

site" catalyst, although because it is possible for some of these catalysts to have multiple sites some prefer to call them "ligand-based catalysts". They are transition metal compounds containing a five-membered carbon ring, and their essential characteristic is that they contain a metal-carbon linkage into which an olefin can insert itself for chain-growth polymerization. The constraint imposed by the ring on geometry of the active site of the catalyst makes the reaction more homogeneous. The first commercial polyethylenes based on metallocene catalysts resulted from work by Welborn and Ewen at Exxon and were marketed under the EXACT[®] label. The overall process for their manufacture was given the name EXXPOL technology.

Single-site catalysts have been used to prepare some interesting new polymers. For example, isotactic polystyrene can be made that cools to a brittle, semi-crystalline solid. Copolymers of ethylene and styrene are also possible, and these have glass transition temperatures that decrease progressively below that of polystyrene as the proportion of ethylene in the copolymer is increased.

Equations that describe several types of molecular weight distribution were presented in Chapter 2. One of these is the "most-probable" or Schulz-Flory distribution that is derived assuming that each catalyst site is equally active and that the probability of termination does not depend on chain length. This distribution has a polydispersity index (M_w/M_n) of two, and the metallocene polymers have values very close to this theoretical value, suggesting that the catalyst sites are indeed nearly equally active. These materials can be used to make products having improved mechanical properties but are more difficult to process, because of the lower degree of shear thinning, as compared with more polydisperse or long-chain-branched polymers. Products with broader distributions can be made from metallocene catalysts by blending or the use of multiple catalysts. Another approach to improving the processability of these materials is the introduction of long-chain branching, which is discussed in the next section.

Metallocene catalysts in their basic form are suitable for solution-phase polymerization. In order to adapt them for use in slurry or gas-phase reactors, they must be immobilized on a support. This is normally carried out in a separate preparatory process, but it has been shown how the catalyst can be reacted with its support *in situ* in the polymerization reactor [79]. The copolymers made using metallocene catalysts, e.g. mLLDPE, have a more uniform distribution of co-monomers among the chains than do LLDPEs made using Ziegler-Natta catalysts, which tend to have more co-monomer in the lower molecular weight fractions [78]. The comonomer distribution, *i.e.*, the chemical composition distribution (CCD) is the key to controlling crystallinity, and models for predicting the CCD have been published for binary [8] and multicomponent [9] copolymers. The key factor controlling crystallinity is the distribution of longest ethylene sequences; a more even distribution leads to shorter ethylene sequences, which enhance the reduction in crystallinity for a given fraction of comonomer. Because mLLDPE is more compositionally homogeneous than LLDPE [80] it makes more effective use of the comonomer. For example, a traditional, gas-phase, hexene LLDPE with a density of 0.98 g/cm³ has about 18 short branches per thousand carbon atoms, while an mLLDPE with the same density made by the same type of reactor requires only about 11 branches per carbon atom. Finally, mLLDPE has a narrower molecular weight distribution than LLDPE, and the reduced amount of low molecular weight material ("hexane extractable") is particularly advantageous for food packaging applications.

Johnson *et al.* [81] reported the properties of a series of ethylene-octene copolymers made using Dow CGC technology. In addition to LLDPE, these products included "plastomers" having densities from 0.89 to 0.91 and crystallinities between 23 and 39 percent and "thermoplastic elastomers" having densities below 0.89 and crystallinities between 10 and 23.

Metallocene catalysts now form the basis of polymerization technologies used by many companies to make polyolefins, including SPHERIPOL[®] (PP, Basell), BORSTAR[®] (PE and PE Borealis), INNOVENE[®] (PE, BP), MPACT[®] (PE, ChevronPhillips), INSITE[®] (PE, Dow), and EXXPOL[®] (PE, PP, ExxonMobil).

3.9.2 Long-Chain Branching in Metallocene Polyethylenes

Long chain branches can be introduced into any nominally linear polyethylene by crosslinking, which may occur unintentionally when a sample is heated without adequate thermal stabilization. In addition, it is possible that some metallocene catalysts intended for synthesis of linear chains have the ability to generate vinyl macromonomers and incorporate them into the growing chain to produce branches under certain conditions. Thus, samples thought to be linear sometimes show evidence of low levels of long-chain branching that have a significant effect on rheological behavior [68]. These issues complicate the study of the structure and topology of metallocene polyolefins [82, 83]

However, single-site catalysts and polymerization processes have now been discovered [84] that introduce long-chain branching in a very controlled and predictable way, and a range of commercial products are now produced using this polymerization system. Lai *et al.* [85] at Dow Chemical were the first to report a catalyst system and polymerization conditions able to synthesize polyethylene homopolymer, as well as α -olefin copolymers, having precisely-controlled levels of long chain branching ranging from 0.01 to 3 branches per 1000 carbon atoms. The catalyst used to prepare these "substantially linear" polyolefins is called "constrained geometry catalyst" (CGC), and the overall polymerization system is called "HATF" technology (Dow Chemical Co.). A broad range of products can be made using this technology [86]. The reaction proceeds in the liquid phase in a continuous, stirred-tank reactor or an equally well-mixed loop reactor. Soares and Hamielec [87] have explained why this arrangement is optimal for LCB formation. Using this combination of catalyst and reactor, Lai *et al.* [85] reported that it was possible to make homopolymers having long chain branching frequencies, λ , the average number of branch points per 1000 carbon atoms, in the range of 0.01 to 3. The branching process starts with the formation of a "macromonomer", *i.e.*, a dead polymer chain with a terminal double bond, by β -hydride elimination. Then, this unit is incorporated into a growing chain at the active center of the catalyst. The introduction of the LCB has an important effect on the viscosity, substantially increasing the degree of shear thinning. It thus became possible to have the advantages of a controlled, narrow molecular weight distribution along with good processability.

