1
Introduction to Polyolefins

> It is a near perfect molecule [. . .].
>
> *Jim Pritchard, Phillips Petroleum Company*

1.1
Introduction

Polyolefins are used in a wide variety of applications, including grocery bags, containers, toys, adhesives, home appliances, engineering plastics, automotive parts, medical applications, and prosthetic implants. They can be either amorphous or highly crystalline, and they behave as thermoplastics, thermoplastic elastomers, or thermosets.

Despite their usefulness, polyolefins are made of monomers composed of only carbon and hydrogen atoms. We are so used to these remarkable polymers that we do not stop and ask how materials made out of such simple units achieve this extraordinary range of properties and applications. The answer to this question lies in how the monomer molecules are connected in the polymer chain to define the molecular architecture of polyolefins. By simply manipulating how ethylene, propylene, and higher α-olefins are bound in the polymer chain, polyolefins with entirely new properties can be produced.

Polyolefins can be divided into two main types, polyethylene and polypropylene, which are subdivided into several grades for different applications, as discussed later in this chapter.[1] Taking a somewhat simplistic view, three components are needed to make a polyolefin: monomer/comonomer, catalyst/initiator system, and polymerization reactor. We will start our discussion by taking a brief look at each of these three components.

Commercial polyethylene resins, despite their name, are most often copolymers of ethylene, with varying fractions of an α-olefin comonomer. The most

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[1] Ethylene-propylene-diene(EPDM) terpolymers, another important polyolefin type, are elastomers with a wide range of applications. They are made using catalysts and processes similar to those used to produce polyethylene and polypropylene. Even though they are not discussed explicitly in this book, several of the methods explained herein can be easily adopted to EPDM processes.

Polyolefin Reaction Engineering, First Edition. João B. P. Soares and Timothy F. L. McKenna.

commonly used α-olefins are 1-butene, 1-hexene, and 1-octene. They are used to decrease the density and crystallinity of the polyolefin, changing its physical properties and applications. Industrial polypropylene resins are mostly isotactic materials, but a few syndiotactic grades are also available. There are two main types of propylene copolymers: random propylene/ethylene copolymers[2] and impact propylene/ethylene copolymers.

At the heart of all polyolefin manufacturing processes is the system used to promote polymer chain growth. For industrial applications, polyethylene is made with either free radical initiators or coordination catalysts, while polypropylene is produced only with coordination catalysts. Low-density polyethylene (LDPE) is made using free radical processes and contains short chain branches (SCB) and long chain branches (LCB). Its microstructure is very different from that of polyethylenes made with coordination catalysts. Coordination catalysts can control polymer microstructure much more efficiently than free radical initiators and are used to make polyolefins with a range of properties unimaginable before their discovery. The quotation at the beginning of this chapter was motivated by the revolutionary synthesis of unbranched, linear polyethylene, the ‘‘near perfect molecule,’’ using a Phillips catalyst.

Catalyst design is behind the success of modern industrial olefin polymerization processes because the catalyst determines how the monomers will be linked in the polymer chain, effectively defining the polymer microstructure and properties. Industrial and academic research on olefin polymerization catalysis have been very dynamic since the original discoveries of Ziegler and Natta (Ziegler–Natta catalysts) and Hogan and Banks (Phillips catalysts), with many catalyst families being developed and optimized at a rapid pace. There are basically four main types of olefin polymerization catalysts: (i) Ziegler–Natta catalysts, (ii) Phillips catalysts, (iii) metallocene catalysts, and (iv) late transition metal catalysts. Ziegler–Natta and Phillips catalyst were discovered in the early 1950s, initiating a paradigm shift in olefin polymerization processes, while metallocene and late transition metal catalysts (sometimes called *post-metallocenes*) were developed in the 1980s and 1990s, respectively. In Chapter 3, olefin polymerization catalysts and mechanisms are discussed in detail, while polymerization kinetic models are developed in Chapter 5. For our purposes in this chapter, it suffices to say that polymerization with all coordination catalyst types involves monomer coordination to the transition metal active site before insertion in the metal–carbon bond at one end of the polymer chain. The coordination step is responsible for the versatility of these catalysts: since the incoming monomer needs to coordinate to the active site before propagation may occur, the electronic and steric environment around it can be changed to alter polymerization parameters that control the chain microstructure, such as propagation and chain transfer rates, comonomer reactivity ratios, stereoselectivity, and regioselectivity. This concept is illustrated in Figure 1.1.

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2) Propylene/1-butene copolymers and propylene/ethylene/α-olefin terpolymers are also manufactured, but in a smaller scale.

