p	$CH_2=CH\text{-}PPh_2$	OC_6H_4*p*-$CH_2CH_2N(CH_2PPh_2)_2$	1	64

(*Continued*)

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Table 1 (*Continued*)

Number	*RPZ₂*	*X*	*Highest* G_n	*References*
20q	$CH_2=CH\text{-}PPh_2$	$OC_6H_4p\text{-}CH=NNMeCH_2PPh_2\ RuCl_2p\text{-cym}$	1	64
21a	$CH_2=CH\text{–}CH_2\text{-}PPh_2$	Cl	3	24
21b	$CH_2=CH\text{–}CH_2\text{-}PPh_2$	$OC_6H_4\ p\text{-}CHO$	3	24
21e	$CH_2=CH\text{–}CH_2\text{-}PPh_2$	OC_6H_5	2	24
22a	$CH_2=CH\text{–}p\text{-}C_6H_4\text{-}PPh_2$	Cl	1	24
22b	$CH_2=CH\text{–}p\text{-}C_6H_4\text{-}PPh_2$	$OC_6H_4\ p\text{-}CHO$	1	24
23a	$Me\text{-}PPh_2$	Cl	1	58
23j	$Me\text{-}PPh_2$	$NHCH_2CH_2NHEt_2^+$	1	58
24a	$[\text{-}CH_2O\text{-}]_2CH\text{–}p\text{-}C_6H_4\text{-}PPh_2$	Cl	1	58
24b	$[\text{-}CH_2O\text{-}]_2CH\text{–}p\text{-}C_6H_4\text{-}PPh_2$	$OC_6H_4\ p\text{-}CHO$	1	58
24k	$[\text{-}CH_2O\text{-}]_2CH\text{–}p\text{-}C_6H_4\text{-}PPh_2$	$OC_6H_4\ p\text{-}CH=NNH_2$	1	58
24l	$[\text{-}CH_2O\text{-}]_2CH\text{–}p\text{-}C_6H_4\text{-}PPh_2$	$OC_6H_4\ p\text{-}CH=NN(CH_2PPh_2)_2$	1	58
25a	$(EtO)_3SiCH_2CH_2CH_2\text{-}PPh_2$	Cl	1	59
25b	$(EtO)_3SiCH_2CH_2CH_2\text{-}PPh_2$	$OC_6H_4\ p\text{-}CHO$	1	59
25f	$(EtO)_3SiCH_2CH_2CH_2\text{-}PPh_2$	$OC_6H_4\ p\text{-}PPh_2$	1	59
26a	$(EtO)_2P(O)CH=CHp\text{-}C_6H_4\text{-}PPh_2$	Cl	1	27
26b	$(EtO)_2P(O)CH=CHp\text{-}C_6H_4\text{-}PPh_2$	$OC_6H_4\ p\text{-}CHO$	1	27
26m	$(EtO)_2P(O)CH=CHp\text{-}C_6H_4\text{-}PPh_2$	$OC_6H_4p\text{-}N=CH\text{-}o\text{-}C_6H_4\text{-}PPh_2$	1	27
26n	$(EtO)_2P(O)CH=CHp\text{-}C_6H_4\text{-}PPh_2$	$OC_6H_4p\text{-}N=CH\text{-}o\text{-}C_6H_4\text{-}PPh_2PdCl_2$	1	27
27a	$P[(NMe\text{-}NMe)]_3P$	Cl	1	61
27j	$P[(NMe\text{-}NMe)]_3P$	$NHCH_2CH_2NEt_2$	1	61
28j	$(p\text{-cym})Cl_2RuP[(NMeNMe)]_3P$	$NHCH_2CH_2NEt_2$	1	61

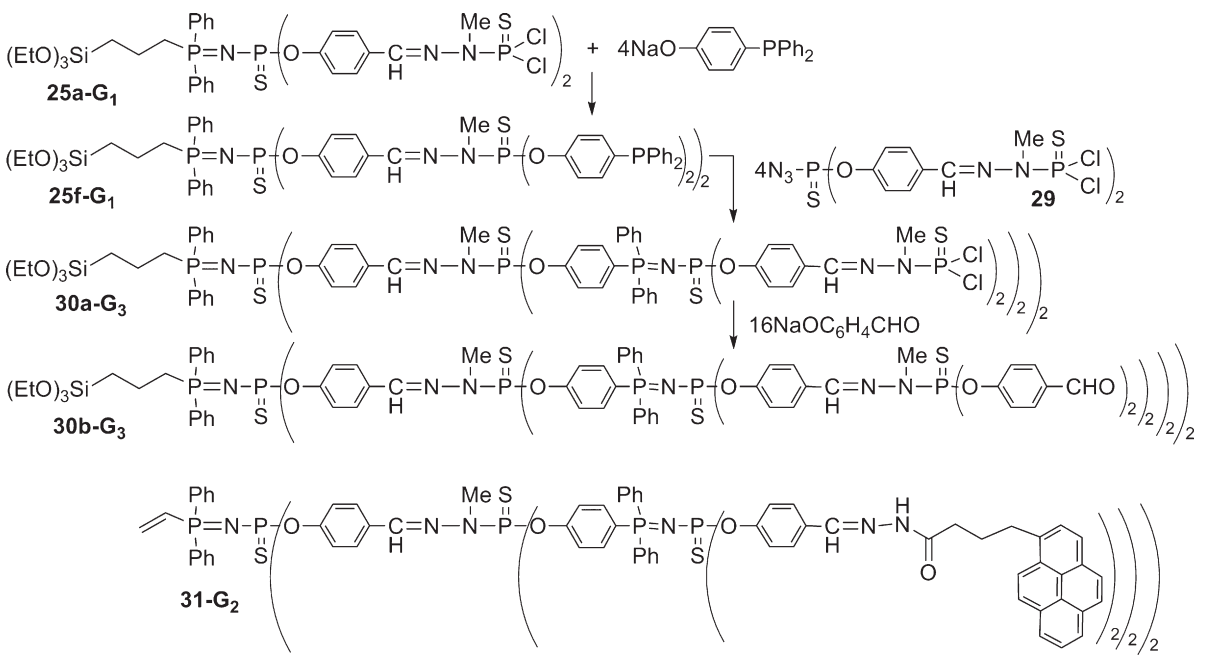

Figure 29 Synthesis of dendrons possessing P = N–P = S linkages for avoiding the condensation step assumed to be hydrolysis sensitive.

reacted via condensation reactions. The use of a large excess of methylhydrazine, necessary to prevent a polymerization reaction between the NH_2 of the core and the aldehydes, afforded the dendrons **44-G$_n$**. Their subsequent reaction with Ph_2PCH_2OH yielded the dendrons **45-G$_n$** possessing a diphosphine at the core and monophosphines as end groups (**Figure 33**).[26] With dendrons having a NH_2 as core such as **42c,d-G$_n$**, it was possible to obtain another dendron having an azide as core, as shown, for instance, by the condensation of two equivalents of the dendrons with one equivalent of the azidodialdehyde **CD$_2$**. The azide remaining at the core of **46c,d-[G$_3$]$_2$** (**Figure 33**)[26] could be used later to afford more

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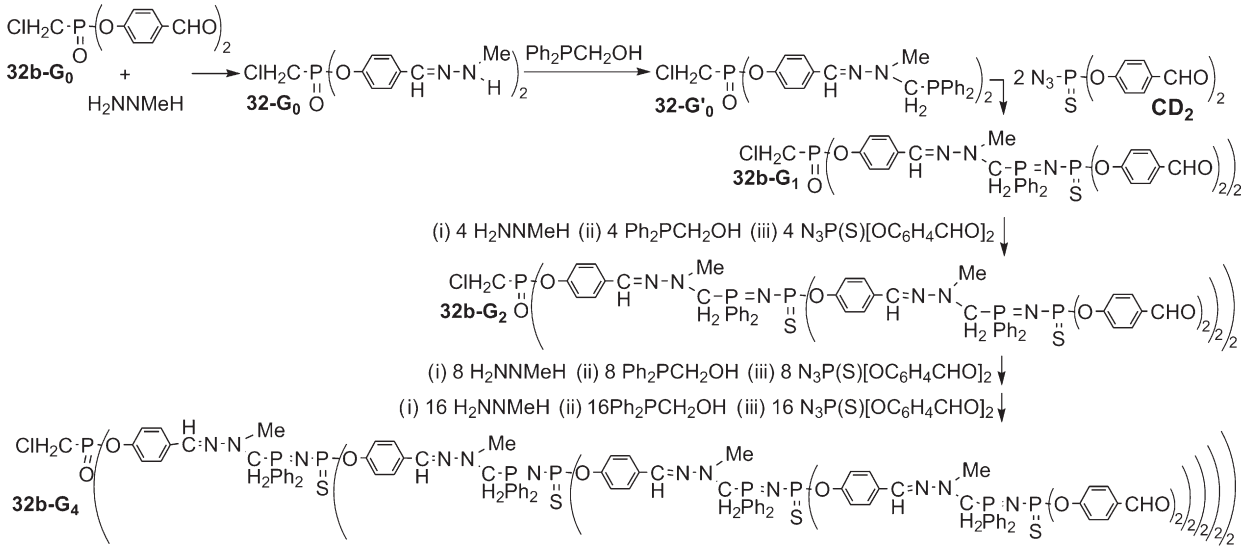

Figure 30 Three-step method of synthesis of dendrons.

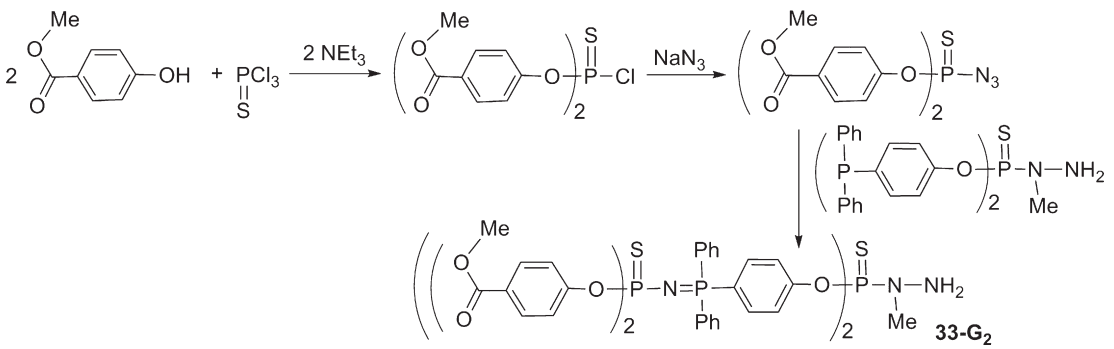

Figure 31 Convergent method of synthesis of a dendron.

elaborated structures. In fact, most of the reactions at the core of dendrons described in the previous sections were applied for the elaboration of special dendritic architectures, as we will see in the next part.

If the functions at the core and the surface of dendrons are chemically orthogonal, it is possible to develop independently a selective reactivity at both levels, as illustrated in Figure 34. The $P(S)Cl_2$ terminal functions of dendron **20a-G$_2$** were first reacted to graft triphenylphosphine, affording **20f-G$_2$**. In the second step, the core of **20f-G$_2$** was reacted with aminopentanol, affording **47-G$_2$**, and finally the phosphine terminal groups were complexed with rhodium affording **48-G$_2$**.[60] This sequence of reactions illustrates the versatility of the reactivity of dendrons.

5.24.4 Syntheses of Special Phosphorus-Containing Dendritic Architectures

Due to the presence of one (or a few) functional groups at the core of dendrons as shown in the previous paragraphs, they are useful bricks for building special dendritic architectures.

5.24.4.1 Special Dendritic Architectures Elaborated by Coupling Dendrons

The classical association of dendrons to cores can be applied also to very particular species such as the oligophosphazene **49**. The condensation of the NH_2 group located at the core of dendron **42h-G$_1$** affords the dendritic species **50-G$_2$**, possessing four different types of functions at the core, but only one type of end groups (Figure 35).[59]

The phosphorus-containing dendron **33-G$_2$** was especially synthesized to be grafted to the tetraphosphorus macrocycle **51** (Figure 36). The presence of such bulky substituents allowed for the first time the amplification of topological differences in the macrocycle. These differences become detectable by ^{31}P NMR, with the appearance of several signals for the phosphorus atoms included in the macrocyclic part of compound **52-G$_2$**.[62] Combination of both types of macromolecules (macrocycles and dendrimers) may increase the level of preorganization and may induce cooperative effects affording specific properties different from those produced by the separated parts.[64]

Another example of non-fully-symmetrical dendritic species but possessing only one type of end groups was

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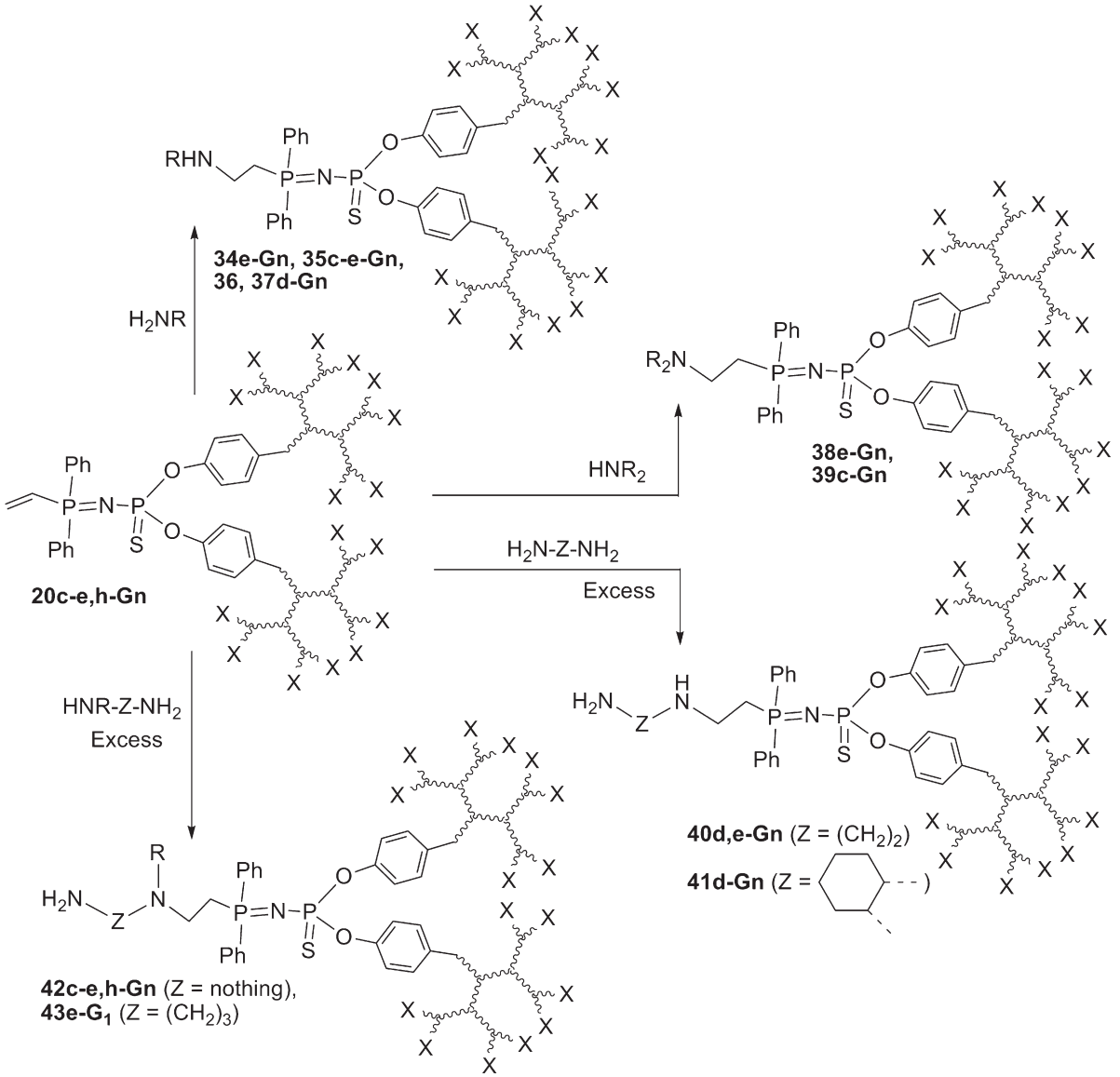

Figure 32 Addition of functionalized amines to the vinyl core of dendrons. See **Table 2** for the types of substituents R and X.

Table 2 Functional groups linked to the CH_2CH_2 group located at the core (R) and on the periphery to the most external PS groups (X) of the dendrons shown in **Figure 32**

Number	*R*	*X*	*Highest generation*	*References*
34e	$NHCH_2C{\equiv}CH$	$O–C_6H_5$	3	58
35c	$NH(CH_2)_3Si(OEt)_3$	$O–C_6H_4–p\text{-}CN$	3	56
35d	$NH(CH_2)_3Si(OEt)_3$	$O–C_6H_4–m\text{-}NMe_2$	3	56
35e	$NH(CH_2)_3Si(OEt)_3$	$O–C_6H_5$	1	63
36	$NH(CH_2)_3Si(OEt)_3$	Pyrene[a]	2	56
37d	$NH(CH_2)_2–p\text{-}C_6H_4–OH$	$O–C_6H_4–m\text{-}NMe_2$	3	58
38e	$N(CH_2CH=CH_2)_2$	$O–C_6H_5$	3	58
39c	$N[\text{-}CH_2–CH_2\text{-}]_2S$	$O–C_6H_4–p\text{-}CN$	3	58
40d	$NH–CH_2–CH_2–NH_2$	$O–C_6H_4–m\text{-}NMe_2$	3	26
40e	$NH–CH_2–CH_2–NH_2$	$O–C_6H_5$	3	58
41d	$NH–o\text{-}C_6H_{10}–NH_2$	$O–C_6H_4–m\text{-}NMe_2$	2	58
42c	$NMeNH_2$	$O–C_6H_4–p\text{-}CN$	3	26
42d	$NMeNH_2$	$O–C_6H_4–m\text{-}NMe_2$	3	26
42e	$NMeNH_2$	$O–C_6H_5$	3	58
42h	$NMeNH_2$	$O–C_6H_4–p\text{-}CF_3$	1	59
43e	$N((CH_2)_3NH_2)_2$	$O–C_6H_5$	1	63

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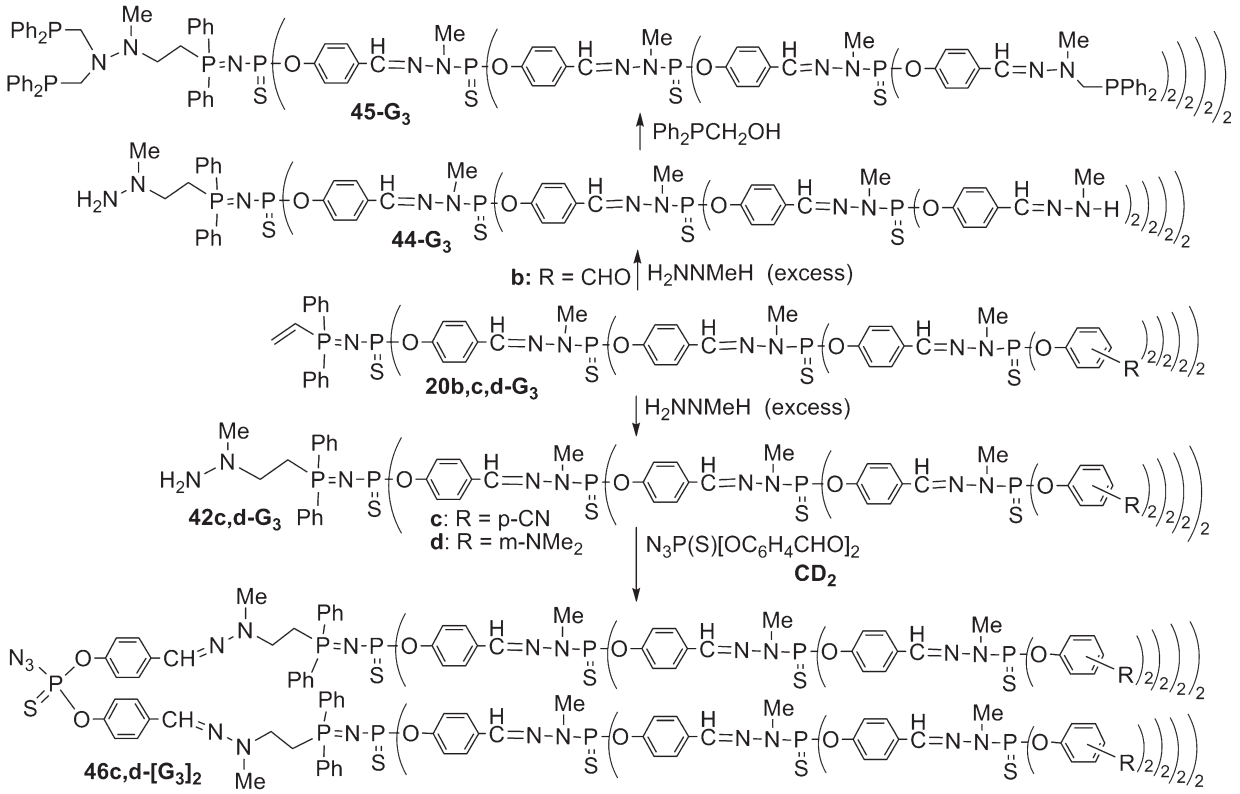

Figure 33 Identical reactivity at the core and surface of a dendron and association of two dendrons by their core.

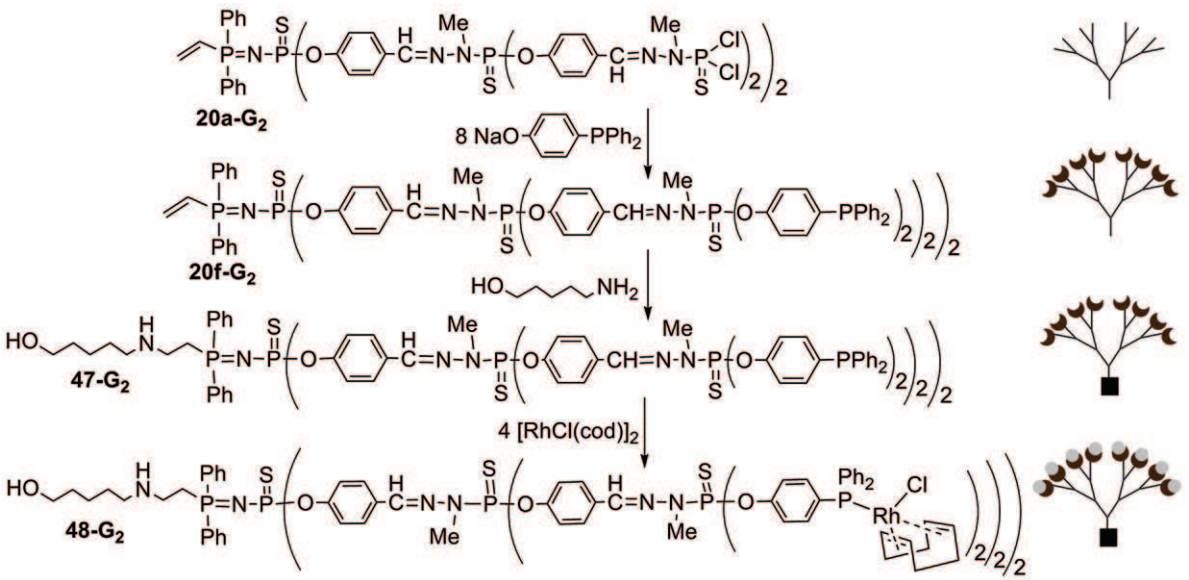

Figure 34 Different reactivity at the surface and the core of a dendron.

provided by the third-generation dendron 45-G_3 having phosphines both at the level of the core (2) and as terminal groups (16). The Staudinger reaction of this species with 18 equivalents of dendron 46d-$[G_3]_2$ possessing an azide as core occurred simultaneously at the level of the core and the surface of 45-G_3, affording the complex dendritic species 53. This is a kind of layered segment-block dendritic compound having a nonsymmetrical internal structure, despite the presence of 576 identical end groups (dimethylamino groups) (Figure 37).[26]

Analogous types of reactions were applied to two dendrons having a different type of terminal groups. In particular, the

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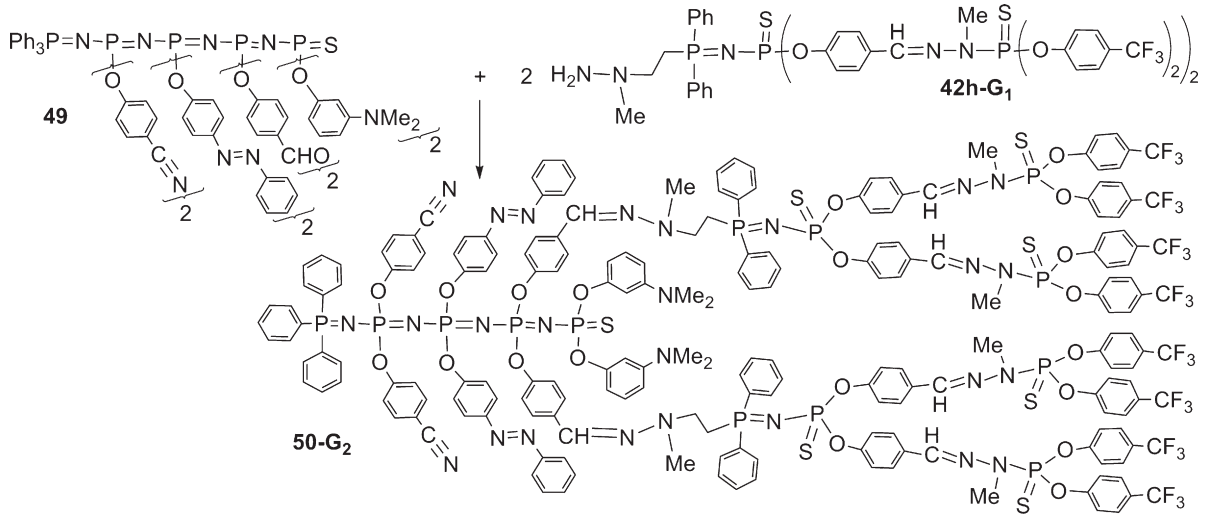

Figure 35 Multifunctionalized core of a dendrimer.

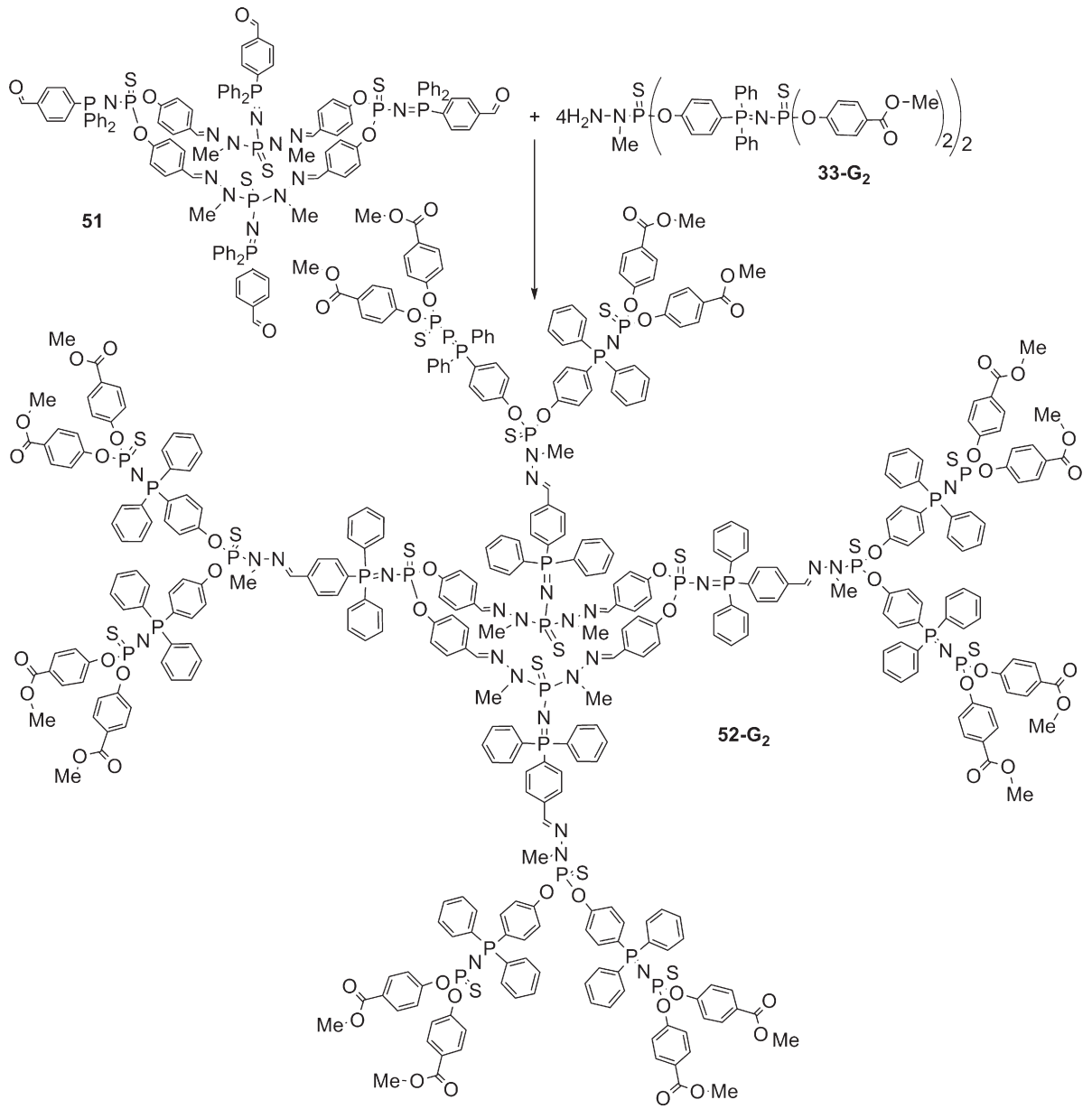

Figure 36 Synthesis of a dendrimer having a macrocyclic core.

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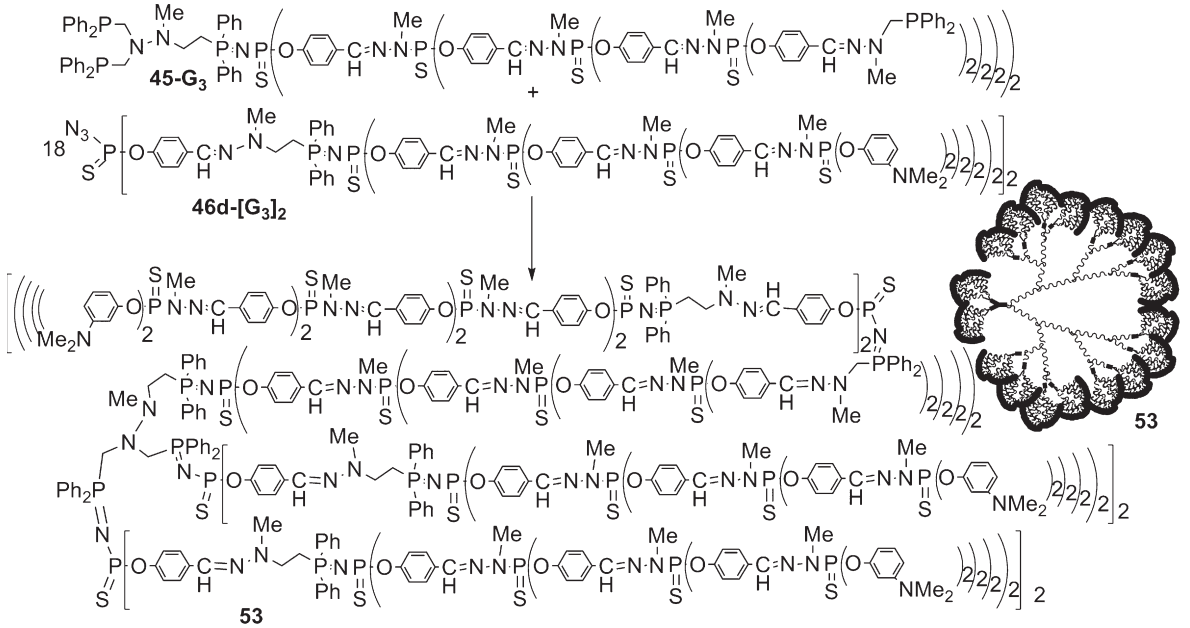

Figure 37 An unsymmetrical dendrimer possessing a single type of terminal groups.

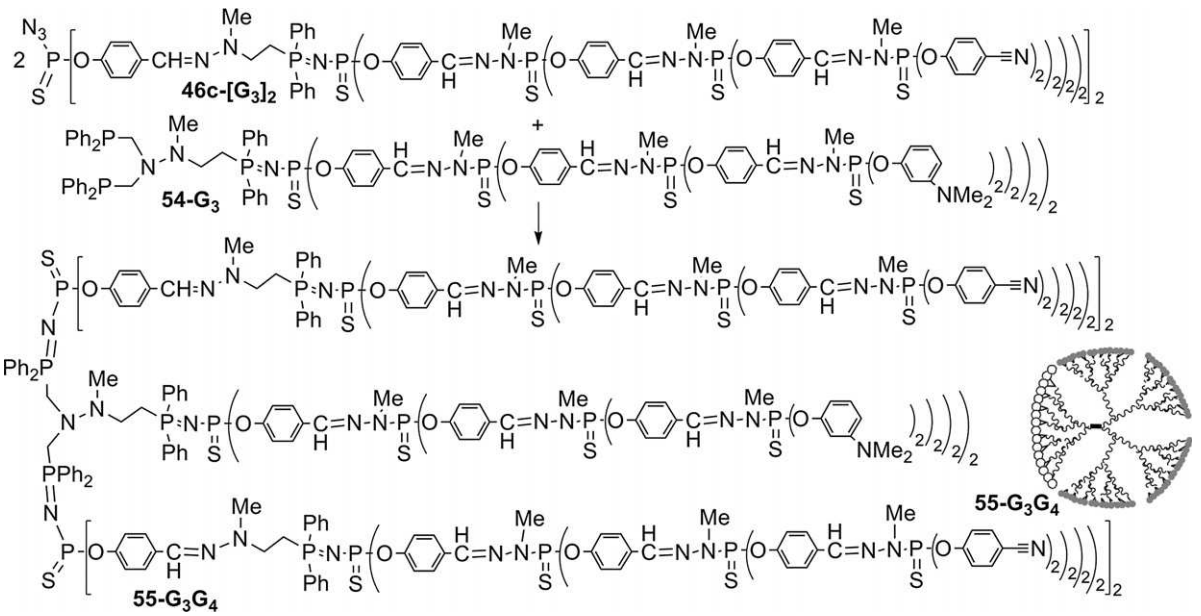

Figure 38 Unsymmetrical dendrimer having two types of terminal groups obtained by the coupling of two types of dendrons via Staudinger reactions.