Soares and Hamielec developed kinetic models for the synthesis of both homopolymers [87] and copolymers [88] and have used these to show how reaction conditions affect the distributions of molecular weight and degree of branching. Beigzadeh *et al.* [89] proposed the use of a combined catalyst system to enhance the level of long chain branching. By

combining a constrained geometry catalyst with a conventional (linear) metallocene catalyst, their kinetic model indicated that it would be possible to obtain higher degrees of LCB while controlling the molecular weight, polydispersity, and copolymer distribution. They later validated this model using data from polymerization experiments [90]. Beigzadeh *et al.* [91] then carried out extensive simulations based on this model and showed how reactor conditions could be manipulated to produce a polymer having prescribed molecular structure. Kolomba *et al.* [92] have demonstrated the long-chain branching of single-site catalyzed polyethylene in a slurry reactor. Soares [93] has reviewed work on the prediction of branching structures in polyolefins made using single-site coordination catalysts.

The level of branching is often expressed simply in terms of λ , the average number of branch points per thousand carbon atoms, and this is related to β , the average number of branch points per molecule through Eq. 3.3 for the case of polyethylene.

$$\beta = \frac{M_N \lambda}{14 \cdot 10^3} \quad (3.3)$$

However, this single parameter contains no information about the distributions of branch points per molecule and the molecular weights of the various types of segment. For example, we note that many combinations of M_N and β can give the same value of λ . To determine the detailed structure, it is necessary to make a more detailed analysis of the reaction. Because this reaction system has been analyzed in great detail, it will be of interest to summarize the models used. Soares and Hamielec [87] developed a kinetic model based on the following reactions:

1. Addition of a monomer to increase the chain length
2. β -hydride elimination by the catalyst to give a dead chain with a terminal vinyl unit, i.e. a *macromonomer*
3. Addition of a macromonomer to form a branch
4. Termination by transfer to a chain transfer agent

If one is interested only in the final structures of the molecules formed rather than the rate of reaction, only two parameters are important [94]: pp , the probability of propagation ($1 + \beta$) relative to that of termination (4), and lp , the probability of adding a monomer (1) relative to that of adding a macromonomer (3). Given only these two parameters, one can, in principle, calculate all the quantities of interest. A simple example of such a relationship is shown in Eq. 3.4.

$$\lambda = \frac{10^3}{2} pp(1 - lp) \quad (3.4)$$

To obtain the distributions of segment lengths and branch point, it is necessary to carry out a detailed analysis. Soares and Hamielec [87] used a Monte Carlo computational scheme to calculate all the relevant structural parameters. A diagram of the Monte Carlo algorithm used is shown in Fig. 3.2. Polymer molecules are built up one by one and added to a pool. As the number of molecules created in this manner increases, the distributions become closer and closer to that in the polymer.

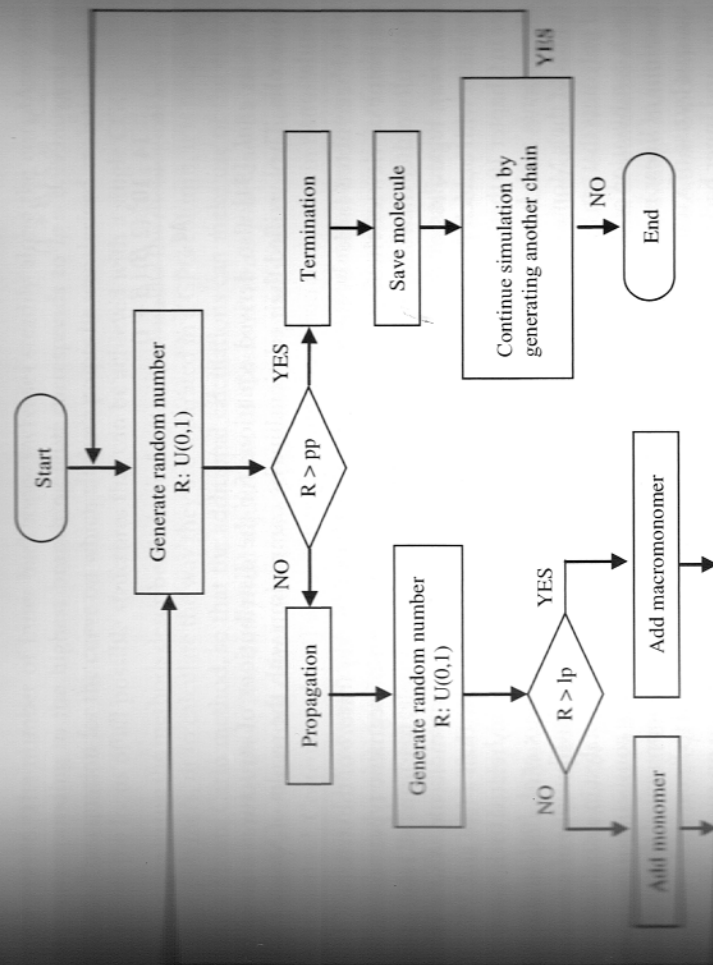


Figure 3.2 Algorithm for Monte Carlo simulations of branching distribution in branched metallocene polyethylenes made using a constrained-geometry catalyst. A large number of molecules are "created" according to rules based on the relative probabilities of propagation (pp) and monomer addition (lp). From Soares and Hamielec [87].

Soares *et al.* [95] later derived analytical expressions for all the relevant average parameters, a few of which are shown below.

$$M_{n,s} = \frac{28}{1 - pp \cdot lp} \quad (3.5)$$

$$M_{w,s} = 28 \left(\frac{1 + pp \cdot lp}{1 - pp \cdot lp} \right) \quad (3.6)$$

$$M_w = 2(\beta + 1)(2\beta + 1)M_{n,s} \quad (3.7)$$

$$M_n = (2\beta + 1)M_{n,s} \quad (3.8)$$

In these equations, the subscript s indicates a segment average. From Eqs. 3.7 and 3.8, the following useful relationships can be derived:

$$\frac{M_w}{M_n} = 2(\beta + 1) \quad (3.4)$$

$$\lambda = \frac{14 \cdot 10^3 (2\beta)(\beta + 1)}{M_w} \quad (3.5)$$

Costeux *et al.* [94] also derived equations for the distributions of structures among the molecules. They verified their relationships by comparison with the results of Monte Carlo simulations.

