OLEFIN POLYMERS, INTRODUCTION

1. Introduction

"Polyolefin (PO) resins" is the generic name for a large family of homopolymers and copolymers derived from olefins (chemical name "alkenes"), unsaturated hydrocarbons with one or several C=C double bonds. Most of the olefins used for the synthesis of PO resins are α-olefins of the general formula $CH_2{=}CH{-}R$, where R=H in ethylene, $-CH_3$ in propylene, $-C_2H_5$ in 1-butene, $-CH_2-CH(CH_3)_2$ in 4-methyl-1pentene, etc. Molecular weights of PO resins vary from very small, 300–600, in olefin oligomers, waxes, and base stocks for lubricating oils, to very large, >3,000,000, in PO resins with the ultrahigh molecular weight. The family of PO resins also includes homopolymers and copolymers of cycloolefins and cyclodiolefins.

The PO resins are commonly divided into five large classes:

1. Ethylene polymers and copolymers.
2. Propylene polymers and copolymers.
3. Ethylene–propylene elastomers and synthetic rubbers.
4. Polymers and copolymers of higher olefins.
5. Polymers and copolymers of cycloolefins and cyclodiolefins.

The PO resins are produced worldwide in a very large volume, $\sim 100 \times 10^6$ metric tons/year in 2005, which corresponds to >50% of the total production of all plastic materials. Ethylene polymers and copolymers account for 60–65% of the total PO production and propylene polymers for ~35%; other types of PO resins are manufactured in much lower volumes.

2. Ethylene Polymers and Copolymers

2.1. Definitions. All semicrystalline polymers and copolymers derived mostly from ethylene and used as commodity plastics are called polyethylene (PE) resins. These resins are produced in radical polymerization reactions at a high pressure and in catalytic polymerization reactions. Most PE molecules contain branches in their chains. In very general terms, the molecular structure of a PE resin can be represented by a formula

$$-(CH_2-CH_2)_x-\mathrm{Branch}_1-(CH_2-CH_2)_y-\mathrm{Branch}_2-(CH_2-CH_2)_z-\mathrm{Branch}_3-$$

where the $-CH_2-CH_2-$ unit comes from ethylene, x, y, and z values can vary from 4 to 5 to a very large number, and the branches are either formed spontaneously in the course of polymerization reactions or introduced deliberately.

Industry produces a variety of PE resins that differ in several features:

The Origin and the Types of Branches. In high pressure ethylene polymerization processes, the branches are formed spontaneously, due to peculiarities of ethylene radical polymerization reactions at high pressures. These branches are linear or branched alkyl groups. Their lengths vary widely, even within a single polymer molecule. Two types of the branches are distinguished, short-chain branches, from the methyl to the isooctyl group, and long-chain alkyl branches, up to several thousands carbon atoms long. The PE resins produced in radical polymerization reactions are called low density PE (LDPE) resins (see the article "Ethylene Polymers, Low Density").

In catalytic polymerization processes, the branches are introduced deliberately, by copolymerizing ethylene with α-olefins. These copolymers, depending on the content of α-olefin, are called either medium density PE (MDPE) resins, linear low density PE (LLDPE) resins, or very low density PE (VLDPE) resins (see Table 1). Polymerization processes utilizing metallocene catalysts can also introduce long-chain branches in LLDPE and VLDPE resins. Some metallocene catalysts can copolymerize ethylene with cycloolefins, such as cyclopentene, cyclooctene, norbornene, etc. In this case, the branches are either small cycles consisting of from 5 to 10 carbon atoms, or two fused cycles. These materials are called in industry cycloolefin copolymers (COC) (see the article "Polymers of Higher Olefins").

Content of Branches. Some PE resins are produced in ethylene homopolymerization reactions; they contain no branches at all. The commercial name of these resins is high density PE (HDPE). These resins found broad commercial applications (see the article "Polyethylene, High Density"). In other PE resins, the number of branches can be quite significant: The content of the branches in some VLDPE resins is 25–30 wt.%.