Staudinger reaction of two equivalents of dendrons **46c-[G$_3$]$_2$** (32 nitrile end groups) with one equivalent of the dendron **54-G$_3$** (16 dimethylamino groups) afforded the dendritic species **55-G$_3$G$_4$** possessing 16 NMe_2 and 64 nitrile terminal groups (**Figure 38**).[26]

Michael-type additions are also a useful way for coupling two types of dendrons. For instance, Michael-type addition of the primary amine located at the core of dendron **41d-G$_2$** with the activated vinyl group of the core dendron **20e-G$_2$** afforded the 'Janus' species **56-G$_2$G$_2$**. This dendritic compound had eight phenoxy groups on one side and eight dimethylamino groups on the other side (**Figure 39**).[58]

The same Michael-type addition was performed with larger species, in particular with dendrons **20c,f-G$_3$** and **40d,e-G$_3$**. This reaction was compatible with several types of end groups, as shown by the isolation of the 'Janus' species **57cd-G$_3$G$_3$** and **57ef-G$_3$G$_3$**. The latter one is particularly interesting, because it possesses 16 diphenylphosphino groups on one side. The

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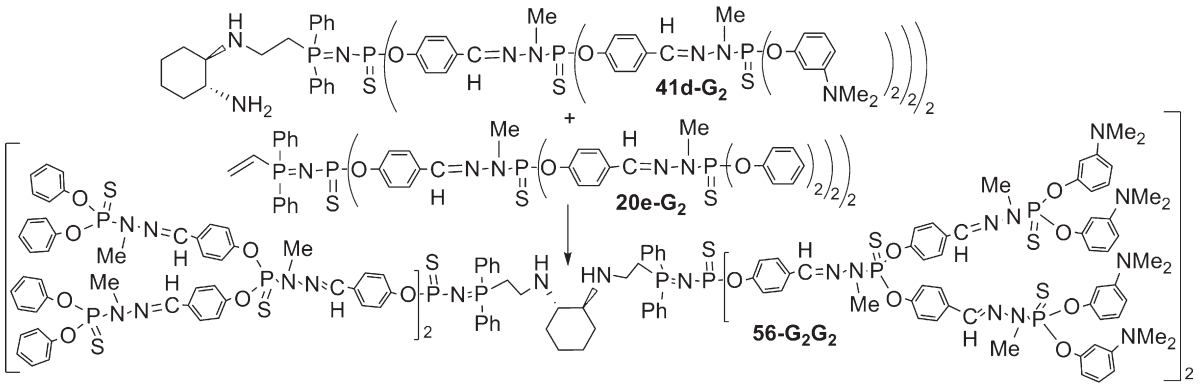

Figure 39 A dendrimer possessing two types of terminal groups obtained by Michael-type additions.

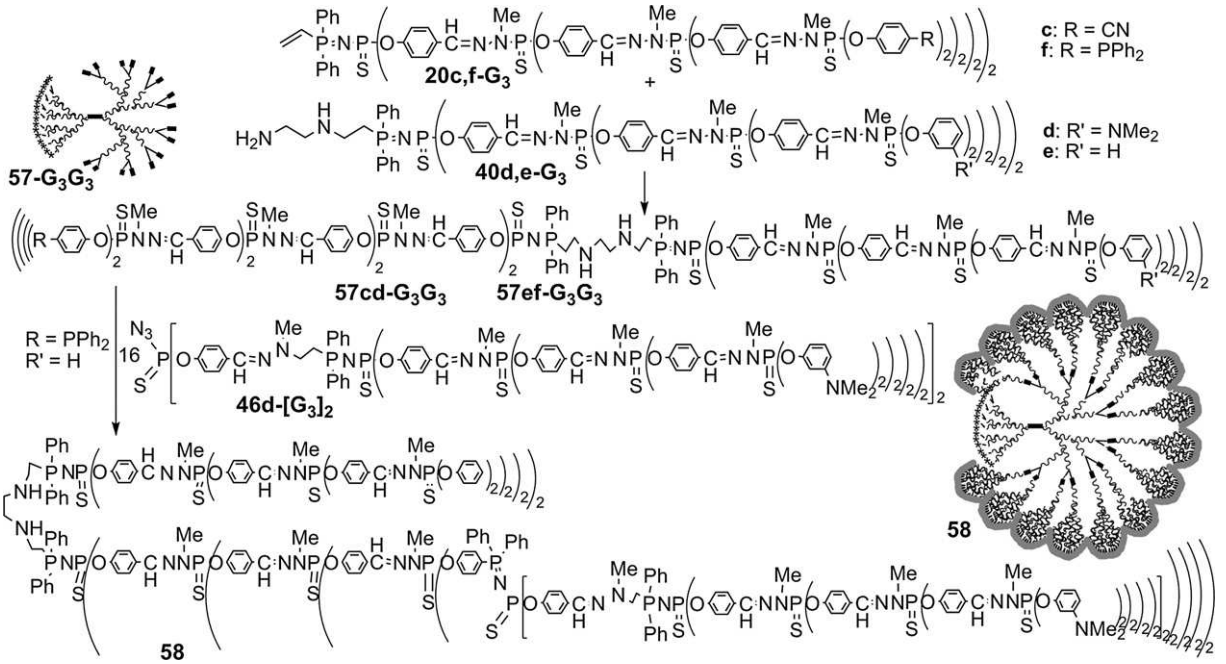

Figure 40 Association of two dendrons by Michael-type addition, followed by Staudinger reactions on one side of the surface.

reaction of 16 equivalents of dendron **46d-[G$_3$]$_2$** via Staudinger reactions afforded the dendritic species **58**, reminiscent of **53**. However, contrarily to **53**, compound **58** possesses two types of end groups, 16 phenoxy groups on one side and 512 dimethylamino groups on the other side (**Figure 40**).[58]

The Michael-type addition was also applied to dendrons having amines as terminal groups together with dendrons having carboxylates as terminal groups. Such an association was performed with dendrons of the same generation, affording in particular compounds **59-[G$_1$]-[G$_1$]** and **59-[G$_2$]-[G$_2$]**, but also to dendrons of different generations (see **Figure 41**). The amino groups of the bis-dendrons could be alkylated with MeI to afford ammoniums on one side and carboxylates on the other side.[65]

Other types of reactions could be used for coupling two dendrons, such as the classical 'peptide' coupling method applied to a dendron having a carboxylic acid as core (**60-G$_0$**) and a dendron having a primary amine as core (**61-G$_0$**), affording the fluorescent bis-dendron **62**. The other fluorescent bis-dendron **65** was obtained by condensation reaction between dendron **63-G$_1$** having hydrazine as core and dendron **64-G$_0$** having aldehyde as core (**Figure 42**). In both cases, the Boc-protected tyramine groups were deprotected by triflic acid, affording dendritic species having fluorophores on one side and ammonium groups on the other side.[66]

5.24.4.2 Special Dendritic Architectures Elaborated from Dendrons

The presence of P = N–P = S linkages inside dendrimers, obtained by Staudinger reactions as shown in particular in **Figures 14, 15, 17, 20–23, 25,** and **29–31** are particularly useful to obtain original types of dendritic structures. Indeed, these linkages have a mesomeric form ($^{+}$P–N = P–S^{-}) in which a

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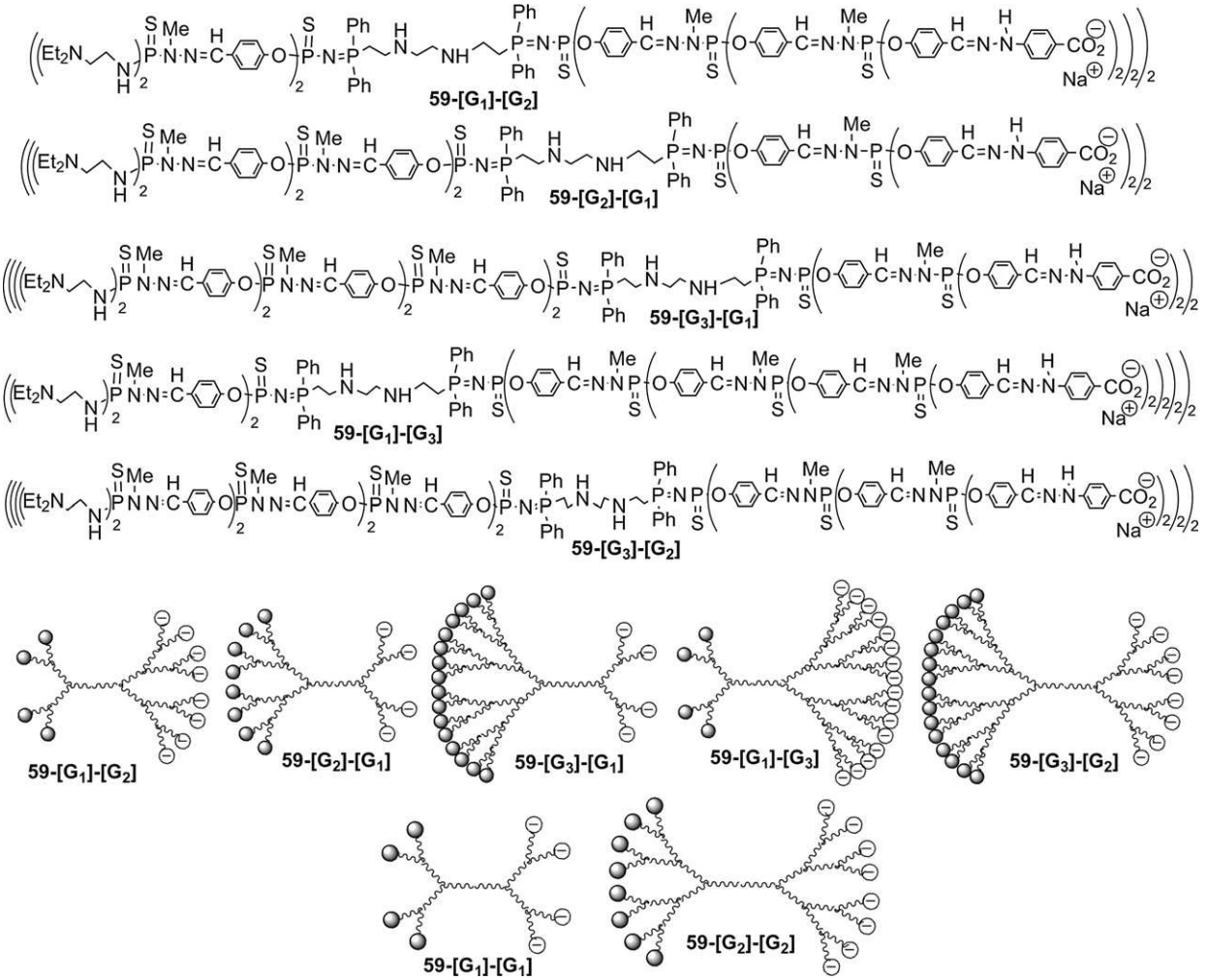

Figure 41 Chemical structure of unsymmetrical bis-dendrons of generations 1, 2, or 3, and their schematization.

negative charge is located on sulfur. Due to this particular structure, these linkages are able to undergo a specific alkylation on sulfur with alkyl triflates,[29] eventually functionalized.[67] This reaction is compatible with the presence of the other P = S groups in the dendrimer, which are not alkylated, as well as with P–Cl functions. The alkylation of sulfur induces a weakening of the phosphorus–sulfur bond, which can be easily cleaved by a nucleophilic phosphine such as $P(NMe_2)_3$,[68] affording tricoordinated phosphorus atoms (P^{III}) inside the structure, which can react in Staudinger reactions with various functionalized azides. This sequence of reactions was mainly applied to obtain special dendritic architectures from dendrimers (see the next paragraph) but it was also applied to the core of the dendron **66-G$_1$**. The alkylation affording **67a-G$_1$** was followed by anion exchange to avoid formation of triflic acid in the next step, giving **67b-G$_1$**. Reaction of four equivalents of *N*,*N*-diethylethylenediamine afforded **68-G$_1$**. The cleavage of the P–S bond by $P(NMe_2)_3$, followed by reaction of an azide gave the bis-dendritic species **69-G$_1$G$_0$**. Methylhydrazine, Ph_2PCH_2OH, and iron pentacarbonyle were successively added to **69-G$_1$G$_0$**, to finally afford compound **70-G$_1$G$_0$**. This compound had four ammonium groups on one side, ensuring the solubility in water, and two iron complexes on the other side (**Figure 43**).[55]

Another example of stepwise growing of new branches after the synthesis of a dendron was provided by compound **71-G$_1$**, which possesses two functional groups (phosphines) at the core. The reaction of **71-G$_1$** with the dialdehyde azide **CD$_2$** afforded **72-G$_1$G$_1$** having four aldehyde groups, which was used for the growing of new branches on one side. The building was carried out up to the third generation, applying the method of synthesis already shown in **Figure 9**. The resulting very unsymmetrical compound **72-G$_1$G$_3$** had four phenoxy groups on one side, and 16 aldehyde groups on the other side, which might be used for further reactions (**Figure 44**).[55]

5.24.4.3 Special Dendritic Architectures Elaborated from Dendrimers

The sequence of reactions applied to the P = N–P = S groups shown in **Figure 43** (alkylation, desulfurization, and Staudinger reaction) was in particular applied to the third-generation dendrimer **73-G$_3$**, having one layer of P = N–P = S groups constituting the first layer. The alkylation afforded

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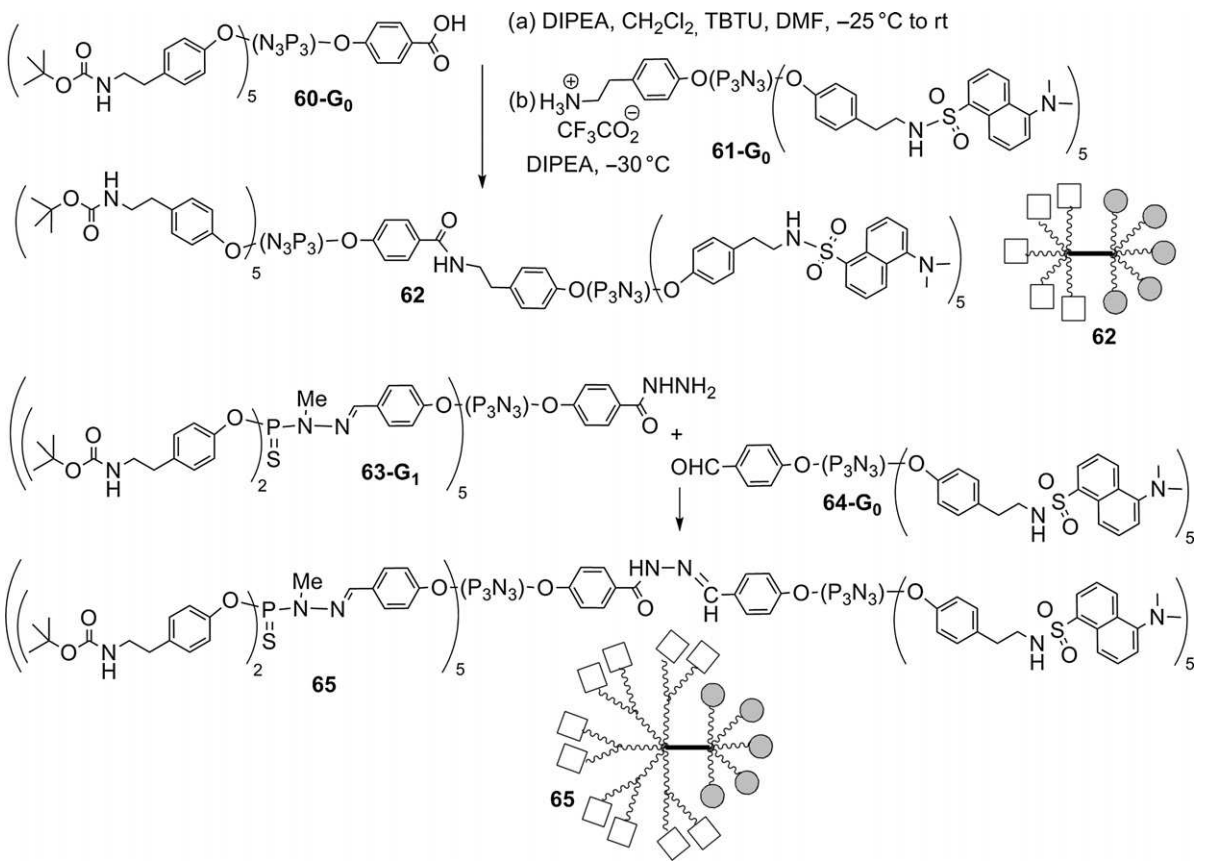

Figure 42 Two methods used for coupling functionalized dendrons.

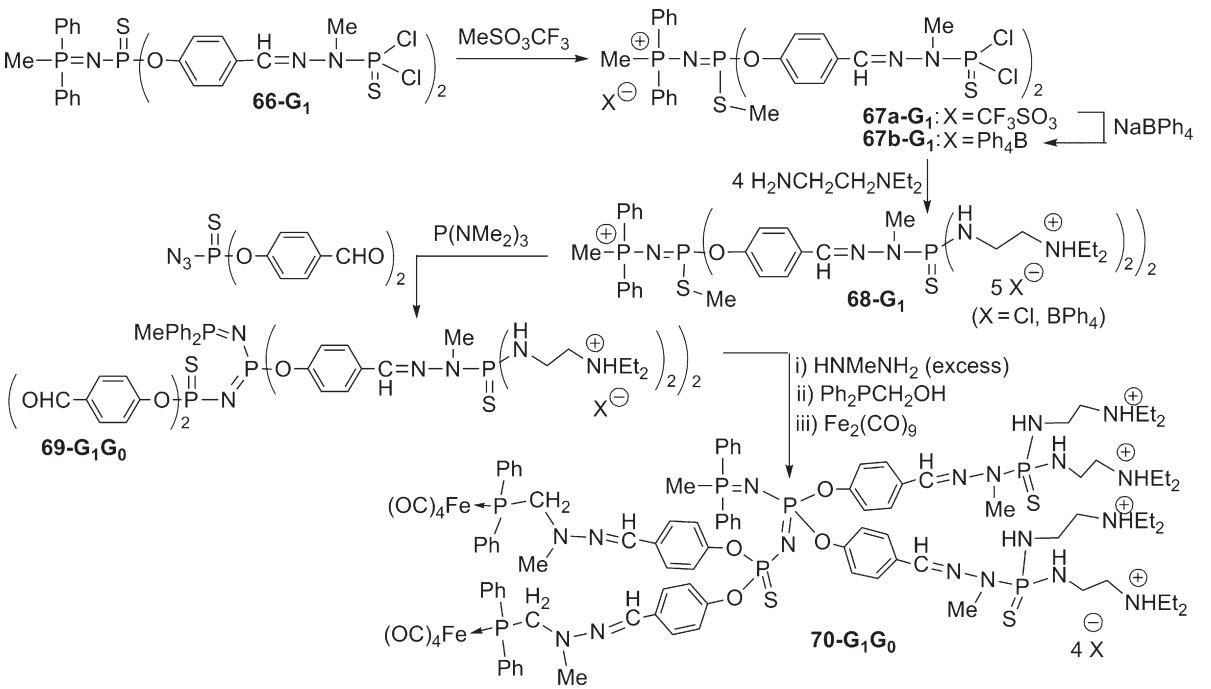

Figure 43 Growing of small branches from the core of a small dendron.

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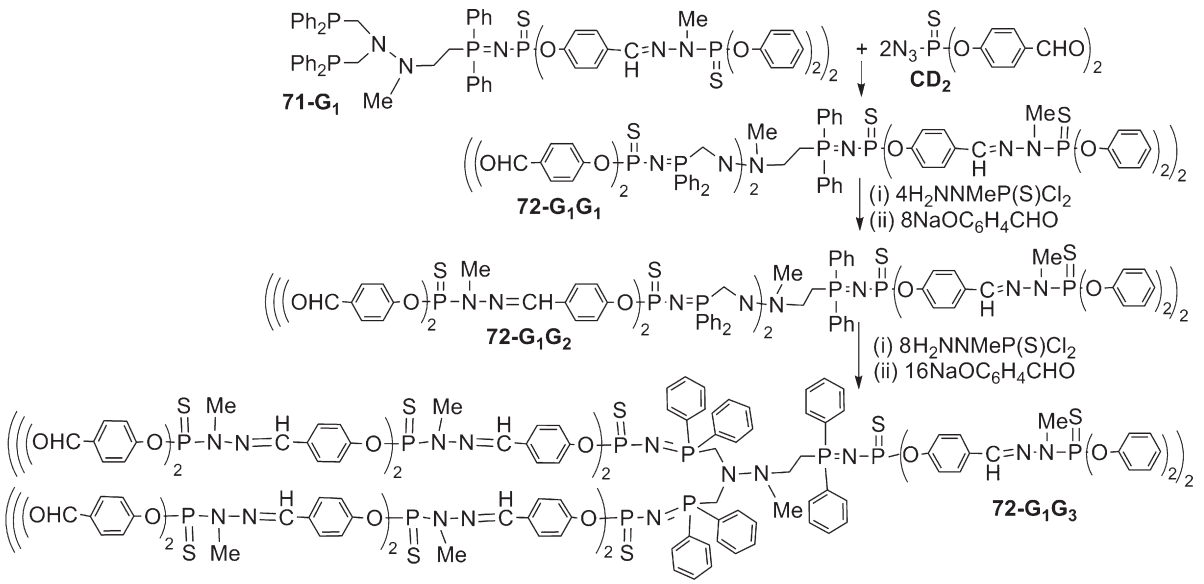

Figure 44 Step-by-step growing of G_3 branches from the core of a G_1 dendron.

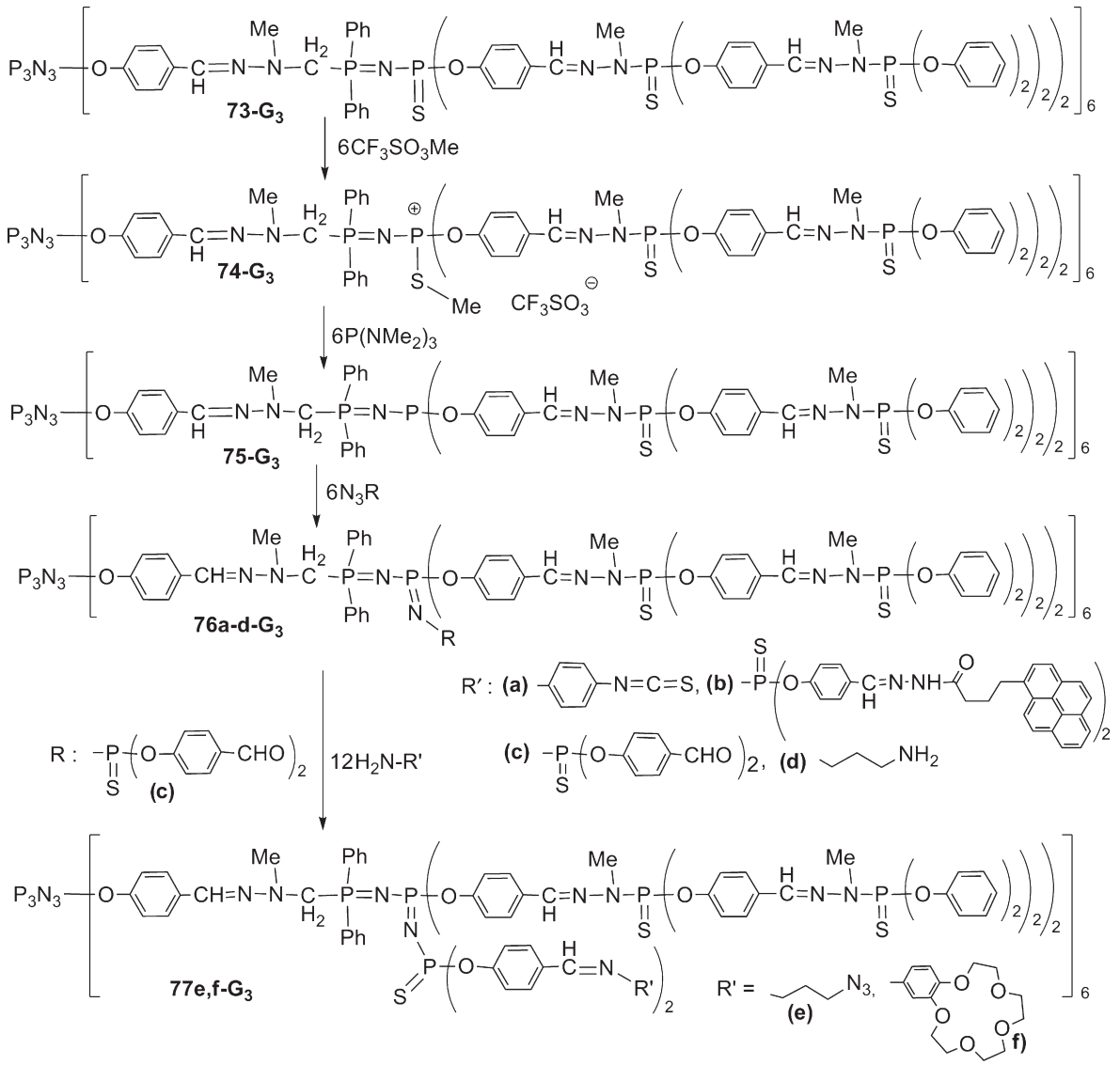

Figure 45 Various examples of internal functionalization of dendrimers.

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dendrimer **74-G$_3$**, and the desulfurization led to compound **75-G$_3$** possessing six phosphino internal groups. The Staudinger reaction with various azides allowed the internal functionalization with different functions such as primary amines, isothiocyanates,[69] or pyrene derivatives.[70] However, the most interesting function to be grafted in this way was aldehyde, using $N_3P(S)(OC_6H_4CHO)_2$ (**CD$_2$**). Indeed, from dendrimer **76c-G$_3$**, it is possible to condense various functional amines on the internal aldehydes, leading in particular to azides or macrocycles covalently included inside these dendrimers (**Figures 45** and **46**).[69]

Obviously, many reactions could be performed starting from the aldehyde internal groups of dendrimer **76c-G$_3$**, and in particular the methods of synthesis shown in **Figures 9** (two-step method) and **14** (three-step method) were used to grow new branches inside the starting dendrimer. The two-step method shown in **Figure 9** was applied up to the growing of four generations inside the dendrimer **76c-G$_3$** (**Figure 47**). The largest compound synthesized (**78-G$_3$G$_4$**) had 48 phenoxy end groups coming from the initial dendrimer, and 96 aldehyde end groups, coming from the reactivity inside the dendrimer, and the growing of new branches.[71] Up to now, no other type

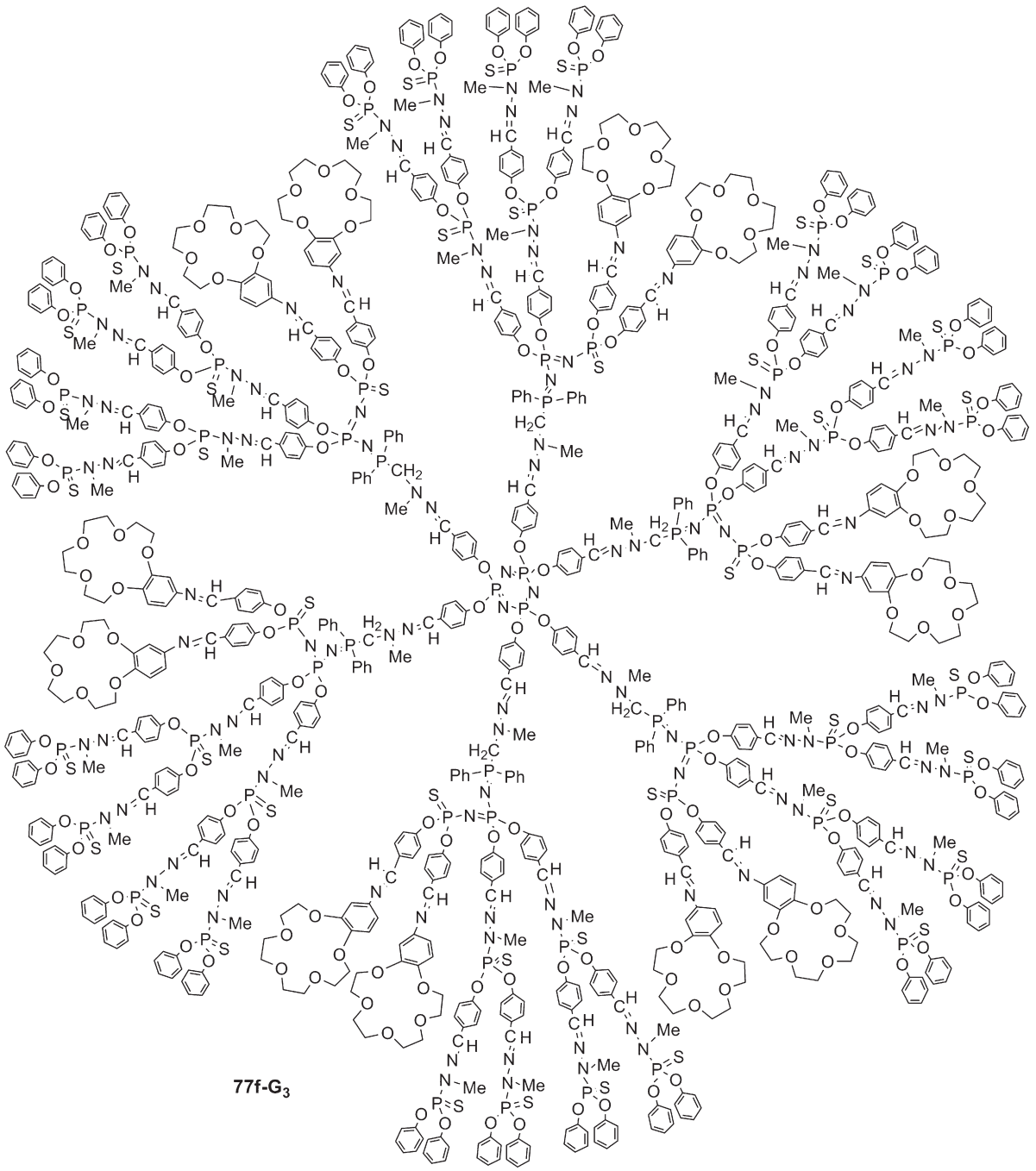

Figure 46 Full structure of a dendrimer with internal functions.

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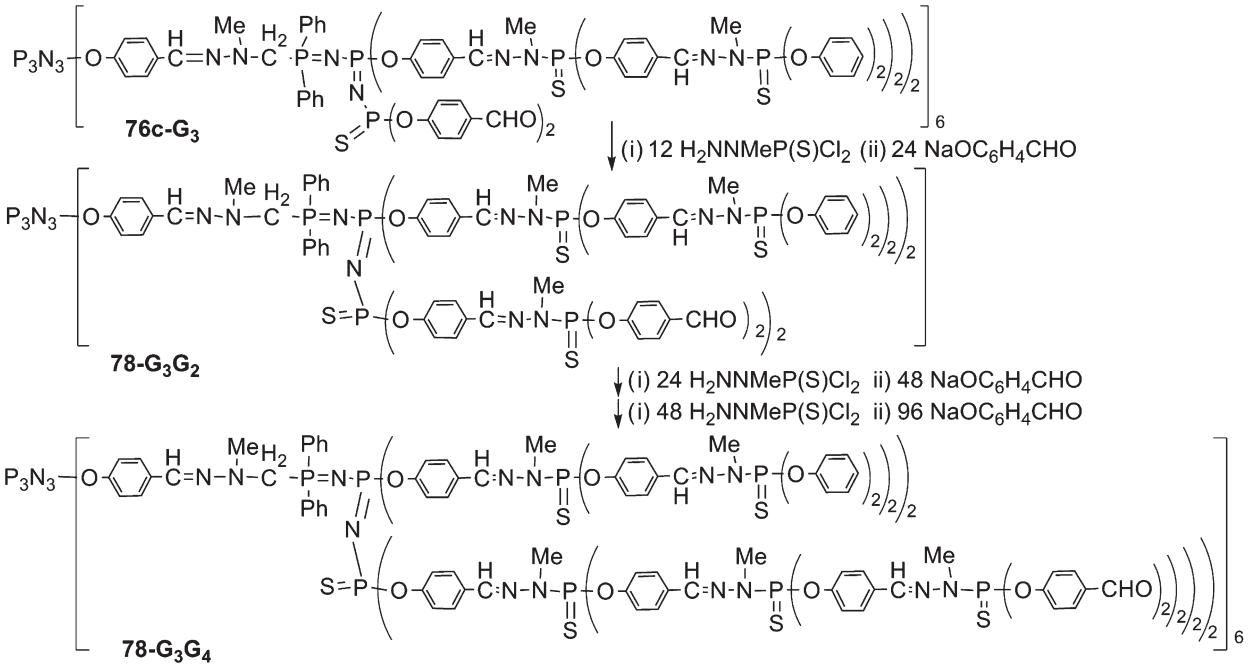

Figure 47 Two-step method applied for the growing of new branches inside a dendrimer.

of dendrimer (including organic dendrimers) has been able to afford so original structures.

The three-step method shown in **Figure 14** was also applied to grow new branches inside dendrimer **76c-G$_3$**. This three-step process afforded very original dendrimers **79-G$_3$G$_4$** in which two different types of branches are forced to coexist, but keep their own properties.[71] This fact is illustrated by the reactivity of gold; only the newly synthesized branches, constituted of P = N–P = S linkages were able to complex gold on P(S), whereas the other branches having simple P = S groups could not, affording compound **80-G$_3$G$_4$** (**Figure 48**).[72]

The functional groups afforded by the three-step method in the internal structure were used for other reactions. For instance, after the reaction of methyl hydrazine and Ph_2PCH_2OH, the phosphine internal groups of **79-G$_3$G$_1$** were used for the complexation of gold, which occurs also on the P = N–P = N–P = S linkages, affording compound **81-G$_3$G$_1$**.[69] Zwitter-ionic groups were also grafted inside the next generation **79-G$_3$G$_2$**, by reaction with a zirconocene derivative on aldehydes (**Figure 49**).[73]

The last example for the elaboration of special dendritic species was obtained using dendrons to functionalize the interior of dendrimer **76c-G$_3$**. Condensation reactions of the second-generation dendron **42c-G$_2$** with the internal aldehydes were used to obtain the dendritic species **83-G$_3$G$_4$**. These condensation reactions were slow and necessitated 10 days to go to completion, due to the steric hindrance induced by the use of dendrons instead of small molecules. However, the dendritic species **83-G$_3$G$_4$** was finally isolated (**Figure 50**).[58]

5.24.5 Conclusions

We have shown in this chapter the synthesis of phosphorus-containing dendrimers and of highly sophisticated dendritic superstructures. The focus was on the synthesis, but many of these compounds were not synthesized for their aesthetic aspect, but have found applications, mainly along three main axes that are catalysis, materials, and biology.