It had been noted earlier by Read and McLeish [96] that the key feature of the structure from the point of view of rheological behavior is the distribution of segment types among the molecules rather than simply the number of branches. For example, free arms all relax in the same way, regardless of the total number of branches on the same molecule. And a chain segment with branch points at both ends relaxes much more slowly than a free end. We will see in Chapter 10 that a key aspect of extensional flow behavior is directly related to the presence of segments with branch points at both ends. This inspired Costeux *et al.* [94] to use the results of their Monte Carlo simulations to calculate the branching distributions of a number of polymers that can be formed using a single, constrained-geometry catalyst in a single reactor. Each combination of the parameters pp and lp corresponds to a system consisting of particular fractions of linear molecules, free arms and inner backbones. They represented these ternary systems by use of a ternary diagram in which the vertices correspond to linear molecules, free arms, and inner backbone segments. Ten simulated systems are shown on such a diagram in Fig. 3.3. The point nearest the lower-right-hand vertex corresponds to a system made up mostly of linear molecules with a few three-armed stars. This point corresponds to $lp = 0.99984$ and

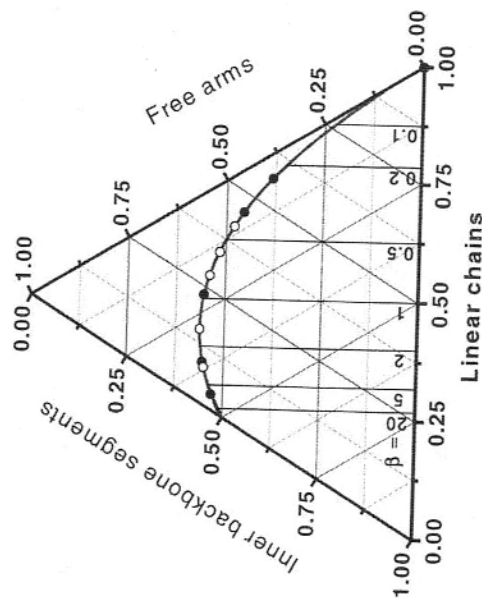


Figure 3.3 Ternary diagram based on Monte Carlo simulations showing all possible combinations of linear molecules, free arms and inner backbones in long-chain branched polyethylenes made using a single, constrained-geometry catalyst in a single reactor. From Costeux *et al.* [94].

$pp = 0.999176$. The number of inner backbones increases steadily along the curve, and the lp corresponding to the highest branching level corresponds to $lp = 0.99980$ and $pp = 0.99980$. The equation for the curve on which all these points lie was derived analytically and represents the locus of all possible structures that can be achieved with a single CGC.

One wants to use the methods described in later chapters to simulate the rheological behavior of these polymers, or to calculate the way they are separated in a GPC column, it is necessary to use a Monte Carlo method, so that the additional calculations can make use of the entire ensemble of molecules. The analytical equations of Costeux *et al.* [94] can be used to automatically accelerate this calculation. Using a personal computer with an advanced Monte Carlo method, Costeux *et al.* [94] were able to simulate 10 million molecules in two minutes, that is, the mass of linear molecules M in each elution volume is calculated. Then for molecules with one branch point, one determines the mass required to be in the same portion of column area. These steps are repeated for each number of branch points, and the weight fractions are summed. The weight fractions are used to calculate the average g for each apparent molecular weight using Eq. 2.25. Finally, to simulate the output of a LALLS detector, M_w of each elution volume is used instead of the mass of linear chains M .

As an example of this use of this method, computations were made for the seven materials whose segment compositions correspond to the points in Fig. 3.4. The values of M_w , λ and β for these materials are given in Table 3.1, and the rheological behavior of these materials is discussed in Chapters 5 and 10. Fig. 3.5 is a plot of g versus M for portions of simulated elute having weight average molecular weights of M , and Fig. 3.6 shows the average number of branches per molecule β as a function of M . These were computed using the Zimm-Stockmayer equations.

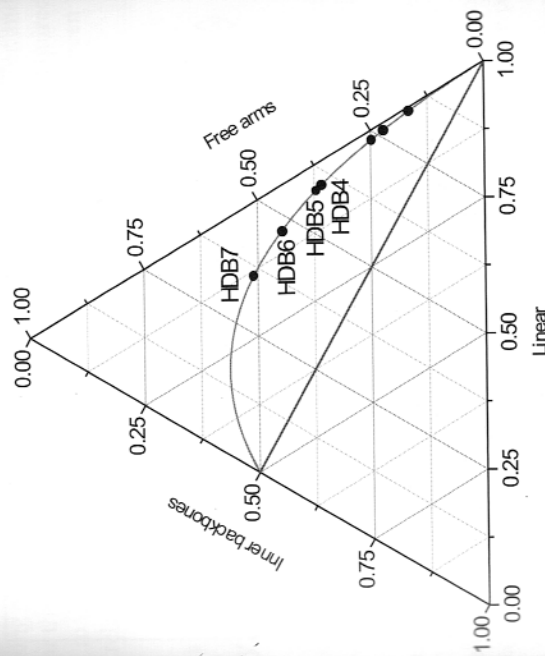


Figure 3.4 Ternary diagram of Fig. 3.3 showing the segment compositions of the seven branched metalocene polyethylenes whose GPC separations were simulated using the method of Costeux *et al.* [94]. Key parameters for these polymers are given in Table 3.1.