Molecular Weight. The total number of monomer units in an average polymer chain can vary from very small, 10–20, in PE waxes to very large, >100,000, for PE resins with the ultrahigh molecular weight. Respectively, the molecular weights of PE resins range from several hundreds to several millions.

Uniformity of Branching Distribution. The content of branches in different polymer molecules in a given PE resin can be nearly the same or it can be quite different, depending on the production method. Some PE resins have uniform branching distributions: Any polymer molecule contains about the same fraction of branches as any other polymer molecule. Polyethylene prepared in high pressure processes (LDPE) and most LLDPE and VLDPE resins produced with metallocene catalysts belong to this group. In contrast, LLDPE and VLDPE resins produced with Ziegler catalysts and chromium oxide-based catalysts are mixtures of polymer molecules with very different branching degrees (different contents of an α-olefin). Some of the macromolecules in such mixtures contain very few branches while other polymer molecules contain a relatively large number of branches.

2.2. History.

Von Pechmann synthesized the first polymer with the PE structure from diazomethane in 1898 (1). The history of PE polymers as commercial plastics has four milestones (1):

1. In 1935, A. Perrin at the ICI laboratories in the United Kingdom discovered that ethylene could be polymerized at a very high pressure into a solid semicrystalline material with a melting point of ~120°C and density of 0.920–0.930 g/cm^3 (1). This discovery was the starting point in the commer-

cial manufacture of LDPE resins. It began in the United Kingdom in 1938 and in the United States in 1943.

2. In the early 1950s, J. P. Hogan and R. L. Bank at Phillips Petroleum Company in United States discovered that ethylene can be catalytically polymerized under moderate reaction conditions, at pressures of 3–4 MPa and temperatures of 70–100°C, into a crystalline plastic with density of 0.960–0.970 g/cm^3. These reactions require the use of a catalyst containing chromium oxides supported on silica and called Phillips catalyst (1). These resins (HDPE) are currently produced worldwide on a very large scale.
3. In 1953, K. Ziegler and co-workers in Germany discovered that PE resins of a similarly high density could be prepared under even milder conditions in the presence of catalyst systems containing titanium halides and alkylaluminum compounds (Ziegler catalysts) (1,2). Ziegler catalysts can also copolymerize ethylene and α-olefins. Depending on the amount of the olefin, the copolymers range from highly crystalline to nearly completely amorphous. The discovery of Ziegler brought to life a large industry of manufacturing PE resins with a broad range of properties.
4. In 1976, W. Kaminsky and H. Sinn in Germany discovered a new family of catalysts for ethylene polymerization (1-3). The catalysts contain two components: a metallocene complex and an organoaluminum compound called methylalumoxane (1-3). Kaminsky catalysts and a variety of their later modifications afford the synthesis of ethylene copolymers with a high degree of branching uniformity.

Classification of PE resins is given in Table 1. It is based on two easily measured parameters: resin density and its melt index (see the definitions in articles on HDPE and LLDPE). This classification provides a simple means for basic differentiation of PE resins.

2.3. Catalysts and Technologies of PE Manufacture.

A variety of catalysts and technological processes are used for the PE manufacture:

Polymerization in Supercritical Ethylene. If a polymerization process is carried out at a very high ethylene pressure and at a temperature above the PE melting point, 110–140°C, the mixture of supercritical ethylene and molten PE serves as a polymerization medium (1). This process can accommodate radial initiators, such as oxygen or organic peroxides, Ziegler catalysts, and metallocene catalysts. The radical polymerization reaction proceeds at a pressure from ~60 to 350 MPa and at a temperature in a 200–350°C range. This reaction also affords synthesis of ethylene copolymers with α-olefins and with some polar monomers, the most important of them being vinyl acetate.

Polymerization in Solution. Many hydrocarbon solvents dissolve PE at elevated temperatures, 120–150°C. Solution polymerization processes require, as their last step, removal of the solvent from the polymer. A variety of Ziegler and metallocene-based catalysts can be used in such processes (2).

Polymerization in Slurry. Catalytic polymerization reaction in hydrocarbon slurry, usually a light saturated hydrocarbon, was historically the first commercial ethylene polymerization process using Phillips and Ziegler catalysts.