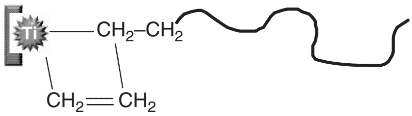

Figure 1.1 Coordination step before ethylene insertion on a polyethylene chain (active site control).

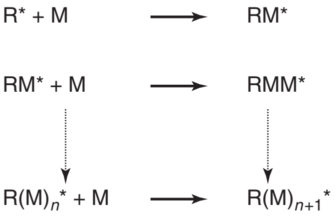

Figure 1.2 Generic free radical polymerization (chain-end control). R*, free radical initiator; M, monomer.

This mechanism controls the polymer microstructure better than free radical polymerization, where the chemical nature of the free radical initiator stops being important after a few propagation steps since the polymerization locus moves away from the initiator molecule, as illustrated in Figure 1.2. Free radical processes for LDPE production are not the main topic of this book and are only discussed briefly as comparative examples.

Even though a few processes for ethylene polymerization use homogeneous catalysts in solution reactors, most olefin polymerization processes operate with heterogeneous catalysts in two-phase or three-phase reactors. This adds an additional level of complexity to these systems since inter- and intraparticle mass and heat transfer resistances during polymerization may affect the polymerization rate and polymer microstructure. If significant, mass and energy transport limitations create nonuniform polymerization conditions within the catalyst particles that lead to nonuniform polymer microstructures. Many other challenging problems are associated with the use of heterogeneous catalysts for olefin polymerization, such as catalyst particle breakup, agglomeration, growth, and morphological development, all of which are discussed in Chapter 7.

All the phenomena mentioned above take place in the polymerization reactor. The variety of polyolefin reactors can be surprising for someone new to the field: polyolefins are made in autoclave reactors, single- and double-loop reactors, tubular reactors, and fluidized-bed reactors; these processes may be run in solution, slurry, bulk, or gas phase. Each reactor configuration brings with it certain advantages, but it also has some disadvantages; the ability to select the proper process for a given application is an important requirement for a polyolefin reaction engineer. Chapter 4 discusses these different reactor configurations and highlights some important polyolefin manufacturing processes. Reactor models that take into account micromixing and macromixing effects, residence time distributions, and mass and heat transfer phenomena at the reactor level are needed to simulate these processes, as explained in Chapter 8.

Catalyst type, polymerization mechanism and kinetics, inter- and intraparticle mass and heat transfer phenomena, and macroscale reactor modeling are essential for the design, operation, optimization, and control of polyolefin reactors. Figure 1.3

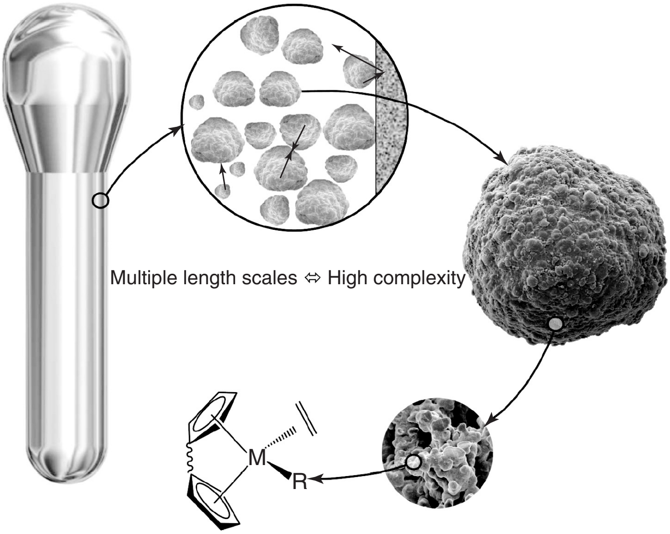

Figure 1.3 Modeling scales in polyolefin reaction engineering.

shows how these different length scales are needed to help us understand olefin polymerization processes.

In summary, much science and technology is hidden behind the apparent simplicity of everyday polyethylene and polypropylene consumer goods. No other synthetic polymer is made with such a variety of catalyst types, reactor configurations, and microstructural complexity. In this book, we will explain how, from such simple monomers, polyolefins have become the dominant commodity plastic in the twenty-first century.