Most catalytic properties are studied using organometallic derivatives, most often linked to the surface of dendrimers.[74] The main advantage of dendritic catalysts is that they can be easily recovered and reused several times – thanks to their large size.[75] The phosphorus dendrimers we synthesized were used, in particular, for Knoevenagel condensations and Michael additions, Stille couplings, asymmetric allylic alkylation, asymmetric benzoylations, C–C cross-coupling reactions, and Mizoroki-Heck reactions. In some examples, a positive dendritic effect was observed, that is, an increase of the catalytic efficiency with increasing generation number (and with an identical number of catalytic sites used). This effect was observed in particular for O- and N-arylation and vinylation of phenol and pyrazole[76] and in aqueous media.[77]

In the field of materials, it is possible to build new materials incorporating dendritic structures inside their structure,[78,79] which were used also for the elaboration of organic light-emitting diodes (OLEDs) from fluorescent dendrimers.[80] However, the simple functionalization of the surface of materials at the nanometric scale by a single layer of covalently grafted dendrimers or by multiple layers of dendrimers using electrostatic interactions can greatly modify the properties of the materials. For instance, glass slides functionalized by a single layer of dendrimers bearing oligonucleotides usable as sensitive DNA chips,[81] nanotubes made of dendrimers,[82,83] and a titanium film functionalized by fluorescent dendrons usable as a chemical sensor for phenols[84] were obtained in this way. In addition, soft matter dendrimers bearing two-photon absorption fluorophores[85] are able to replace hard matter quantum dots (generally toxic), in particular for biomedical imaging.[35]

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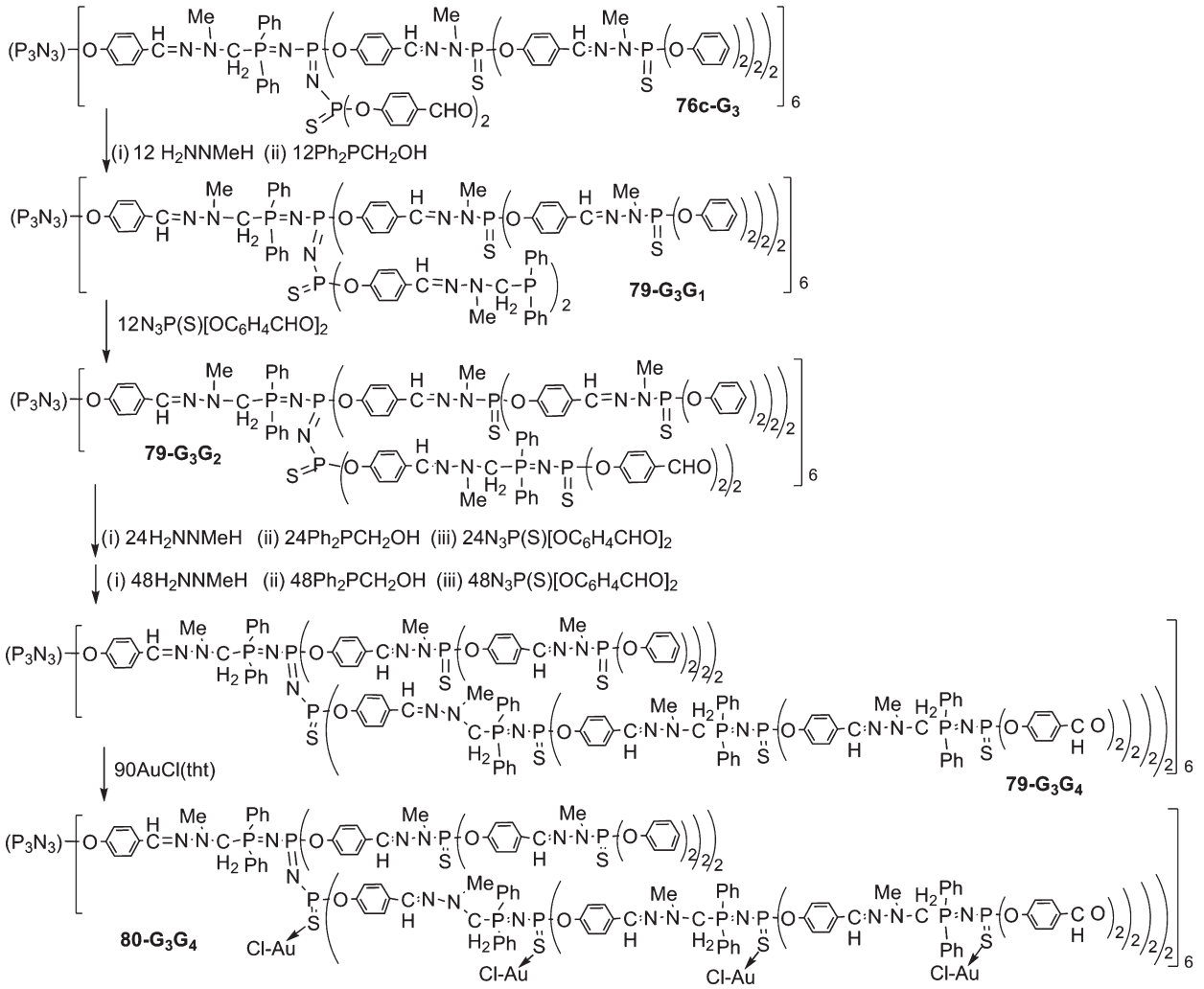

Figure 48 Three-step method applied for the growing of new branches inside a dendrimer. The new branches are chemically different from the other ones; only the P = S groups of the newly synthesized branches are able to complex gold.

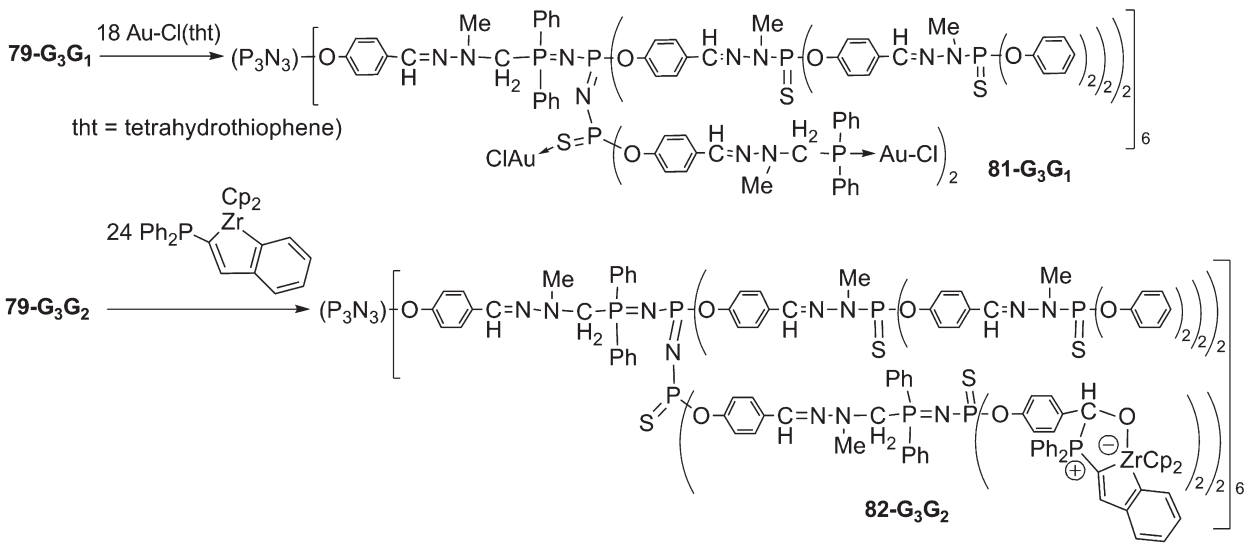

Figure 49 Reactivity of new branches inside dendrimers.

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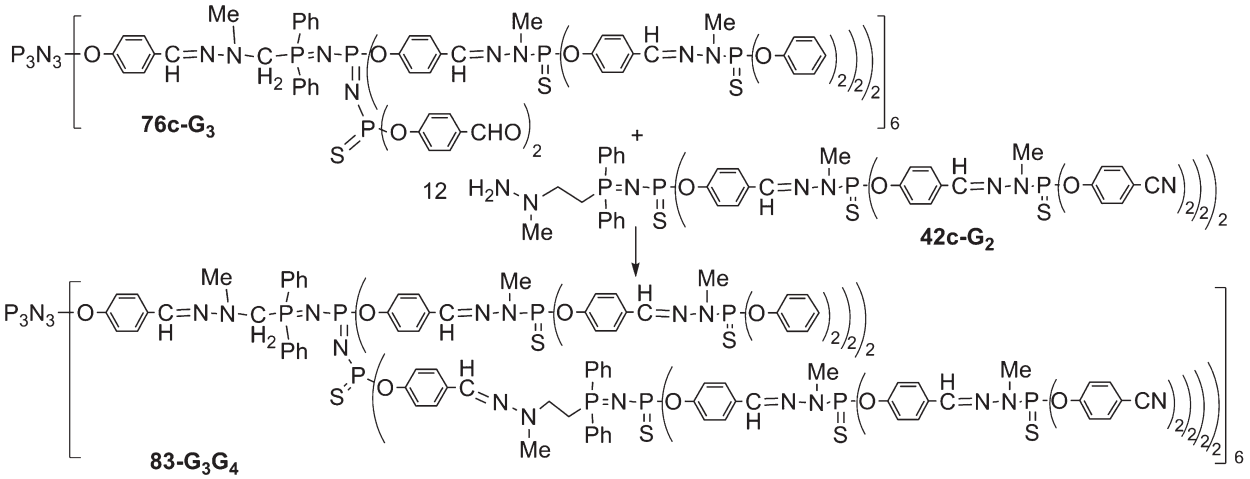

Figure 50 Grafting of dendrons inside a dendrimer.

Many water-soluble phosphorus-containing dendrimers have important biological properties.[86] Ammonium-ended dendrimers are efficient transfection agents (the ability to induce the insertion of genetic materials inside cells),[87] and have a high antiprion activity (for instance, against mad-cow disease), including *in vivo*.[88] Carboxylic acid terminated dendrimers when reacted with amino functionalized biologically active compounds generate saline species, which display anti-HIV activity,[89] or are usable for ocular drug delivery.[28] However, the most important properties that we have obtained up to now concerns phosphorus dendrimers ended by phosphonate salts. Indeed, several of them display surprising properties toward the human immune blood system: they are able to induce monocytes activation,[32] to multiply Natural Killer cells that play a key role against infections and many cancers,[90] and possess anti-inflammatory properties,[91] particularly interesting against Rheumatoid Arthritis.[92]

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5.25 Epoxy Resins and Phenol-Formaldehyde Resins

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5.25.1 Introduction of Epoxy Resins

An epoxy resin is defined as a molecule containing more than one epoxy group capable of being converted to a thermoset form. The term, epoxy, is used to indicate the resins in both the thermoplastic (uncured) and thermoset (cured) state.

Epoxy functional groups are prepared (1) by the reaction of olefins with oxygen-containing compounds such as peroxides or peracids, and (2) by dehydrohalogenation of chlorohydrines (**Figure 1**). But, the most important preparation method for epoxy resins is (3) by the reaction of epichlorohydrin with a suitable di- or polyhydroxy

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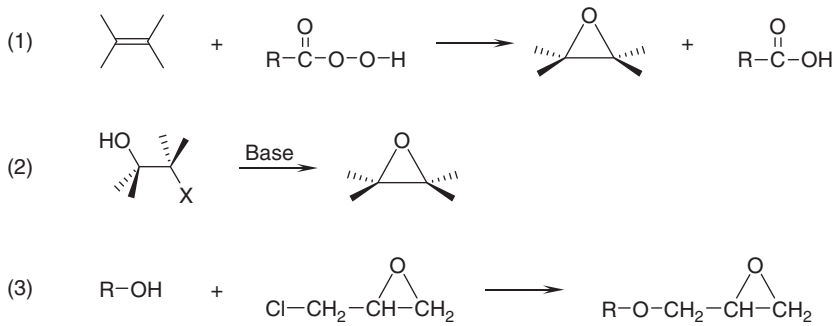

Figure 1 Preparation of epoxy functional group.

compound or other active hydrogen-containing compounds.

In 1927, Schrade reported the first attempt to prepare resins from epichlorohydrin. In 1936, Castan produced a low-melting, amber-colored epichlorohydrin – bisphenol A resin which was then reacted with phthalic anhydride to produce a thermoset. In 1939, Greenlee explored the epichlorohydrin–bisphenol A synthesis route for the production of new resins for coatings. The epichlorohydrin–bisphenol resins were the outgrowth of research by many workers on the substituted ethylene oxide derivatives. The first resins, the reaction products of epichlorohydrin and bisphenol A, were produced commercially in 1947. Due to the many researches devoted to epoxy, rapid commercial utilization of the diglycidyl ether of bisphenol A resins became possible after World War II.

5.25.2 Basic Characteristics of Epoxy Resins

A number of advantageous properties have led to the rapid growth of epoxy resins and their use in a wide range of industries. The liquid resins are low-viscosity liquids, which readily convert to the thermoset upon mixing with the curing agent. Other liquid resins, such as phenolics, polyesters, acrylics, and so on, cure in a similar fashion, but the liquid epoxy resins possess a rather unique combination of properties as follows.[1]

1. Low viscosity: The liquid resins and their curing agents form low viscosity and easy-to-process (or modify) system.
2. Easy cure: Epoxy resins cure quickly and easily at the temperature range from room temperature to 150 °C, depending on the selection of the curing agent.
3. Low shrinkage: One of the most advantageous properties of the epoxy resin is the low shrinkage during the cure. Epoxy resins react without evolving volatile by-products.
4. High adhesive strength: Because of the presence of polar hydroxyl and ether groups, the epoxy resins are excellent adhesives. The resins cure with low shrinkage; therefore, the various surface contacts between the liquid epoxy resin and adherents are not disturbed during cure.
5. Good chemical resistance: The chemical resistance of the cured epoxy resin depends considerably on the curing agent used. Outstanding chemical resistance can be obtained. Overall, most epoxy resins possess extremely high resistance to alkali and good to excellent resistance to acid.
6. High electrical insulation: Epoxy resins are excellent electrical insulator.
7. High mechanical properties: The strength of properly formulated epoxy resins usually surpasses that of other type of resins. This is probably the result of their low shrinkage, which minimizes stresses that otherwise would weaken the mechanical structure.
8. Versatilities: The epoxy resins are one of the most versatile among the plastics. The basic properties may be modified in many ways: by blending of the resin types, by selecting curing agent, and by use of modifiers and fillers.

On the other hand, solid epoxy resins are mainly used for solution coatings. The higher molecular weight materials are reacted with methylol-containing resins. The epoxy resin backbone affords toughness, scratch resistance, and chemical resistance. Solid resins of intermediate molecular weight may be crosslinked by heating, and cured films may be developed which provide excellent properties. The excellent adhesion, ease of cure, mechanical strength, and high chemical resistance are also the important advantages of the solid epoxy resins as the liquid epoxy resins.

5.25.3 Synthesis of Epoxy Resins

5.25.3.1 Synthesis of Glycidyl-Type Epoxy Resins

The first commercial epoxy resins were the reaction products between epichlorohydrin and bisphenol A, the reaction giving the diglycidyl ether of bisphenol A (DGEBA) of higher molecular weight species. The structure of the resin is shown in Figure 2.[1]

The low-molecular-weight liquid products have an n value about 1 or below. When the n value is above 1, the resins are brittle solids. DGEBA is obtained by reacting epichlorohydrin with bisphenol A in the presence of sodium hydroxide. The reaction occurs in two steps (Figure 3): (1) the formation of a chlorohydrin intermediate, and (2) the dehydrohalogenation of the intermediate to the glycidyl ether. Sodium hydroxide catalyzes the reaction to produce the chlorohydrin intermediate, acts as the dehydrohalogenating agent, and neutralizes the formed HCl. In order to obtain the monomeric DGEBA, 2 mol of epichlorohydrin is theoretically required for each mole of

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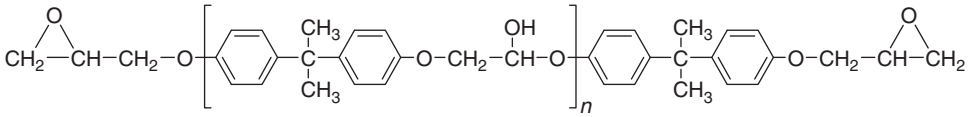

Figure 2 Structure of typical epoxy resin.

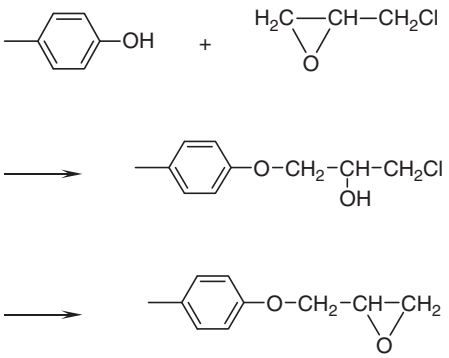

Figure 3 Reaction of epichlorohydrin with phenol.

bisphenol A. However, when this ratio is employed, the yield of monomer is less than 10%, with the remaining material being higher molecular weight products. To obtain high yield of monomeric product, excess epichlorohydrin is employed, and yields of 90% or higher are then possible. The usual DGEBA having an average molecular weight of approximately 380 is the commercial liquid epoxy resin.

It is possible to synthesize higher molecular weight epoxy resins by reacting epichlorohydrin and bisphenol A in the presence of excess sodium hydroxide. It should be noted that such a molecule contains many alcoholic hydroxyls (Figure 4) and contains no more than two epoxy groups. Synthesis of higher molecular weight epoxy requires not only the consumption of the epoxy group in the epichlorohydrin, but also, in order to connect successive bisphenol A groups, the consumption of some of the epoxy groups formed by dehydrohalogenation.

Therefore, it should be possible to control the degree of polymerization by regulating the ratio of epichlorohydrin and bisphenol A when employing sodium hydroxide in excess of the amount required to carry out the reaction. Typical data for various ratios in terms of resultant molecular weight are summarized in Table 1.

5.25.3.2 Syntheis of Glycidyl Ethers of Novolac Resins

Novolac resins are also suitable intermediates for the synthesis of polyglycidyl ether resins. The novolac-based epoxy resins (Figure 5) are synthesized by the reaction with epichlorohydrin in the same fashion as are the bisphenol A-based resins. The number of glycidyl groups per molecule in the resin is dependent on the number of the phenolic hydroxyls in the starting novolac, the extent to which they are reacted, and extent to which the lowest molecular weight species are polymerized during synthesis. Theoretically, all the phenolic hydroxyls may be reacted. But, in practice, selective epoxidation offers an advantage when the novolac contains more than three phenolic hydroxyls. If complete epoxydation is accomplished, steric factors will prevent the reaction of some of the epoxy groups during cure. The glycidyl ethers of novolacs are also commercially important because of their high functionality.[1]

5.25.4 Curing of Epoxy Resin

Epoxy functional groups react readily with various chemicals as shown in Figure 6. As a result, the most valuable property of epoxy resins is their ability to transform readily from the liquid (or thermoplastic) state to hard thermoset solids. The conversion normally occurs without the evolution of by-products. The conversion is accomplished by the addition of curing agent (hardener, activator, or catalyst). Some curing agents catalytically promote curing, and others participate directly in the reaction and are chemically bound into the resin. The cured structure may be a homo epoxy polymer or a hetero polymer composed of epoxy resin and curing agent, or a mixture of both types. Depending on the particular agent, curing may be

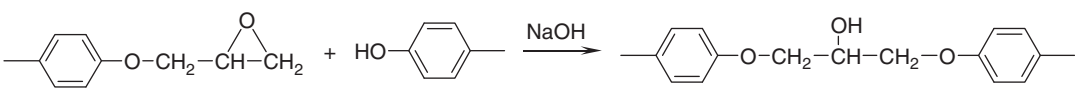

Figure 4 Reaction of epoxy resin.

Table 1 Effect of varying ratios on molecular weight of epoxy resins

Mole ratio epichlorohydrin/ bisphenol A	*Mole ratio NaOH/ epichlorohydrin*	*Softening point (°C)*	*Molecular weight*	*Epoxide equivalent*	*Epoxy groups per molecule*
2.0	1.1	43	451	314	1.39
1.4	1.3	84	791	592	1.34
1.33	1.3	90	802	730	1.10
1.25	1.3	100	1133	862	1.32
1.2	1.3	112	1420	1176	1.21

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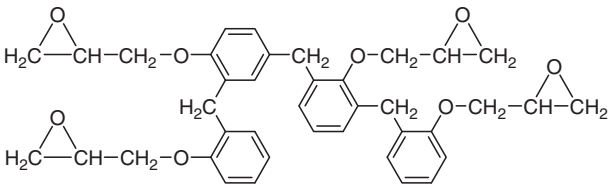

Figure 5 Structure of novolac-based epoxy resin.

accomplished at room temperature with heat produced by exothermic reaction, or require external heat. The reactivity of the epoxy differs, depending on whether the epoxy is located terminal or internal.

The epoxy group may react either anionically or cationically. Both types of reaction are important in epoxy resin technology.[1,2] In the anionic mechanism, the epoxy ring may be opened in various fashions to produce an anion (Figure 7(a)). The anion is an activated species, and capable of further reaction. In the cationic mechanism, the epoxy groups may be opened by acids (Figure 7(b)).

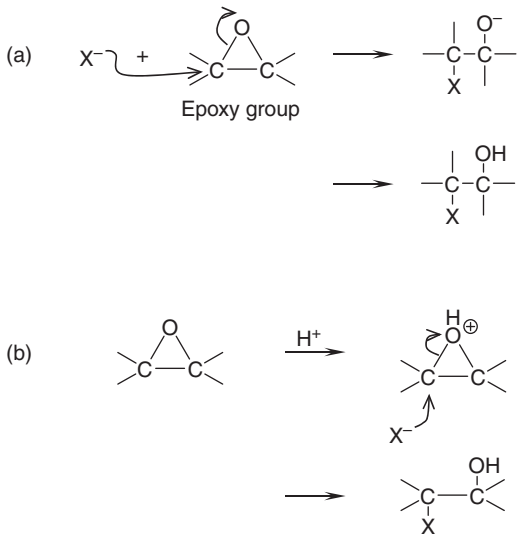

Figure 7 Ring-opening reaction of epoxy resin.

5.25.4.1 Curing by Primary Amines

One of the most important and most frequently used curing agents is amine. The reaction of primary amine with epoxy proceeds as shown in Figure 8. The reaction proceeds in two steps. (1) At the first step, the primary amine reacts with epoxy, forming secondary amine and a hydroxyl group. (2) At the second step, the secondary amine reacts with another epoxy, forming tertiary amine and another hydroxyl group. (3) The hydroxyl groups thus formed also react with epoxy, contributing the development of the network.

In the case of aliphatic amines, the k_1/k_2 ratio is approximately 2. After the initial reaction between primary amine and epoxy, the reaction between secondary amine and epoxy proceeds in parallel with the initial chain extension reaction. In the case of aromatic amines, the k_1/k_2 ratio is as large as 7–12. Therefore, in this case, chain extension of epoxy with primary amine preferentially proceeds, and Lewis acid is used as an accelerator.

The primary amines can be used effectively as epoxy curing agents, since the primary amine group is bifunctional with the epoxy resin. If more than one primary amine is present in a molecule, crosslinked structure results through the reaction with diepoxides. Generally, the tertiary amines formed by the reaction of two epoxy groups with a primary amine are not effective catalysts, though tertiary amines may cause further reaction as Lewis bases.

5.25.4.2 Curing by Anhydrides

Another important and frequently used curing agent for epoxy is cyclic anhydride. Cyclic anhydride does not react directly with epoxy group. In order for the reaction to occur, first of all, ring opening of the anhydride is necessary. The ring may be opened either by active hydrogen as water or hydroxyls.

In the absence of an accelerator, the curing of epoxy by anhydride proceeds as shown in Figure 9. At first, anhydride reacts with the hydroxyl group of epoxy, affording ester and carboxylic groups. The carboxylic group then reacts with epoxy, forming hydroxyl group, which reacts further with another anhydride. This curing system is acidic, and ether linkage also forms from the reaction between epoxy and hydroxyl group.

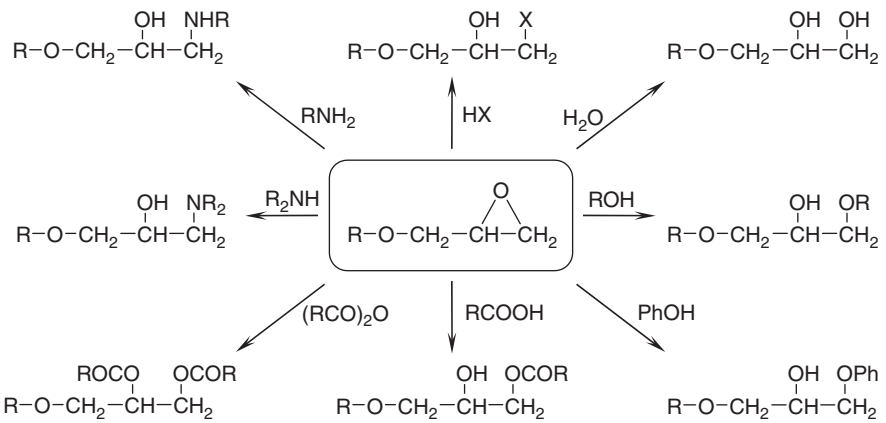

Figure 6 Reaction of epoxy functional group.

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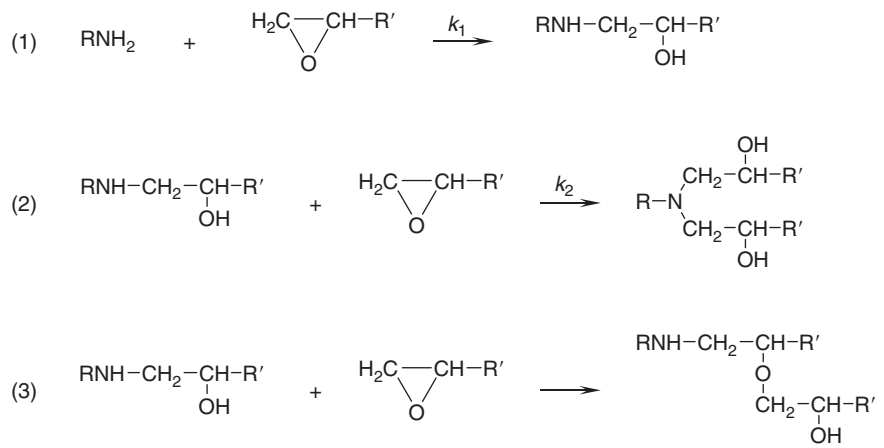

Figure 8 Ring-opening of epoxy by primary amine.

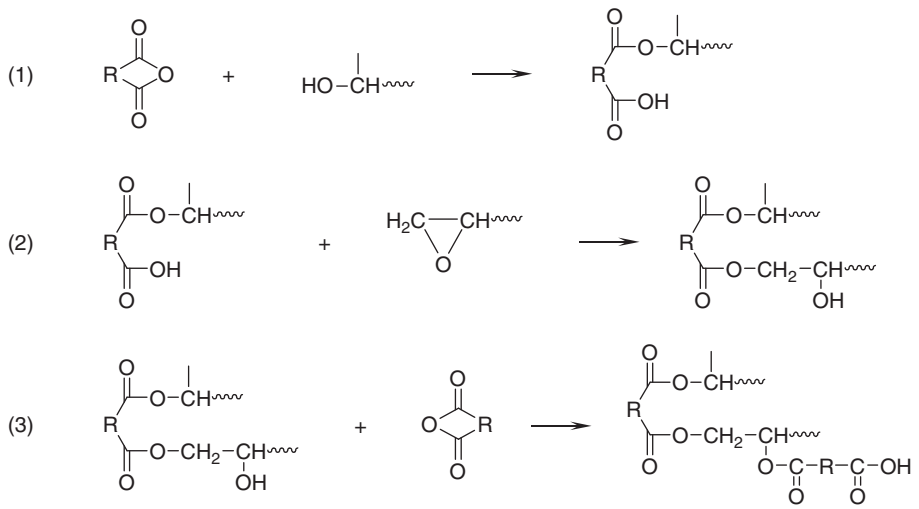

Figure 9 Ring-opening of epoxy by anhydride.

Generally, anhydrides cure epoxy slowly, and shrinkage at the cure is relatively small. The resulting epoxy resin has high heat distortion temperature (HDT) with excellent mechanical and insulation properties. The problem of using anhydrides as curing agents is that relatively high temperature (above 80 °C) is needed, and the processing cycle becomes long.

As suggested from the above mechanism, the reaction rate is governed by the concentration of hydroxyl functional groups in the epoxy resin. In the liquid resin, the concentration of hydroxyl group is low, and the reaction proceeds very slowly at approximately 150 °C. In the solid epoxy resin that contains high concentration of hydroxyl groups, the cure reaction proceeds very quickly.

The curing reaction by anhydrides is accelerated in the presence of bases. In the presence of Lewis base accelerator such as tertiary amine, the curing reaction starts by the attack of accelerator to anhydride. The reaction product then reacts with epoxy, giving alkoxide to which another anhydride reacts. In the basic conditions, ester linkages predominantly form, and ether linkage formation is minimum.

5.25.4.3 Other Curing Agents

Another important curing agent for epoxy resins is phenol novolac. The cured resins are water and heat resistant. Phenols react with epoxy resins when elevated temperatures are applied. Without accelerators, phenol groups work as catalyst, and the reaction between the epoxy and alcoholic hydroxyl groups predominates. But, with basic accelerators such as KOH and tertiary amine, the reaction between epoxy and phenolic hydroxyl groups preferentially occurs.

Liquid polymercaptans and oligomeric polysulfide resins are also used as curing agents. The terminal mercaptan functional groups works for the cure.

5.25.4.4 Catalytic Curing Agents

Differently from the above-mentioned curing agents that are incorporated in the cured networks, catalytic curing agents homopolymerize epoxy resins by inonic mechanism.

Imidazoles and tertiary amines are the important anionic catalysts. Imidazoles, especially those with high basicity,

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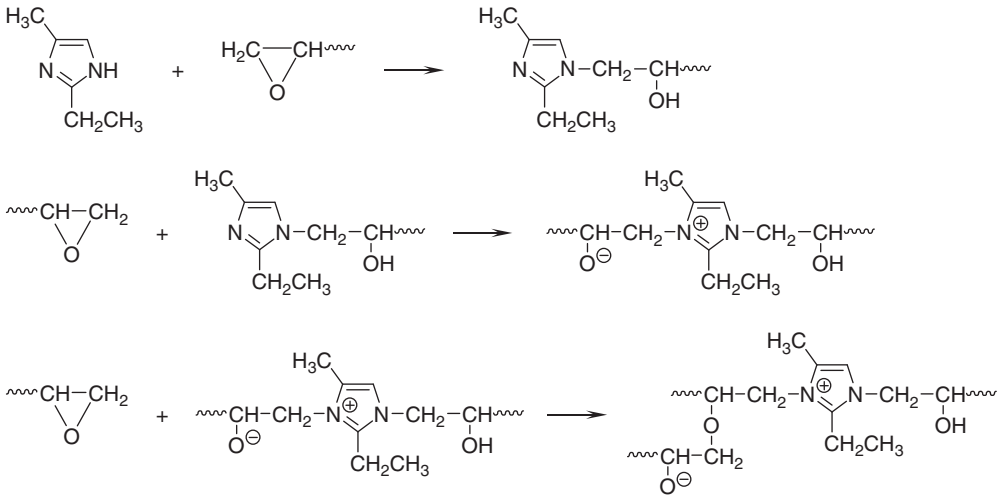

Figure 10 Curing of epoxy by imidazole.

catalyze effectively at relatively low temperature, and afford cure products with good thermal properties. Catalytic mechanism of imidazole is shown in Figure 10. At first, secondary amine reacts with epoxy, and then another amine reacts with epoxy to form ionic complex, followed by further reaction of the ionic complex with another epoxy.

Tertiary amines, representative reactive Lewis bases, are highly basic compounds and catalyze the curing of epoxy. The tertiary amine approaches one of the carbon atoms of the epoxy and attaches itself. Once the alkoxide ion is available, it will then react directly with an epoxy to generate a new alkoxide ion. The process continues in a chain mechanism.

As the cationic catalyst, Lewis acid such as boron trifluoride (BF_3) is used. Usually, BF_3 is complexed with amine as a Lewis base, thereby controlling the reactivity. The complex is stable at room temperature, and works as a latent curing agent which becomes active at elevated temperatures.

5.25.5 General Properties of Epoxy Resins

Epoxy resins are available in a range of molecular structures, suitable for reaction with a large variety of different curing agents, for a multitude of end uses. At the early stages of cure of an epoxy resin, before the molecules are fully crosslinked, the resin exists as a thermoplastic or B-stage resin. It is hard but soluble in solvents such as acetone. At this stage, the cure reaction has been initiated at a number of widely separated points by the formation of branched and linear molecules. With the progress of cure, crosslinking becomes general. Epoxy resin forms network and becomes thermoset.[1–4]

5.25.5.1 Glass Transition Temperature of Cured Epoxy Resins

One of the advantages of thermosets such as epoxy over the thermoplastics is thermal properties. Thermal properties are evaluated from glass transition temperature (T_g) or HDT.

A major factor that determines the T_g value is chemical structure of epoxy and curing agent. Increase of rigidity, for example, by the higher content of aromatics, increases the T_g value, but tends to become brittle. The introduction of flexible groups, on the other hand, decreases T_g but increases toughness. Introduction of polar groups in the polymer chains increases the molecular interactions between adjacent chains and hence decreases the chain flexibility, resulting in increased T_g. Bulky side groups, such as aromatic rings, also hinder segmental motion and, therefore, reduce flexibility, resulting in increased T_g.

Another major factor that determines the T_g values is crosslink density. Crosslink density is defined as the number of effective crosslinks per unit volume. It is important to know how far apart the functional groups are located, since this determines crosslink density. In the DGEBA ($n = 0$), the epoxy groups are separated by seven units (the aromatic ring being counted as one unit). In general, short spacing gives rigidity, medium spacing gives semi-rigid properties, and long spacing gives flexibility or softness.

T_g of network polymer is determined by the crosslink density (ρ) as shown in the following equation:

$$T_g = K_1 \log K_2\rho = K_1 \log \rho + K_2$$

where K_1 is a constant that suggests how the crosslink density affect T_g, and in the range of 50–250. K_2' ($K_1 \log K_2$) is a constant that depends on various factors such as rigidity, steric hindrance, and intermolecular interaction. Aromatic polymers have high K_2'. Among the similar polymers, K_1 and K_2' are constant. Crosslink density, ρ, is estimated from the modulus at the rubbery plateau region above T_g using the following equation:

$$\rho = \frac{(dN_A)}{Mc} = \frac{E}{(3\varphi RT)}$$

where E is usually the storage modulus measured from the viscoelastic analyses. N_A is Avogadro constant, d is density, R is gas constant, and $\varphi = 1$ is very often used.

Various epoxy resins with improved thermal properties have been examined aiming for high-temperature applications such as matrix resin for advanced composite materials. Some of the proposed epoxy resins are shown in Figure 11.

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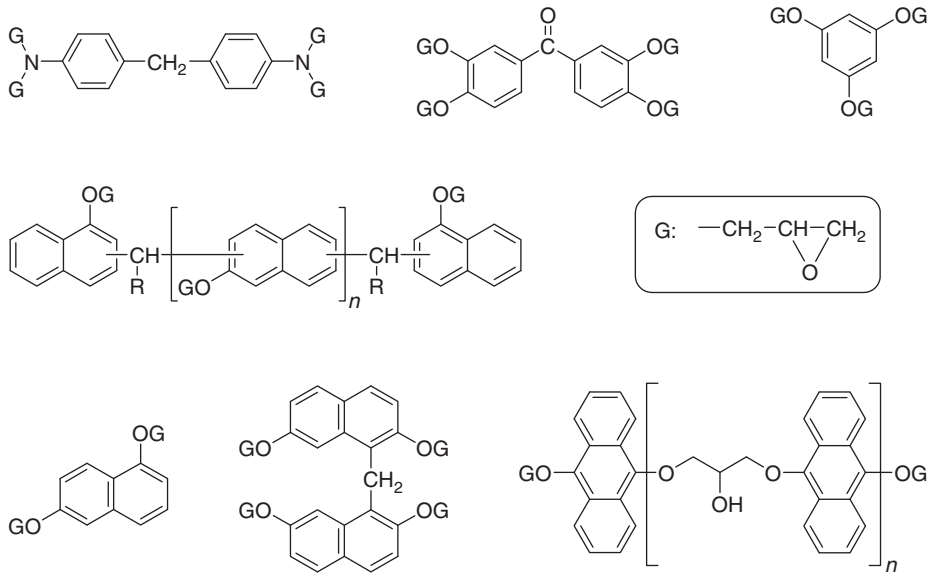


Figure 11 High-performance epoxy resins.