These processes still enjoy high popularity due to their versatility and convenience of operation (2,4).

Polymerization in the Gas Phase. Many polymerization catalysts, both Ziegler catalysts and metallocene catalysts supported on inert carriers, can be adopted for the use in the gas phase (2,5). A gas-phase reactor contains a bed of polymer particles with imbedded catalyst ingredients. The particle bed is agitated either by a mechanical stirrer or by employing the fluidized-bed technique. Such processes are very economical due to the absence of solvent recovery and recirculation streams.

2.4. Control of PE Properties and Its Uses. Tailoring PE properties in commercial processes is achieved by the following means:

1. Density and crystallinity of a catalytically produced PE resin are primarily determined by the amount of an α-olefin in an α-olefin copolymer. It is achieved by varying relative amounts of ethylene and an α-olefin in a polymerization reaction. Density of LDPE resins produced in free-radical processes is usually controlled by temperature.
2. Molecular weight of a PE resin is controlled by two means: (a) reaction temperature, the principal control method in polymerization processes with Phillips catalysts and in radical polymerization reactions; and (b) the use of special chemical agents for chain transfer, mostly hydrogen, with Ziegler catalysts.
3. A variety of PE resins, after their synthesis, can be modified by cross-linking with peroxides, hydrolysis of silane-grafted polymers, ionic bonding of carboxyl groups in polymer chains (ionomers), chlorination, graft copolymerization, hydrolysis of ethylene–vinyl acetate copolymers, and in other reactions. These modifications afford the manufacture of a large family of PE products with broad differences in physical properties, such as the softening temperatures, stiffness, hardness, clarity, impact and tear strength, etc.

Polyethylene resins enjoy a large range of applications, both as commodity resins, engineering resins and, in some cases, as specialty polymers. The largest application is thin film that is made from LDPE, HDPE, and LLDPE. The film is mostly used for bags and packaging. These resins are also used to manufacture coating for paper, metal, and glass; household and industrial containers such as bottles of different sizes and shapes for water, food products, detergents, liquid fuels, etc; for wire and cable insulation, toys; pipe, and tubing of various types. Because of its versatility, PE has become the largest commercially manufactured polymer in the world. The 2005 world capacities were $\sim 19 \times 10^6$ metric tons of LDPE, $\sim 16 \times 10^6$ tons of LLDPE and VLDPE, and $\sim 26 \times 10^6$ ton of HDPE.

3. Propylene Polymers and Copolymers

3.1. Definitions. Four types of propylene polymers (PP) are produced by industry:

1. Isotactic PP, a tough semicrystalline material widely used as a commodity and engineering plastic.
2. Impact resistant PP, a mixture of isotactic PP and amorphous ethylene–propylene copolymer.
3. Syndiotactic PP, a semicrystalline material used as an engineering plastic.
4. Atactic PP, an amorphous material used as a binder for a variety of plastics and inorganic materials, especially in construction industry.

The definitions of the molecular structure of isotactic and syndiotactic PP are given in the article "Propylene Polymers".

3.2. History. Isotactic PP was produced in 1954 independently by two groups of researchers, J. P. Hogan and R. L. Bank in the United States and G. Natta and his co-workers in Italy (1). The first commercial production of isotactic PP was started in 1957 in Italy (Montecatini) and in the United States (Hercules). Atactic PP is a by-product in the synthesis of isotactic PP; it is also known since early 1950s. G. Natta first synthesized syndiotactic PP in 1960s (1). All these products were prepared using polymerization catalysts named Ziegler–Natta catalysts and based on titanium compounds. W. Kaminsky and H. Sinn in 1976 discovered another class of catalyst suitable for polymerization of propylene, metallocene catalysts (1,4,5). Depending on the structure of the latter catalysts, they produce isotactic, syndiotactic, or atactic PP.

3.3. Catalysts and Technologies of PP Manufacture. Two types of catalysts are used for the synthesis of isotactic PP: supported catalysts based on $TiCl_4$ and $MgCl_2$, and metallocene catalysts (4,6-8). Propylene polymers synthesized with the $TiCl_4/MgCl_2$ catalysts dominate the word production, 93–95%. Syndiotactic PP is produced exclusively with metallocene catalysts.

