POLYMERS OF HIGHER OLEFINS

1. Introduction

This article describes polymeric materials derived from higher olefins, α-olefins and cycloolefins with carbon atom numbers 4 and higher. These olefins produce both homopolymers and copolymers with lighter olefins, mostly with ethylene. Crystalline polymers of higher α-olefins belong to two classes of stereoregular polymers, isotactic and syndiotactic: see the definitions in the article "Polymers of Propylene". Presently, isotactic polymers of α-olefins are produced with two types of catalysts, heterogeneous Ziegler–Natta catalysts and bridged metallocene catalysts. Other types of metallocene catalysts produce either crystalline syndiotactic polymers or amorphous atactic polymers. Higher α-olefins can also be polymerized with cationic initiators to liquid oligomeric materials.

G. Natta and co-workers reported the synthesis of isotactic polymers of higher α-olefins in 1954, 1 year after the synthesis of isotactic polypropylene (1). First commercial production of crystalline isotactic poly(1-butene) (PB) and poly(4-methyl-1-pentene) (PMP) began in 1964–1965. Syndiotactic polymers of higher α-olefins were first prepared in 1990 (2,3). In addition, higher α-olefins can be polymerized with cationic initiators to liquid oligomeric materials with isomerized structures. These liquids are manufactured commercially and used as components of synthetic lubricating oils (4).

Cycloolefins are polymerized via two different mechanisms. Catalysts based on tungsten, ruthenium, and molybdenum compounds induce ring-opening polymerization through the double-bond metathesis reaction in cycloolefins, such as cyclooctene and norbornene, with the formation of linear elastomers containing regularly spaced double bonds in polymer chains. Grubbs and Schrock discovered these catalytic polymerization reactions of cycloolefins, called ring-opening metathesis polymerization (ROMP) reaction, in the 1970s (5). If dicycloolefins, such a dicyclopentadiene, are used in this reaction, the same catalysts produce cross-linked resins. The ROMP polymers of several cycloolefins, dicyclopentadiene, cyclooctene, and norbornene, are produced commercially. Metallocene-based catalysts polymerize the cycloolefins without ring opening into linear, stereoregular, highly crystalline polymers. Kaminsky discovered this catalytic polymerization reaction of cycloolefins in the 1980s. The same catalysts copolymerize cycloolefins and ethylene into tough amorphous transparent plastics, usually called COC resins, with high glass points (T_g). One more type of polymeric products derived from higher α-olefins, their copolymers with ethylene containing from 6 to 50 wt% of higher α-olefins, is described in a separate article "Polyethylene, Linear Low Density".

2. Monomers

2.1. Manufacture of Monomers. The monomers of the greatest commercial interest are produced by oligomerization of ethylene and propylene. Some olefins are also available as by-products from refining of petroleum and as the products of thermal cracking of hydrocarbons.

1-Butene.   Commercial production of 1-butene, as well as the manufacture of other linear α-olefins with even carbon atom numbers, is based on ethylene oligomerization reactions. The reactions are catalyzed by triethylaluminum at 180–280°C and 15–30-MPa pressure (6) or by nickel-based catalysts at 80–120°C and 7–15-MPa pressure (7,8). Another commercially developed method includes ethylene dimerization with the Ziegler dimerization catalyst, Ti(OR)$_4$-AlR$'_3$, where R and R$'$ are small alkyl groups (9). In addition, several processes are used to manufacture 1-butene from mixed butylene streams in refineries (10).

4-Methyl-1-Pentene.   This compound is produced commercially by dimerization of propylene in the presence of potassium-based catalysts at 150–160°C and at a pressure of ~10 MPa. Commercial processes are carried out in fixed-bed reactors and utilize several catalysts, such as sodium-promoted potassium carbonate and sodium- and aluminum-promoted potassium hydroxide (11,12). The reaction produces a mixture of C$_6$ olefins containing 80–85% of 4-methyl-1-pentene.

Other Higher Olefins.   Linear α-olefins, such as 1-hexene, 1-octene, 1-decene, etc, are produced by catalytic oligomerization of ethylene with triethylaluminum (6) or with nickel-based catalysts (8). 1-Hexene is also produced commercially in an ethylene trimerization reaction using an organochromiun catalyst (13). Olefins with branched alkyl groups are usually produced by catalytic dehydration of corresponding alcohols.

Cycloolefins.   Cyclooctene is synthesized in a two-step reaction, cyclodimerization of 1,3-butadiene to 1,5-cyclooctadiene followed by hydrogenation of one double bond in the latter compound. Dicyclopentadiene is recovered as a by-product from the off-stream of ethylene crackers.

2.2. Physical Properties of Higher Olefins.   1-Butene is a colorless, flammable, noncorrosive gas. Its physical properties are listed in Table 1. Butene has a very low flash point and represents a strong fire and explosion hazard (14-16).

4-Methyl-1-pentene is a light, colorless, flammable liquid; its physical constants are also given in Table 1. It is an irritant and, in high concentrations, a narcotic. Because of a low flash point, this chemical compound also represents a significant fire hazard when exposed to heat, flame, or oxidizing agents (15).