5.25.5.2 Thermal Degradation of Epoxy Resins

A number of epoxy resin systems have been thermally degraded, and the degradation products were studied. When epoxy resin is cured with a primary amine, the unreacted epoxy is evaporated, and the higher molecular weight fractions are degraded to release H_2, CO, CH_4, C_2H_6, C_3H_6, and C_3H_8, the latter four possibly from decomposition of polyamine radicals. The presence of hydroxyl groups in amine-cured systems may be one of the causes for their relatively poor thermal stability, perhaps dehydration due to the cleavage. In addition, it is possible that amine hydrochloride is formed and decomposes to HCl, which initiates cleavage of bisphenol A structure. In the anhydride-cured system, the diester can undergo β-elimination to release olefin and carbon dioxide, with other decomposition products preceding through cleavage at the ether links following dehydration.

5.25.5.3 Toughening of Epoxy Resin

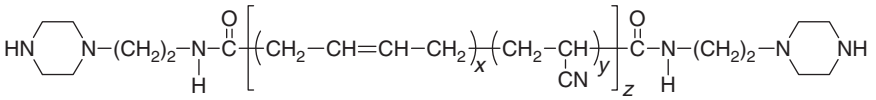
Epoxy resin is naturally a brittle material, and needs modification for toughening depending on the use. An effective method for this purpose is modification by rubber, especially amine- or carboxylic-terminated liquid rubber (ATBN or CTBN). The structure of ATBN is shown in Figure 12. At the initial stage, liquid rubber dissolves in epoxy. With the progress of cure of epoxy, liquid rubber is phase separated into particles. The particle size affects the mechanical properties of the cured resin. Therefore, the particle size control is very important. The terminal functional group reacts with epoxy to make strong the interface between liquid rubber and epoxy. With the increase of liquid rubber, epoxy resin becomes tough. The toughening effect is most significant at a rubber content of around 20%. A disadvantage of using liquid rubber as a toughening agent is that T_g decreases with the addition of liquid rubber.

For the toughening of epoxy without decreasing the T_g of epoxy, the use of engineering thermoplastics shown in Figure 13 is effective.[5–10] In the case of polyethersulfone, phase separation did not occur, and fracture toughness (K_{1c}) did not improve. But, in the case of polyetherimide (PEI), sea-island type phase separation occurred, and fracture toughness increased linearly with the addition of PEI up to $\sim$1.5 MPa m$^{1/2}$ at 20% inclusion from $\sim$0.5 MPa m$^{1/2}$ of the pristine epoxy. End-reactive oligomers such as amine- and hydroxyl-terminated polysulfones and amine-terminated polyaryletherketones were also effective without sacrificing T_g and flexural modulus.

5.25.5.4 Liquid Crystalline Epoxy Resins

It has been reported that the liquid crystalline (LC) epoxy resins containing mesogenic groups in the backbone moiety and having controlled network structures show high thermal stability and fracture toughness.[11–14]

Recently, Takezawa and Akatsuka used LC epoxy resins (Figure 14), and succeeded in preparing isotropic cured resins that have 5 times higher thermal conductivity than that of the conventional epoxy resins by controlling the high-ordered structure because mesogens were highly ordered to form crystal-like structure.[15]



ATBN

Figure 12 Structure of ATBN.

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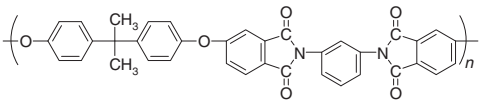
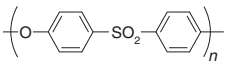
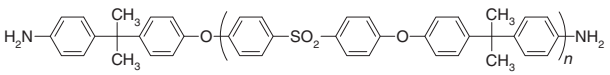
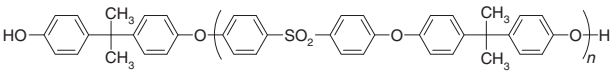
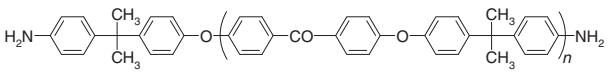
Name		Structure	T_g
Polyetherimide (PEI)			215 °C
Polyethersulfone (PES)			225 °C
Polysulfone (PSF)	Amine-terminated		–
	Hydroxy-terminated		180 ~ 183 °C
Polyaryletherketone (PAEK)	Amine-terminated		–

Figure 13 Engineering thermoplastics for toughening epoxy.

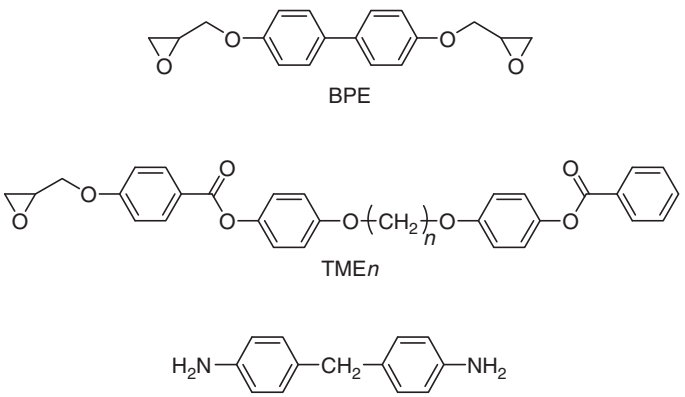


Figure 14 Liquid crystalline epoxy resin.

Harada *et al.* cured LC epoxy resin, shown in Figure 15, under a magnetic field to obtain a highly ordered network structure. They found that the thermal conductivity in the direction along the applied field had a significantly high value (0.89 W m^{-1} K) as compared with that (0.32 W m^{-1} K) of the cross direction.[16]

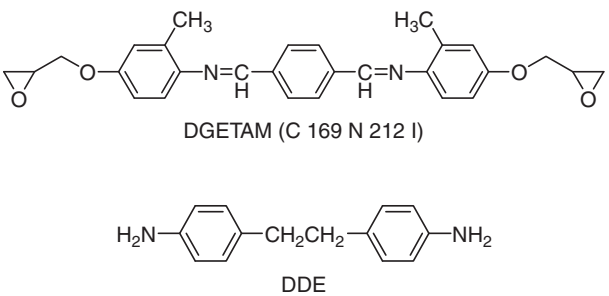


Figure 15 Liquid crystalline epoxy resin and curing agent.

5.25.6 Introduction of Phenolic resins

Phenolic resin was produced in 1910 as the first man-made synthetic plastic, and now has the history for more than 100 years. Phenolic resin possesses excellent characteristics such as excellent heat and flame retardance, high strength, long-term thermal and mechanical stability, excellent electrical and thermal insulating properties, good chemical resistance, low water absorption, and excellent cost-performance characteristics due to the inexpensive raw materials and fabricating processes. Therefore, phenolic resin is widely used in various applications from commodity and construction materials to the high-technology aerospace industry in the form of electric

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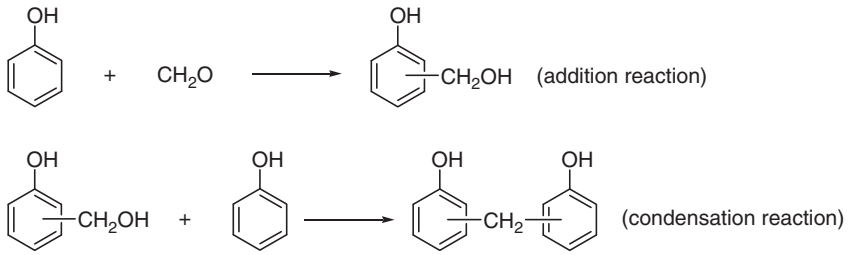

Figure 16 Addition and condensation reactions of phenol and formaldehyde.

laminates, adhesives, molding compounds, fiber-reinforced composites, glass fiber or rock wool insulation, honeycomb paneling, acid-resistant coatings, wood panels, binder in friction linings, or automobile brakes.

Phenolic resin is prepared from phenols and aldehydes using various organic and inorganic acids and alkalis or their salts as catalysts. Two types of reactions, addition and condensation reactions (Figure 16), take place depending on the reaction conditions, such as the type of catalyst or pH, and molar ratio of aldehyde to phenol. The obtained materials with low to medium molecular weight are reactive intermediates that can be cured, or can undergo various transformations utilizing phenolic hydroxyl group that have new utility. These transformations include epoxy, cyanate ester, and benzoxazine.

For the production of phenolic resins, mono-hydroxybenzenes, especially phenol, are of greatest importance. Alkylphenols such as cresols (monomethyl derivatives of phenol) and xylenols (dimethyl derivatives) are also important. Resorcinol (1,3-dihydroxybenzence) has a very high reaction rate toward formaldehyde. Bisphenol A is used for the production of special resins.

Formaldehyde is practically the only carbonyl component used in the synthesis of industrial phenolic resins. It is highly reactive, and commonly handled in aqueous solutions containing variable amounts of methanol. Paraformaldehyde, obtained by the distillation of formaldehyde solutions, is a polycondensation product whose degree of polymerization ranges between 10 and 100. Commercial grades contain up to 6% water. Paraformaldehyde is seldom used in resin production because of the high costs compared to aqueous formaldehyde solution, and problems with the high heat evolution. Paraformaldehyde is used for resins with a high solids content or to avoid distillation of waste water. Trioxane, a cyclic trimer of formaldehyde, is a colorless solid, and can be used as a source of formaldehyde in prepolymer formation or as a resin curing agent. Hexamethylenetetramine (HMTA or very often called hexa), prepared from formaldehyde and ammonia, is stable white crystal at room temperature (Figure 17). Hexa is soluble in water, and is by far the most important compound to cure novolac resin. Special resins are made with other aldehydes such as acetaldehyde, butylaldehyde, furfural, glyoxal, and benzaldehyde.

The reaction of formaldehyde (F) with phenol (P) leads to either novolac (or novolak) or resol (or resole) depending on the mode of catalyst and molar ratio of F to P.

Under acidic conditions, the reaction rate of condensation reaction is faster than the addition reactions. Therefore, by feeding an excess amount of P against F, linear or branched condensation products in which phenolic moieties are linked together through methylene linkages are obtained (Figure 18). These products are called 'novolac'. Novolac is normally solid at room temperature, having number average molecular weight between 500 and 800. It is soluble in organic solvents such as acetone and tetrahydrofuran (THF), and melts on heating. But novolac is stable, is not curable as it is, and is 'thermoplastic'.

On the other hand, under basic conditions, the reaction rate of the addition reaction is faster than the condensation reaction. Therefore, by feeding an excess amount of F to P, addition of aldehydes to phenols occurs preferentially, and eventually, hydroxymethyphenols called 'resols' are formed as viscous liquid at room temperature. The number average molecular weights of resols are generally as low as 200–500, and resols are soluble in alcohols and acetone.

Different curing conditions are necessary to crosslink novolacs and resols. Novolacs require a source of formaldehyde, which is commonly hexa as a latent source of formaldehyde. Other curing methods of novolac besides hexa consist of solid resol, bismethylol cresol, bisoxazolines, and bisbenzoxazines.

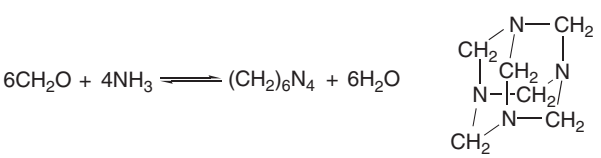

Figure 17 Hexa as the source of formaldehyde.

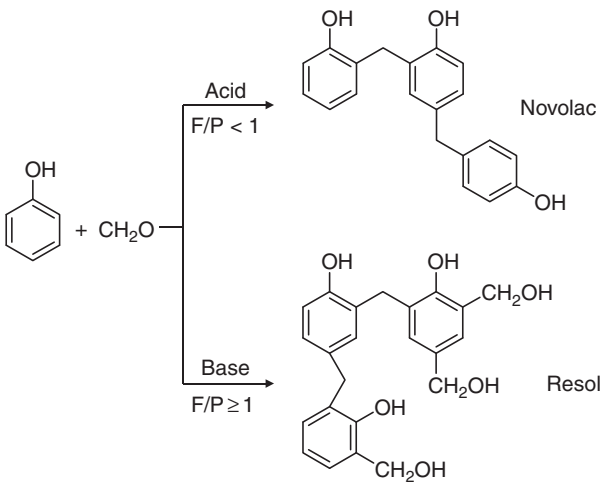

Figure 18 Chemical structures of typical novolac and resol.

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Resols are readily cured on heating or even at room temperature under acidic or special basic conditions, through condensation reactions between methylol groups and phenolic core at *ortho* and *para* positions, affording intractable network polymers.

5.25.7 Novolac

5.25.7.1 Bisphenol F

The simplest novolac, bisphenol F, is prepared by conducting the reaction of phenol (P) and formaldehyde (F) with a large excess of P under acidic conditions. The mechanism of formation involves initial protonation of methylol glycol, which reacts with phenol at the *ortho* and *para* positions (Figure 19). Among the mixtures of isomers obtained, *o,p′* isomer predominates, followed by *p,p′*, and *o,o′* the lowest.

Recently, synthesis of bisphenol F was examined over microporous H-beta zeolites, with different Si/Al ratios.[17] With an increase in the aluminum content in beta zeolite, the acidity is increased gradually. The catalyst with Si/Al ratio of 75.0 mol mol^{-1} showed the highest yield and selectivity at 90 °C (yield of 68% with 91% Bis F selectivity). Isomer distribution was considerably different, and *p,p′* isomer ratio was as high as 54%, with *o,p′* 35%, and *o,o′* 11%.

5.25.7.2 Random Novolac

Novolacs with varying molecular weight can be prepared under acidic conditions using an excess amount of P to F in a typical ratio of P:F = 1.0:0.75–0.85. The overall reaction scheme showing isomeric structural changes that occur during oligomerization is shown in Figure 20. Beyond bisphenol F, the number of isomeric structural oligomers increases significantly.

As the acid catalyst, oxalic acid is preferably used rather than the strong acid like HCl or H_2SO_4. When low reactive phenols and aldehydes are used, strong acid like *p*-toluenesulfonic acid or H_3PO_4 will be used.

Novolac synthesis was studied by conducting the oxalic acid-catalyzed reaction in an NMR tube.[18] *o*-Methylolphenol

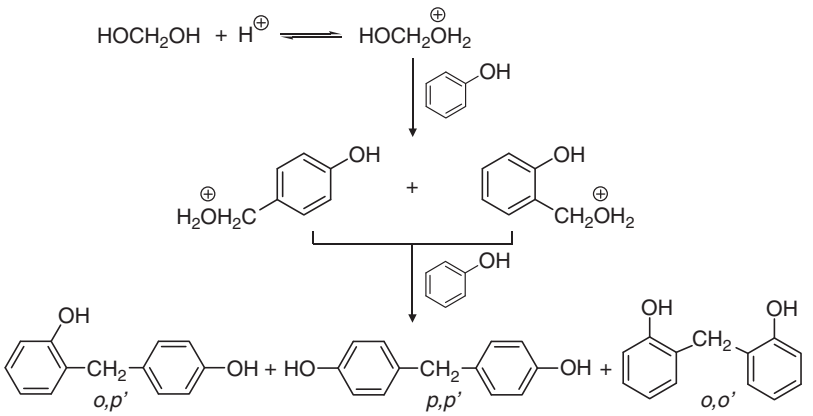

Figure 19 Preparation of bisphenol F.

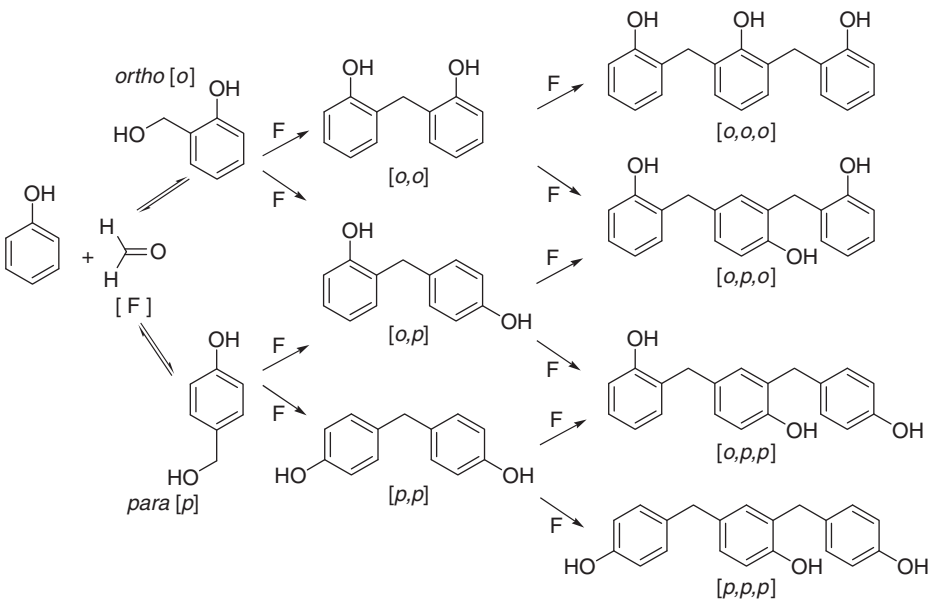

Figure 20 Preparation of novolac.

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Table 2 Isomeric content of various novolacs

	% Methylene bridges		
Novolak	*p–p′*	*o–p′*	*o–o′*
Random	25.8	49.1	25.1
Oxalic acid	27.6	49.1	23.3
Phosphoric acid	25.4	51.1	23.5
Sulfuric acid	25.6	48.5	25.9
High *ortho*	2.3	40.2	57.5
PAPS	40.1	45.3	14.6

Table 4 Reaction condition and the molecular weight of novolac

No.	*Solvent*	*Reaction time (h)*	M_n	M_w
1	2-Propanol	4	2990	16 700
2	Ethyl propionate	2.5	2830	18 600
3	2-Methoxyethanol	8	3870	22 900
4	water	5	2550	12 100
5	4-Methyl-2-pentanone	5	3030	24 100
6	Dioxane	22	3580	75 700

was identified, but *p*-methylolphenol was not identified. It was proposed that *o*-CH_2OH is more stable than *p*-CH_2OH due to the intramolecular H-bonding of methylol group and adjacent phenolic group. It should be noted that, in the latter stage of reaction, *p,p′* and *o,p′* methylene linkages were observed, which proves the existence of *p*-methylolphenol.

In the random novolac, the ratio of *ortho* and *para* is almost 1:1. This means that *para* position is twice more reactive than *ortho* position because there are two *ortho* positions and only one *para* position in phenol. Various factors affect *ortho*:*para* ratio (Table 2). There is a tendency that, under weakly acidic conditions, high *ortho* resin is obtained, and under strong acidic condition, high *para* resin is obtained. Reaction media also affects the ratio, and at high concentrations of water, high *para* resin is obtained. Whilst the use of paraformaldehyde, instead of formalin, results in high *ortho* resin, because of the small content of water and high reaction temperature. Higher reaction temperature gives high *ortho* resin. Heterogeneous two-phase method yields a high *para* resin.

5.25.7.3 High-Molecular-Weight Novolac

In order to improve thermal and mechanical properties of phenolic resins, various approaches have been examined to obtain high-molecular-weight novolac. As the molar ratio of F to P is increased, higher melting novolacs are obtained (Table 3), which is due to the increase of higher molecular weight materials. When the ratio increases above 0.9, the reaction tends to cause gelation.

In an attempt to prepare higher molecular weight novolacs, Yamagishi *et al.*[19,20] conducted an acid-catalyzed reaction in polar organic solvents. Using equimolar amounts of F (paraformaldehyde) to P, reactions were carried out using HCl in solvents such as isopropanol, ethyl propionate, 2-methoxy ethanol, 4-methyl-2-pentanone, dioxane, and acetic acid (Table 4). It was found that relatively high-molecular-weight novolacs with weight-average molecular weight greater than 1×10^6 were obtained. It was also indicated from ^{13}C NMR that this solution-based novolac gives higher branching with the progress of the reaction.

Table 3 Relationship of F/P ratio to novolac softening point

F:P	*Softening point (°C)*
0.65:1	60–70
0.75:1	70–75
0.85:1	80–100

Konishi *et al.* have been preparing various types of phenolic resins using polycondensation from phenols whose phenolic OH was protected.[21] The kinds of protecting groups for the phenolic OH affords variation of monomers and solvents usable for the reaction, and the control of reactive sites became possible. As a result, it became possible to control the structures of the obtained polymers including main chain structure, molecular weight, and stereochemistry. When anisole was used as the most simple protected phenol, by using sulfuric acid as the catalyst in acetic acid, anisole reacted with formaldehyde as a bifunctional monomer, and linear polymer was obtained without branching, though the methylene linkage was random (Figure 21). The use of large excess formaldehyde did not cause gelation, and molecular weight of the polymer reached as high as 5×10^6 in only 10 min.

The reaction of trimethyl ether of 1,3,5-trihydroxybenzene with formaldehyde using HCl as a catalyst gave completely different products depending on the solvents (Figure 22). Linear polymer was obtained in THF, highly branched polymer in chloroform, and crosslinked nanoparticle in acetic acid/chloroform. The result indicates that the kind of solvent controlled the number of reactive sites of monomer.

5.25.7.4 High *Ortho* Novolac

Under weak acidic conditions (pH 4–6) with an excess of P to F, the use of divalent metal salt such as Zn, Mg, Cd, Pb, Cu, Co, and Ni, preferably acetate, yields a uniformly structured phenolic resin known as high *ortho* novolac. The initial reaction is proposed to occur through chelation of P and F through metal carboxylate (Figure 23). The chelated intermediate is then transformed into *o*-methylol phenol.

Huang *et al.* described many different catalysts for high *ortho* novolac and confirmed the use of divalent salts as the preferred catalyst.[22] Optimum reaction conditions required a molar ratio of 1.25 for P/F, 4% zinc acetate, 5 as pH, xylene as a solvent, and 5 h at 125 °C. *Ortho* content was greater than 90%.

Solution properties of all *ortho* linear oligomer (Figure 24) were examined by Yamagishi *et al.*[23] All the oligomers (n – 2–7) were highly solvated in acetone and molecularly dispersed, while strong H-bonding was observed in chloroform. Both inter- and intramolecular H-bonding facilitated bimolecular aggregation of dimer and trimer into tetramer and hexamer-like

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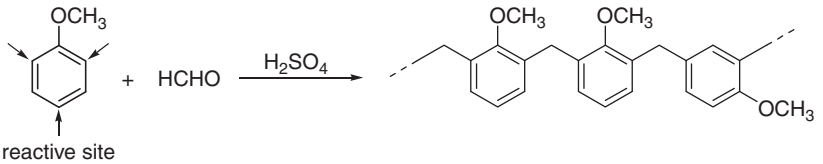

Figure 21 Preparation of linear polymer from anisole.

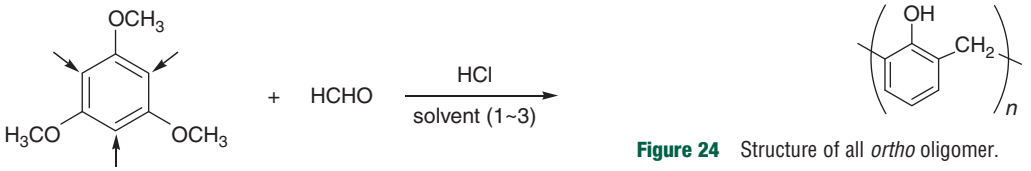

Figure 24 Structure of all *ortho* oligomer.

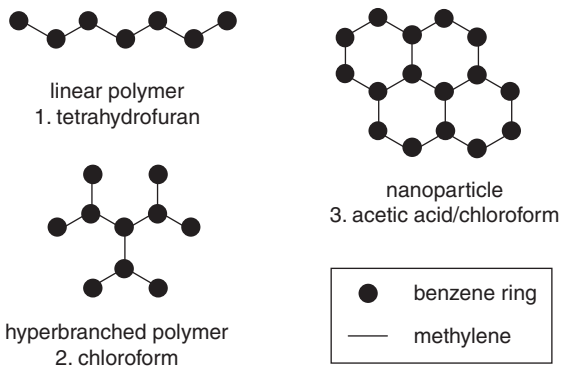

Figure 22 Reaction of protected phenol with formaldehyde.

calixarene structure (Figure 25). Tetramer ($n = 4$) and hexamer ($n = 6$) formed pseudo-calixarene structures by intramolecular H-bonding.

5.25.7.5 Heterogeneous Two-Phase Process

A unique heterogeneous two-phase process was reported by Sumitomo Bakelite for the production of novolacs.[24] In the process, large quantities of an organophosphonic acid (usually 20–100 wt.% based on phenol) was used with molar ratios of P/F = 0.5–1.0 at 110–200 °C. 1-Hydroxyethylidene-1,1′-diphosphonic acid, known as Ferriox 115, is a preferred acid. The resulting novolac is obtained in virtually 100% yield with less free phenol (about 1%) and a narrower molecular weight distribution (MWD) of 1.3–3 than a comparable novolac prepared under oxalic acid conditions.

The organophosphonic acid is highly water soluble, whereas phenol has lower water solubility followed by an even lower water solubility of novolac. These different water solubility characteristics result in a heterogeneous two-phase reaction process, in which P and F and low-molecular-weight materials are within the aqueous organophosphonic phase and react rapidly and go out of the aqueous phase as the molecular weight of novolac increases. Due to these factors, a novolac-type resin with less unreacted P and a narrow MWD is obtained in high yield.

Another unique heterogeneous two-phase novolac process, known as 'phosphoric acid phase-separation' (PAPS) process, was developed by Asahi.[25,26] The heterogeneous two-phase process uses a high amount of phosphoric acid as catalyst/phase reactant by reacting P with 0.4–0.93 mol of F. Molar ratios between 0.4 and 0.8 are for lower molecular weight novolac, and molar ratios between 0.8 and 0.93 are for high-molecular-weight novolac. The high-molecular-weight novolasc has extremely low amount of free P, low amount of dimers (~5%), and an MWD between 1.5 and 2.0. The low-molecular-weight novolac has less than 3% of free P, higher amount of dimer (20–60%), and a narrow MWD between 1.1 and 1.8.

A comparison of PAPS resins with current resins (oxalic acid catalyzed) is shown in Table 5. It is clearly shown that PAPS resin has very low MWD, lower amount of dimer, and lower bulk viscosity with similar softening point as well as higher softening point for similar bulk viscosity. Gel permeation chromatography (GPC) shows a significantly narrow MWD for the

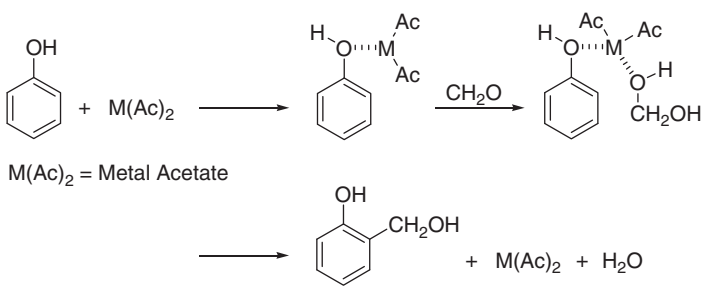

Figure 23 Mechanism for the high *ortho* novolac.

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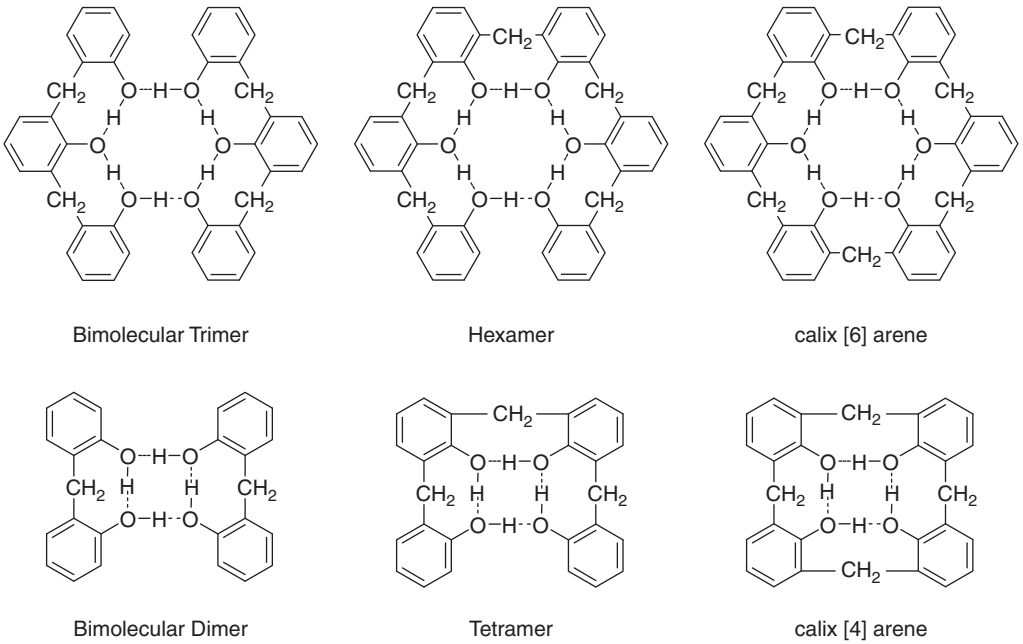

Figure 25 Aggregation of *ortho* oligomers through H-bonding.

Table 5 Comparison of PAPS resins with current resins

Novolaks		M_n[a]	M_w[a]	M_w/M_n	*Dimer (GPC)*	*Softening point (°C)*	*Melt viscosity at 150 °C (Pa s)*
PAPS resins	Low (1)	340	412	1.21	45	49	0.04
	Middle (2)	615	720	1.17	6	83	0.21
	High (3)	688	1035	1.50	1	111	3.03
	Ultra high (4)	1535	7696	5.01	1	150	–
Current resins	Middle (5)	631	2028	3.22	12	85	0.97
	High (6)	864	2623	3.04	11	105	1.38
	Ultra high (7)	950	7926	8.34	8	120	–

[a] Reduced value (polystyrene).

PAPS resin, while the peak for dimer is substantially reduced (Figure 26). An overview of the types of PAPS resin that can be obtained by controlling F/P ratios is shown in Figure 27.

The PAPS yields a high *para* resin as was shown in Table 1. The higher *p,p′* functionality affects the reactivity with hexa, and PAPS resins are slower in cure than standard resins. The PAPS resin also exhibit improved thermal stability because of the lower amount of free phenol and low-molecular-weight components.

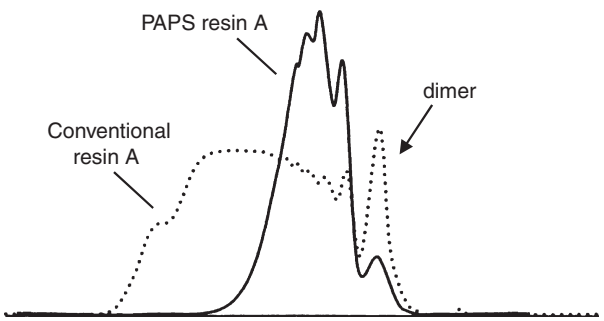

Figure 26 Molecular weight distribution of PAPS and conventional novolac.

5.25.7.6 Curing of Novolac

Hexamethylenetetramine (HMTA or hexa) is by far the most important curing agent for novolac. Typically, about 10% of hexa will be added to novolac. The hydrolysis of hexa by the water in novolac affords, via aminoalcohols (Figure 28), methylene carbocations which attack phenol moieties. A complete understanding of the mechanism of hexa-cured novolac has been lacking due to the crosslinking and intractability of the product.

In 1987, Hatfield and Maciel identified 15 possible intermediates involved in hexa-cured novolac.[27] They used ^{13}C-labeled and ^{15}N-labeled hexa for the study of the curing reaction, and presented solid state ^{13}C and ^{15}N CS/MAS spectra.

More recently, Solomon and co-workers expanded Maciels's proposed mechanistic scheme by undertaking a study on the novolac/hexa curing mechanism by synthesizing many phenolic oligomers with known configuration.[28,29] They studied

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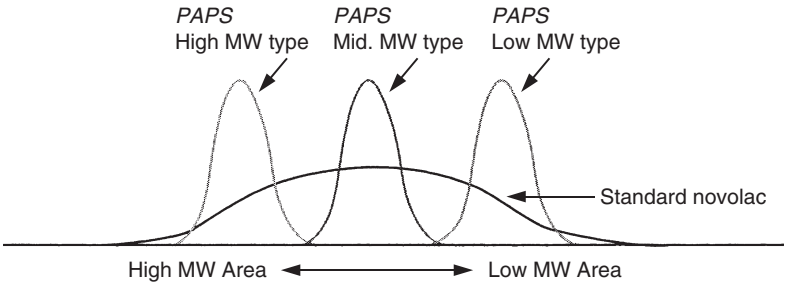

Figure 27 An overview of PAPS and standard novolac.

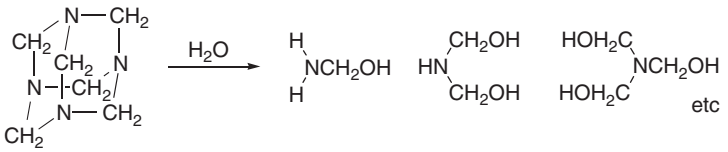

Figure 28 Hydrolysis of hexa.

reaction of hexa with model compounds,[30] studied the fate of novolac/hexa intermediates generated from model compounds/hexa,[31] and analyzed the novolac/hexa cure reaction by ^{13}C and ^{15}N NMR.[32]

Individual reactions of hexa with xylenols, cresols, and phenol showed that when an *ortho* site is unoccupied, a benzoxazine structure is formed. Benzoxazines formed with 2,4-xylenol, *o*- and *p*-cresol, and phenol, whereas 2,6-xylenol led to benzyl amines. The model studies by Solomon *et al.* established the intermediacy of benzoxazine by attack of hexa at vacant *ortho* position. But if *ortho* positions are occupied, benzyl amine is formed by the reaction of hexa at the open *para* site. The curing reaction of novolac with hexa was also conducted with a conventional novolac with novolac/hexa weight ratios of 80/20, 88/12, and 94/6. Accordingly, the curing reaction was proposed to occur in two stages (Figure 29). At the first stage, benzoxazine and benzyl amines form as the initial intermediates. Other intermediates such as triazine, diamine-, and ether-type structures are also formed. At the second stage, by the decomposition, oxidation, and/or further reactions, these initial intermediates are transformed into methylene bridges between phenol rings. At this stage, various amines, amides/imides, imines, methyl phenols, benzaldehydes, and other trace species also forms. Some of the boiling species are considered to remain in the final cure products. The chemical structure of the final cured novolac was proposed to be controlled by the amount of initial hexa introduced and the ratio of *ortho*/*para* sites of the starting resin.