1.2
Polyethylene Resins

Polyethylene resins are classified into three main types: LDPE, linear low-density polyethylene (LLDPE), and high-density polyethylene (HDPE). This traditional classification distinguishes each polyethylene type according to its density range: $0.915–0.940\ \mathrm{g\,cm^{-3}}$ for LDPE, $0.915–0.94\ \mathrm{g\,cm^{-3}}$ for LLDPE,[3] and $0.945–0.97\ \mathrm{g\,cm^{-3}}$ for HDPE, although these limits may vary slightly among different sources. Lower-density polyethylene resins ($<0.915\ \mathrm{g\,cm^{-3}}$) are sometimes called ultra low-density polyethylene (ULDPE) or very low-density polyethylene (VLDPE). HDPE with molecular weight averages of several millions is called ultrahigh molecular weight polyethylene (UHMWPE). To reduce the

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[3] Sometimes polyethylene resins in the range $0.926–0.940\ \mathrm{g\ cm^{-3}}$ are called medium-density polyethylene (MDPE).

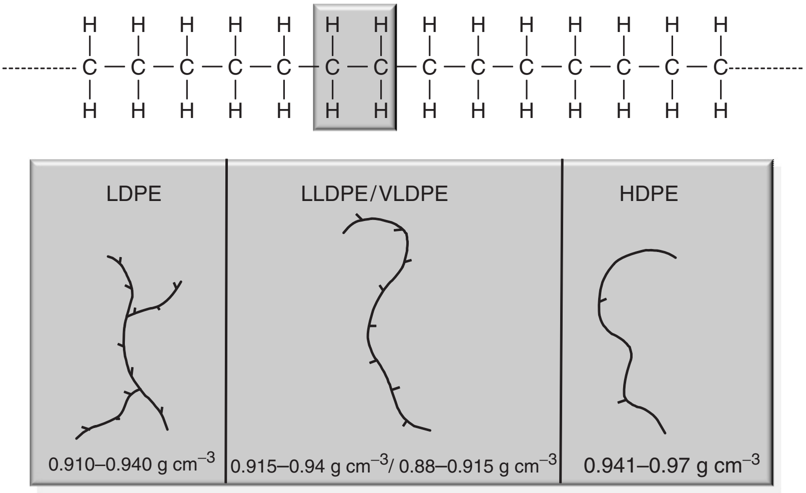

Figure 1.4 Classification of polyethylene types according to branching structure and density.

number of acronyms in this book, we have often grouped MDPE, LLDPE, ULDPE, and VLDPE under the generic term LLDPE and have made no distinction between HDPE and UHMWPE; these resins are very similar from a structural point of view, as explained below.

This division according to polyethylene density or molecular weight, although standard for commercial resins, tells us little about their microstructures. A more descriptive classification, based on their microstructural characteristics, is presented in Figure 1.4.

HDPE and LLDPE are made with coordination catalysts, while LDPE is made with free radical initiators. LDPE has both SCB and LCB, while polyethylenes made by coordination polymerization generally have only SCBs. Some polyethylene resins made with specific metallocenes or Phillips catalysts may also have some LCBs, but their LCB topology is distinct from that of LDPE resins. Most commercial HDPE and LLDPE grades are made with Ziegler–Natta or Phillips catalyst. Phillips catalysts are very important for the production of HDPE but are not used for LLDPE manufacture. Metallocenes can be used in making both HDPE and LLDPE, but metallocene resins are very different from the ones made with either Ziegler–Natta or Phillips catalyst, as explained below. The market share of metallocene resins is still relatively small but has been increasing steadily since the 1990s. Resins made with late transition metal catalysts have had no significant commercial applications to date.

The mechanism of SCB and LCB formation in LDPE is different from that in coordination polymerization; in LDPE, LCBs are formed by transfer-to-polymer reactions, while SCBs result from backbiting reactions. Contrarily, SCBs in HDPE and LLDPE are produced by the copolymerization of α-olefins added to the reactor as comonomers. LCBs, when present, are also formed by copolymerization reactions