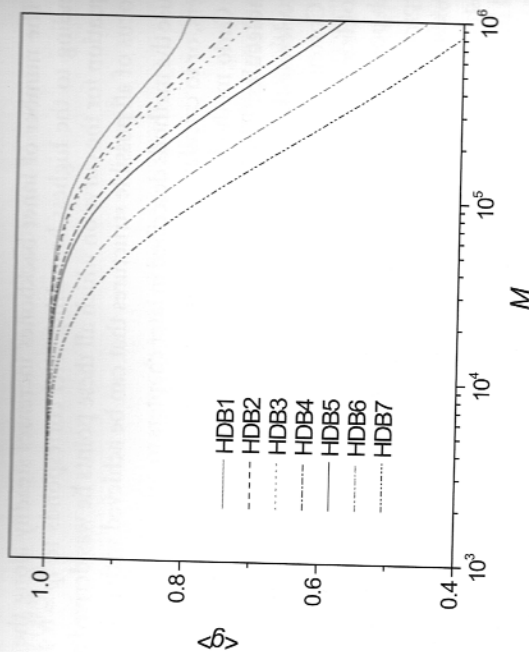


Figure 3.5 Branching factor g versus M for portions of simulated elute having weight average molecular weights M for the polyethylenes whose segment compositions fall on the curve in Fig. 3.4. These were computed using the Zimm-Stockmayer equations and the method of Costeux *et al.* [94] (calculations carried out by S. Costeux).

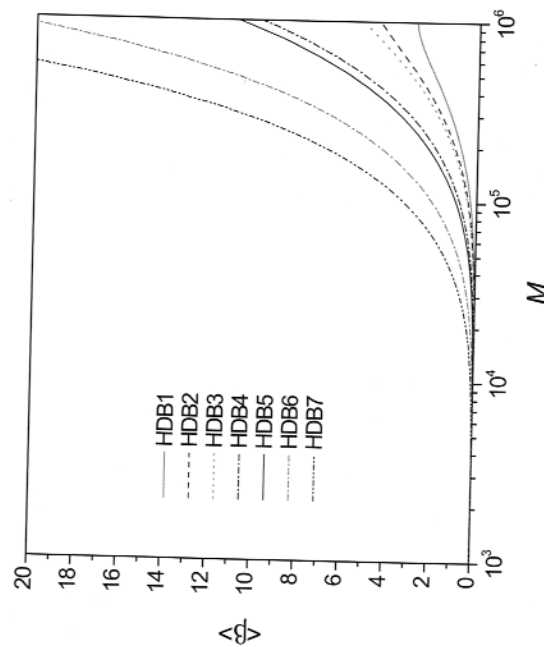


Figure 3.6 Average number of branch points per molecule β versus M for portions of simulated elute having weight average molecular weights M for the polyethylenes whose segment compositions are shown in Fig. 3.4. These were computed using the method of Costeux *et al.* [94] and the Zimm-Stockmayer relationships (calculations carried out by S. Costeux).

Table 3.1 Molecular Weights and Branching Levels of the Polymers Corresponding to the Seven Points in Fig. 3.4.

	M_w	λ	β
(1)	77,000	0.026	0.067
(2)	82,000	0.037	0.099
(3)	86,000	0.042	0.116
(4)	96,000	0.080	0.224
(5)	79,000	0.090	0.210
(6)	68,000	0.190	0.343
(7)	70,000	0.330	0.537

An important conclusion of the theoretical studies of these polymers is that the more complex, hyperbranched structures tend to occur in the largest chains. This implies that if one tries to increase the type of branching that has a strong effect on stretching-flow behavior, the viscosity may increase sharply at the same time. In order to achieve better control of branching structure, the use of more than one catalyst has been examined [90, 91]. Costeux [95] used a statistical model to predict the molecular weight distributions and branching structures of polymers produced in a reactor containing several single-site catalysts with the objective of optimizing the melt flow properties. Later, we will show that long-chain branching strongly influences both the linear and nonlinear behavior of polymers and can be used to "tune" the rheology to optimize processing performance. Such tuning is a delicate process, however, and a quantitative understanding of the relationship between branching and rheology is required to do it in an effective way. A major goal of this book is to review progress that has been made towards developing this relationship.

3.10 Polypropylene

Polypropylene is usually said to have one of three tacticities: isotactic, syndiotactic, and atactic, although we saw in Chapter 2 that there are intermediate structures in which the distribution of methyl units is neither regular nor perfectly random. Atactic polypropylene is a viscous amorphous liquid with limited industrial applications. Both isotactic and syndiotactic versions are crystallizable, but because of its much faster rate of crystallization, the isotactic polypropylene is the commercially important type, second only to polyethylene in global level of production. Nearly monodisperse polypropylene for use in research can be prepared by the polymerization of a suitable diene, with subsequent hydrogenation [49].

It is often credited with the discovery that the catalysts developed by Ziegler are capable of controlling the tacticity of α -olefins, and these catalysts are generally referred to as Ziegler-Natta catalysts. The ability to control tacticity made it possible for the first time to manufacture