5.25.7.7 Non-Hexa Cure

Other than hexa, methylol derivatives of phenol, bisoxazines, bisbenzoxazines, and solid resol are used as the non-hexa curing agents.

Sergeev *et al.* reported the use of methylol derivatives of phenols as curing agents for novolacs.[33] Besides bismethylol cresol (1), other bismethylol compounds based on cresol trimer (2), cresol novolac (3), and bisphenol A tetramethylol (4) were evaluated (Figure 30). Curing behavior of methylol derivatives and hexa with novolac is compared in Table 6. All methylol materials were satisfactory curing agents for novolac with low extractibles as hexa. Mechanical properties such as impact strengths and ultimate bonding strengths of the methylol-cured novolac were higher than those of the hexa-cured novolac.

Bisoxazolines (A), known as 1,3-PBOX, is reported to co-react with novolac using triphenyl phophine catalyst[34] (Figure 31). The ring-opening reaction of the bisoxazoline is facilitated by the phenolic hydroxyl group without evolving volatiles. As will be described in detail, benzoaxazines also co-react with novolacs. At low cure temperature, the use of benzoxazines for the cure of novolac does not emit ammonia, and yields cured product with lower weight loss. Solid resol is also a curing agent for novolacs. Special formulations based on solid novolac/resol systems are used in molding compounds for electrical applications and others.

5.25.8 Resol

The reaction of F and P using excess amount of F to P under basic condition gives the mixture of products named 'Resol'.

5.25.8.1 Methylol Phenols

Under basic conditions, the reaction of P with F is the addition of F to phenolate (Figure 32), leading to *ortho*- or *para*-methylol phenol, the simplest phenolic components that can be cured into a phenolic resin.

Preparation of *o*- and *p*-methylol phenol has been studied using complexation with cyclodextrin.[35,36] The base-catalyzed reaction of P with F using β-cyclodextrin increased the ratio of *para* isomer to 3:1. Mechanism of selective synthesis of *para* isomer is shown in Figure 33. Phenolate anion is located in the β-cyclodextrin cavity, and approach of F from the bottom of the cavity is more facile to react with the *para* position of the phenolate. Approach of F to the *ortho* position is hindered by

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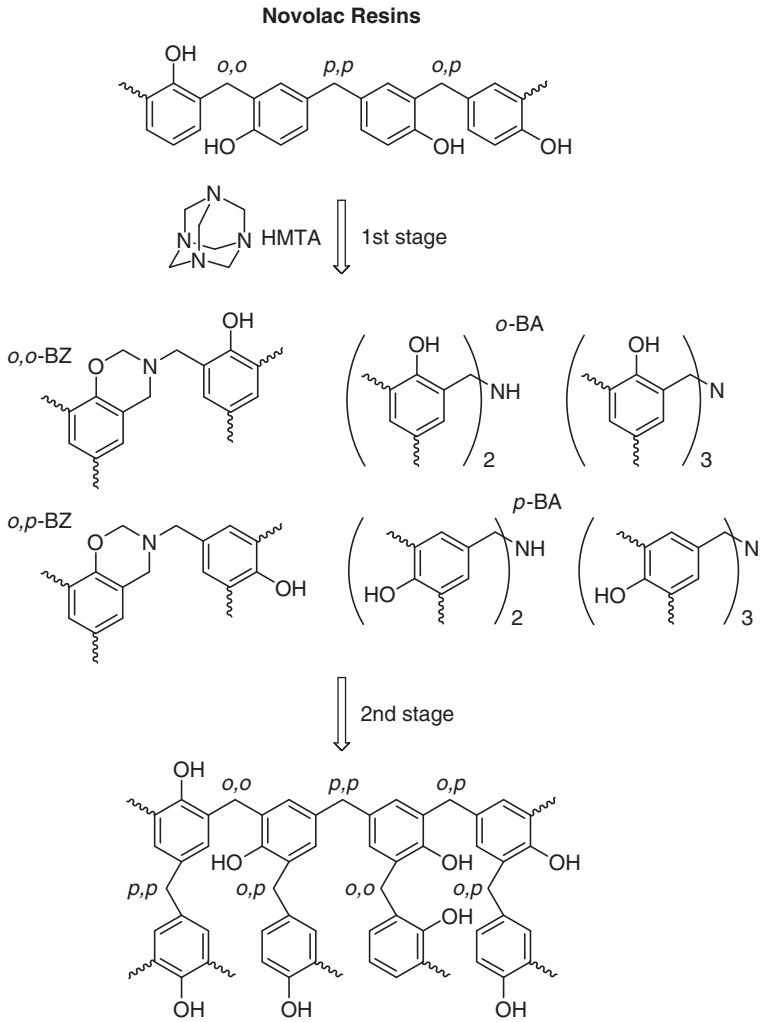

Figure 29 Curing reaction of novolac by hexa.

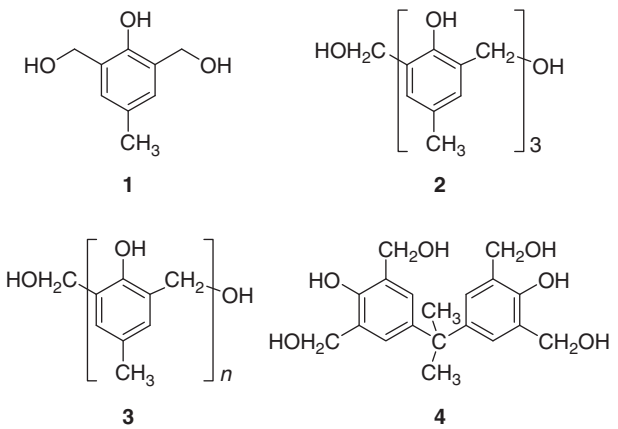

Figure 30 Methylol derivatives of phenols as curing agents for novolac.

the complexation of phenolate and β-cyclodextrin. With a 2-hydroxypropyl group on the bottom side of the cavity, the selectivity of *para* over *ortho* was increased up to 94%. Use of crown ether, 18 crown 6, also led to a high selectivity of *p*-methylol phenol of up to 88%.

Besides the monomethylol phenols, some di- and tri-methylol phenols are formed when the reaction is carried out with more than an equimolar amount of F (Figure 34). These mono-, di-, and tri-methylolated phenols act as transient intermediates and undergo oligomerization into dimeric, trimeric, and higher oligomers depending on F content, reaction basicity, and temperature during reaction.

5.25.8.2 Oligomers

At low temperatures below 60 °C, only addition of F to P occurs. Above 60 °C, condensation reactions of methylol phenols with P and/or methylol phenol occur, and leads to resol resin (Figure 35). Resols are a mixture of the monomethylol phenols, oligomers, residual-free P and F.

The structure of resol depends strongly on the ratio of P and F, the kind of catalyst, and reaction conditions. The ratio of F/P is usually between 1 and 3. The catalysts used are NaOH, Na_2CO_3, oxide and hydroxide of alkali earth metals, aqueous ammonia, hexa, and tertiary amines.

Grenier-Loustalot *et al.* analyzed the resol resin.[37] They showed that resol resin structure depends on reaction

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Table 6 Comparison of methylol derivatives of phenol and hexa on cure of novolacs

Curing agent	*% Wt*[a]	*Cure time*[b]	*% Extractibles*[c]	*Impact strength (kJ m^{-2})*	*Ultimate bending strength (MPa)*
1	36	6.0	2.8	6.2	108.0
2	87	7.5	2.6	2.6	41.5
3	100	6.5	2.9	5.0	64.5
4	38	7.0	2.6	3.6	69.3
Hexa	10	5.5	2.7	1.8	38.9

[a] Comparable amount of reactive groups as hexa.
[b] 180 °C min^{-1}.
[c] Acetone extraction/1 h.

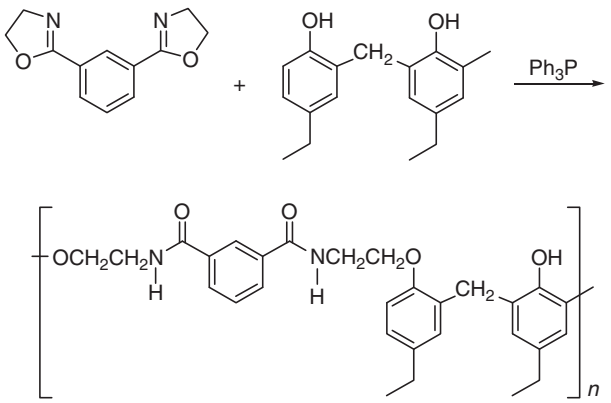

Figure 31 Curing of novolac by bisoxazolines.

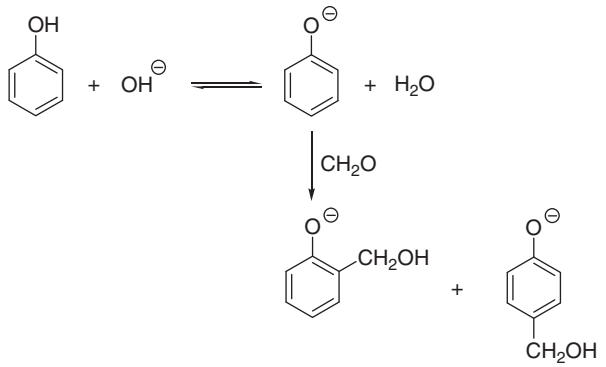

Figure 32 Reaction of phenol and formaldehyde under basic condition.

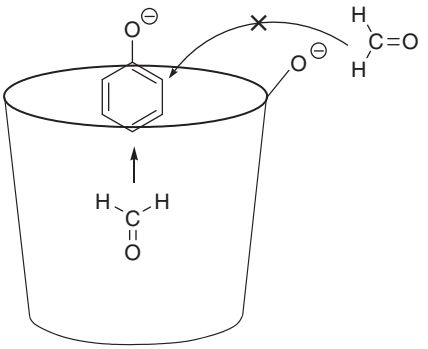

Figure 33 Reaction profile of phenol and formaldehyde in cyclodextrin.

conditions and that all the methylol phenols shown in Figure 34 were formed along with dimers and trimers. Analyses of the dimers (Figure 36) indicated that the dimers were linked by *p,p* methylene bridges.

They also studied catalytic activity at F/P = 1.5 and at pH = 8 from the decrease of F.[38] It was found out that activity was in the following order:

$$Mg(OH)_2 > Ca(OH)_2 > Ba(OH)_2 > LiOH > NaOH > KOH$$

This result concludes that divalent alkali earth metals have higher catalytic activity than monovalent alkali metals and that cations with larger ionic radius have higher catalytic activity. *Ortho/para* ratio of resol has been examined from the ratio of *o*- and *p*-methylol phenol, and found to increase by using metals that have higher chelation ability[39] (Table 7).

5.25.8.3 Curing of Resol

Resols are readily cured by thermal conditions or even at room temperatures by the help of acid or base. The reactions involved in the curing of resol are shown in Figure 37. As the cure of resol proceeds, molecular weight increases, leading to a gel state. Complete cure of phenolic resol leads to a highly cross-linked material exhibiting high modulus, excellent moisture and heat resistance, and high T_g (~150 °C).

There are some other special systems that accelerate the cure of resol resins, such as anhydrides, amides, carboxylic acid esters, and carbonates.

5.25.9 Transformation of Phenolics

Selective reactions can be directed to the hydroxyl functionality of the phenolic group whereby the transformed product has a new utility in applications that are not attainable by the phenolic resin. Moreover, in many instances, these transformations eliminate evolution of by-product such as water and minimize void formation. These transformations are preferably conducted on the stable novolac system. The new functional groups include epoxy, cyanate ester, and benzoxazine. Introduction of epoxy is the most important transformation of phenolics. Cyanate ester and benzoxazine offer promise in many high-temperature applications such as electronics and primary structural components for aircrafts.

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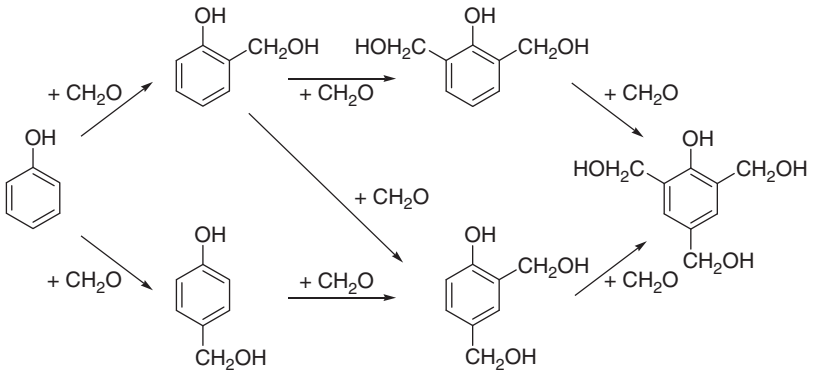

Figure 34 Addition of formaldehyde with phenol.

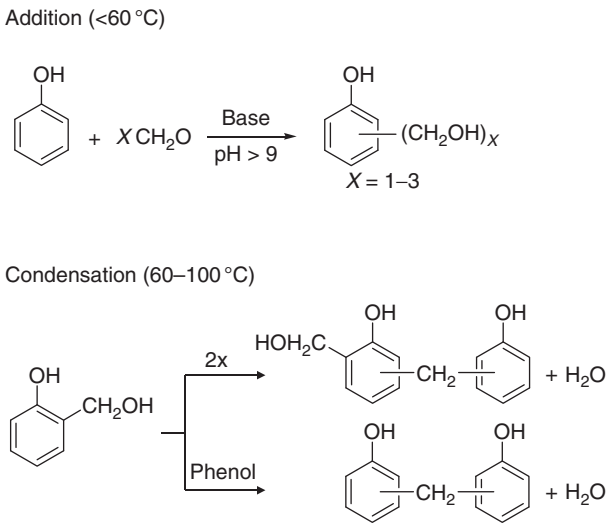

Figure 35 Addition and condensation reactions for resol.

5.25.9.1 Epoxy

By introducing epoxy groups onto the phenolic hydroxyl groups, transformation of phenolic to epoxy is achieved, and a variety of epoxy compounds are obtained. A commodity epoxy resin, bisphenol A epoxy resin, is prepared by the reaction of epichlorohydrin with bisphenol A (**Figure 38**). The average degree of polymerization, *n*, changes depending on the ratio of the reagents. The simplest novolac, bisphenol F, is transformed into the corresponding epoxy resin as a low-viscosity epoxy resin system. Details on epoxy were described before.

5.25.9.2 Cyanate Esters

The cyanate esters were developed in a manner analogous to epoxy resins. Bisphenol A dicyanate ester is obtained in high yield from bisphenol A by using cyanogens chloride and base (**Figure 39**). The cyanate ester trimerizes into a cyanurate ring structure at elevated temperature catalyzed by metal salts, affording crosslinked resin having T_g above 250 °C, excellent thermal stability, low water absorption, low dielectric constant (D_k), and dissipation factor (D_f).[40,41] Only Teflon and polyethylene possess lower D_k and D_f values than cyanate esters.

The problem with this material is its brittleness. Toughening by high-performance thermoplastics such as PES, PSF, PPO, PEI, and PI was successful without sacrificing high T_g.[42,43] Iijima *et al.* studied the effect of *N*-phenylmaleimide-styrene copolymers (PMSs) for the toughening of cyanate ester, and found that cocontinuous phase is effective for the toughening[44] It was found out that *in situ* polymerization of PMS was

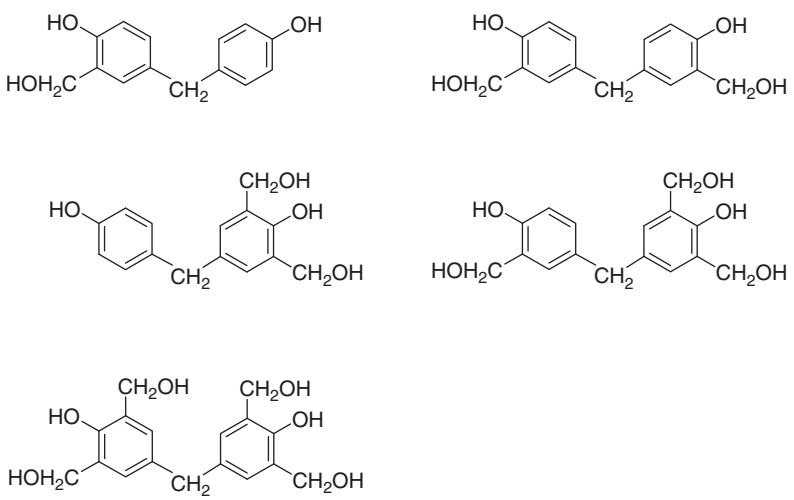

Figure 36 Dimer structures.

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Table 7 Effect of catalyst on the *o*/*p* ratio of hydroxymethylphenols

Catalyst	*Mg(OH)₂*	*Ca(OH)₂*	*Sr(OH)₂*	*Ba(OH)₂*	*LiOH*	*NaOH*	*KOH*	*(CH₃)₄NOH*
o-/*p*- ratio	4.39	3.08	2.68	2.52	1.75	1.56	1.33	0.88

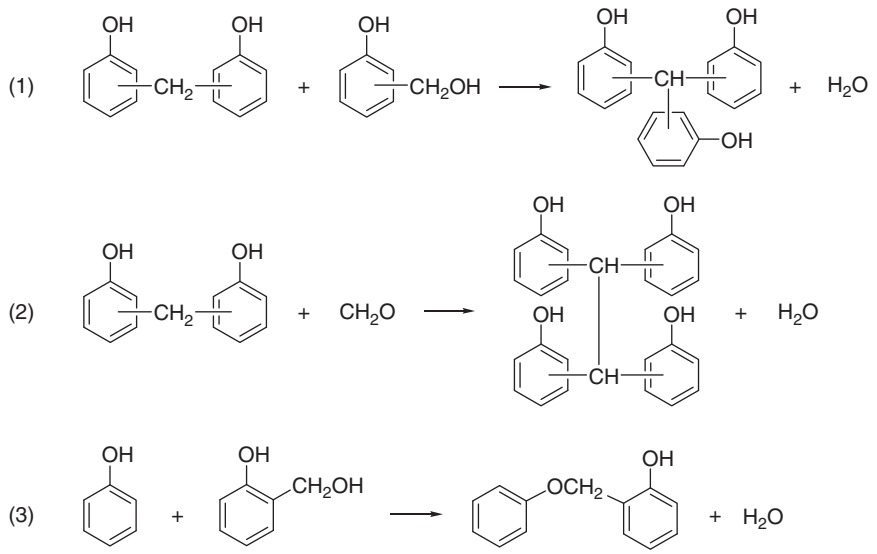

Figure 37 Curing reactions of resol.

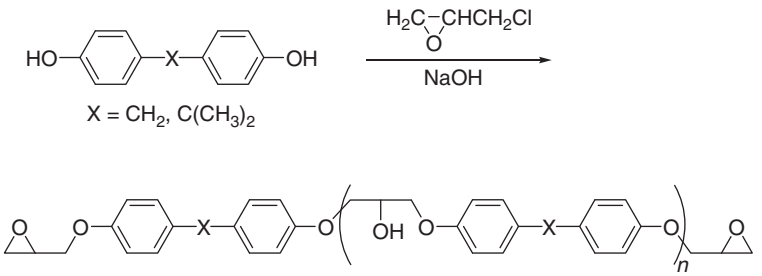

Figure 38 Preparation of epoxy from phenols.

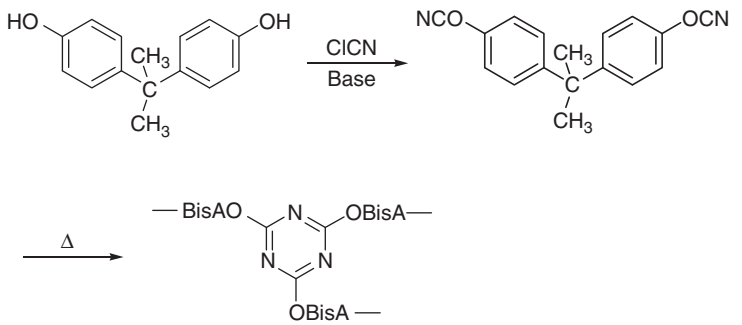

Figure 39 Preparation of cyanate ester and the cure reaction.

effective for the toughening of cyanate esters keeping the flexural properties and T_g.

As a family of cyanate ester, 'BT resin' that consists of bisphenol A dicyanate and bismaleimide is an important resin that is used in high T_g electrical laminates.

5.25.9.3 Benzoxazines

Benzoxazine has been known as the intermediate of the hexa-cured novolac. But, detailed study on benzoxazine was not performed until Ning and Ishida showed that benzoxazines

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are obtained from the reaction of phenols, amines, and formaldehyde.[45] They reported that the ring-opening polymerization of benzoxazine is facilitated by active hydrogen-containing chemicals such as unreacted starting phenolics and oligomeric phenolics[46,47] and that the cured resin shows various interesting features.[48] Now, benzoxazines are emerging as a novel type of phenolic resin. Review papers[49–51] reveal the synthesis and interesting properties of benzoxazines. The first book on polybenzoxazine will be published in 2011.[52]

5.25.9.3.1 Typical benzoxazines

Benzoxazines are easily prepared from phenols, primary amines, and formaldehyde. The wide variations of raw materials, phenols and amines, allow tremendous molecular design flexibility for the cyclic monomers. Formation of one of the typical benzoxazines, B-a, and the structure of the ring-opened resin is shown in Figure 40.

Benzoxazines are typically prepared in one step using phenols, amines, and formaldehyde as starting materials with or without solvent. It is reported that in the benzoxazine formation, triazine is an intermediate.[53] Benzoxazines can be prepared through a two step reaction, in which triazine will be formed first from the reaction of amine and formaldehyde, and in the second step the triazine will be reacted with phenols to give benzoxazine (Figure 41).[54]

Benzoxazines undergo ring opening only by heat treatment without the need of catalysts and without emitting volatiles during cure, and thus offering an excellent dimensional stability for the cured products. The ring-opening reaction is autocatalytic and can be catalyzed by organic and inorganic acids, bases, and metal compounds to lower the cure temperature. Polymerization occurs with near zero shrinkage or slight expansion.[47] The uniqueness of expansion of benzoxazine on polymerization is attributed to molecular packing via H-bond formation.[48] Benzoxazine is a six-membered ring and very stable at ambient atmosphere. This outstanding stability of the monomer makes the curing by the ring-opening polymerization occur at relatively high temperature.

On the mechanism of the ring-opening polymerization, from the detailed study using model compounds, the reaction pathway is proposed as shown in Figure 42: (1) formation of an intermediate polymer having *N,O*-acetal-type linkage in the main chain, and (2) its rearrangement into Mannich-type linkage in the solid state.[56] The mechanism explains that when formation of polymer A in Figure 42 is hindered, weight loss through evolution of imines increases. Therefore, the use of small aliphatic amine such as methylamine is advantageous in

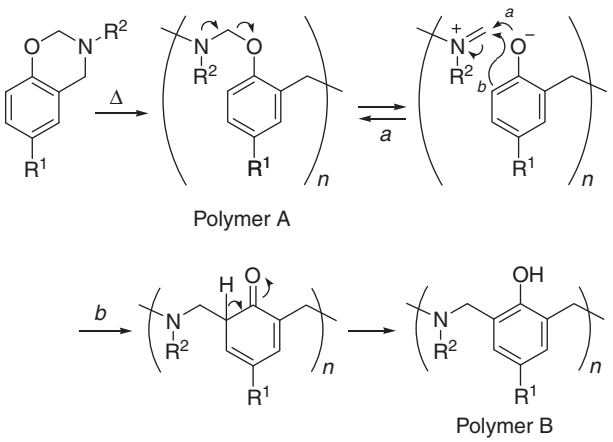

Figure 42 Mechanism of ring-opening reaction of benzoxazine.

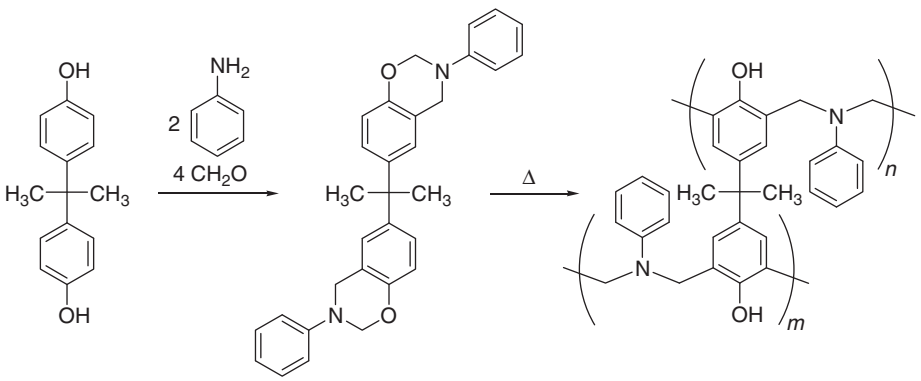

Figure 40 Preparation of typical benzoxazine and the structure of cured product.

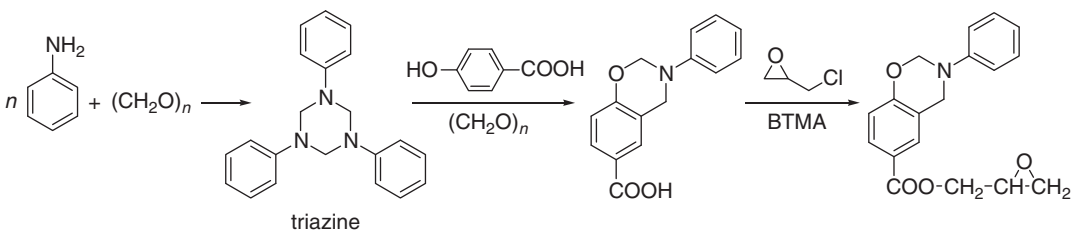

Figure 41 Preparation of benzoxazine through triazine intermediate.

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lowering the ring-opening temperature and reducing the amount of volatiles at the cure.

Benzoxazines differ from the traditional phenolics in that the phenolic moieties are connected by a Mannich base bridge [$-CH_2-N(R)-CH_2-$] instead of methylene ($-CH_2-$) bridge. Polybenzoxazines provide characteristics found in the traditional phenolic resins such as excellent heat resistance and flame retardance. They also provide characteristics that are not found in the traditional phenolic resins such as excellent dimensional stability, low water absorption, and stable low dielectric properties. Therefore, it is considered that polybenzoxazines have overcome the disadvantages of the traditional phenolic resins including poor shelf life of the precursors, the use of harsh catalyst for polymerization, evolution of volatiles during the cure leading to a large volumetric shrinkage upon cure, and formation of voids. These attractive features are responsible for its large volume use in electronics and Fiber Reinforced Plastics (FPR). It was also reported that polybenzoxazine has very low surface free energy.[57] The surface free energy is as low as 16.4 mJ m^{-2}, which is even lower than that of pure Teflon (21 mJ m^{-2}).

A comparison of thermal properties of benzoxazines with other important thermosetting resins is shown in **Table 8**.[58] Both polybenzoxazine and phenolic are favorable based on T_g and char yield as compared to expensive BMI.

However, polybenzoxazines are brittle as is common for thermosets. They also need relatively high temperature (~200 °C) for the ring-opening polymerization. The typical polybenzoxazine, PB-a, has T_g at ~160 °C and storage modulus drops considerably at around T_g due to the low crosslink density. Therefore, further enhancement of the thermal properties is also expected. Another shortcoming is the difficulty to process into thin films from the typical monomers. Aiming for performance enhancement and lowering the polymerization temperature, various approaches have been developed.

Table 8 Comparison of benzoxazines with thermosetting resins

Resin family	*T_g (°C)*	*T_d[a] (°C)*	*Char yield (%)*
Polybenzoxazines	150–260	250–400	45–65
Phenolics	~175		40–50
Epoxies	150–261		≤40
Bismaleimides	250–300	450–500	50–70

[a] Temperatures when 5% weight loss during TGA in N_2, 20 °C min^{-1} heat rate.

5.25.9.3.2 Molecular design of benzoxazines

Taking advantage of the tremendous molecular design flexibility, various types of benzoxazine can be prepared, and properties of polybenzoxazines are easily tuned from the combination of raw materials. Benzoxazines with improved properties are prepared. Such properties include toughness, thermal properties, flame retardant properties, and so on.

For the toughness enhancement, the inclusion of flexible linkages into the backbone of benzoxazine is effective. Such linkages include long alkylene groups[59] and siloxane groups.[60] In some cases, however, the introduction of flexible linkage lowers the thermal properties of the cured polymer.

For the enhancement of thermal properties, introduction of crosslinkable units into the benzoxazine moiety is very effective. It is proposed that polybenzoxazines decompose by volatilizing aniline fragments during the thermal degradation.[61] Therefore, the introduction of crosslink sites into an aniline moiety is expected to enhance thermal properties of polybenzoxazine.

Various double and triple bonds have been found to be effective as crosslink sites. For example, an allyl group is an effective crosslink site that works at moderate temperature.[62] The allyl-containing monomers, P-ala and B-ala, were prepared from phenol and bisphenol A with allylamine and formaldehyde (**Figure 43**). Differential scanning calorimetry (DSC) of P-ala showed two separate exotherms with maxima at 207 °C and 260 °C, which correspond to the polymerization of the allyl groups and the ring opening of benzoxazines, respectively. The obtained thermosets exhibit much higher T_g (~300 °C), which is nearly 150 °C enhancement. Another series of allyl-containing monofunctional benzoxazine, prepared by reacting various cresols with allylamine and paraformaldehyde,

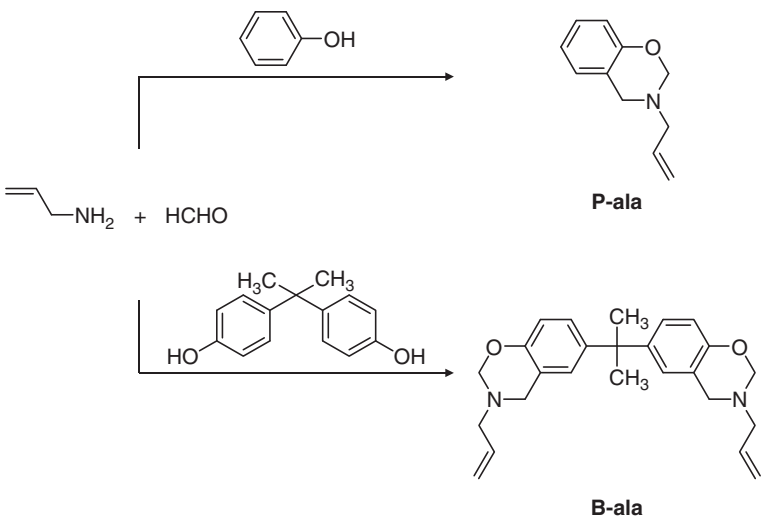

Figure 43 Preparation of allyl-containing benzoxazine.

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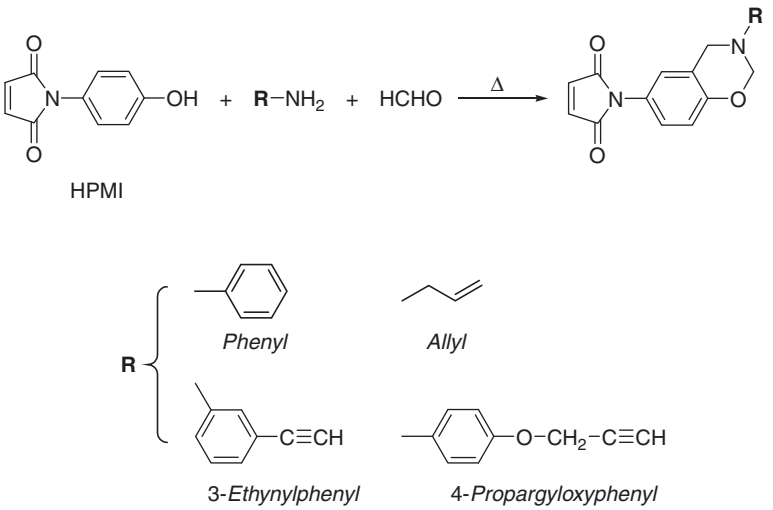

Figure 44 Preparation of novel benzoxazines containing crosslink sites.

also showed increased thermal properties.[63] The *ortho* position in cresol was more reactive than the *para* position.

Other double and triple bonds attached to amine moieties were similarly effective to enhance the thermal properties of polybenzoxazines. The examples are propargyl,[64] ethynyl,[65] and nitrile groups.[66]

Crosslink sites can also be introduced into phenol moiety. An example is the introduction of maleimide double bond through the use of hydroxyphenylmaleimide (HPMI). By reacting HPMI with formalin and various amines (e.g., aniline, allylamine, and aminophenyl propargyl ether), a series of maleimide-containing benzoxazines are obtained (**Figure 44**).[67] The thermal cure of the monomers at 250 °C afforded polybenzoxazine having novel network structures. The T_gs were as high as 241–335 °C with improved thermal stability and higher char yield (62–70%). Other than the double and triple bond, epoxy group was introduced as another crosslink site of benzoxazine as shown in **Figure 41**.[54]

The introduction of a mesogenic group in benzoxazines was attempted to provide LC benzoxazines, which give, upon cure, polybenzoxazine resins with enhanced thermal conductivity as well as improved thermal and mechanical properties. In the first report on LC benzoxazines, a cyanobiphenyl unit was used as the mesogen. The LC benzoxazine showed a nematic phase only upon cooling and did not show any LC phase upon heating, indicating a monotropic LC phase.[68] Another type of LC benzoxazines was recently reported, in which ester and azomethine linkages were used as the mesogenic unit. The benzoxazine showed an LC phase not only upon cooling down but also upon heating.[69]

5.25.9.3.3 High-molecular-weight benzoxazine precursors

As the precursors of polybenzoxazines, only low-molecular-weight cyclic benzoxazines, prepared by the reaction of bisphenol, amine, and formaldehyde, have been studied in detail. The yield of monomer is ~80%, and the reaction mixture contains ring-opened oligomers. The combination of diamine and bisphenols with formaldehyde could give polymers that contain benzoxazine in the backbone. Though Ishida reported the modification of polyphenol with a monofunctional amine to get a benzoxazine-functional polymer,[70] a high-molecular-weight polymer containing the cyclic benzoxazine structure as a repeating unit in the main chain has not yet been prepared.

Takeichi *et al.* reported the first successful synthesis of high-molecular-weight polybenzoxazine precursors containing cyclic benzoxazine groups in the backbone.[71,72] The reaction of bisphenol A, various diamines, and paraformaldehyde (**Figure 45**) afforded various precursors in the range of 77–87% yield after purification. The M_w was in the range of 6000–8900 and M_n was 2200–2600, showing that the molecular weight is not so high. But, it should be emphasized that self-standing thin films were easily obtained by casting the precursor solutions. All the polybenzoxazine films cured by the heat treatment up to 240 °C gave remarkably improved tough films (**Figure 46**). They also had much improved tensile strength and the elongation at break. The T_g values of the polybenzoxazines from the high-molecular-weight precursors were as high as 238–260 °C, much higher than the T_g of the typical polybenzoxazine. The significant increase in T_g indicates the beneficial effect of the linear long backbone and the high crosslink density.