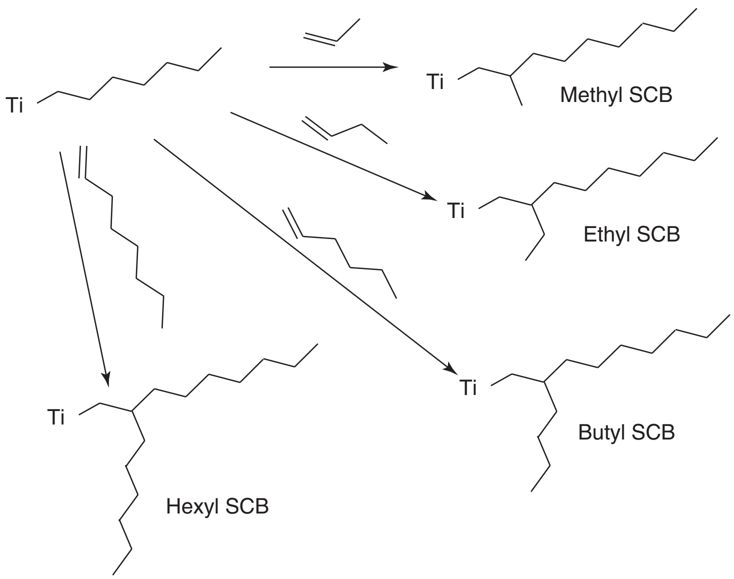

Figure 1.5 Short-chain branch formation mechanism in coordination polymerization. The chains are shown growing on a titanium active site.

with a polymer chain having a terminal group containing a reactive double bond (macromonomer).

Figure 1.5 illustrates the SCB formation mechanism during the copolymerization of ethylene and α-olefins. The SCB behaves as a defect in the polymer chain, decreasing polymer density, crystallite size, and melting temperature. Therefore, the higher the molar fraction of α-olefin in the polymer chain, the lower its crystallinity. HDPE resins have very low α-olefin comonomer fractions (typically below a few mole percentage), while the comonomer content increases from LLDPE to ULDPE to VLDPE.

Density is, therefore, a reflection of the α-olefin molar fraction in the polyolefin chain, and it also depends, to a lower degree, on its molecular weight; all other factors being the same, polyolefins with higher molecular weight averages tend to have a slightly lower density than those with lower molecular weight averages.

Density has been used for decades to classify polyethylene resins, but it is a poor descriptor for these materials because the microstructure of commercial polyethylenes is too complex to be captured with a single density value. Let us first focus on the chemical composition distribution (CCD) of LLDPEs, that is, the distribution of α-olefin fraction in the polymer chains. Most commercial LLDPEs are made with heterogeneous Ziegler–Natta catalysts. These catalysts have more than one type of active site, each one producing polymer chains with different average comonomer fractions and molecular weights. In addition, active sites that favor α-olefin incorporation also result in polymers with lower average molecular weights. As a consequence, the CCDs of Ziegler–Natta LLDPE resins are very

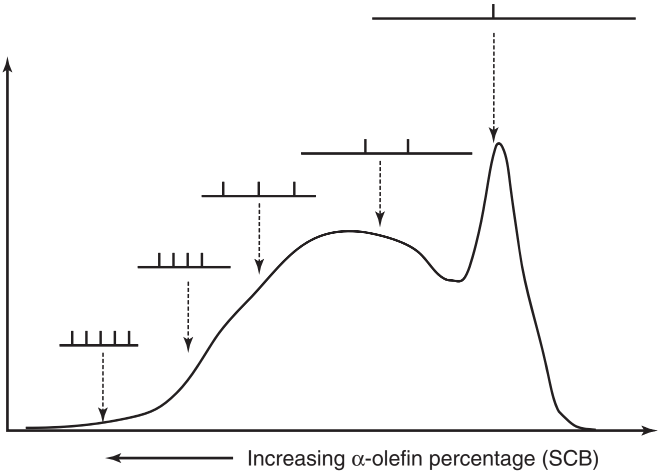

Figure 1.6 Generic chemical composition distribution of an LLDPE resin made with a heterogeneous Ziegler–Natta catalyst.

broad, generally bimodal, and the average α-olefin content is correlated to the polymer molecular weight, as illustrated in Figure 1.6.

Two distinct regions can be identified in Figure 1.6: a sharp high-crystallinity peak (low α-olefin fraction) and a broad low-crystallinity peak (high α-olefin fraction). These two regions are associated with at least two types of active sites, one with much lower reactivity ratio toward α-olefin incorporation than the other. As the relative amounts of polymer made under these two modes vary, polyethylene resins vary from HDPE, with a unimodal, high-crystallinity peak and sometimes a small, lower-crystallinity tail, to MDPE, LLDPE, ULDPE, and VLDPE, with increasingly pronounced lower-crystallinity peak. The shape of the CCD is a strong function of the catalyst type, but it also depends on ethylene/α-olefin ratio, α-olefin type, and polymerization temperature.

From the discussion of Figure 1.6, it is apparent that classifying these complex microstructures according to a single density value is inadequate. The picture becomes even more complex when we take a look at the joint distribution of molecular weight and chemical composition (MWD × CCD) for Ziegler–Natta LLDPE, such as the one depicted in Figure 1.7. This tridimensional plot summarizes the complexity inherent to most commercial polyolefin resins. It also demonstrates that microstructural characterization techniques are indispensable tools to understand these polymers, as discussed in Chapter 2.