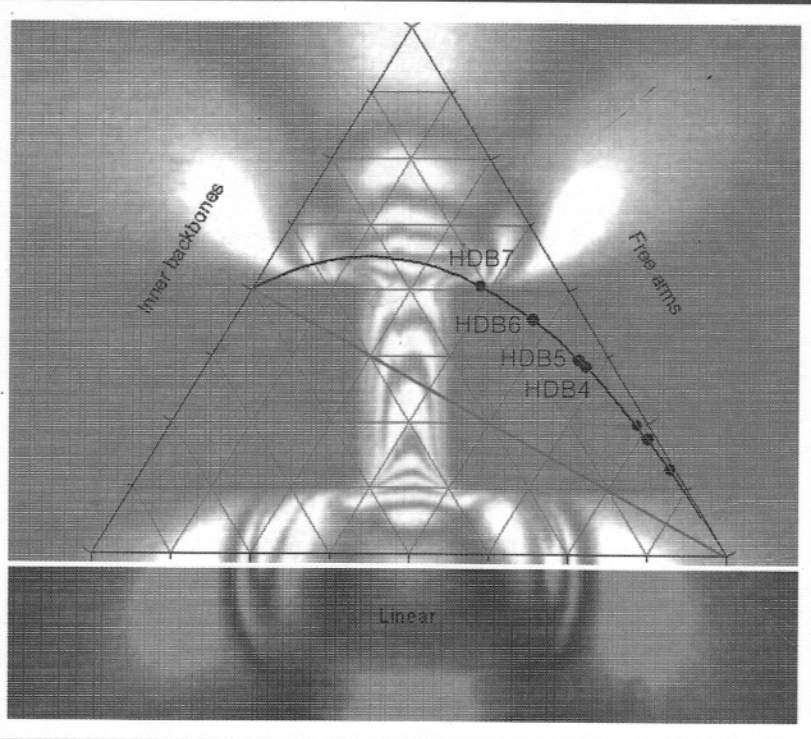
- [35] Hawker, C. J., "Living" free radical polymerization: A unique technique for the preparation of controlled molecular architecture. *Acc. Chem. Res.* (1997) 30, pp. 373–382
- [36] Keoshkerian, B., Georges, M. K., Quinlan, M., Veregin, R. P. N., Goodbrand, B., Polyacrylates and polydiemnes to high conversion by a stable free radical polymerization process: use of a reducing agent. *Macromol.* (1998) 31, pp. 7559–7561
- [37] Pasquale, A. J., Long, T. E., Synthesis of star-shaped polystyrenes via nitrogen-mediated stable free-radical polymerization. *J. Polym. Sci. A, Polym. Chem.* (2000) 39, pp. 216–223
- [38] Percec, V., Kim, H.-J., Barboiu, B., Disulfonyl chlorides: A universal class of initiators for melt-catalyzed "living" diradical polymerization of styrene, methacrylates and acrylates. *Macromol.* (1997) 30, pp. 6702–6705
- [39] Harth, E., Hawker, C. J., Fan, W., Waymouth, R. M., Chain-end functionalization in nitroxide-mediated "living" free-radical polymerizations. *Macromol.* (2001) 34, pp. 3856–3862
- [40] Wang, J.-S., Matyjaszewski, K., Controlled "living" radical polymerization. Halogen atom transfer radical polymerization. *Macromol.* (1975) 28, pp. 7901–7910
- [41] Matyjaszewski, K., Jo, S. M., Paik, H.-J., Gaynor, S. G., Mechanistic and synthetic aspects of atom transfer radical polymerization. *J. Macromolec. Sci. - Part A* (1997) 34, pp. 1785–1801
- [42] Matyjaszewski, K., Miller, P. J., Pyun, J., Kicelbick, G., Diamanti, S. Synthesis and characterization of star polymers with varying arm number, length and composition. *Macromol.* (1999) 32, pp. 6526–6535
- [43] Chong, Y. K., Le, T. P. T., Moad, G., Rizzardo, E., Thang, S. H., A more versatile route to block copolymers and other polymers of complex architecture by living radical polymerization: the RAFT process. *Macromol.* (1999) 32, pp. 2071–2074
- [44] Summerlin, B. S., Donovan, M. S., Mitsukami, Y., Lowe, A. B., Water-soluble polymers. Controlled polymerization I aqueous media of anionic acrylamoido polymers via RAFT. *Macromol.* (2001) 34, pp. 6561–6564
- [45] H. Rachapudy, G. G. Smith and V. R. Raju, Properties of amorphous and crystallizable hydrocarbon polymers. III Studies of the Hydrogenation of Polybutadienes. *J. Polym. Sci., Polym. Phys. Ed.* (1979) 17, pp. 1211–1235
- [46] V. R. Raju, H. Rachapudy and W. W. Graessley, Properties of amorphous and crystallizable hydrocarbon polymers. IV. Melt rheology of linear and star-branched hydrogenated polybutadienes. *J. Polym. Sci., Polym. Phys. Ed.* (1979) 17, pp. 1223–1235
- [47] Hadjichristidis, N., Xenidou, M., Iatrou, H., Pitsikalis, M., Poulos, Y., Avgeropoulos, A., Sioulas, Paraskeva, S., Vellis, G., Lohse, D. J., Schulz, D. N., Fetters, L. J., Wright, P. J., Mendelson, R. A., Garcia-Franco, C. A., Sun, T., Ruff, C. J. Well-defined, model long chain branched polyethylene I. Synthesis and characterization. *Macromol.* (2000) 33, pp. 2424–2436.
- [48] Lohse, D. J., Milner, S. T., Fetters, L. J., Xenidou, M., Hadjichristidis, N., Mendelson, R. A., Garcia-Franco, C. A., Lyon, M. K. Well-defined, model long chain branched polyethylene. 2. Melt rheological behavior. *Macromol.* (2002) 35, pp. 3066–3075
- [49] Pearson, D. S., Fetters, L. J., Younghouse, L. B., Mays, J. W. Rheological properties of poly(1,3-dimethyl-1-butene) and model atactic polypropylene. *Macromol.* (1988) 21, pp. 478–484
- [50] Tarmy, B. L. Reactor Technology, in *Encyclopedia of Polym. Sci. and Technol.*, John Wiley & Sons, NY (1988) vol. 14, pp. 189–237
- [51] Ballard, D. G. H. The discovery of polyethylene and its effect on the evolution of polymer science in Seymour, R. B., Cheng, Tai (eds.), *History of Polyolefins*. D. Reidel Publ. Co., Dordrecht 1986, pp. 9–53