High-molecular-weight precursors were also synthesized from aminophenols and formaldehyde (**Figure 47**).[73] The precursors also gave self-standing thin films. Upon a gradual thermal cure up to 250 °C, they afforded polybenzoxazine films, having T_g as high as 260–300 °C. Decomposition temperature and char yield of the thermosets were higher than those of the typical polybenzoxazine.

The above approach to prepare high-molecular-weight polybenzoxazine precursors employs the benzoxazine formation as the method of polymerization. The reaction to make benzoxazine is known to give benzoxazine only in 70–80% yield. It is therefore not a good reaction to be used for polymer formation. But because of this unique reaction feature, the obtained high-molecular-weight benzoxazines have various advantageous unique properties as follows: (1) the oligomers are low molecular weight, (2) the solubility in the ordinary solvents is excellent, (3) the uncured films can be obtained as self-standing films, and (4) cured films are very tough with much improved thermal

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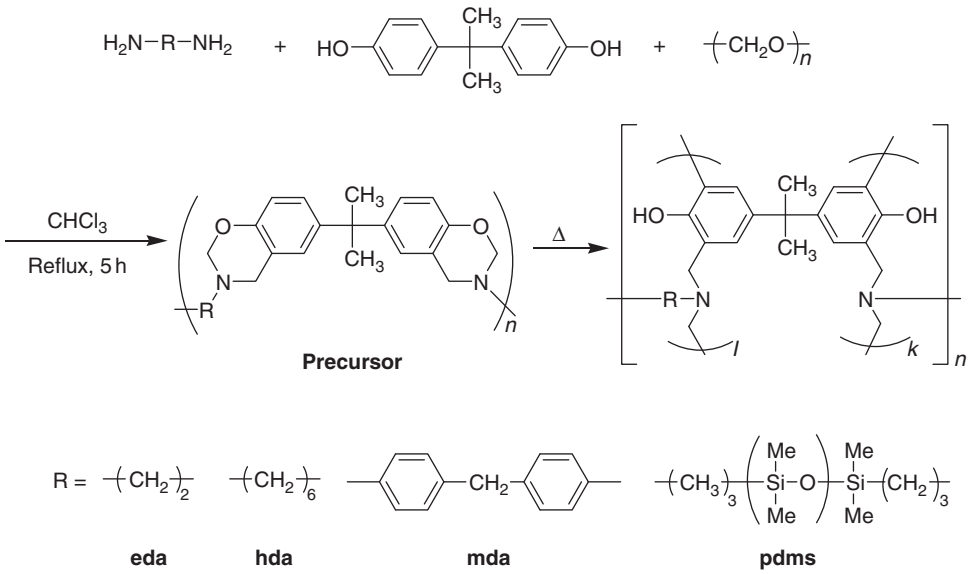

Figure 45 Preparation of high-molecular-weight polybenzoxazine precursor.

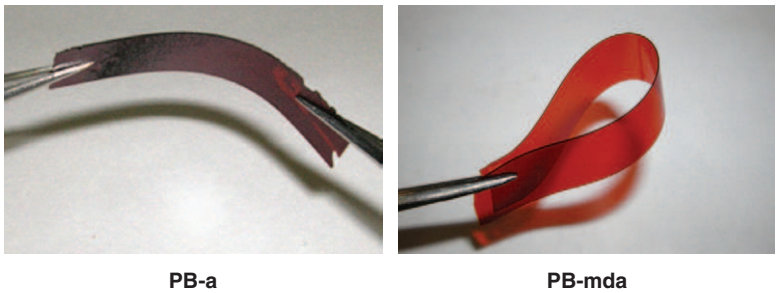

Figure 46 Appearance of polybenzoxazine films.

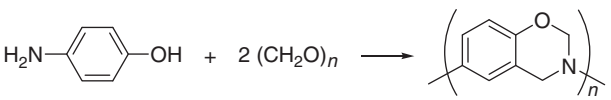

Figure 47 Preparation of polybenzoxazine from aminophenols and formaldehyde.

properties (T_gs are around 250 °C). Other research groups also employed the same chemistry and examined the structure and properties of the obtained polymers.[74–77]

The disadvantage of the above method is that the chemical structure is not well defined. Various attempts have been examined to prepare high-molecular-weigh polybenzoxazine precursors with well-defined structure, having benozxazine in the polymer backbone or as a pendent. For that purpose, difunctional monomer containing benoxazine in the backbone (main-chain type) will be first prepared, and then reacted to give a polymer containing benzoxaszine. Various reactions have been employed for the polymerization of benzoxazine-containing monomers such as ester formation between diol and adipoyl chloride,[78] Diels–Alder reaction,[79] click reaction,[80] and hydrosilylation[81] (Figure 48). These approaches give well-characterized polymer. But one of the problems of the approach is that the solubility of the polymers is generally low and that it is often difficult to get soluble high-molecular-weight polymers. Side-chain or pendant-type polybenzoxazines have also been prepared using similar chemistry.[82–87]

5.25.10 Natural Products as Phenolics

Various natural products are known to contain phenolic groups within their structure such as lignin, tannin, and cashew nut shell liquid. These natural products undergo similar reactions as were shown for novolacs. An epoxy group has been introduced into lignin,[88] and hydroxymetylation was examined with lignin[89] and tannin.[90] The chemistry of cashew nut shell liquid was reviewed.[91]

Lignin is actually a naturally occurring phenolic compound, but phenolic activity is rather low. Funaoka *et al.* developed a method to isolate lignin from cellulose and hemicellulose mixtures and convert them into lignophenol by the cleavage of benzyl aryl ether through the phase-separation system.[92–94]

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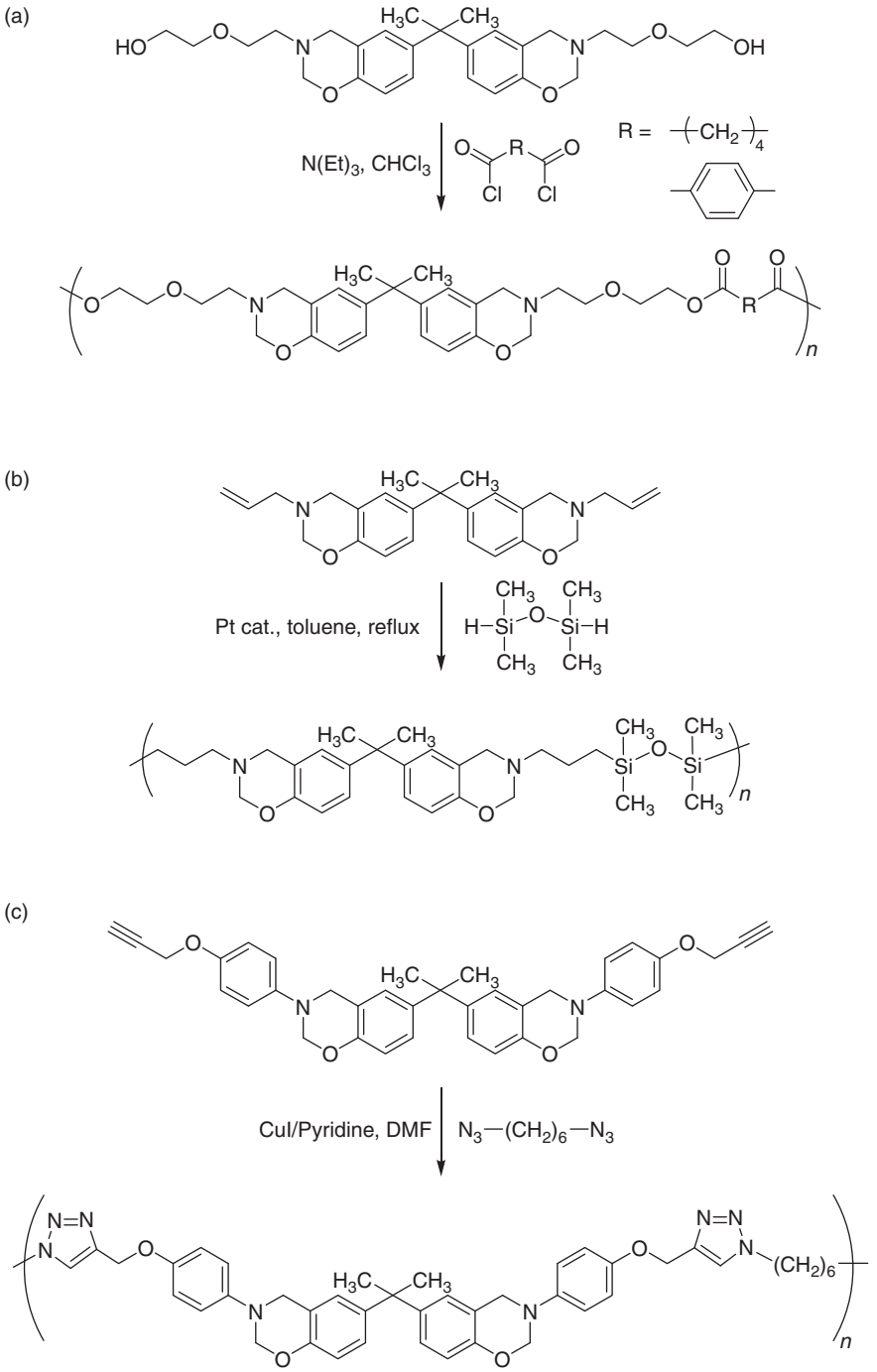

Figure 48 Preparation of polymers containing benzoxazine in the main chain.

The lignophenols have improved activity as phenolic compounds, and various studies to utilize the lignophenol are being carried out.[95]

5.25.11 Modification by Alloys and Co-curing

5.25.11.1 Modification of Phenolics by Alloying

Brittle characteristics have been always a problem for thermosets. Several methods have been used to toughen the phenolics. A method that has been mainly applied to novolac is the introduction of rubber modifiers. Rubber emulsion or latex is added to crude novolac and then dehydrated so that the rubber component is uniformly dispersed in the novolac. These rubber-modified novolac are used by curing with hexa. They exhibited marginal toughness.

Another method which is mainly applicable to resols consists of a co-reaction of resol methylol with the double bond/acid end group of nitrile butadiene rubber or resol methylol reacting with polyol/isocyanate (PUR rubbery phase). The flexible rubbery phase is introduced into the resol phase by the proposed co-reaction.

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An interpenetrating network system (IPN) is reported on phenolic resin combined with oligomeric silanol or siloxane leading to a toughened phenolic resin system.[96] The phenolic resin modified with siloxane showed better impact and burst strength than phenolic control.

A technique that has been successful in enhancing the toughness of thermosets is the introduction of thermoplastic, ductile phase into matrix resin.[97] High-performance, high T_g engineering plastics are co-reacted or uniformly dispersed in the thermoset. Poly(aryl ether)s are high T_g (~200 °C), high modulus/strength polymers, and poly(aryl ether)s with and without hydroxyl end group were evaluated in hexa-cured novolac.[98]

5.25.11.2 Modification of Benzoxazine by Alloying

The performance of polybenzoxazines can be improved much more easily than novolac or resol by alloying with various polymers. Also, benzoxazines appear to be versatile in that they can undergo co-reaction with a variety of materials such as epoxy, isocyanates, and bismaleimide (BMI).

Alloying with epoxy and/or phenolic resins has been one of the well-studied examples.[47,99,100] Epoxy reacts with polybenzoxazine through its phenolic OH, and the traditional phenolic resin works as an acid catalyst for the ring-opening polymerization of benzoxazine. Addition of the low viscous epoxy resin is also advantageous in processing.

Toughness of the brittle polybenzoxazine can be remarkably improved by alloying with elastomers like liquid rubber and polyurethane (PU). Jang and Seo evaluated the effect of amine-terminated butadiene acrylonitrile (ATBN) and carboxyl-terminated butadiene acrylonitrile (CTBN) rubbers, and reported that ATBN exhibited better distribution of rubber particles in the matrix phase than CTBN.[101] Higher fracture toughness and smaller rubber particle size was observed in benzoxazine modified with ATBN than that modified with CTBN.

The performance of the ATBN-modified polybenzoxazines can be further improved by the addition of HPMI.[64] HPMI is activated by its OH group and copolymerize with benzoxazine (Figure 49). The blend with HPMI effectively lowers the cure temperature of B-a as large as 40–60 °C. The maleimide double bond in HPMI further crosslinks to give a cured resin having improved properties such as higher T_g, tensile modulus, and thermal stabilities. Thus, the combination of HPMI and ATBN was effective to lower the curing temperature, to increase toughness, T_g, and degradation temperature at the same time.

PU is one of the most important functional polymers that are being used in various applications. Alloying of PU with polybenzoxazine can be considered as a novel polymer alloy of PU and phenolic resin, in which improvement of both the thermal properties of PU and the toughness of polybenzoxazine can be achieved. The blend of an NCO-terminated PU prepolymer and a benzoxazine was thermally treated at 190–200 °C to give yellow, transparent films.[103,104] The network structure is formed by the reaction of the NCO functionality with the phenolic OH that was formed through the ring-opening polymerization of the benzoxazine (Figure 50). Films became a plastic or an elasomer depending on the ratio of the benzoxazine and the PU prepolymer. Only one T_g was observed, and the T_g value increased with the increase of the

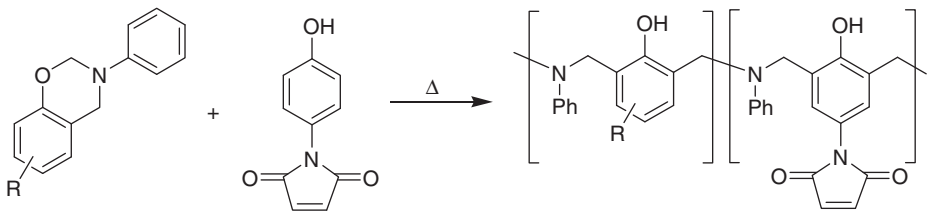

Figure 49 Reaction of benzoxazine and hydroxyphenylmaleimide.

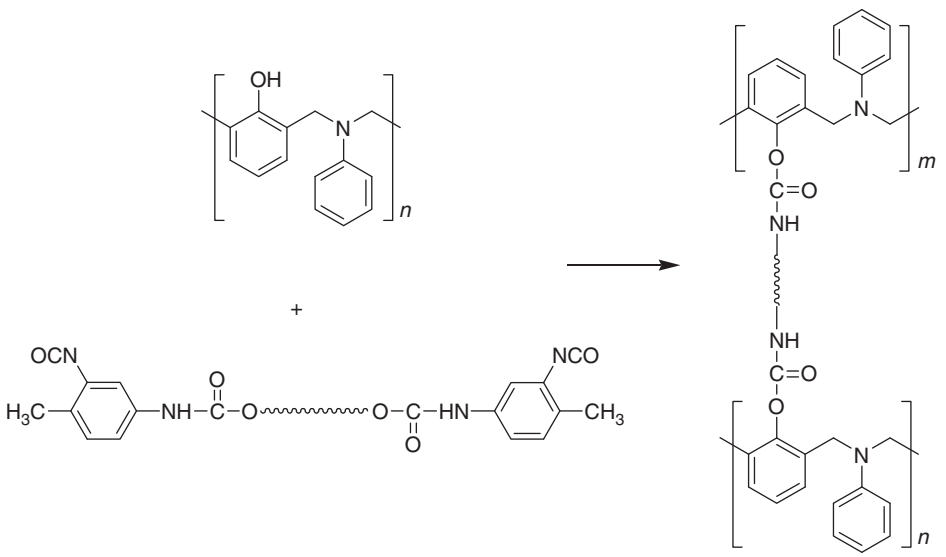

Figure 50 Reaction scheme of benzoxazine and polyurethane prepolymer.

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benzoxazine content. By the introduction of PU, the toughness of benzoxazine was improved. On the other hand, the thermal stability of the PU was improved by the addition of a small amount of the benzoxazine.

5.25.11.3 Alloying of Benzoxazine with Polyimide

Polyimide is the most important thermally stable polymers. Wide variations of the monomers and the precursors make polyimide a suitable candidate to be used as one component of a polymer alloy.

Polymer alloys of a polybenzoxazine and a polyimide was prepared by blending B-a as a benzoxazine with a poly(amide acid), PAA, as a precursor of polyimide, followed by film casting and thermal treatment for the ring-opening polymerization of the benzoxazine and imidization.[105] Various types of PAA were prepared as shown in Figure 51. It was observed that the onset temperature of the exotherm due to the ring-opening polymerization decreased by as much as ~80 °C by blending B-a with a PAA because of the catalytic effect of the carboxylic group in the PAA. The resulting alloy films are considered to form a semi-interpenetrating polymer network (semi-IPN) consisting of a linear polyimide and a crosslinked polybenzoxazine or to form an AB-co-crosslinked polymer network by the copolymerization of benzoxazine with polyimide containing a pendent phenolic hydroxyl (Figure 52).[122] The semi-IPN polymers gave two T_gs, while the AB-co-crosslinked polymers gave only one T_g. Both types of polymer alloys were effective to improve the brittleness, the T_g and the thermal degradation temperature of polybenzoxazine. The semi-IPN formation

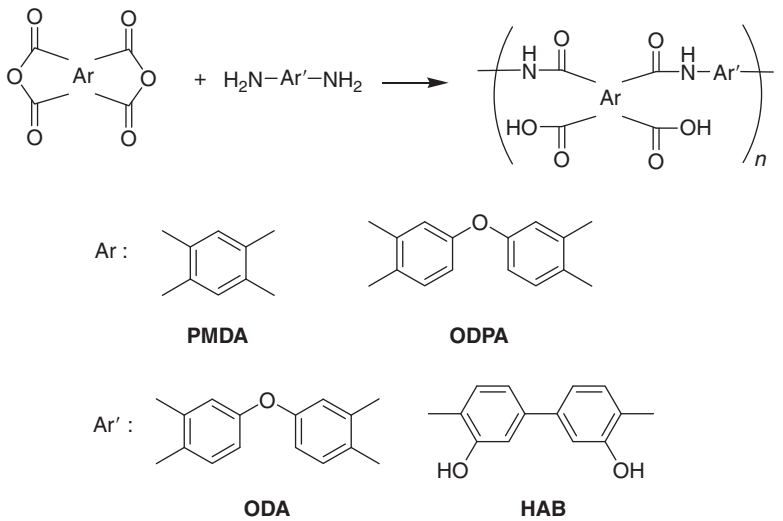

Figure 51 Preparation of various poly(amide acid) as polyimide precursor.

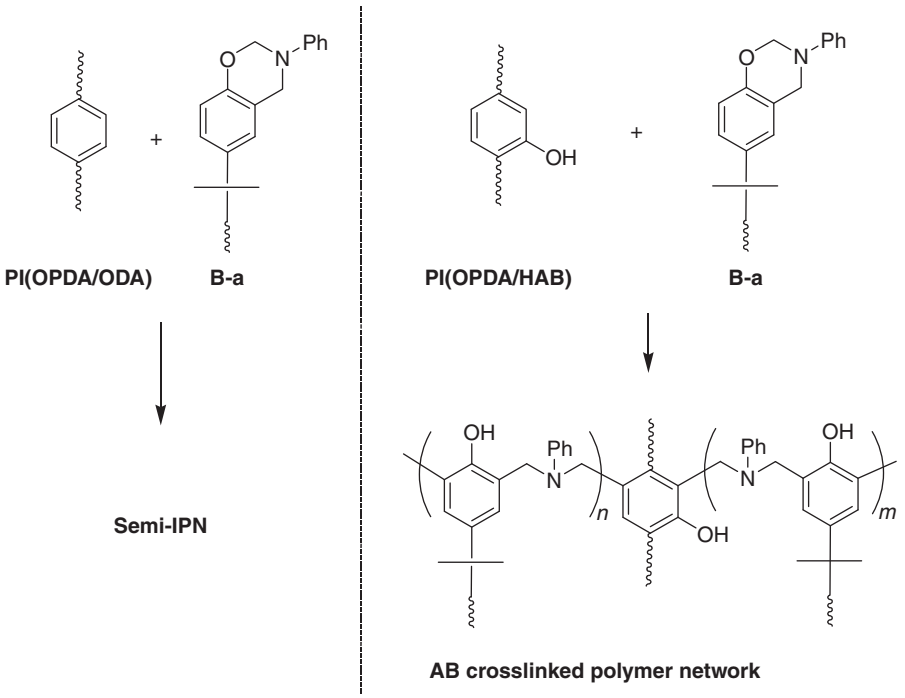

Figure 52 Scheme of reaction between polyimide and benzoxazine.

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was especially effective for toughening the polybenzoxazine, while the AB-co-crosslinked polymer network was effective for increasing T_g.[123]

5.25.11.4 Alloying of Benzoxazine with Bismaleimide

Another type of polymer alloy was prepared by mixing a typical benzoxazine, such as P-a and B-a, and a typical bismaleimide, 4,4-bismaleimidodiphenyl methane (BMI), followed by a thermal cure.[51,124] IR and DSC analyses indicated the thermal reaction between the hydroxyl group of the polybenzoxazine and the double bond of BMI, forming an AB-co-crosslinked structure as supported by the model reaction of phenol and *N*-phenylmaleimide. Dynamic mechanical analysis (DMA) of the polymer alloys showed only one T_g, also suggesting the formation of the AB-co-crosslinked structure. Interestingly, T_g of the polymer alloys shifted to higher temperature by the increase of the BMI content, and were even higher than those of each resin due to the formation of the AB-co-crosslinking (Figure 53). The thermal stability also increased with the increase of the BMI content.

5.25.12 Hybrids and Composites

Nanotechnology has been applied to phenolic resins, benzoxazines, and cyanate esters using various nanomaterials such as nanoclay, carbon nanofiber, carbon nanotubes, nanosilica, POSS, and metal oxide nanoparticles by the sol–gel process.

5.25.12.1 Preparation of Hybrids by Layered Clay

Polymer–clay hybrid is a new class of composite material, in which a clay, a layered silicate, is dispersed in a polymeric matrix in nanoscale size.[106,107]

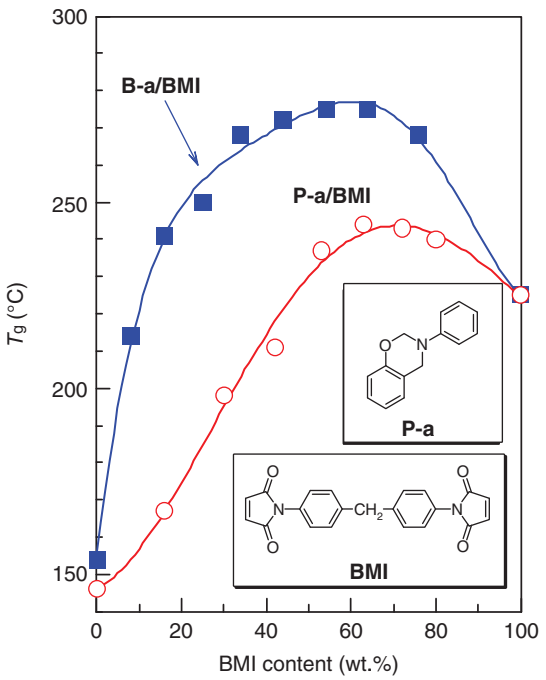

Figure 53 T_g profile of benzoxazine/bismaleimide blend.

The first study on the successful preparation of polybenzoxazine/clay hybrids was reported by Takeichi *et al.*, in which the inclusion of an organically modified-montmorillonite (OMMT) into a polybenzoxazine matrix led to a considerable improvement of its properties.[108,109] Polybenzoxazine/clay hybrids were prepared by two different methods; a melt method and a solvent method. X-ray diffraction (XRD) measurements of the hybrids showed that the blending method and the kind of solvent play crucial roles for the dispersion of OMMT in the polybenzoxazine matrix. In the melt method and in the solvent method using NMP as a solvent, a complete exfoliation of clay nanolayers into the polybenzoxazine matrix was achieved. Interestingly, the inclusion of any type of OMMT significantly lowered the curing exotherm of the benzoxazines, suggesting a catalytic effect of the onium ions of the clay surface and/or the silanol groups at the edge of the clay on the ring-opening polymerization of the benzoxazines. The hybrids exhibited higher T_g (for 25–30 °C) and increased storage moduli than the pristine resins. Dynamic and isothermal TGA clearly showed the improvement of the thermal stability by the inclusion of the clay. The effect of the clay was most significant at around 2–5 wt.% of inclusion for the improvement of various properties.

The effect of OMMT inclusion was also examined in the epoxy/polybenzoxazine[110,111] and the PU/polybenzoxazine[112] alloys. In both cases, lowering of the cure temperature and the enhancement of the thermo-mechanical properties were achieved.

Polybenzoxazine–clay hybrids were also prepared using a synthetic mica.[113] The storage moduli of the hybrids were much enhanced because of the reinforcing effect of the mica nanolayers that have large aspect ratio. The hybrids also showed an improved thermal and thermoxidative stability with higher char yield.

5.25.12.2 Preparation of Hybrid by Sol–Gel Process

The sol–gel process is a common and a convenient technique to develop a homogeneous and high-purity metal oxide (Figure 54). Therefore, it is convenient to grow an inorganic ceramic network within a polymer matrix through the sol–gel process, thus producing organic–inorganic hybrids.

Polybenzoxazine/silica hybrids were prepared by blending various content of tetraethoxysilane (TEOS) with B-a using THF, followed by the curing up to 240 °C for 1 h.[114] Polybenzoxazine/titania hybrids were similarly prepared by using titanium isopropoxide (TIPO).[115] The hybrid films were optically transparent with loading of silica or titania up to 10–20%, and the transparency decreased at higher loading. In the blends of B-a and TEOS or TIPO, the onset and the maximum of the exotherm due to the ring opening of the benzoxazine was shifted to lower temperature at small loading of the metal oxide precursor. This implies that the acidity of the residual Si–OH and Ti–OH group in silica or titania network is high enough to initiate the ring-opening polymerization of B-a. The morphology study of the hybrids indicates that the inorganic domains are homogenously dispersed into the organic matrix in a nanosacle. The viscoelastic analyses revealed that the inclusion of silica or titania shifted the T_g to higher temperature than the neat resin. The decomposition temperatures and the char yield of PB-a considerably increased by the

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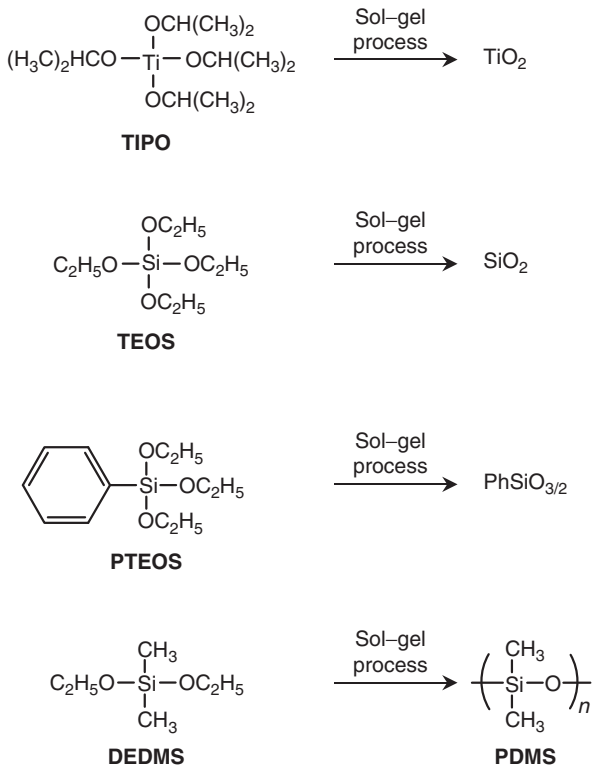

Figure 54 Sol–gel reactions of various precursors.

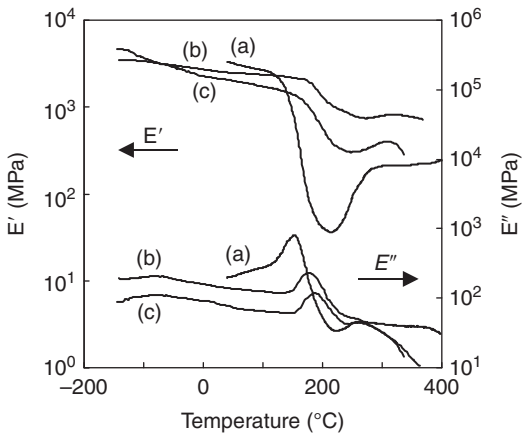

Figure 55 Dynamic mechanical properties of polybenzoxazine/PDMS hybrids.

inclusion of a small amount of silica or titania, demonstrating that the metal oxide dispersed into the matrix acts as a thermal insulator to protect the polybenzoxazine network.

Polydimethylsiloxane (PDMS) is an inorganic polymer that shows not only flexibility but also unique properties such as good thermoxidative stability, low surface energy, high hydrophobicity, and high gas permeability. Polybenzoxazine/PDMS hybrids were successfully prepared by blending a benzoxazine and diethoxydimethylsilane (DEDMS), followed by the thermal curing that induce the ring-opening polymerization of the benzoxazine and the sol–gel process of DEDMS (Figure 54).[116] The introduction of PDMS improved the tensile strength and the elongation at break of the pristine PB-a, because of the toughening effect of the PDMS. Surprisingly, in spite of the introduction of the flexible and low T_g PDMS, T_g of the polybenzoxazine shifted to higher temperature (Figure 55). The decrease of the storage modulus above T_g was also suppressed by the hybridization with PDMS. These results suggest that the *in situ* formed PDMS behaves as a plasticizer for the polymerization of benzoxazine accompanied with the increase of the crosslink density. Moreover, the decomposition temperature and the weight residue at 850 °C increased with an increase in the PDMS content.

5.25.13 Conclusion

Epoxy and phenolic resins are the most important thermosets widely used in various fields such as electronics and aerospace industries. These thermosets are indispensable because of the excellent thermal and mechanical properties, and creep resistance. Thermosetting materials are becoming more and more important as evidenced by the recent increasing application in commercial airplanes such as the Airbus A380 and Boeing B787.

It is true that thermosets are old polymers, but there continues to be new developments. For epoxy resins, toughening without sacrificing thermal properties is always expected. The enhancement of thermal conductivity is also a challenge nowadays. For phenolic resins, PAPS resin is a promising new material. Remarkable development can be seen in the progress of benzoxazine resin as an emerging high-performance thermoset. The designing of novel monomers and high-molecular-weight precursors of benzoxazines are a promising approach for obtaining polybenzoxazines for specific applications, taking advantage of the wide selection of mono- and diamines and mono- and bisphenols. Polymer alloys and organic–inorganic hybrids are also promising approaches for the design of benzoxazine-based materials with required performance.

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Biographical Sketches

Tsutomu Takeichi received his PhD degree in 1979 from The University of Tokyo under the direction of Professor Teiji Tsuruta. He joined Toyohashi University of Technology and was promoted to Professor in 2002. Meanwhile, he spent 2 years from 1984 to 1986 at Colorado State University in the USA as a postdoctoral fellow with Professor J. K. Stille, where he started research on polyimide. His current research interests include designing of novel high-performance polymers based on polyimide and polybenzoxazine.

Nobuyuki Furukawa received his Master degree from Kyoto University in 1982 and joined Nippon Steel Chemical Co., Ltd., Japan. He received his PhD degree from Kyoto Institute of Technology in 1999 under the supervision of Professor Yoshiharu Kimura. In 2005, he moved to Sasebo National College of Technology as a Professor. His current research interests include development of functional network polymers, polymer alloys, molecular composites, and composite materials especially for the application in the microelectronic applications.

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5.26 High-Temperature Thermosets

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5.26.1 Introduction

5.26.1.1 High-Temperature Polymers

The development of high-temperature polymers began in the late 1950s, mainly in support of the growing electronics and aerospace industry. Although the term 'high-temperature polymer' or 'high-performance polymer' is somewhat arbitrary, it has generally been reserved for polymers, which display exceptional thermal stability over prolonged periods of time in combination with mechanical performance and solvent resistance. Such polymers often make extensive use of aromatic monomers, that is, all carbon atoms have a high sp^2-bonding character and preferentially lack sp^3-type bonding. The primary reason is that the C═C bond dissociation energy of 614 kJ mol^{-1} is substantially higher than the 348 kJ mol^{-1} bond dissociation energy for the C–C bond. High-temperature polymers typically exhibit high glass-transition temperatures (>200 °C), high decomposition temperatures (>450 °C), and excellent mechanical properties. Examples of first-generation high-temperature polymers include polyimides (e.g., Kapton™ and Upilex™), main-chain all-aromatic liquid crystal (LC) polymers such as *para*-aramid (e.g., Twaron™ and Kevlar™), polybenzoxazoles (e.g., Zylon™), and polybenzimidazoles (PBIs; e.g., Celazole™). Although these polymers display excellent thermomechanical properties, they are inherently difficult to process. They do not melt and they can only be processed from a soluble precursor state, for example, the polyamic acid state, or the final polymer must be processed from aggressive solvents such as sulfuric acid or polyphosphoric acid.

In an attempt to provide high-temperature polymers with melt-processing capability, new aromatic polymers were developed in the 1970s and examples include Fortron™ (polyphenylene sulfide), Ultem™ (polyetherimide), poly(arylene ether)s such as Radel™ (polyetherketone), and Victrex™ (polyetheretherketone). Although most of these polymers can indeed be processed from their melt phase, their thermomechanical properties remain far below what could be achieved by the first-generation high-temperature polymers and their high degree of crystallinity results in challenging processing considerations. One needs to control the degree of crystallinity in the final part, in order to obtain the desired mechanical properties, and minimize thermal stresses. Several books and reviews on high-temperature/high-performance polymers, covering the applications, history, synthesis, and processing considerations, are available.[1–6]

5.26.1.2 High-Temperature Thermosets

In the 1980s, an increasing demand for high-temperature polymers for adhesives, composite matrices, dielectric films, foams, and moldings prompted polymer chemists to explore new reactive all-aromatic architectures. The shape complexity of the final products, especially in microelectronic and fiber-reinforced composite applications, required resins with low melt viscosities and low after-cure coefficients of thermal expansion (CTEs). In general, one can distinguish two approaches: the 'reactive monomer' approach and the 'reactive oligomer' approach.

In the first case, as shown in **Scheme 1**, a suitable diamine monomer is functionalized with two reactive functionalities. All reactive monomers have identical molecular weights, which are typically in the range of 200–500 g mol^{-1}. The advantage of this approach is the low melt viscosity of monomeric species, which allows for rapid processing and the ability to fabricate complex parts. The downside, however, is that the high concentration of reactive functionalities results in products, which are typically very stiff and brittle. The use of reactive monomeric species is also not attractive from a commercial point of view since multiple synthetic and workup steps may be required. In addition, high concentrations of (often) expensive end-groups are needed.