The MWD × CCD correlation exemplified in Figures 1.6 and 1.7 is not desirable for certain polyolefin applications. A notable example are bimodal pipe resins, where better mechanical properties are achieved if the higher molecular weight chains also have a higher α-olefin fraction than the lower molecular weight component. The reason for this improved performance has been linked to the presence of tie molecules, a subject that is, unfortunately, beyond the scope of this book. The reader is directed to the references at the end of the chapter for more information on

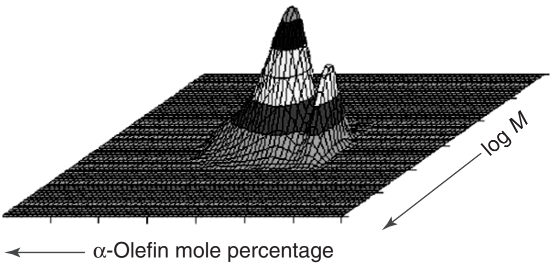

Figure 1.7 Joint distribution of molecular weight and chemical composition (MWD × CCD) for an LLDPE made with heterogeneous Ziegler–Natta catalysts.

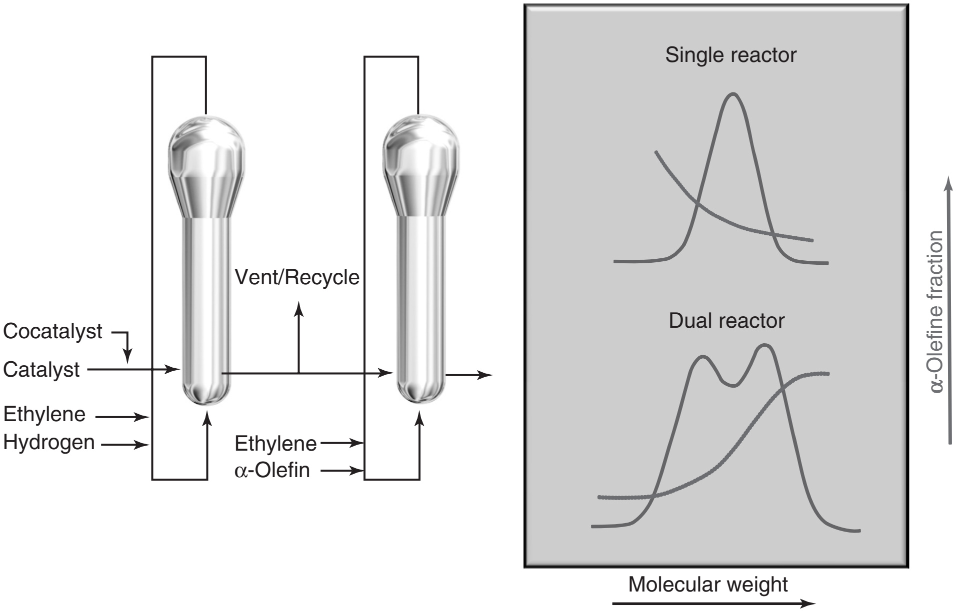

Figure 1.8 Polyethylene with regular and reverse comonomer incorporation made in single- and dual-reactor systems, respectively.

this subject. The usual MWD × CCD correlation observed in polyethylene resins made with heterogeneous Ziegler–Natta catalysts can be *partially* reversed using at least two reactors in series, as depicted in Figure 1.8. The polymers are called *bimodal polyethylenes* because they have broad, and sometimes bimodal, molecular weight distribution (MWD). The first reactor makes low molecular weight HDPE in the absence, or under very low concentration, of α-olefin. Hydrogen, the standard chain transfer agent in olefin polymerization, is used in the first reactor to lower the polymer molecular weight. The polymer made in the first reactor is then transferred continuously to the second reactor, which is operated under higher α-olefin concentration in the absence, or under a much lower concentration, of hydrogen, thus producing an LLDPE component with higher average molecular