- [52] Roedel, M. The molecular structure of polyethylene. I. Chain branching in polyethylene during polymerization. *J. Am. Chem. Soc.* (1953) 75, pp. 6110–6112
- [53] Flory, P. J. The mechanism of vinyl polymerization. *J. Am. Chem. Soc.* (1937) 59, pp. 241–253
- Bradley, J. K. The molecular structure of polyethylene. IV. Kinetic calculation of the effect of branching on molecular weight distribution. *J. Am. Chem. Soc.* (1953) 75, pp. 6123–6127
- Usami, T., Takayama, S. Fine-branching structure in high-pressure, low-density polyethylenes by an 10-MHz ¹³C-NMR analysis. *Macromol.* (1984), 17, pp. 1756–1761
- Radom, D. E., Levy, G. C., Mandelkern, L. A quantitative analysis of low-density (branched) polyethylenes by Carbon-13 Fourier transform nuclear magnetic resonance at 67.9 MHz. *Macromol.* (1979) 12, pp. 41–52
- Shaw, W., Marshall, E., Oshinowo, L. Modeling LDPE tubular and autoclave reactors. *Ind. Eng. Chem.* (2001) 40, pp. 5533–5542
- Yamaguchi, M., Takahashi, M., Rheological properties of low-density polyethylenes produced by tubular and vessel processes. *Polymer* (2001) 42, pp. 8663–8670
- Wagner, M. H., Yamaguchi, M., Takahashi, M. Quantitative assessment of strain hardening of low-density polyethylene melts by the molecular stress function model. *J. Rheol.* (2003) 47, pp. 779–803
- Hansen, D. E. Shear modification of polyethylene. *Polym. Eng. Sci.* (1969) 9, pp. 405–414
- Abokuda, M., Mihara, S., Fujiki, T. J. Influence of shear history on the rheological properties and processability of LDPE. *Journ. Appl. Polym. Sci.* 32 (1979), 3289–3294
- Heldens, P. J. R., Bastiaansen, C., Shear modification of LDPE. *Macromol.* (1989) 22, pp. 3312–3317
- Yamaguchi, M., Takahashi, M. Rheological properties of low-density polyethylenes produced by tubular and vessel processes. *Polymer* (2001) 42, pp. 8663–8670
- Parsons, A. Mathematical models for polymerization processes of Ziegler-Natta type. Chapt 1 of *Mathematical modeling for polymer processing*, V. Capasso, Ed., Springer, Berlin 2000
- Koel, E. J. UNIPOL gas phase copolymerization with SSC metallocene technology. in *Metallocene Catalyzed Polymers*, Benedikt, G. M. and Goodall, B. L., Eds., Plastics Design Lib, Norwich, NY 1998, pp. 35–42
- F. J. Karol, Catalysis and the polyethylene revolution. In Seymour, R. B., Cheng, Tai (eds.), *History of Polyolefins*, D. Reidel Publ. Co., Dordrecht 1986, pp. 193–211
- Bousfield, R. et al. A fully integrated high-throughput screening methodology for the discovery of new polyolefin catalysts. *J. Am. Chem. Soc.* (2003) 125, pp. 4306–4317
- Agar, J. P., Santamaria, A. Small-amplitude oscillatory shear flow measurements as a tool to detect very low amounts of long chain branching in polyethylenes. *Macromol.* (1998) 31, pp. 3639–3647
- Benham, E., McDaniel M., Ethylene Polymers, HDPE. *Encyclop. Polym. Sci. Technol.* (2002) John Wiley & Sons, NY
- McDaniel, M. P., Rohlfing, D. C., Benham, E. A. Long-chain branching in polyethylene from the Phillips chromium catalyst. *Polym. React. Eng.* (2003) 11, pp. 101–132
- Shoob, P., Dev, D., Chakrabarti, A. Reactive melt processing of polyethylene: Effect of peroxide action on polymer structure, melt rheology and relaxation behavior. *Polymer* (1997) 38, pp. 6175–6180
- Isaac, M., Kleinova, A., Fiedlerova, A., Janigova, I., Borsig, E. Role of minority structures and mechanism of peroxide crosslinking of polyethylene. *J. Polym. Sci. A: Polym. Chem.* (2003) 42, pp. 675–688
- Shou, W., Zhu, S. ESR study of peroxide-induced cross-linking of high density polyethylene. *Macromol.* (1998) 31, pp. 4335–4341
- Isaac, P., Mackley, M. R. The structure and rheology of molten ultra-high-molecular-mass polyethylene. *Polymer* (1994) 35, pp. 5210–5216