Another route toward high-temperature thermosets is the reactive oligomer approach. High-molecular-weight all-aromatic polymers are often intractable and do not melt. In

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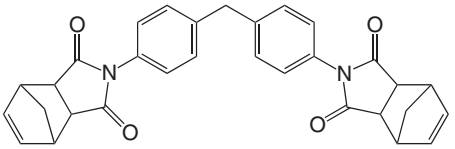
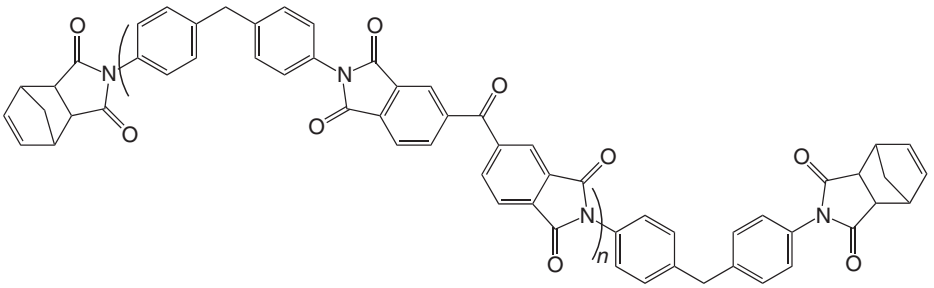


Reactive bisnorbornene monomer, molecular weight = 490 g mol^{-1}



Reactive bisnorbornene oligomer, with $n \sim 5$ gives $M_n \sim 3000$ g mol^{-1}

Scheme 1 A reactive bisnorbornene-terminated monomer with a well-defined molecular weight of 490 g mol^{-1} and below a reactive bisnorbornene-terminated oligomer (PMR) with an $M_n \sim 3000$ g mol^{-1} (including end-groups).

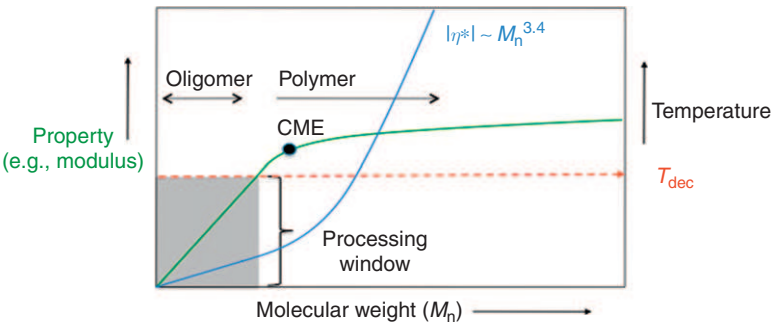


Figure 1 Polymer properties (T_g, E, etc.) increase rapidly with increasing polymer molecular weight (M_n) and level off after the CME has been reached. The shaded area represents the melt-processing window for most high-temperature polymers and is limited by the polymer decomposition temperature (T_{dec}).

fact, their oligomers decompose (T_{dec}) far below their critical molecular weight of entanglement (CME), as can be seen in Figure 1. Reducing the molecular weight (M_n) such that the oligomer melting temperature stays well below T_{dec} offers a potential route toward melt processing. Reactive end-groups, which can survive the polymerization and melt-processing conditions, are used to perform a postprocessing polymerization. Polymerization could either be achieved via chain extension and/or cross-linking and should result in a significant improvement in the thermomechanical properties.

The reactive oligomer approach, which constitutes about 80% of the high-temperature thermoset market, circumvents some of these issues. Although melt viscosities of oligomer species are typically higher, the processing window tends to be broader due to the broad melting range of oligomer species. Other advantages include better after-cure properties such as less shrinkage, improved fracture toughness, and more control over the cross-linking reaction. The last factor should not be underestimated because in both the reactive oligomer and reactive monomer cases the use of thermally cross-linkable end-groups is generally preferred. Cross-linking proceeds via radical-type chemistry and especially in the reactive monomer case the high concentration of end-groups could result in difficulty to control exothermic reactions.

Reactive oligomers, as, for example, the norbornene-terminated imide-based oligomer shown in Scheme 1, are typically prepared with an M_n of 1000–13 000 g mol^{-1}, but M_n greatly depends on the desired processing characteristics and targeted after-cure properties. The chemical nature of the polymer backbone determines the chemical stability and the backbone length, that is, the targeted M_n, determines the final after-cure mechanical properties. A reactive oligomer with a target M_n of 1000 g mol^{-1} has a high concentration of reactive end-group functionalities and this results in a high after-cure cross-link density. A densely cross-linked network displays high stiffness but low toughness, whereas a network prepared from a similar backbone but 9000 g mol^{-1} precursor would result in a less stiff but more tough after-cure thermoset. From a processing perspective, a low-molecular-weight oligomer is to be

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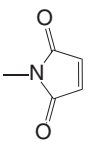
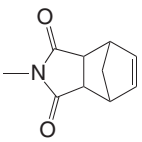
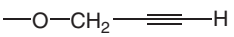
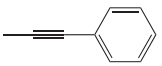
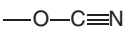
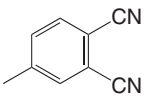
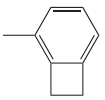
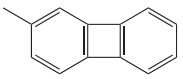
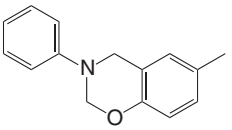
preferred over a high-molecular-weight precursor because the melting temperature and melt viscosity are usually lower.

Over the years, a wide variety of reactive end-groups have been explored. Table 1 lists several reactive end-groups used for preparing high-temperature thermosets via melt processing and subsequent thermal cross-linking. The selection of end-group type and concentration (M_n range) depends strongly on the cure rate, stability during processing, that is, the reactive end-group needs to remain latent during processing, and, of course, price and availability.

The reactive monomer and oligomer approach presents in principle a route toward processing intractable, often all-aromatic, polymers from their low melting monomer or oligomer state. After processing, the temperature is increased to induce cross-linking via the reactive end-group functionalities. Whereas the reactive precursor state exhibits favorable processing characteristics, the mechanical properties are poor. The T_g is low and injection-molded parts show brittle fracture behavior. After the cross-linking reaction, melt processing is no longer possible but the thermomechanical properties will improve considerably. The T_g of a fully cured thermoset can increase by 20–40 °C, and mechanical properties such as tensile strength, fracture toughness, and elongation at break will improve. As mentioned earlier, the final thermomechanical properties are determined by the reactive precursor backbone architecture, and the end-group concentration. Although a variety of architectures are possible, most reactive oligomers are linear and are prepared from AA + BB-type monomers. Star-shaped and branched reactive precursors as well as side-chain functionalized oligomers have been prepared but their after-cure properties vary.

When designing a high-temperature thermoset, one has to consider the fabrication method first. Take for example manufacturing of complex composite parts for automotive, aerospace, and sports applications. Resin film infusion (RFI),

Table 1 End-groups used for the preparation of reactive monomers and oligomers

Entry	*Structure*	*Name*	*Cure Temperature (°C)*
I		Maleimide	200–300
II		Norbornene	300–375
III		Ethynyl	200–250
IV		Propargylether	300
V		Phenylethynyl	300–400
VI		Cyanate ester	300
VII		Phthalonitrile	300
VIII		Benzocylcobutene	300
IX		Biphenylene	300
X		Benzoxazine	200–300

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resin transfer molding (RTM), vacuum-assisted RTM (VARTM), and reaction injection molding (RIM) are all processing methods with different demands on resin viscosity and stability.[7,8] In the case of RFI and RIM, the melt viscosity is not a critical factor and rapid cross-linking (< 10 min) could even be desirable. When producing a large carbon fiber-reinforced composite panel, however, a low melt viscosity (< 10 Pa s) and a melt stability (∼ 1–3 h) are required to facilitate resin impregnation to take place without premature cross-linking. In order to control the oligomer melt viscosity, one needs to control the number average molecular weight (M_n) of the reactive oligomer. This can be achieved by controlling the stoichiometry. When high-molecular-weight polymers using AA- and BB-type monomers are wanted, it is critical that both monomers are of high purity and added in a 1:1 molar ratio. When the aim is to produce an oligomer, the stoichiometry needs to be offset in that either a slight excess of AA or BB needs to be added or a XA or XB monomer with one A- or one B-functionality and X being a thermally cross-linkable end-group as listed in Table 1. This will act as a temporary chain stopper as it effectively terminates the polycondensation reaction, but the molecular weight may increase in a later stage via a high-temperature-induced cross-linking mechanism.

In order to control the molecular weight in step polymerizations, the Carothers equation is employed.[9] This equation can be used to calculate the ratio between the various monomers and the reactive end-groups which is required to prepare an oligomer with a prespecified molecular weight. The general Carothers equation, valid for reactions in which a monofunctional compound is used to control the anticipated number average degree of polymerization ($\overline{x_n}$), that is, AA + BB + XB (X = reactive end-group) type of reactions, is given by eqn [1].

$$\overline{x_n} = \frac{1 + r}{1 + r - 2rp} \quad [1]$$

In this equation, p is the extent of the reaction, which is assumed to approach 1 upon complete polymerization, r is the reactant ratio defining the ratio of various functional groups present prior to reaction, and $\overline{x_n}$ is the number average degree of polymerisation. This number average degree of polymerization can be calculated from the anticipated number average molecular weight $\overline{M_n}$ and the mean molar mass of a monomer unit $\overline{M_0}$ following eqn [2]. Upon calculating $\overline{x_n}$ and the reactant ratio r from eqns [2] and [3], respectively, the ratio between the number of functional groups N_{AA} and N_{BB} from the difunctional monomers on one hand and the number of monofunctional groups N_{XB} from the end-group on the other hand can be calculated.

$$\overline{M_n} = \overline{M_0} \cdot \overline{x_n} \quad [2]$$

and

$$r = \frac{N_{AA}}{N_{BB} + 2N_{XB}} \quad [3]$$

Typically, N_{AA} and N_{BB} are predetermined, for example, 1 mol, so N_{XB} can now easily be determined.

As a practical example, let us consider the norbornene end-capped oligomer shown in Scheme 1. The mean molar mass ($\overline{M_0}$) of a monomer unit in this imide-based oligomer is 242 g mol^{-1}. For an anticipated oligomer with a number average molecular weight $\overline{M_n}$ equal to 3000 g mol^{-1}, this results in $\overline{x_n} \sim 12$. Assuming complete polymerization, the extent of the reaction p will approach 1 so the reactant ratio is calculated to be 0.85. Using eqn [3], the stoichiometric offset can now be calculated. To prepare a 3000 g mol^{-1} oligomer from 1 mol diamine (N_{AA}) and 1 mol dianhydride (N_{BB}), 0.09 mol of norbornene dicarboxylic acid (N_{XB}) will be needed.

Other examples, including the effects on oligomer T_g, oligomer melt viscosity and after-cure T_g are available in the literature.[5] In general, this approach works really well for target M_n's in the range of 5000 g mol^{-1} and above. Calculated M_n's of 5000 g mol^{-1} and below have a tendency to deviate since the contribution of the end-group becomes significant but is not included in the calculation.

5.26.2 Thermosetting Monomers and Oligomers

5.26.2.1 Bismaleimide- and Bisnadimide-Based Systems

Bismaleimide (BMI)- and bisnadimide (BNI)-terminated monomers and oligomers, end-groups **I** and **II** in Table 1, are among the most extensively studied thermosets. Introduced in the 1960s and applied in countless industrial applications, this approach has been proven to be successful for a variety of backbone chemistries. Over the years, researchers have explored a variety of backbone all-aromatic chemistries, including imide-, etherimide-, arylether-, polycarbonate- and aryletherketones. The reactive double bond may be substituted with different groups such as halogens and methyl and phenyl groups. Introducing substituents could be used to control the cure temperature and time but the advantages appear limited. Most commercial BMIs and BNIs, however, make use of unsubstituted maleimide or nadimide end-groups, which is from a commercial perspective most attractive.

The most well-known example of a BNI is maybe PMR-15, shown in Scheme 2. PMR stands for polymerization of monomer reactants and 15 refers to 1500 g mol^{-1}. Researchers at National Aeronautics and Space Administration (NASA) developed this material in the 1970s as a resin for fiber-reinforced composites.[10] Overall PMR-15 is an interesting material with useful processing characteristics and a high after-cure T_g of 370 °C. Over the years, many different backbone modifications emerged, which were aimed at improving the low fracture toughness of the fully cured PMR network and dealing with the poor long-term thermo-oxidative stability. The latter, however, met with limited success and can be understood considering the nature of the aliphatic (sp^3-type) functionalities formed after cross-linking. The insoluble nature of the fully cross-linked networks has made it impossible to fully elucidate the cross-linking mechanism and the composition of the final cross-linked product. Solid-state nuclear magnetic resonance (NMR) spectroscopy, using ^{13}C-labeled PMR-15, seems to support the idea that cross-linking takes place via the cycloaliphatic double bond, leaving the norbornene ring intact.[11]

Most BMIs and BNIs may be polymerized directly via thermal curing but BMIs have the additional advantage that they can also be used in mixed systems where the electrophilic double bond may be reacted with diamine-terminated monomers and oligomers via a Michael-type addition reaction, or with propargyl-terminated and cyanate ester (CE)-terminated

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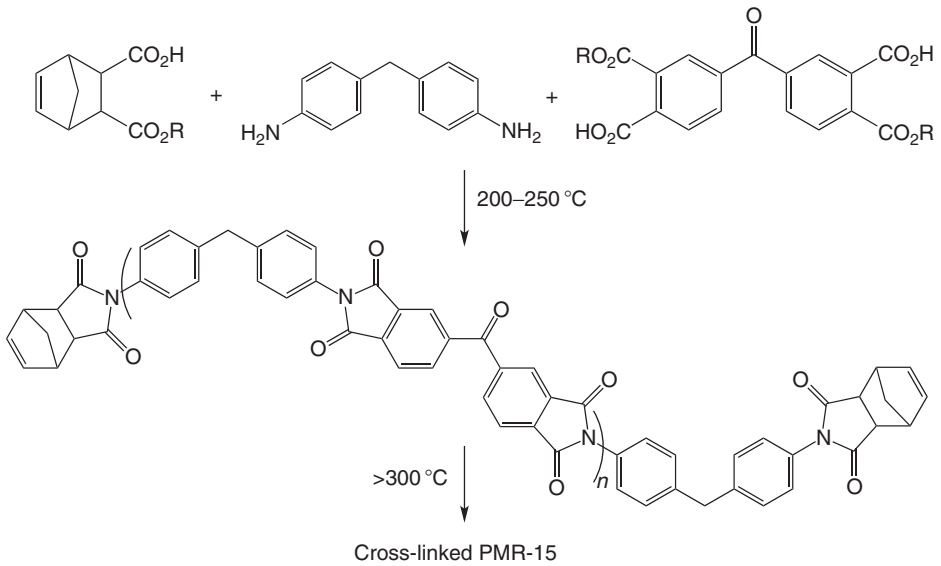


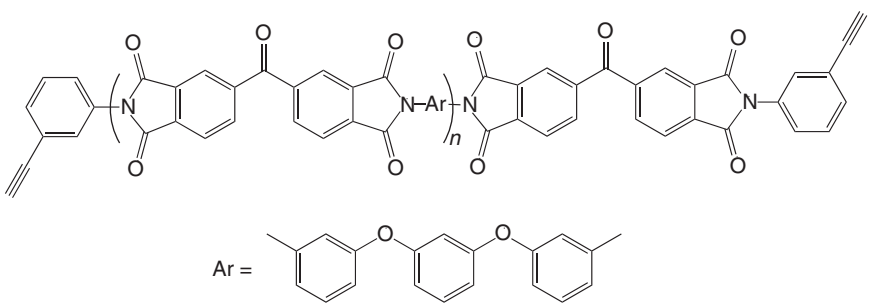
Scheme 2 Polymerization of monomer reactants (PMRs) and subsequent cross-linking of PMR-15.

resin systems. The chemical structure–property relationship, cure behavior, and the nature of the after-cure products have been presented in several excellent monographs and review articles.[5,12–17] Although BMIs and BNIs show excellent processability via melt- or solution-based processing, in general their after-cure products tend to be brittle and out-gassing of cyclopentadiene, as is the case for BNI curing, could pose a problem when void-free articles are needed such as for composites and microelectronic applications. As already mentioned, BMIs and BNIs are well-known thermosetting resins that have found application in a wide range of industrial applications. The versatility of BMI chemistry is still under investigation by several groups. Research has shifted, however, toward mixed end-group chemistries, that is, BMI-bisallylether-, BMI-CE-, BMI-benzoxazine-, BMI-benzocyclobutene-, and BMI-propargyl-based systems.[18–25] The aim is to find high T_g (> 250 °C) thermosets with low CTEs and improved mechanical properties over traditional BMIs and BNIs. Another area of interest is the use of BMIs as resin matrices for nanocomposite applications, where clay, ceramics, and carbon nanotubes are explored as the reinforcing phase. Small concentrations, typically in the order of 1–6 wt %, result in improved barrier properties, higher values for the after-cure T_g and storage modulus, and lower friction coefficients and wear loss.[26–30]

5.26.2.2 Ethynyl- and Phenylethynyl-Based Systems

BMIs and BNIs, as discussed in Section 5.26.2.1.1, suffer from several shortcomings. Although they are often presented in literature to be high-temperature thermosets, they lack long-term (> 10 000 h) stability at temperatures in excess of 150 °C. This combined with their low toughness and outgassing problems has prompted researchers to explore new reactive end-group chemistries that could circumvent these problems. Acetylene-based reactive functionalities, entries **III** and **IV** in Table 1, have been shown to be useful as reactive end-groups for low T_g polymers. In the early 1970s, LaBNIs *et al.*[31] used 3-ethynylaniline as a chain terminator for the synthesis of polyetherimides, or acetylene-terminated imides (ATI resins). Curing takes place via a radical mechanism and the after-cure thermomechanical properties appeared promising. An all-aromatic etherimide acetylene-terminated oligomer marketed at the time under the name Thermid 600, shown in Scheme 3 below, showed an after-cure T_g of 370 °C and reasonable thermo-oxidative stability.

Unfortunately, acetylene starts to polymerize around 200 °C and this results in a limited processing range for all-aromatic high-melting oligomers. Propargylether derivatives, entry **IV** in Table 1, have the same processing limitation with a rather low onset of cure (150–200 °C)



Scheme 3 Thermid 600, an ATI resin.[32]

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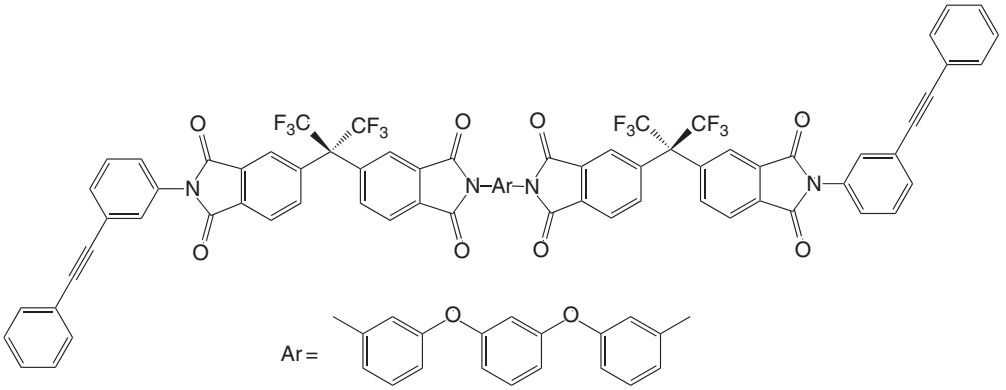


Scheme 4 First example of a phenylethynyl-terminated model compound.[36]

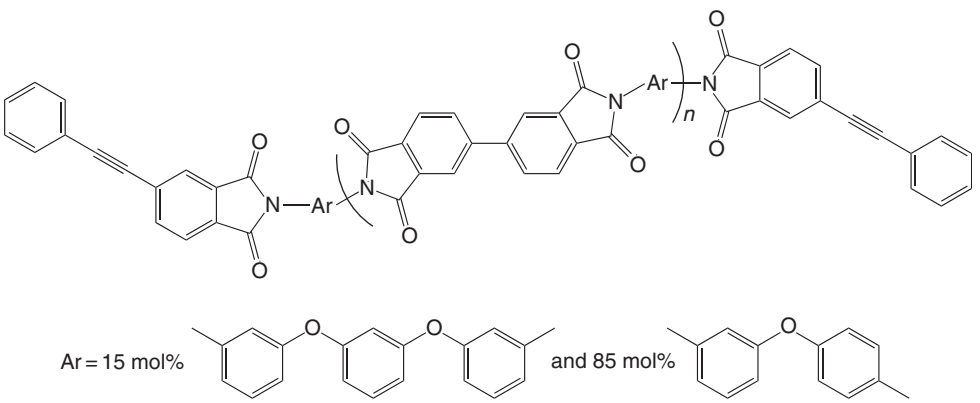
and therefore only practical for low-melting precursor formulations.[33–35]

In 1983, a breakthrough was reported by Harris *et al.*[36] They published their results on a phenylethynyl (entry **V** in Table 1) end-capped polyetherimide-based model compound, as shown in Scheme 4, which is a structure very similar to the Thermid 600 acetylene-terminated imide shown in Scheme 3.

Replacing the terminal acetylene proton with a phenyl ring slows radical formation and postpones cross-linking to temperatures in excess of 300 °C. This now provides a useful processing window for high-melting polymers with all-aromatic backbone formulations. It did not take long to appreciate the possibilities phenylethynyl could offer. In several years' time, a wide variety of polyetherimide formulations were prepared and their properties investigated. The potential of this chemistry was maybe best demonstrated by scientists at the NASA Langley Research Center. In support of the High Speed Civil Transport program, new high-temperature polymers were required as matrix material for carbon fiber-reinforced composites. The most challenging requirements, which needed to be met, included long-term stability of 60 000 h at 177 °C, solvent resistant under stress, nontoxic, and excellent resin shelf life. In addition, the resins were required to be affordable and amendable to different composite processing techniques.[37] This program yielded a series of phenylethynyl-terminated polyetherimides, or PETIs, with truly remarkable properties. In fact, the PETI thermosets are among the few high-temperature thermoset polymers, which are have actually been tested under high-temperature conditions and found to perform well. The most well-known example is a 5000 g mol^{-1} reactive linear oligomer based on 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA), 1,3-bis (3-aminophenoxy)benzene (APB), 3,4′-oxydianiline (ODA), and 4-phenylethynylphthalic anhydride (PEPA), shown in Scheme 5.[38]

This reactive oligomer met all of the above-mentioned processing and after-cure criteria. PETI-5 displays a T_g of 270 °C after a 1 h cure at 371 °C, a room temperature modulus of 3.0 GPa, a 130 MPa tensile strength, and 32% elongation at break. The synthesis, properties, composite properties, and long-term behavior of several phenylethynyl-terminated imides are well documented and available in several excellent review papers.[6,7,37,39] Over the years, a whole family of PETIs has emerged. Modifications with phosphine oxide-based monomers resulted in flame-resistant high T_g thermosets with low smoke and toxic volatile evolution. Phenylethynyl modifications of commercial available poly(etherimide)s, such as Ultem™, were also explored.[40]

Besides linear oligomers with phenylethynyl at the chain termini, researchers also investigated etherimide-based oligomers containing pendant phenylethynyl functionalities, oligomers with multiple phenylethynyl groups, and branched oligomers with phenylethynyl reactive functionalities.[37] All



Scheme 5 PETI. A 5000 g mol^{-1} oligomer shows an after-cure (1 h at 371 °C) T_g of 270 °C.[38]

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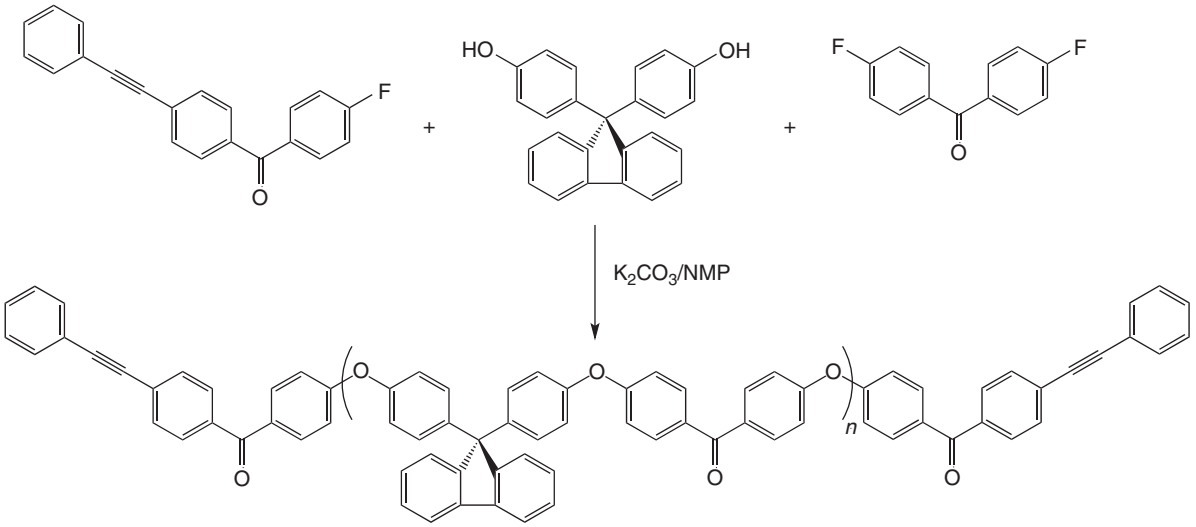


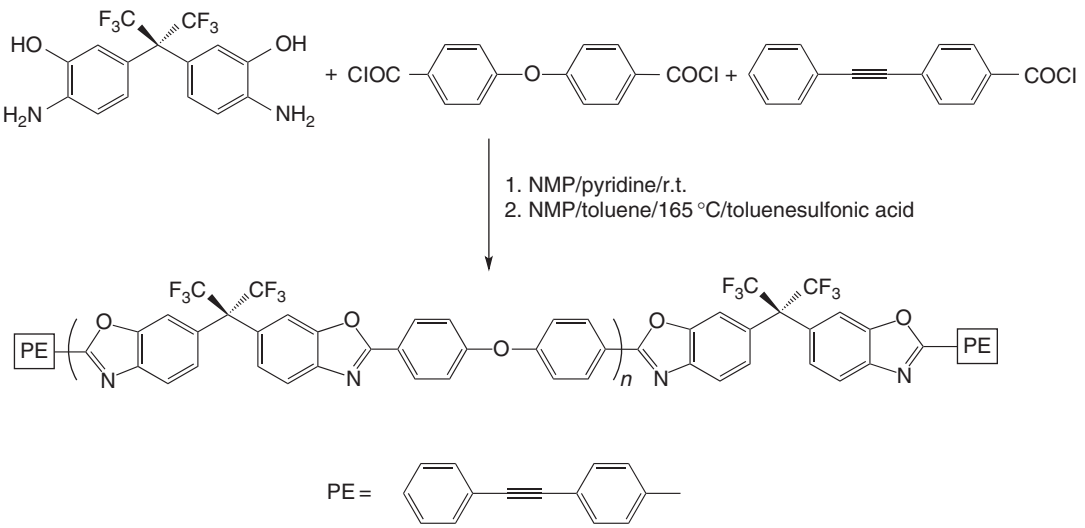
Scheme 6 Synthesis of a phenylethynyl-terminated polyarylether.[41]

these approaches allow the user to tailor specific processing conditions or after-cure properties.

In addition to poly(etherimide)s, other polymer backbones have been explored as well. Phenylethynyl-terminated arylethers were reported by Bryant *et al.*[41] 4-Fluoro-4′-phenylethynylbenzophenone could be incorporated as a reactive end-group via standard nucleophilic substitution conditions. Reactive oligomers, as shown Scheme 6, could be prepared and a 5000 g mol^{-1} oligomer showed a T_g of 263 °C after a 1 h cure at 350 °C. All oligomers displayed excellent processing characteristics and could be used as adhesives and composite matrix resins.

High-performance polymers, which are notoriously difficult to process, are polybenzoxazoles, PBIs, and phenylquinoxalines. For this reason, phenylethynyl-terminated benzoxazole oligomers were explored by Joseph *et al.*[42] according to Scheme 7. Oligomer precursors of 5000, 10 000, and 15 000 g mol^{-1} were prepared and successively melt processed into isotropic films and cross-linked.

The mechanical properties of these films showed an interesting trend in that it deviates from what was observed for etherimide- and arylether-based oligomers. When the molecular weight of the precursor oligomer increases, and so the concentration of phenylethynyl decreases, the tensile strength, modulus, and elongation at break increase significantly. This is a strong indication that the phenylethynyl end-groups react mainly via chain extension chemistry and cross-linking is just a minor contribution. A cured film from the 15 000 g mol^{-1} precursor gave a tensile strength of 353 MPa, a storage modulus of 7.7 GPa, and an elongation at break of 16 %. These values are exceptionally high and almost double that of the 5000 g mol^{-1} reactive precursor. Reactive benzimidazole oligomers were prepared as well, but the advantage of cross-linking via phenylethynyl end-groups appeared minimal.[43,44] Connell and Hergenrother investigated both linear and star-shaped phenylquinoxaline phenylethynyl-terminated oligomers. All oligomers displayed low melt viscosities and could be processed into films and carbon fiber-reinforced composites with



Scheme 7 Phenylethynyl end-capped arylether-based benzoxazole oligomer.[42]

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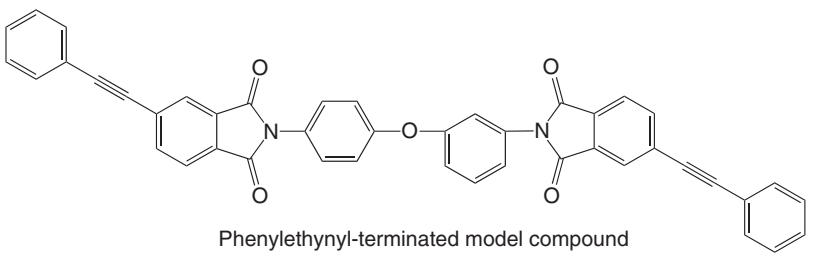
excellent thermomechanical properties.[45] A 2500 g mol^{-1} linear oligomer showed a T_g of 329 °C, after a 1 h cure at 350 °C, a room temperature tensile strength of 94 MPa, a storage modulus of 2.8 GPa, and elongation at break of 5%.[46]

5.26.2.2.1 Curing of phenylethynyl-based systems

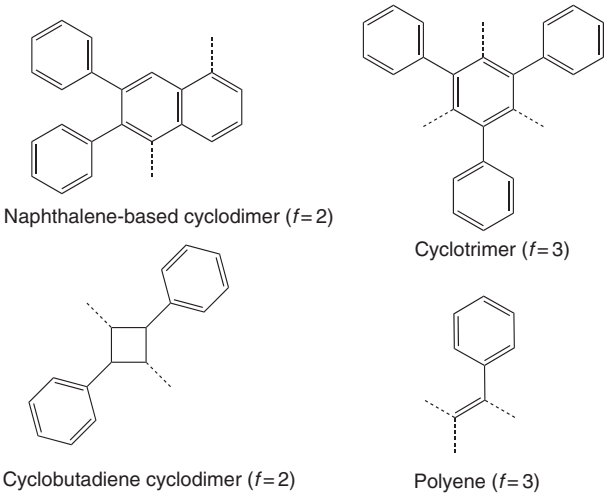
There is strong evidence that thermal curing of phenylethynyl-based oligomers proceeds via a free-radical mechanism.[47] Phenylethynyl-terminated oligomers may be cured between 300 and 400 °C, but it was experimentally found that curing between 350 and 370 °C provides the best after-cure thermomechanical properties such as T_g, storage modulus, tensile strength, and elongation at break. Besides obvious parameters such as cure temperature, time, and phenylethynyl concentration, other factors appear to play a critical role as well. It was found that the T_g of phenylethynyl-cured oligomers is higher when cured in the presence of oxygen (air) as compared to curing in an inert environment. Most phenylethynyl-based reactive end-groups are prepared starting from phenylacetylene and a functionalized arylhalide such as 4-bromophthalic anhydride. Coupling takes place in the presence of a palladium catalyst and failure to remove this catalyst completely, or its Pd(0) form, results in a lowering of the cure exotherm and an increase in the rate of cure. Although potentially interesting from a processing point of view, the long-term thermo-oxidative stability of the cured polymer becomes compromised.

As previously mentioned, indirect evidence suggests that cross-linking is not the only reaction in phenylethynyl-based systems. Most fully cured thermosets show excellent toughness and elongation at break, which support the idea that chain extension could be a major reaction as well. Understanding the cure kinetics and nature of the final products is therefore important when it comes to designing new high-temperature polymer applications. Fang and Takekoshi have investigated the cure kinetics in some detail. They investigated the cure kinetics of simple phenylethynyl-terminated model compounds, such as the compound shown below, and found that curing followed first-order kinetics, with activation energies of 153–170 kJ mol^{-1}.[48,49]



Phenylethynyl-terminated model compound

Insight with respect to the after-cure products was provided by Roberts *et al.*[50] They used ^{13}C-labeled phenylethynyl model compounds and solid-state NMR techniques to investigate the after-cure products. Their work seems to confirm that phenylethynyl is indeed capable of forming chemical functionalities, which lead to chain extension ($f = 2$) and cross-linking ($f = 3$), as shown in Scheme 8 below.



Scheme 8 Proposed cure products of phenylethynyl end-group chemistry. Both chain extension ($f = 2$) and cross-linking ($f = 3$) are possible and depend on factors such as temperature, presence of O_2, and concentration.[50]

Rheology experiments performed by Iqbal *et al.*[51] confirmed the fact that phenylethynyl is able to undergo both chain extension and cross-linking reactions. They prepared a 5000 g mol^{-1} phenylethynyl end-capped LC oligomer, based on terephthalic acid (TA) and chlorohydroquinone (Cl-HQ), and investigated the melt viscosity as function of time and temperature. When this oligomer was heated to 310 °C, the observed viscosity increase was mainly due to chain extension during the first 131 min. At this point, G′ and G″ crossover occurred and cross-linking became the predominate reaction. Experiments were also performed at 340, 370, and 400 °C and chain extension was taken over by cross-linking after 54, 10, and 5 min, respectively.

From the available literature, the following general statements with respect to the use of phenylethynyl as a reactive end-group can be made:

- Phenylethynyl reacts between 310 and 400 °C. Kinetics are slow at 310 °C, and chain extension is the predominate reaction. At 400 °C, kinetics are fast and cross-linking predominates.
- Oligomers with $M_n \sim 1000$ g mol^{-1} have a high concentration of reactive end-groups and after-cure products have a tendency to be brittle. Oligomers with $M_n \sim 5000$ g mol^{-1} or higher have a low concentration of reactive end-groups and after-cure products show improved toughness.

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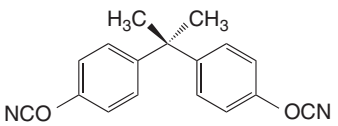
- Metal catalysts (e.g., Pd), added or residual, accelerate chain extension/cross-linking. The thermo-oxidative stability, however, decreases.
- Curing in the presence of air (O_2) results in polymers with a higher T_g as compared to curing in inert atmosphere or vacuum.

The high curing temperatures of phenylethynyl-terminated polymers have limited their use to specific applications such as carbon-reinforced composites. Over the years, attempts were made to lower the cure temperature to more acceptable levels (<300 °C), which should make this class of reactive oligomers processable via existing melt-processing equipment. The use of phenylethynylnaphthalic end-groups lowers the onset of cure by 10–40 °C over their phenylethynyl analog,[52] whereas the use of anthracenyl-ethynyl end-groups are capable of lowering the cure temperature by as much as 80 °C.[53] In both cases, no catalysts were needed and the thermomechanical post-cure properties were maintained. Gong *et al.*[54] demonstrated that the addition of a mixed solvent system, such as NMP/PEG-400, could lower the cross-linking temperature of a phenylethynyl end-capped polyimide to 200–250 °C. The working principle is based on the thermolysis of polyethylene glycol and the free radicals formed initiate the cure of the phenylethynyl end-groups.