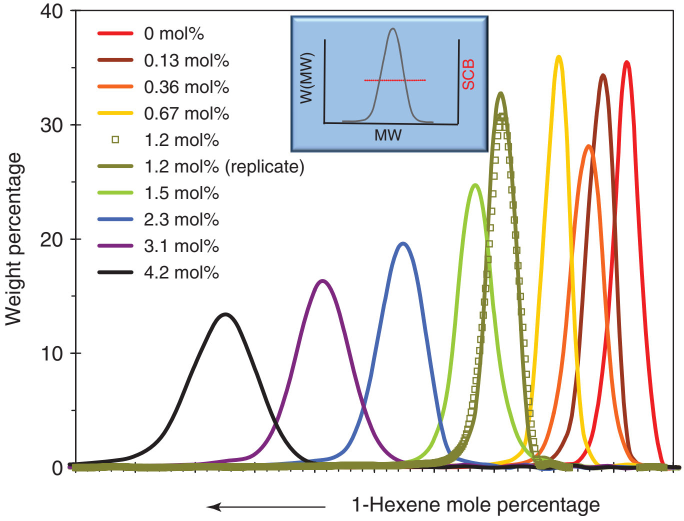

Figure 1.9 Chemical composition distributions of ethylene/1-hexene copolymers made with a metallocene catalyst.

weight than the HDPE component made in the first reactor. Many polyethylene industrial processes include two reactors in series to broaden the range of product properties, as described in Chapter 4.

The advent of metallocene catalysts added a new dimension to commercial polyolefin resins. Metallocenes are single-site catalysts that are used to make polyethylenes with completely different microstructures from those made with Ziegler–Natta and Phillips catalysts, but are still classified loosely as HDPE and LLDPE. Polyethylenes made with metallocene catalysts have uniform microstructures, with narrow MWDs and CCDs. Figure 1.9 shows the CCDs for a series of ethylene/1-hexene copolymers made with a metallocene catalyst. All distributions are narrow and unimodal in sharp contrast to the behavior observed for Ziegler–Natta LLDPEs. Notice the uniform incorporation of 1-hexene and the absence of the high-crystallinity peak. In addition, their average copolymer composition is independent of their MWD.

From a polymerization reaction engineering point of view, polyolefins made with metallocene catalysts provide an excellent opportunity for model development because they have "well-behaved" microstructures. Chapter 6 shows that models developed for single-site catalysts can also be extended to describe the more complex microstructures of polyolefins made with multiple-site complexes such as Ziegler–Natta and Phillips catalysts.

Substantially linear polyethylenes are an important new class of polyolefins. These polymers are also made with single-site catalysts, but their main characteristic is the presence of LCBs formed by terminal branching. They are called *substantially linear* because their LCB frequencies are typically below a few LCBs per 1000 carbon atoms. Terminal branching is illustrated in Figure 1.10, showing a polymer

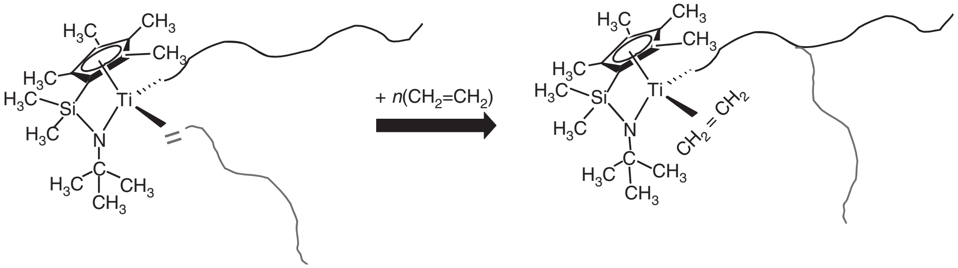

Figure 1.10 Long-chain branch formation through terminal branching promoted by a single-site catalyst.

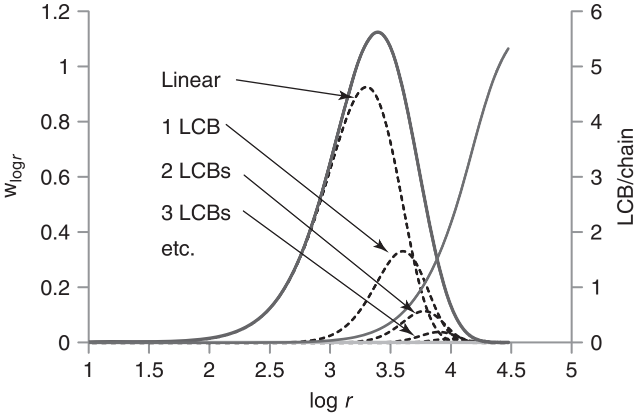

Figure 1.11 Model predictions for the long-chain branch and chain length (r) distributions of substantially linear polyethylene.

chain with a reactive terminal bond being copolymerized with ethylene to form an LCB. The branching topology resulting from this mechanism is very different from that of LDPE resins. Figure 1.11 illustrates a model prediction for the chain length distribution and LCB frequency for a polyolefin formed via this mechanism. More details on this LCB formation mechanism are provided in Chapter 6.