Polymerization in Slurry. Two different slurry processes are used in industry (6). The first one uses liquid propylene as a reaction medium; it is called a "bulk" polymerization process. This is the most important technology for the PP manufacture, it accounts for nearly 60% of its worldwide production. The second type of a slurry process uses a hydrocarbon diluent, $\sim$15% of the world production (6).

Polymerization in the Gas Phase. The second most important technology of PP manufacture is the fluidized-bed gas-phase technology, $\sim$25% of the world production (6). Both Ziegler–Natta and supported metallocene catalysts can be used in gas-phase reactors.

Multistage Polymerization Processes. Demand for isotactic PP with improved impact resistance at low temperatures resulted in the development and commercial production of impact resistant PP, a mixture of isotactic PP and amorphous ethylene–propylene copolymer. These resins account for $\sim$25% of the total world production of PP. They are manufactured in two stages. First, highly crystalline isotactic PP is produced and then the PP resin particles with a still active catalyst are transferred into a second reactor where an ethylene–propylene copolymerization reaction takes place.

3.4. Properties. Isotactic PP is a rigid semicrystalline plastic (1,4-8). It has density of $\sim$0.903 g/cm^3, its melting point is $\sim$165°C and its glass point is ca. -10°C. The resin has high mechanical strength: its tensile strength is 35 MPa, elongation at break ~10–12%, and the flexural modulus is 1.2–1.7 GPa. Crystalline isotactic PP is less stiff than HDPE, but it has a higher flexural modulus and its tensile properties are also much higher than those of HDPE. This allows isotactic PP to be used as an engineering thermoplastic competing with other engineering thermoplastics, such as ABS. When isotactic PP is mixed with 10–15% of ethylene–propylene copolymer (impact-resistant PP), its glass point decreases to afford its uses under below zero temperatures. Isotactic PP prepared with metallocene catalysts has a small fraction of chemical defects in its polymer chains and, as a consequence, it usually has a lower melting point, 155–160°C. This resin is also very tough and is used as a general purpose and an engineering plastic.

Syndiotactic PP is a rigid semicrystalline plastic with density of ~0.88 g/cm^3. It has a lower melting point than isotactic PP, ~130°C. Its crystallinity, tensile strength (~15 MPa), and the modulus (480–500 MPa), are also lower than for isotactic PP. However, syndiotactic PP has exceptional softness, much higher clarity and gloss, and good scratch resistance (4,7,8).

Atactic PP is an amorphous material with a glass point of ca. −20°C. Atactic PP is always present in small quantities, 1–5%, in commercial PP resins produced with Ziegler–Natta catalysts. The presence of a small amount of atactic PP modifies properties of commercial PP resins; it improves their low temperature performance, processability and optical properties, but decreases stiffness and long-term aging properties (8).

3.5. Uses of PP. Over 50% of all isotactic PP and impact resistant PP is converted by injection molding into a variety of articles with complex profiles (4,5,8). Important markets for injection-molded articles are automotive, mostly internal trim in cars; household appliances; toys; rigid packaging including food containers suitable for microwave heating; and medical products such as single-use syringes, trays, etc.

Melt spun fibers and nonwoven fibers represent the second most significant use of isotactic PP, 25–30% (5). The biggest fraction of spun PP fiber is consumed in the manufacture of rugs and wall-to-wall carpeting. Fabrics from nonwoven fiber are the principal material for the production of various hygiene products and for single-use medicine uses such as patient clothes, surgical gowns, etc. Other applications of isotactic PP include biaxially oriented film and cast film (10–13%), extruded sheet of various thickness, and pipes (3–4%). The PP film is widely used for packaging cigarettes, snacks, candy, etc, as replacement for cellophane.

Syndiotactic PP is produced in a relatively small volume, ~2% of the overall PP production. It is mostly used for the manufacture of sheet, film, both cast and oriented, and for injection molding. Other markets for syndiotactic PP include blends with other polymers, sterilizable medical products, elastomers, and plastomers as an alternative to flexible poly(vinyl chloride) (PVC).