- [75] Rastogi, S., Kurelec, L., Cuijpers, J., Lippits, D., Wimmer, M., Lemstra, P. J. Disentangled star-like polymer melts; a route to ultimate physical and mechanical properties. *Macromol. Mater. Eng.* (2003) 288, pp. 964–970
- [76] Utracki, L. A., Schlund, B. Linear low density polyethylenes. Part 1. Molecular characterization. *Polym. Eng. Sci.* (1987) 27, pp. 359–366
- [77] Mirabella, F. M., Ford, E. A. Characterization of low-density polyethylene: Cross fractionation according to copolymer composition and molecular weight. *J. Polym. Sci. B, Polym. Phys.* (1991) 25, pp. 777–790
- [78] Zhang, M., Lynch, D. T., Wänke, S. E. Effect of molecular structure distribution on melting and crystallization behavior of 1-butene/ethylene copolymers. *Polymer* (2001) 42, pp. 3067–3073
- [79] Chu, K.-J., Soares, J. B. P. Effect of experimental conditions on ethylene polymerization with in situ supported metallocene catalysts. *J. Polym. Sci., Polym. Chem.*, (2000) 38, pp. 1803–1810
- [80] Simpson, D. M., Vaughan, G. A. Ethylene Polymers. LLDPE. *Encyclopedia of Polymer Science and Technology* (2002) John Wiley & Sons, NY.
- [81] Bensason, S., Minick, J., Moet, A., Chum, S., Hiltner, A., Baer, E. Classification of homogeneous ethylene-octene copolymers based on comonomer content. *J. Polym. Sci. B, Polym. Phys.* (1996) 34, pp. 1301–1315
- [82] Malmberg, A., Gabriel, C., Steffl, T., Münstedt, H., Lofgren, B. Long-chain branching in metallocene catalyzed polyethylenes investigated by low oscillatory shear and uniaxial rheometry. *Macromol.* (2002) 35, pp. 1038–1048.
- [83] Gabriel, C., Kokko, E., Löfgren, B., Seppälä, J., Münstedt, H. Analytical and rheological characterization of long-chain branched metallocene-catalyzed ethylene homopolymers. *Polymer* (2001) 43, pp. 6383–6390
- [84] Stevens, J., INSITE™ catalyst structure/activity relationships for olefin polymerization. *Stud. Surf. Sci. & Catal.* (1994) 89, pp. 277–284; Constrained geometry and other single site metallocene polyolefin catalysts, *ibid* (1996) 101, pp. 11–20
- [85] Lai, S. Y., Wilson, J. R., Knight, G. W., Stevens, G. W. Elastic substantially linear olefin polymers. US Patent 5,272,236 (1993)
- [86] Chum, P. S., Kao, C. I., Knight, G. W. Structure, properties and preparation of polyolefins produced by single-site catalyst technology, Chapter 12 of *Metallocene-based Polyolefins*, Vol. 1. Scheirs, J. Kaminsky, W., Eds. John Wiley & Sons, NY (2000)
- [87] J. B. P. Soares and A. E. Hamielec, Bivariate chain length and long chain branching distribution by copolymerization of olefins and polyolefin chains containing terminal double-bonds. *Macromol. Theory Simul.* (1996) 5, pp. 547–572
- [88] J. B. P. Soares and A. E. Hamielec, The chemical composition component of the distribution of chain length and long chain branching for copolymerization of olefins and polyolefin chains containing terminal double bonds. *Macromol. Theory Simul.* (1997) 6, pp. 591–596
- [89] D. Beigzadeh, J. B. P. Soares and A. E. Hamielec, Study of long-chain branching in ethylene polymerization. *Polym. React. Eng.* (1997) 5, pp. 141–180
- [90] Beigzadeh, J. B. P. Soares and T. A. Duever, Combined metallocene catalysts: An efficient technique to manipulate long-chain branching frequency of polyethylene. *Macromol. Rapid Commun.* (1999) 20, pp. 5541–5545
- [91] Beigzadeh, J. B. P. Soares and A. E. Hamielec, Recipes for synthesizing polyolefins with tailor made molecular weight, polydispersity index, long-chain branching frequencies, and chemical composition using combined metallocene catalyst systems in a CSTR at steady state. *J. Appl. Polym. Sci.* (1999) 71, pp. 1753–1770
- [92] Kolodka, E., Want, W.-J., Charpenier, P. A., Zhu, S., Hamielec, A. E. Long-chain branching in slurry polymerization of ethylene with zirconocene dichloride/modified methylaluminoxane. *Polymer* (2000) 41, pp. 3985–3991
- [93] Head, D. J., McLeish, T. C. B. Molecular rheology and statistics of long chain branched metallocene-catalyzed polyolefins. *Macromol.* (2001) 34, pp. 1928–1945
- [94] Costeux, S., Wood-Adams, P., Beigzadeh, D. Molecular structure of metallocene-catalyzed polyethylene: Rheologically relevant representation of branching architecture in single catalyst and blended systems. *Macromol.* (2002) 35, pp. 2514–2528
- [95] Costeux, S. Statistical modeling of randomly branched polymers produced by combination of several single-site catalysts: Toward optimization of melt properties. *Macromol.* (2003) 36, pp. 4168–4187
- [96] Soares, J. B. P. Polyolefins with long chain branches made with single-site coordination catalysts: A review of mathematical modeling techniques for polymer microstructure. *Macromol. Mater. Eng.* (2004) 289, pp. 70–87
- [97] Hoogen, J. P., Banks, R. L. History of crystalline polypropylene. In Seymour, R. B., Cheng, Tai (eds.), *History of Polyolefins*. D. Reidel Publ. Co., Dordrecht (1986) pp. 103–115
- [98] Haer, K., White, J. L. Peroxide induced and thermal degradation of polypropylene. *Intern. Polym. Proc.* (1994) 9, pp. 233–239
- [99] Pabedinskas, A., Cluett, W. R., Balke, S. T. Modeling of polypropylene degradation during reactive extrusion with implications for process control. *Polym. Eng. Sci.* (1994) 34, pp. 598–612
- [100] Mead, D. W. Evolution of the molecular weight distribution and linear viscoelastic rheological properties during reactive extrusion of polypropylene. *J. Appl. Polym. Sci.* (1995) 57, pp. 151–173
- [101] Vergnes, B., Berzin, F. Peroxide-controlled degradation of polypropylene. *Macromol. Symp.* (2000) 158, pp. 77–90
- [102] Sato, K., Wozumi, Kaji, E. Synthesis of isotactic polypropylene by metallocene and related catalysts, Chapter 17 of *Metallocene-based Polyolefins*, Vol. 1, J. Scheirs and W. Kaminsky, Eds. John Wiley & Sons, NY (2000)
- [103] Wang, W., Hu, W., Dekmezian, A. H., Ruff, C. J. Long chain branched isotactic polypropylene. *Macromol.* (2002) 35, pp. 3838–3843
- [104] Xu, Z., Alabaldi, E., Zhu, S. Synthesis and rheological properties of long-chain-branched isotactic polypropylenes prepared by copolymerization of propylene with nonconjugated dienes. *Ind. Eng. Chem.* (2004) 43, pp. 2860–2870
- [105] Xu, Z., Zhu, S. Synthesis of branched polypropylene with isotactic backbone and atactic side chains. *J. Polym. Sci. Part A* (2003) 41, pp. 1152–1159
- [106] Yoshii, E., Makuuchi, K., Kikukawa, S., Tanaka, T., Saitoh, J., Koyama, K. High-melt-strength polypropylene with electron beam irradiation in the presence of polyfunctional monomers. *J. Appl. Polym. Sci.* (1996) 60, pp. 617–623
- [107] Matsub, M., Reaction mechanism in long chain branched PP. *J. Macromol. Sci., Pure Appl. Chem.* (1999) 36, pp. 1759–1769
- [108] Papendijk, R. P., Hogt, A. H., Buijtenhuijs, Gotsis, A. D. Peroxydicarbonate modification of polypropylene and extensional flow properties. *Polymer* (2001) 42, pp. 10035–10043
- [109] Gotsis, A. D., Zeevenhoven, B. L. E., Tsenoglou, C. Effect of long branches on the rheology of polypropylene. *J. Rheol.* (2004) 48, pp. 895–914
- [110] He, C., Costeux, S., Wood-Adams, P., Dealy, J. M. Molecular structure of high-melt-strength polypropylene and its application to polymer design. *Polymer* (2003) 44, pp. 7181–7188
- [111] American Society for Testing and Materials (ASTM) Standard Test Method for Flow Rates of Thermoplastics by Extrusion Plastometer (D1238) West Conshohocken, PA
- [112] Kubo, R., Krömer, H., Structures and properties of different low density polyethylenes. *Colloid & Polym. Sci.* (1982) 260, pp. 1083–1092
- [113] Meissner, J. Basic parameters, melt rheology, processing and end-use properties of three similar low density polyethylenes. *Pure & Appl. Chem.* (1975) 42, pp. 553–612