1.3
Polypropylene Resins

Because propylene is an asymmetrical monomer, polypropylene can be produced with different stereochemical configurations. The most common types of polypropylene, shown in Figure 1.12, are isotactic, syndiotactic, and atactic. In isotactic polypropylene, the methyl groups are placed on the same side of the backbone; in syndiotactic polypropylene, on alternating sides; and in atactic polypropylene, the methyl groups are arranged randomly along the chain. Atactic polypropylene

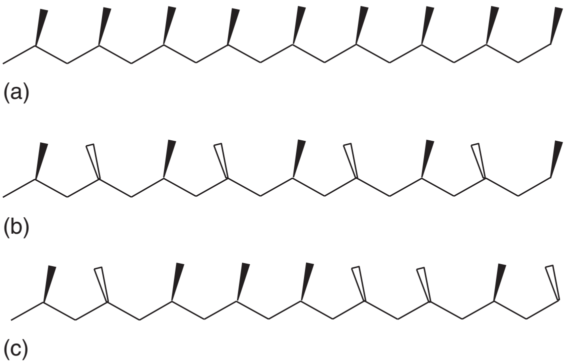

Figure 1.12 Main polypropylene types: (a) isotactic, (b) syndiotactic, and (c) atactic.

is amorphous and has little commercial value. Both isotactic and syndiotactic polypropylene are semicrystalline polymers with high melting temperatures. Isotactic polypropylene dominates the market, likely because it is easily produced with heterogeneous Ziegler–Natta and metallocene catalysts; syndiotactic polypropylene can be produced only with some metallocene catalysts and has much less widespread commercial use.

Modern Ziegler–Natta catalysts used for propylene polymerization make isotactic polypropylene with a very small fraction of atactic polypropylene. Non-specific sites are responsible for the formation of atactic chains in Ziegler–Natta catalysts. Many years of catalyst development were required to minimize the fraction of these catalyst sites, as discussed in Chapter 3.

Ziegler–Natta catalysts also are used to make chains with very high regioregularity, favoring 1-2 insertions and head-to-tail enchainment (Figure 1.13). Defects such as a 2-1 insertion following a 1-2 insertion create irregularities along the polymer chain, decreasing its crystallinity and melting temperature. Several metallocene catalysts produce polypropylene with very high isotacticity but lower regioregularity, which causes their melting temperatures to be lower than of those made with Ziegler–Natta catalysts. Metallocene catalysts can also make polypropylenes with other stereostructures such as atactic–isotactic block chains, but these products have not found commercial applications yet.

Impact propylene/ethylene copolymers[4] are produced using at least two reactors in series with heterogeneous Ziegler–Natta catalysts or supported metallocenes. The first reactor makes isotactic polypropylene, and the second produces propylene–ethylene random copolymer. The copolymer component is amorphous or has very low crystallinity, and is intimately dispersed in the homopolymer phase, even though the two phases are immiscible. The copolymer phase dissipates

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4) These materials are sometimes (erroneously) called *block copolymers*. In fact, they are heterophasic materials composed of isotactic polypropylene and random propylene/ethylene copolymer chains.

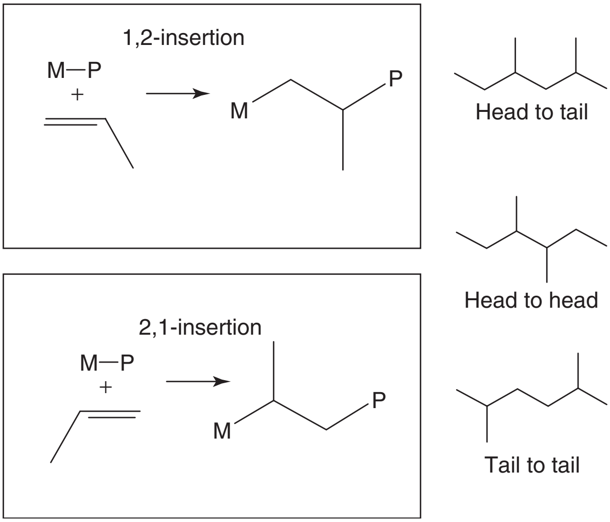

Figure 1.13 Regioregularity in polypropylene polymerization.