Atactic PP is used for modified bitumen roofing, as an adhesive and a sealant, for asphalt modification and in cable flooding compounds. Atactic PP forms uniform matrix with asphalt. This enhances the bitumen's performance by increasing its flexibility at low temperatures, ultraviolet (uv) resistance, and flow resistance at high temperatures.

4. Ethylene–Propylene Elastomers

4.1. Definitions. Two types of ethylene–propylene elastomers are manufactured commercially. The first one is a random copolymer of ethylene and propylene containing from 40 to 60 wt% of ethylene. This material has the industrial name "EP elastomer"; it is completely amorphous. The second type is a random ternary polymer of ethylene, propylene and a diolefin, such as ethylidene norbornene or dicyclopentadiene. These copolymers are called "EPDM elastomers". They contain 55–60 wt% of ethylene, 35–40 wt% of propylene, and 5–10% of the diolefin. The presence of diolefin units in EPDM elastomers affords their vulcanization (cross-linking) with peroxides and other cross-linking agents.

4.2. History. G. Natta in Italy synthesized first ethylene/propylene elastomers in 1957 using vanadium-based polymerization catalysts (1). Exxon Chemical Company in the United States produced the first commercial EP elastomers in 1961; Montedison Company in Italy produced the first EPDM rubbers in 1963.

4.3. Catalysts and Technologies for EP and EPDM Manufacture. - The early copolymerization catalysts developed in the 1960s are still widely used for the EP and EPDM production (1). They are based on VCl_4 or $VOCl_3$ as transition-metal ingredients, diethylaluminum chloride or triethylaluminum as cocatalysts, and various modifiers, mostly chlorinated aliphatic hydrocarbons. The second type of catalyst used in the commercial manufacture of EP and EPDM elastomers is based on metallocene complexes. Both catalysts perform under commercially accepted conditions as single-site catalysts; they produce copolymers in which the composition of all macromolecules is approximately the same, independently on their molecular weight.

Both EP and EPDM are readily soluble in aliphatic and aromatic hydrocarbons. A large part of the world EP and EPDM production is based on continuous stirred-tank solution processes under moderate reaction conditions, at 20–50°C, using light hydrocarbons as solvents. The monomer conversion is usually limited to $<10\%$ because the solution becomes progressively more viscous as the copolymer concentration increases. The second technology of EP and EPDM manufacture is based on a continuous stirred-tank slurry process in which propylene is used as a reaction medium. The EP–propylene slurry has a relatively low viscosity and the reactant conversion up to 30% is possible before the slurry becomes excessively viscous. The third technology for the manufacture of the elastomers is a fluidized-bed gas-phase process similar to those used for the manufacture of HDPE, LLDPE, and PP. Synthesis of sticky amorphous polymers in gas-phase reactors is difficult. To avoid agglomeration of polymer particles, addition of a significant quantity of an inorganic filler powder to the reactor, mostly carbon black, is necessary.

4.4. Properties and Uses. The EP and EPDM elastomers are amorphous materials with a glass point of -50 to 60°C. The elastomers are usually used in a cross-linked form. Three types of cross-linking are practiced, radiation, best suitable for EP resins; with organic peroxides; and with sulfur-based agents similar to those used for vulcanization of natural and synthetic rubber. Vulcanized EPDM rubbers have tensile strength of $\sim$20MPa (for reinforced materials), their tear strength is ~20–40 kN/m^2 and their temperature exploitation limit is 150–170°C.

Two properties of the elastomers make them attractive for industrial use. The first one is their exceptionally high chemical stability to a variety of corrosive inorganic compounds, to heat, light, and to oxidation, particularly by ozone. Due to complete absence of double bonds in the polymer structure in EP rubbers and their low content in EPDM rubbers, the ozone resistance of the elastomers is significantly higher that that of natural rubber, butyl rubber or poly(chloroprene). The second distinctive feature of the elastomers is their high extension ability, ie, ability to accommodate very large quantities of oils and inorganic fillers, up to 90%, with retention of elasticity and physical strength.