John M. Dealy
Ronald G. Larson

Structure and Rheology of Molten Polymers

From Structure to Flow Behavior
and Back Again



HANSER

Preface

Results of recently developed molecular models suggest the possibility of predicting the rheological behavior of a molten polymer when its molecular structure is well-known. Such models also provide the basis of methods for using rheological data to obtain information about the structure of a polymer whose structure is not known in detail. These models and relationships between structure and rheology are presented here from both phenomenological and molecular-theoretical points of view.

This book is intended to be useful to several types of reader. For those who have a basic knowledge of rheology but little experience with polymers, we have provided in the early chapters sufficient information about polymer physics and chemistry for an understanding of the later chapters. For readers who are currently active in polymer rheology and would like to know the state of the art with respect to quantitative relationships between molecular structure and rheology, the later chapters of the book provide this information. Thus, the book provides both an introduction to polymers and rheological concepts as well as an advanced treatment of potential interest both to polymer scientists and plastics engineers.

Until recent years, there existed major barriers to the development of quantitative relationships between the molecular structure of molten polymers and their rheological behavior. First, reaction systems capable of producing polymers on an industrial scale yielded materials with complex and imprecisely controlled structures. Second, the molecular weight distributions of linear polymers tended to be broad and somewhat irreproducible. And, finally, the branching structure of long-chain branched polymers, particularly low-density polyethylene, involves multidimensional distributions that can neither be predicted nor characterized with precision.

However, over the last ten years, advances in the areas of catalysis and molecular modeling have changed this situation dramatically. Using single-site catalysts, it is now possible to produce on an industrial scale polymers having structures that are much better defined and reproducible than those produced previously. Furthermore, new molecular models, particularly those based on the concept of a "molecule in a tube", have been developed that can predict rheological behavior based on knowledge of molecular structure. While still requiring further work, particularly to deal with broad molecular weight distributions and complex branching structures, the new models show great promise for the quantitative prediction of flow behavior of polymers of commercial importance. The objective of this book is to present these important developments, along with the background necessary to understand them, and to provide industrial and academic researchers with the up-to-date knowledge and expertise required to use them effectively.

It is not feasible to mention here all the people who have helped us in various ways during the several years we spent writing this book, but we would like to mention the following who were helpful in particularly important ways: Ralph Colby, Stéphane Costeux, Richard Graham, Willem de Groot, Teresa Karjala, David Lohse, Guiseppe Marrucci, Hiroshi Watanabe, and Paula Wood-Adams. And we cannot fail to mention that the support of our tolerant families

The Authors:

Dr. John M. Dealy, McGill University, Montreal, Canada
Dr. Ronald G. Larson, University of Michigan, Ann Arbor, USA

Distributed in the USA and in Canada by

Hanser Gardner Publications, Inc.

6915 Valley Avenue, Cincinnati, Ohio 45244-3029, USA

Fax: (513) 527-8801

Phone: (513) 527-8977 or 1-800-950-8977

www.hansergardner.com

Distributed in all other countries by

Carl Hanser Verlag

Postfach 86 04 20, 81631 München, Germany

Fax: +49 (89) 98 48 09

www.hanser.de

The use of general descriptive names, trademarks, etc., in this publication, even if the former are not especially identified, is not to be taken as a sign that such names, as understood by the Trade Marks and Merchandise Marks Act, may accordingly be used freely by anyone.

While the advice and information in this book are believed to be true and accurate at the date of going to press, neither the authors nor the editors nor the publisher can accept any legal responsibility for any errors or omissions that may be made. The publisher makes no warranty, express or implied, with respect to the material contained herein.

Library of Congress Cataloging-in-Publication Data

Dealy, John M.

Structure and rheology of molten polymers :

John M. Dealy, Ronald G. Larson.

p. cm.

ISBN-10: 1-56990-381-6 (hardcover)

ISBN-13: 978-1-56990-381-0 (hardcover)

1. Polymers--Testing. 2. Rheology. I. Larson, Ronald G. II. Title.

TA455.P58D39 2006

620.1'92--dc22

2005033781

Bibliografische Information Der Deutschen Bibliothek

Die Deutsche Bibliothek verzeichnet diese Publikation in der Deutschen Nationalbibliografie; detaillierte bibliografische Daten sind im Internet über <http://dnb.ddb.de> abrufbar.

ISBN-13: 978-3-446-21771-3

ISBN-10: 3-446-21771-1

All rights reserved. No part of this book may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying or by any information storage and retrieval system, without permission in writing from the publisher.

© Carl Hanser Verlag, Munich 2006

Production Management: Oswald Immler

Typeset by Manuela Treindl, Laaber, Germany

Coverconcept: Marc Müller-Bremer, Rebranding, München, Germany

Coverdesign: MCP • Susanne Kraus Gbr, Holzkirchen, Germany

Printed and bound by Druckhaus "Thomas Müntzer" GmbH, Bad Langensalza, Germany