5.26.2.3 Cyanate Ester- and Phthalonitrile-Based Systems

Cyanate esters (entry **VI** in Table 1), such as 2,2′-bis(4-cyanatophenyl)isopropylidene (BACY), have been commercially applied in electronics, adhesives, and composites because of their good processability and excellent after-cure properties. BACY can be melt processed and cured above its melting point of 80 °C and the resulting thermoset exhibits a T_g of 290 °C.[55–57]



2,2′-Bis(4-cyanatophenyl)isopropylidene (BACY)

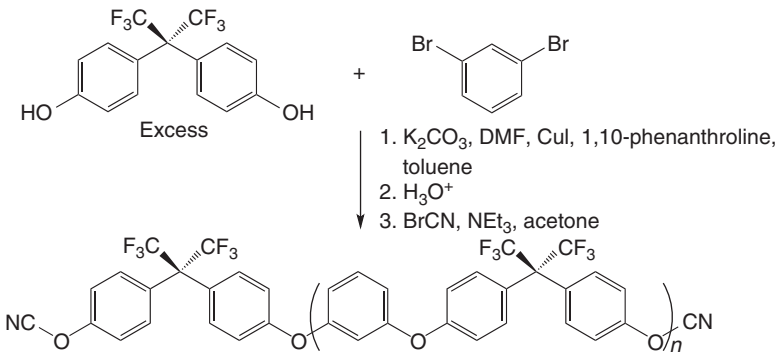
Most CEs, however, make use of aliphatic building blocks. Only a limited number of all-aromatic CE-terminated oligomers have been published to date. In comparison with other high-temperature thermosets, all-aromatic CEs exhibit brittle fracture behavior and this has limited their use in electronic and structural applications. In order to improve toughness, researchers have explored CE-based semi-interpenetrating polymer networks. Low-molecular-weight and oligomeric CEs were reacted in the presence of a high-molecular-weight thermoplastic polymer such as polysulfone,[58] polyetherimide,[59,60] or polyester.[61] It was successfully demonstrated that phase separation during cure indeed resulted in after-cure thermosets with improved toughness, whilst leaving other desirable properties largely unaffected. Very little data, however, is available on the long-term thermal stability of fully cured products.

Another approach toward improving the toughness of cured all-aromatic CE thermosets was presented by Laskoski *et al.*[62–64] They prepared arylether oligomers of different chain lengths and terminated the chains with CE functionalities. This effectively lowers the concentration of reactive end-groups and with a reduction in cross-link density an improvement in toughness was anticipated. The arylether backbone was synthesized using Ullmann-type chemistry and all-aromatic arylether-based oligomers, such as those shown in Scheme 9 below, could be processed into thermosets using a chromium(III)-based catalyst system.

This oligomer showed excellent processability and an after-cure T_g of 175 °C. In a nitrogen atmosphere, the onset of thermal decomposition was 425 and at 1000 °C a char yield of 47% was obtained.[62] Although all polymers are well characterized, no data were presented which could support an improvement in after-cure toughness. Replacing 6F-bisphenol-A with regular bisphenol-A gave a thermoset with a slightly lower T_g of 140 °C. Mechanical properties of cured resin plaques include a storage modulus of 1.3 GPa, flexural strength of 124 MPa, flexural modulus of 3.3 GPa, and an indentation hardness number (HR_M) of 97, respectively. The fully cured resins typically absorb 2–3% water by weight. No data were reported on the stress–strain behavior.[63]

The same group also explored phthalonitrile-terminated monomers and oligomers (entry **VII** in Table 1).[65–69] As depicted in Scheme 10, a polyetherketone was prepared from excess bisphenol-A and 4,4′-difluorobenzophenone under nucleophilic substitution conditions and the terminal phenols were end-capped with 4-nitrophthalonitrile.[65]

The authors prepared a reactive oligomer with a rather high concentration of phthalonitrile end-groups ($n \sim 1$). This gave a low-melting processable compound with a broad processing window of ~110 °C, which could be cured by incorporating 3–5 wt% of a suitable amine. The high concentration of phthalonitrile, on the other hand, resulted in a densely cross-linked thermoset with no apparent T_g and a room temperature storage modulus of 1.3 GPa.[65] A variety of all-aromatic arylether



Scheme 9 Synthesis of a soluble CE-terminated arylether-based oligomer.[62]

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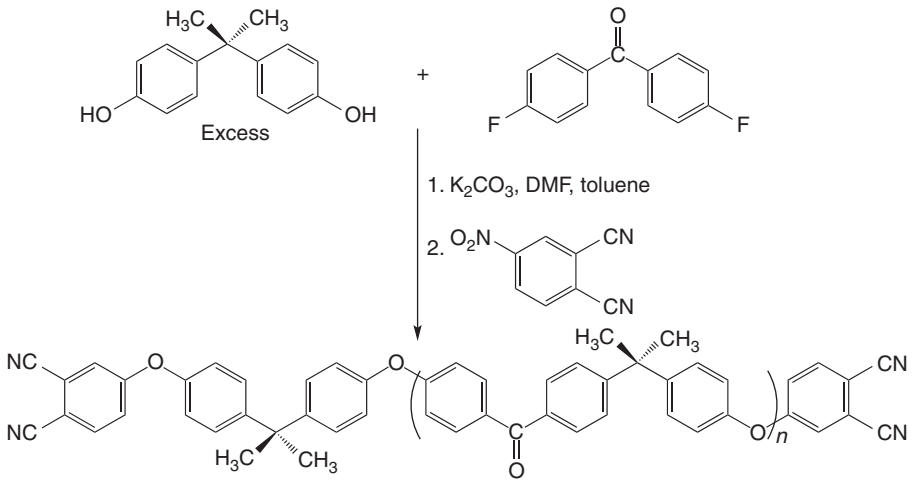
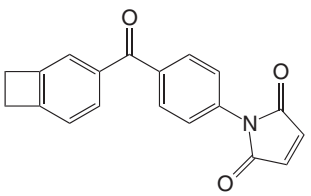


Scheme 10 Synthesis of a soluble phthalonitrile-terminated arylether-based oligomer.[65]

derivatives, that is, devoid of aliphatic isopropylidene units, have been synthesized and characterized by the same group. Ample data were published on the melt behavior and after-cure thermomechanical properties but unfortunately no mechanical data are available on the stress–strain behavior of fully cured all-aromatic phthalonitrile-based thermosets.

5.26.2.4 Benzocyclobutene- and Biphenylene-Based Systems

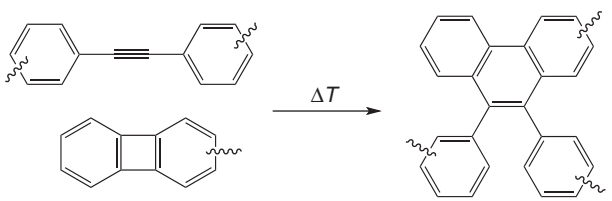
Only a few examples exist where strained ring systems such as benzocyclobutene and biphenylene were used as reactive functionalities in high-temperature thermosets (entries **VIII** and **IX**, Table 1). Their high cost and high curing temperatures may be the reason that their use has been limited to date. Both benzocyclobutene and biphenylene were used as cross-linking agents in low molar mass (mixed) reactive monomers and as reactive functionalities in high-molecular-weight polymers (Section 5.26.3.3) and oligomers. Investigated extensively in the 1990s, benzocyclobutene polymerization proceeds via an *ortho*-quinodimethane intermediate, which results from the thermal-induced opening of the cyclobutene ring. Polymerization takes place at a moderate temperature of 200 °C and without the evolution of volatiles. An excellent review on the application of benzocyclobutene in high-temperature polymers is available by Kirchhoff and Bruza[70] and a more detailed description with respect to the cross-link chemistry and kinetics was published by Deeter *et al.*[71] An interesting example of a maleimidobenzocyclobutene reactive precursor is shown below.



Reactive maleimidobenzocyclobutene monomer

This compound was reported by Labadie *et al.* and could be cross-linked to yield a thermoset with unusual properties. A T_g of 310 °C was measured and despite the high concentration of reactive functionalities, a fully cured film showed an elongation at break of 6% and a fracture energy (G_{1c}) of 610 J m^2. The flexural modulus at 30 °C was 3.6 GPa and only dropped to 2.5 GPa at 300 °C, which demonstrates the potential for high-temperature applications.[72]

Biphenylenes were also explored in the 1990s. Although commercially available, their application has been limited to all-aromatic backbone chemistries due to their high temperature of cure. The strained biphenylene ring opens at 350–400 °C to form a biradical and this radical species can both chain extent and cross-link. Garapon and Stille[73] initially recognized the use of biphenylene as a potential cross-linking agent in 1977. The possibilities with biphenylene were further explored in a series of all-aromatic model compounds,[74] polyquinoxalines,[75] polyquinolines,[73,76] and polyimides.[77] In most cases, processable oligomers were obtained, which could be cross-linked in the neat or in the presence of a catalyst toward high T_g (typically > 250 °C) thermosets. The authors found, however, that curing in many cases appeared to be incomplete. The probability for the biradical to recombine and revert to the biphenylene start compound was thought to be a competing reaction. In an attempt to overcome this reversion, mixed systems based on biphenylene and phenylacetylene were explored. The biradical would be trapped by the phenylacetylene and form a diphenylphenanthrene, shown in Scheme 11 below. An additional advantage of this mixed system was an observed lowering of the cure temperature.



Scheme 11 The reaction between phenylethynyl and biphenylene forming a diphenylphenanthrene functionality.[77]

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5.26.2.5 Benzoxazine-Based Systems

The benzoxazine functionality, entry **X** in Table 1, is another example of a cyclic structure, which can thermally polymerize without the need of a catalyst and cures without the formation of low-molecular-weight volatiles.[78,79] The six-membered ring is cheap and easy to prepare from a phenol, primary amine, and aldehyde. The availability of a wide variety of amine and phenolic starting materials makes this an interesting cross-link functionality. Depending on several factors, such as benzoxazine concentration, purity, and presence of a catalyst, benzoxazines can be cross-linked between 200 and 240 °C. The formation of a polymer network starting from a bisphenol-A-based bisbenzoxazine derivative is shown in Scheme 12 below.[80]

The major disadvantage of low-molecular-weight benzoxazine-based monomers is the brittleness of the fully cured system and the presence of aliphatic (methylene) units, which significantly reduces the continuous final end-use temperature. Several attempts have been undertaken to improve the after-cure toughness via introducing yet another cross-linkable unit such as phenylethynyl,[81–83] nitrile,[84] propargyl,[85] allyl,[80,86] or maleimide.[87] In most cases, low-melting precursors with excellent processing characteristics could be obtained. The reactive precursors could be processed either from solution, from film casting followed by a thermal posttreatment, or directly via the melt. The melt transition (T_m) was typically far below the onset of cross-linking, thus providing an acceptable processing window. Various cure programs can be used and depend on the reactive functionalities present in the monomer, but in order to assure full cure of the benzoxazine a maximum temperature of 240 °C seems to be required.[78–80] Cured films are dark red to brown in color and brittle in nature. Fully cured benzoxazine-based thermosets display relatively high glass-transition temperatures. Dynamic thermomechanical analysis (DMTA) shows that T_g's in the range of 100–300 °C are possible and benzoxazine-maleimide-based monomers are able to form thermosets with T_g's as high as 355 °C, as determined by the maximum of tan δ. The thermal stability, as measured by dynamic thermogravimetric analysis (TGA), is rather poor. Most fully cured thermosets have lost 5% by weight between 290 and 390 °C. The char yield, on the other hand, can be rather high in this class of thermosets, that is, 70% at 800 °C.[87] Very little data have been published on the stress–strain behavior and long-term temperature stability of fully cured benzoxazine-based thermosets.

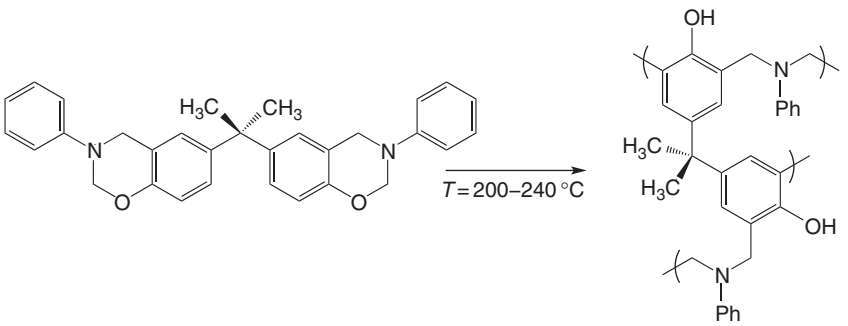
Benzoxazines have also been incorporated into high-molecular-weight polymers prior to cross-linking. This approach resulted in a significant improvement in after-cure toughness as was demonstrated by Takeichi and Agag.[88,89] Despite the low molecular weight of the reactive prepolymer, $M_n \sim 2500\,g\,mol^{-1}$, their cured polymers showed tensile strengths of 37–87 MPa and strain values of 1.6–4.1%.[88]

5.26.3 Thermosetting Liquid Crystals

All reactive monomers and oligomers, as discussed in Section 5.26.2, form amorphous thermosets after cure. Before cross-linking, the precursor molecules might exhibit a high or low degree of crystallinity, as in the case for low-molecular-weight reactive monomers and reactive oligomers, respectively. Chemical cross-linking, however, typically prevents polymer chains between cross-link points to arrange in a highly ordered three-dimensional crystal lattice. Noticeable exceptions to this rule are thermotropic LC thermosets (TLCTs). In this class of polymers, a part, or most, of the positional and long-range order of the molecules in the melt can be preserved after cross-linking.[90,91] Especially the nematic (N) LC phase is attractive from a processing point of view. The melt viscosity is low and very sensitive to shear, making processing of (anisotropic) complex parts, such as electronic parts and composite structures possible. An additional advantage is the low CTE associated with the LC phase, which results in minimal shrinkage of the final part. Since cross-linking in the LC phase and after-cure properties deviate significantly from amorphous thermosets, we will discuss this class of polymers separately.

5.26.3.1 Reactive Thermotropic LC Monomers

The LC thermoset (LCT) concept was initially demonstrated in LC epoxy systems, build around a dihydroxy-α-methylstilbene mesogen by Ober *et al.*[92,93] and aromatic ester-based mesogens by Jahromi *et al.*[94–96] Their results showed that LC thermosets could offer improved physical and mechanical properties over their non-LC counterparts. Over the years, a wide variety of LC epoxy-based thermosets were explored and some compounds and their properties are reviewed by Douglas.[97] At the same time, low-molecular-mass high-temperature, all-aromatic thermotropic monomers end-capped with different reactive functionalities were used to prepare LC networks. Barclay *et al.*[98] demonstrated that the thermal cyclotrimerization of



Scheme 12 Thermal cure of a bisbenzoxazine monomer ($f = 4$) forming a densely cross-linked phenolic network.[80]

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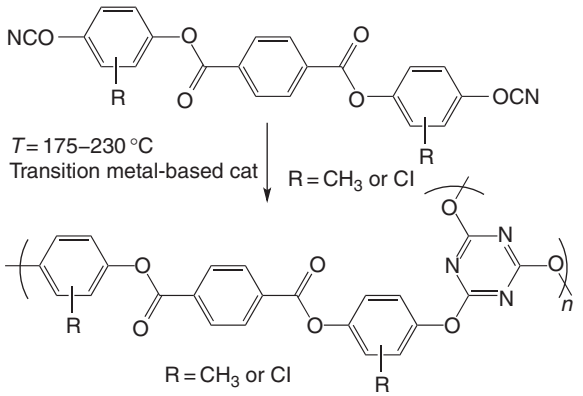
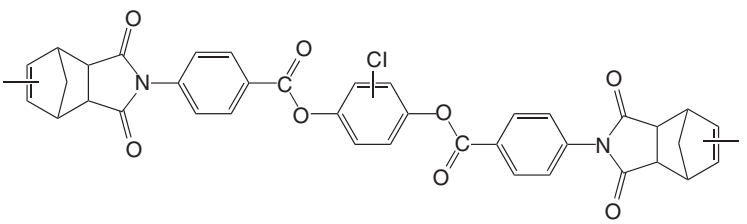


Scheme 13 Formation of a triazine-based LC thermoset.[98]

cyanate-terminated mesogens, Scheme 13 resulted in thermally stable triazine-based smectic networks with high glass-transition temperatures ($T_g \sim 190$ °C) and excellent thermal stability (~ 440 °C). Curing of the reactive monomers in the presence of a magnetic field resulted in well-oriented triazine networks with CTE values as low as 17 ppm °C^{-1} in the direction of the applied field.

Gavrin *et al.*[99,100] prepared LC monomers with acetylene and phenylethynyl end-groups, and observed low viscous nematic melts upon heating. Unfortunately, very limited mechanical and physical properties of the cross-linked thermosets were reported. The same approach was used in a series of bisacetylenes, BMIs, BNIs, and bismethylnadimides, as shown below, by Benicewicz *et al.*[101–103]



Liquid crystal monomer with methylnadimide end-groups. (K-N) 255 °C (N-I) 274 °C

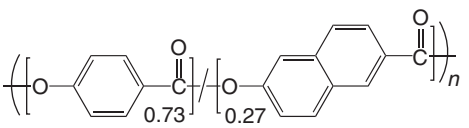
The processing window of these materials was, however, rather limited as cross-linking often started immediately after the crystal-to-nematic (K–N) transition. In addition, starting from low-molar-mass reactive LCs, the cure kinetics and the phase behavior often appeared complex and difficult to control. Due to the high concentration of reactive end-groups, the fully cross-linked materials are brittle and display low fracture toughness.

5.26.3.2 Reactive Thermotropic LC Oligomers

In order to provide TLCTs with useful mechanical, physical, and good processing properties, reactive main-chain all-aromatic liquid crystalline oligomers were explored as well. This route has several advantages over using reactive low-molar-mass LC monomers such as described in Section 5.26.3.1. All-aromatic main-chain thermotropic oligomers end-capped with phenylethynyl functionalities were synthesized using standard one-pot melt condensation techniques. Phenylethynyl is the only reactive functionality, so far, which survives the extreme melt condensation conditions ($T_{max} \sim 310$ °C) and does not cross-link or chain extend prematurely. In addition, phenylethynyl has been used extensively as a reactive end-group functionality in cross-linkable poly (etherimide)s[37,39] and the mechanical properties of the final cured products were found to be outstanding.

Another reason for using phenylethynyl is the fact that this material not only form cross-link functionalities but can also chain extend, depending on the concentration and temperature profile used. As investigated by Roberts *et al.*,[50] phenylethynyl chain extends (e.g., via cyclobutadiene cyclodimers and 1,5-substituted naphthalenes) and forms cross-linking functionalities (e.g., 1,3,5-trisubstituted benzenes and polyenes). In either case, the functionalities formed do not deviate too much from linearity and hence do not disrupt LC formation.

Initial experiments concentrated on modifying a well-known all-aromatic ester-based thermotropic LC polymer (TLCP), Vectra™ (shown below). Vectra™ is a random copolymer of 4-hydroxybenzoic acid (HBA) and 6-hydroxy-2-naphthoic acid (HNA) and this material displays a T_g of 110 °C and melts into a nematic phase around 280 °C.[104]



Vectra™ $T_g = 110$ °C, (K-N) = 280 °C

Two series of oligomers were prepared with the aim to investigate the effects of *oligomer molecular weight* and *oligomer backbone composition* on the thermal and physical properties of reactive HBA/HNA oligomers and their cured polymers. Monofunctionalized phenylethynyl end-groups, as shown in Scheme 14 below, were introduced to effectively control the molecular weight (M_n) of the reactive oligomers.[105,106]

The authors synthesized reactive oligomers with molecular weights of 1000, 5000, 9000, and 13 000 g mol^{-1}, respectively. A high-molecular-weight polymer without reactive end-groups, that is, 30 000 g mol^{-1}, was prepared for reference purposes. As can be expected, the K–N is reduced together with the melt viscosity, which is advantageous with respect to processing complex structures such as fiber-reinforced composites. All fully cured HBA/HNA thermosets show excellent thermal stabilities, that is, $T^{5\%}{}_{dec}$ of 500 °C in both air and inert

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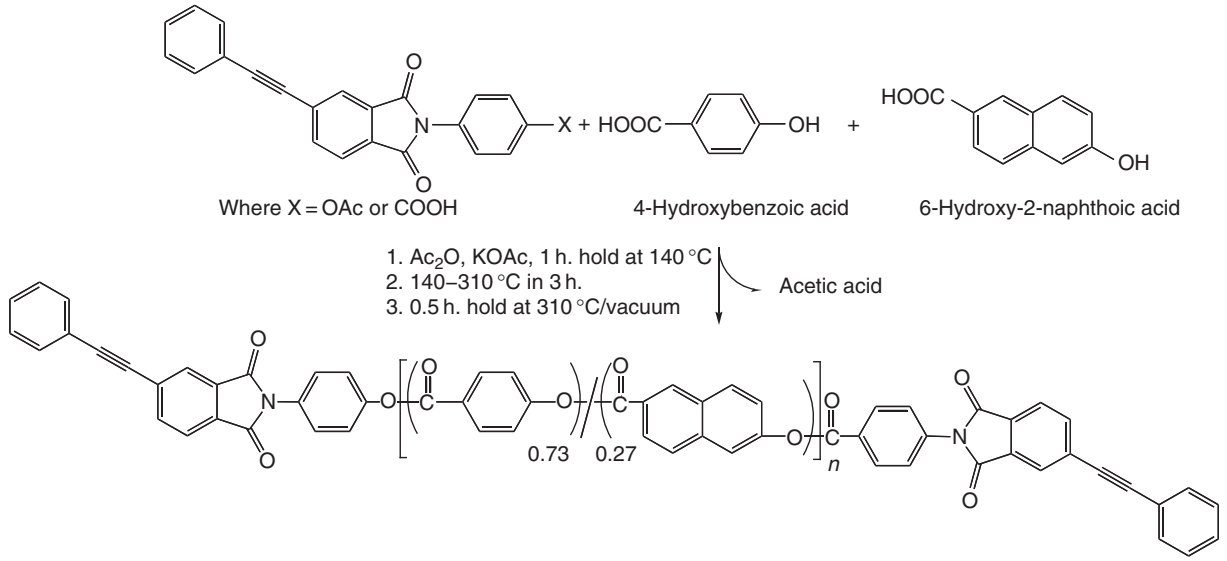


Scheme 14 Synthesis of the reactive, phenylethynyl end-capped, oligomers via standard melt-condensation techniques.[105,106]

environment (N_2). The T_g of the fully cross-linked 1000 g mol^{-1} precursor is 40 °C higher, that is, 150 °C, as compared to the 30 000 g mol^{-1} reference polymer with reactive end-groups. A T_g as high as 203 °C was found when a 5000 g mol^{-1} random reactive oligomer was prepared with a 95 mol% HNA and 5 mol% HBA formulation.[106] The advantage of processing reactive LC oligomers is shown in **Figure 2**. The melt viscosity of a 9000 g mol^{-1} reactive HBA/HNA oligomer is plotted as a function of temperature and shear rate. The melt viscosity of this nematic reactive oligomer is strongly dependent on shear rate and temperature, and this behavior is representative for most reactive LC oligomers.

Most, if not all, commercially available all-aromatic TLCPs are random copolymers of two or more AA/BB/AB-type monomers. All-aromatic LC homopolymers are difficult to synthesize since they become intractable at an early stage of the polycondensation. In order to obtain melt-processable LCPs, a random composition

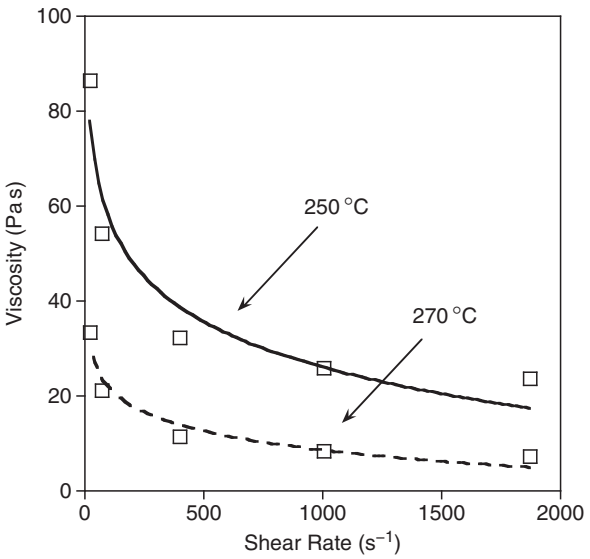
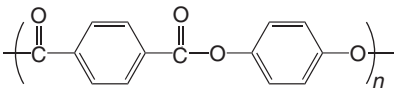


Figure 2 Melt viscosity of a 9000 g mol^{-1} HBA/HNA LC oligomer plotted as function of shear rate and two different temperatures.[105]

is needed to suppress the melting temperature, and thus the processing temperature, to acceptable levels well below 350 °C. As a consequence, the glass-transition temperature (T_g) will also drop, which is not desirable since it will limit the final end-use temperature of the polymer. For example, compositions with HBA or HNA concentrations higher than 80 mol% show a rapid increase in T_m and melt viscosity and are therefore avoided.

The ability to prepare LCPs with, for example, high HBA concentrations, is nevertheless of great interest since they will result in materials with significantly higher T_g's and *E*-modulus. From a commercial point of view, it is also advantageous to formulate LCPs using cheaper backbone monomer compositions. This concept was explored by Iqbal *et al.* where LCTs were prepared using inexpensive and readily available start materials such as TA and hydroquinone (HQ). The main-chain analog, poly-(*p*-phenylene terephthalate), shown below, exhibits a T_g of 267 °C, and a melting point of 610 °C,[104] which makes it rather intractable – the polymer in fact decomposes before it melts– and difficult to synthesize.[107–110]



Poly(*p*-phenylene terephthalate) T_g = 267 °C, (K-N) = 610 °C (dec)

In order to obtain a melt-processable reactive oligomer, M_n has to drop to ~ 1000 g mol^{-1}, which corresponds to $n \sim 4$. This reactive oligomer, labeled TA/HQ-1K, melts at 291 °C and cures at 370 °C to form a nematic thermoset with a T_g of 340 °C and a storage modulus of 5 GPa at room temperature. Due to the high degree of cross-linking, the films are rather stiff and show brittle fracture behavior. In order to obtain TLCTs with improved toughness, Iqbal *et al.* prepared TA/HQ-based oligomer precursor with an M_n of 5000 g mol^{-1}, thereby reducing the concentration of reactive end-groups, and they modified the backbone chemistry with isophthalic acid (IA) and Cl-HQ. In both cases, melt-processable oligomers were obtained, which could easily be processed into fully cured

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thin flexible films with outstanding thermal and mechanical properties. DMTA results showed excellent cryogenic and high-temperature behavior. TA/HQ/IA(50)-5K displays a low temperature β-transition at −100 °C, followed by the α-transition or T_g, as measured at the maximum of tan δ at 1 Hz, at 220 °C. Once the temperature is above T_g, a rubber plateau is reached, which extends from 250–350 °C. The storage modulus remains relatively constant at 200 MPa. After the experiment was terminated at 475 °C, the retrieved film was still flexible, which demonstrates the unusual mechanical behavior of these materials.

The capability of this reactive LC oligomer approach is maybe best demonstrated by a formulation based on HBA, TA, and 4,4′-bisphenol. This 9 000 g mol^{-1} reactive oligomer melts into a low viscous nematic phase at 340 °C. During a 1 h cure at 370 °C, the melt viscosity increases rapidly and after 45 min the nematic melt has solidified completely and a nematic thermoset is obtained. Figure 3 shows the nematic textures before and after cure.[107]

This oligomer can be processed into thin flexible films with excellent thermomechanical properties. The after-cure film displayed a T_g of 429 °C and the decomposition temperature, as determined by the 5% weight loss point, was 495 °C in nitrogen and 487 °C in air, at 10 °C min^{-1}. The storage modulus (E') of this polymer remains high up to 400 °C and in fact, even beyond this temperature the film remains intact up to 500 °C. The storage modulus as a function of temperature for the fully cured polymer 4-HBA/TA/BP(25)-9K is shown in Figure 4.

The reactive LC oligomer approach has proven to be very versatile. One challenge, however, has been to improve the solution processability of this material. Branched LC oligomers were prepared with a mixture of reactive end-groups and carboxylic acid and acetoxy functionalities, but the solubility in all but aggressive solvents remained poor.[108] Several LCTs were successfully used as high-temperature metal adhesives displaying high lap-shear values between 11 and 16 MPa for aluminum, steel, and titanium substrates, respectively.[109] A low-melting LCT based on HBA, HQ, and IA was used to prepare carbon fiber-reinforced composites and the results showed that phenylethynyl-terminated LC oligomers are excellent composite resins with outstanding mechanical properties. Composite panels showed an in-plane shear strength of 154 MPa and an in-plane shear modulus of 3.7 GPa. The tensile strength and modulus were measured to be 696 and 57 GPa, respectively.[110]

5.26.3.3 Reactive Lyotropic Oligomers and Polymers

Another class of high-temperature LC thermosets is based on reactive lyotropic precursors. Although few examples exist to

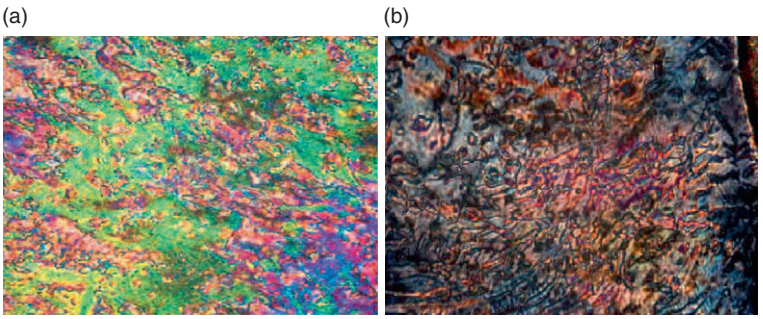

Figure 3 Microphotographs of 4-HBA/TA/BP(25)-9K, a 9000 g mol^{-1} reactive oligomer; Crossed polars and 20X. (a) Low viscous nematic melt at 370 °C. (b) Nematic thermoset after a 1 h cure at 370 °C.[107]

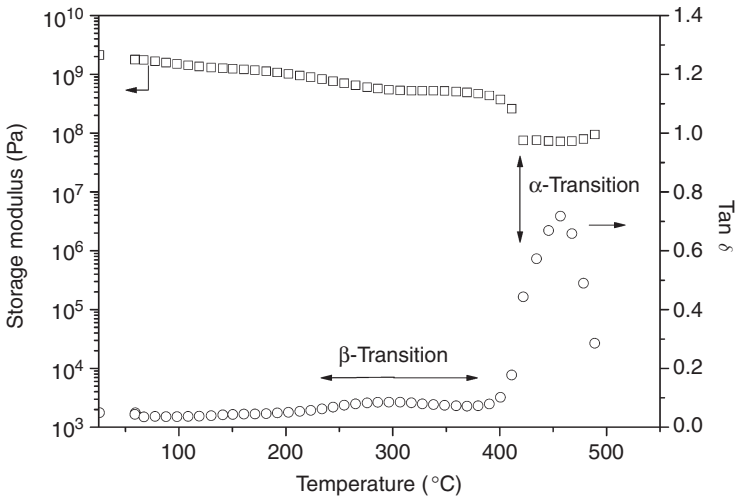

Figure 4 Storage modulus (E') (□) and tan δ (○) of a fully cured HBA/TA/BP(25)-9K film as measured by DMTA using a heating rate of 2 °C min^{-1} and measured at 1 Hz.[107]

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date, several high-temperature lyotropic polymers such as poly (*p*-phenylene terephthalamide) (PPTA) and PBI have been modified with reactive functionalities, which were placed either in the polymer backbone or at the chain termini. The low compressive strength, the major weakness of PPTA and PBI fibers, was recognized at an early stage and introducing cross-linkable units was aimed at improving the fiber compressive strength without compromising the fiber tensile properties. The underlying idea behind introducing interchain cross-links is based on the theory that the lateral cohesive forces largely determine the compressive strength of the final fiber. Several attempts to enhance lateral interactions via cross-linking between polymer chains have been reported. During the mid-1990s, a series of articles were published on the synthesis of 1,2-dihydrocyclobutabenzene-3,6-dicarboxylic acid (XTA) and its incorporation into fibers.[111–114] The formation of cross-links raised the strain to kink band formation and decreased the kink band density at a given strain. At the same time, another monomer, disulfonediamine (DSDA), was developed by Suter and coworkers and incorporated into fibers using it as substituent for *p*-phenylene diamine.[115,116] Other chemical modifications include the incorporation of halogenated monomers into aramid and poly(benzobisthiazole) (PBZT) fibers by Sweeny,[117] incorporation of methyl-pendant monomers into PBI fibers by Jenkins *et al.*,[118] and diacetylene-functionalized polyamide fibers prepared by Beckham and Rubner.[119] However, none of these approaches resulted in an improvement in compressive properties.

It was recognized that placing reactive monomers in the polymer backbone disturbs the delicate intermolecular packing preferences and hence destroys the macroscopic fiber structure. In order to avoid this problem, Knijnenberg *et al.*[120] prepared PPTA oligomers with cross-linkable end-groups. The advantage of a system like this is that the oligomer backbone perfectly fits into the crystal morphology formed by the polymer. The authors investigated several reactive end-groups, which were found to be stable in 100% sulfuric acid, and showed that cross-linking could be achieved during a high-temperature posttreatment of the fibers. After cross-linking, the compressive properties of the fibers were investigated using the 'elastica' single filament compression test and by studying the Raman band shift in axial compressed embedded single filaments.[121] Again cross-linking did not result in a measurable change in compressive strength or compressive failure behavior.

5.26.4 Concluding Remarks

The intent of this chapter is to provide the reader with a starting point on the chemistry, properties, and selection criteria of all-aromatic high-temperature thermosets. Maleimide- and nadimide-based thermosets, introduced in the 1960s and commercialized in many applications over the years, are well understood so the emphasis has been on progress made over the past 25 years. Special emphasis has been placed on phenylethynyl-based systems because of the proven versatility of this end-group. Although the high cure temperatures could be a limiting factor for some applications, their after-cure thermomechanical properties are often unsurpassed. Another advantage of this system is that the long-term properties, over a broad temperature range, are well inventoried and understood. Applicability of phenylethynyl has been demonstrated in a variety of all-aromatic amorphous and liquid crystalline backbone chemistries and some of these reactive oligomers are now commercially available. The market for high-performance/high-temperature polymers is expected to grow considerably over the years. The combination of outstanding physical, thermal, and mechanical characteristics and ease of processing prove them useful for a variety of aerospace, electronic, biomedical, coating, and other demanding applications.

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Biographical Sketch

Theo Dingemans received his chemical engineering degree from the Technische Hogeschool, Eindhoven, The Netherlands, in 1991. He received his PhD in polymer chemistry from the University of North Carolina, Chapel Hill, in 1998. In May 1998, he joined the National Aeronautics and Space Administration (NASA) in Hampton, Virginia. During this period, he worked on several high-temperature polymer systems, including all-aromatic ester-, esteramide-, and esterimide-based liquid crystal thermosets and poly(etherimide)s. He is currently a professor of chemistry and aerospace engineering at the Delft University of Technology, The Netherlands. His current research emphasis is on the design, synthesis, and characterization of novel all-aromatic polymers for structural and functional applications. Research areas include liquid crystal network polymers (LCTs), reactive polyarylethers as matrix resins for composites, carbon nanotube- and graphene-modified aromatic polymers, and novel aramides for high-modulus fiber applications.

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