The EP and EPDM rubbers are widely used in the automotive industry for the manufacture of profiles, especially for car windows, for radiator hoses and seals. These applications account for ~50% of the resin production. Other major applications of the elastomers are binders in roofing materials, cable and wire insulation and jacketing, and in a variety of molded articles.

5. Polymers of Higher Olefins and Cycloolefins

5.1. Definitions. All olefins $CH_2{=}CH{-}R$ with R other than H and CH_3 are called higher olefins in industry. Several types of polymers and copolymers of higher α-olefins and cycloolefins are produced commercially:

1. Isotactic poly(1-butene) (PB).
2. Isotactic poly(4-methyl-1-pentene) (PMP).
3. Oligomers of linear α-olefins.
4. Copolymers of cycloolefins, such as cyclopentene, cyclooctene, cyclodecene, norbornene, etc, with ethylene (COC resins).
5. Homopolymers of cycloolefins and cyclodiolefins such as poly(dicyclopentadiene), poly(cyclooctene), and poly(norbornene) prepared with ROMP catalysts.

5.2. History. G. Natta and co-workers in Italy reported synthesis of isotactic polymers of higher α-olefins in 1954, 1 year after synthesis of isotactic PP (1). Syndiotactic polymers of higher α-olefins were first prepared in 1990 (1). First commercial production of isotactic PB and PMP began in 1964–1965 (1,9).

Cycloolefins are polymerized by means of two different mechanisms. Catalysts based on tungsten, ruthenium, and molybdenum compounds (ROMP catalysts) induce the metathesis reaction, ring-opening polymerization of monocycloolefins with the formation of elastomers containing regularly spaced double bonds in polymer chains. R. H. Grubbs and R. R. Schrock in the United States discovered these catalytic polymerization reactions of cycloolefins in the 1970s (10). If cyclodiolefins are used in this reaction, the same catalysts produce cross-linked materials. W. Kaminsky in Germany has found in the 1980s that metallocene-based catalysts can polymerize the cycloolefins without ring opening into linear, stereoregular, highly crystalline polymers. The same catalysts copolymerize cycloolefins and ethylene into amorphous transparent plastics (COC resins)with high glass points.

5.3. Technologies for PO Manufacture and Their Uses. A variety of catalysts and technological processes are used for the manufacture of PO resins. All isotactic polymers of higher α-olefins are produced with supported titanium-based Ziegler–Natta catalyst systems of the same type that is used for the manufacture of isotactic PP. These polymerization reactions are usually carried out at 50–80°C in slurry in pure monomers or in their mixtures with hydrocarbon solvents (11-13).

Isotactic PB is a semicrystalline plastic; it is used to manufacture pipe and tubing, as well as film. Isotactic PMP is also a semicrystalline plastic. Most of its applications capitalize on high optical transparency of the resin, its excellent dielectric characteristics, high thermal stability and chemical resistance. The uses include medical equipment, such as hypodermic syringes, blood collection and transfusion equipment, etc, as well as chemical and biomedical laboratory equipment.

Higher α-olefins can be also polymerized with catalyst systems based on metallocene complexes. These catalysts polymerize α-olefins with the formation of amorphous atactic polymers or, when the polymerization reactions are carried out at 70–100°C, low molecular weight oligomers which can be used as components of synthetic lubricating oils (1,14). Other metallocene complexes produce isotactic and syndiotactic polymers of higher α-olefins (4,7,8,12,13) (see the article on Polymers of Higher Olefins).

α-Olefins with linear and branched alkyl groups can be readily polymerized at low temperatures with cationic initiators, such as BF_3 or $AlCl_3$, with the formation of low molecular weight oils of an irregular structure (14). These oligomers are used as basestocks for synthetic lubricating oils.