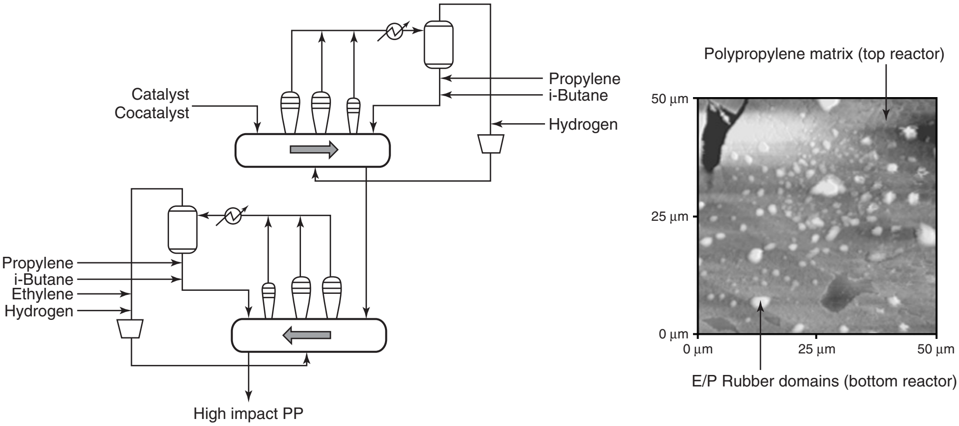

Figure 1.14 Process for the production of impact polypropylene.

energy during impact, greatly increasing the impact resistance of these resins. Several processes have been designed to produce impact polypropylene of high quality, as discussed in Chapter 4. Figure 1.14 schematically illustrates a process for the production of impact polypropylene.

Finally, the same comments made for Ziegler–Natta versus metallocene polyethylene apply to polypropylene resins. Metallocene catalysts make polypropylene with narrower MWD and, in the case of copolymers, narrower CCD.

Further Reading

There are several excellent books on polyethylene and polypropylene properties and applications. The Handbook of Polyethylene is a good source of information on HDPE, LLDPE, and LDPE.

Peacock, A.J. (2000) *Handbook of Polyethylene*, Marcel Dekker, New York.

Two multiauthored books on polypropylene are also recommended.

Karian, H.G. (ed.) (2003) *Handbook of Polypropylene and Polypropylene Composites*, Marcel Dekker, New York.Karger-Kocsis, J. (ed.) (1999) *Polypropylene. An A-Z Reference*, Kluwer Academic Publishers, Dordrecht.

The Encyclopedia of Polymer Science and Technology has excellent entries on HDPE (Benham, E. and McDaniel, M. (2002) Ethylene polymers, HDPE, in *Encyclopedia of Polymer Science and Technology* (ed. H.F. Mark), John Wiley & Sons, New York. doi: 10.1002/0471440264.pst408.pub2), LDPE (Maraschin, N. (2002) Ethylene polymers, LDPE, in *Encyclopedia of Polymer Science and Technology* (ed. H.F. Mark), John Wiley & Sons, New York. doi: 10.1002/0471440264.pst121), LLDPE (Simpson, D.M. and Vaughan, G.A. (2002) Ethylene polymers, LLDPE, in *Encyclopedia of Polymer Science and Technology* (ed. H.F. Mark), John Wiley & Sons, New York. doi: 10.1002/0471440264.pst122), ethylene/propylene elastomers (Noordemeer, J.W.M. (2002) Ethylene-propylene elastomers, in *Encyclopedia of Polymer Science and Technology* (ed. H.F. Mark), John Wiley & Sons, New York. doi: 10.1002/0471440264.pst125), and polypropylene.

Steward, C. (2002) Propylene polymers, in *Encyclopedia of Polymer Science and Technology* (ed. H.F. Mark) John Wiley & Sons, New York. doi: 10.1002/0471440264.pst301

These references are constantly updated by the authors and can be accessed on-line, making them a valuable source of information on these polymers.

We have also published general overviews on olefin polymerization reaction engineering, covering polymerization mechanisms and catalysis, properties, characterization, and mathematical modeling.

Soares, J.B.P. and Simon, L.C. (2005) Coordination polymerization, in *Handbook of Polymer Reaction Engineering* (eds T. Meyer and J. Keurentjes), Wiley-VCH, Weinheim, pp. 365–430.Soares, J.B.P., McKenna, T.F., and Cheng, C.P. (2007) Coordination polymerization, in *Polymer Reaction Engineering* (ed. J.M. Asua), Blackwell Publishing, pp. 29–117.