Polymers of cycloolefins have two different structures, depending on a catalyst used for their synthesis. In the presence of tungsten-, ruthenium-, or molybdenum-based ROMP catalysts, polymerization of cycloolefins proceeds through ring opening with the formation of elastomers (10). These materials from cyclooctene and norbornene are used in industry as components in rubber, PVC-, and PS-based compositions. Dicyclopentadiene also can be polymerized with tungsten-based catalysts. Because this polymerization reaction produces heavily cross-linked resins, the polymer is manufactured in a special process named reactive injection molding (RIM) in which all catalyst components and resin modifiers are slurried in two batches of the monomer and then rapidly combined in a mold. Such processes can produce very large, highly rigid plastic parts.

Polymerization of cycloolefins with metallocene-based catalysts produces polymers and copolymers with a completely different structure. The reaction proceeds via the double bond opening in cycloolefins and the formation of C–C bonds between adjacent rings (15). Copolymers of cycloolefins and ethylene synthesized with metallocene catalysts are tough transparent amorphous materials with high glass points, 70–180°C, depending on copolymer composition (16). They are used in many optical applications, such as lenses, prisms, etc, and for the manufacture of transparent containers and film.

BIBLIOGRAPHY

"Olefin Polymers, Introduction" in *ECT* 4th ed., Vol. 17, pp. 702–707, by Yury V. Kissin, Mobil Chemical company; "Olefin Polymers, Introduction" in *ECT* (online), posting date: December 4, 2000, by Yury V. Kissin, Mobil Chemical Company.

1. B. Seymour and T. Cheng, eds., *History of Polyolefins*, D. Reidel, Dordrecht, The Netherlands, 1986.
2. B. A. Krentsel, Y. V. Kissin, V. I. Kleiner, and S. S. Stotskaya, *Polymers and Copolymers of Higher* α-Olefins, Hanser Publishers, New York, 1997, Chapt. 8.
3. H. Sinn and W. Kaminsky, *Adv. Organomet. Chem.* **18**, 99 (1980).
4. G. M. Benedikt, ed., *Metallocene Technology in Commercial Applications*, Plastics Design Library, Norwich, New York, 1999.
5. C. Mayer and T. Calafut, *Polypropylene, The Definitive User's Guide and Databook*, Plastic Design Library, New York, 1998.
6. E. P. Moor, *Polypropylene Handbook, Hanser Publishers*, Munich, Germany, 1996.
7. J. Scheirs and W. Kaminsky, eds., *Metallocene-Based Polyolefins: Preparation, Properties and Technology*, John Wiley & Sons, Inc., New York, 2000.
8. G. M. Benedikt and B. L. Goodall, eds., *Metallocene Catalyzed Polymers*, ChemTech Publishing, Toronto, Canada, 1998.
9. H. R. Sailors and J. H. Hogan, *J. Macromol. Sci.-Chem.* **A15**, 1377 (1981).
10. A. M. Rouhi, *Chem. Eng. News* **80** (51), 29 (2002).
11. A. M. Chatterjee, *Butene Polymers, in Encyclopedia of Polymer Science and Engineering*, 2nd ed., John Wiley & Sons, Inc., New York, Vol. 2, 1985, p. 590.
12. B. A. Krentsel, Y. V. Kissin, V. I. Kleiner, and S. S. Stotskaya, Ref. (2), Chapt. 3.
13. B. A. Krentsel, Y. V. Kissin, V. I. Kleiner, and S. S. Stotskaya, Ref. (2), Chapt. 5.
14. R. L. Shubkin, *Synthetic Lubricants and High Performance Functional Fluids*, Marcel-Dekker, New York, 1993.
15. W. Kaminsky and M. Arndt, *Adv. Polym. Sci.* **127**, 144 (1997).
16. D. McNally, *Modern Plastics Word Encyclopedia*, Hightstown, NJ, 2001, p. B–8.

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Table 1. **Commercial Classification of Polyethylenes**

Name	Abbreviation	Density, g/cm^3
high density polyethylene	HDPE	0.941 and higher
ultrahigh molecular weight polyethylene, linear polymer with molecular weight $>3 \times 10^6$	UHMW PE	0.935–0.930
Medium density polyethylene	MDPE	0.926–0.940
Linear low density polyethylene	LLDPE	0.915–0.925
Low density polyethylene, produced in high pressure processes	LDPE	0.910–0.940
Very low density polyethylene	VLDPE	0.915–0.880