Properties of other higher α-olefins and those of some commercially significant cycloolefins are given in Table 2. All these monomers are liquids under ambient conditions. They are highly combustible and can form explosive mixtures with air (15). The primary health hazards are associated with inhalation or prolonged skin contact, which can cause irritation.

2.3. Chemical Properties of Higher Olefins.   These olefins are highly reactive because the double bond provides the reactive site for catalytic activation and for numerous radical and ionic reactions. Olefins participate in addition reactions, oxidations, hydrogenation, double-bond isomerization, formation of complexes with transition-metal compounds, polymerization and copolymerization with other olefins in the presence of various catalysts. Olefins readily form peroxides when exposed to air.

3. Polymers

3.1. Physical Properties.   Table 3 lists physical properties of stereo-regular polymers of several higher α-olefins. Crystal cell parameters of these polymers are given in Refs. (17–20). All stereoregular polymers of α-olefins have helix conformations in the crystalline state. Their densities usually range from 0.90 to 0.95 g/cm^3. Crystalline PMP represents an exception; its density is low, only 0.812-0.815 g/cm^3, one of the lowest among plastics; it is even lower than the density of amorphous PMP, which is 0.835-0.840 g/cm^3. Polymers of cycloolefins prepared with some metallocene catalysts are also isotactic crystal-line materials with high melting points as shown in Table 3.

3.2. Polymorphism.   Many crystalline polyolefins (PO) can exist in seve-ral polymorphic modifications (21). The type of the polymorph depends on crys-tallization conditions. Isotactic PB can exist in five crystal forms, Form I (twinned hexagonal), Form II (tetragonal), Form III (orthorhombic), Form I′ (untwinned hexagonal), and Form II′ (17,25). The crystal structures and thermal parameters of the first three forms are given in Table 3. Form II is generated when PB crystallizes from the melt. Over time, it is spontaneously transformed into the thermodynamically stable Form I. At room temperature, the transition takes ∼1 week to complete. Forms I′, II′, and III of PB are rare. They can be formed when the polymer crystallizes from solution, at low temperature or under pressure (25). Syndiotactic PB exists in two crystalline forms, I and II; see Table 3 (17). Form I is produced during crystallization from the melt (this is a very slow process) and Form II is produced by stretching crystalline speci-mens initially crystallized in Form I (17).

Poly (4-methyl-1-pentene) also can crystallize in several crystalline forms (18,20). Form I is generated during crystallization form the melt. This is the only crystalline form present in commercially manufactured articles. Other crys-talline modifications are formed when the polymer is crystallized from solution (18,20).

3.3. Thermal Properties.   Melting points (T_m) of stereoregular polyole-fins depend on the size and the shape of side groups in the polymer chains (Table 3). In the case of isotactic polymers of linear α-olefins, the melting points of the crystalline materials rapidly decrease with increasing the length of the side chain: 175°C for polypropylene, ∼140°C for PB, and 80°C for poly-(1-pentene), while isotactic poly-1-hexene is practically amorphous at room temperature. The crystallinity of isotactic polymers with longer linear side groups is derived from their side chains rather than from the polymer backbone (19). Their T_m values steadily increase with the side-chain length: ∼45°C for poly(1-decene), 50°C for poly(1-tetradecene), 68°C for poly(1-hexadecene), and 75°C for poly(1-octadecene). Polymers of α-olefins with branched alkyl groups generally have much higher T_m values (Table 3); they are the highest for isotactic poly(3-methyl-1-butene) and poly(vinylcyclohexane), >350°C.

Commercial isotactic PB resins melt at ∼125°C. The polymer has two low temperature relaxation transitions. One, in a −17 to −25°C range, is attributed to the glass transition in the amorphous phase, and another, at −158°C, to the onset of the local motion of side groups. Crystalline isotactic PMP has a melting

point of ~245°C and a quite high glass transition temperature, ~50°C. Other thermal transitions in PMP are at 130–180°C, which corresponds to the beginning of crystalline phase disordering, at −120 to −150°C (relaxation movements of short chain segments), and at −250°C. The heat of PMP fusion is 61.65 J/g (14.8 cal/g) (18). Commercial PMP resins are copolymers of 4-methyl-1-pentene and ~3 mol% of linear α-olefins C_{10}–C_{16}. These resins have lower T_m values, 220–225°C; however, their T_g, as well as their brittle point, is also lower compared to pure PMP (18), 20–30°C, which makes them more suitable for many applications.

Melting points of isotactic poly(cycloolefins) are very high, in a 400–600°C range; see Table 3. Crystallinity of cycloolefin–ethylene copolymers rapidly decreases with an increase of the ethylene content; the T_m values of the copolymers also rapidly decrease. When the ethylene content in these copolymers approaches a 30–40 mol% range, they become completely amorphous.

3.4. Melt Crystallization.   Isotactic PB crystallizes from the melt in the spherulitic morphology (26). Its crystallization rate increases with increasing molecular weight (27). The crystallization rate can be significantly increased by using nucleating agents as well as by stress and pressure (26). Some nucleating agents also increase hardness, modulus, yield strength, and the heat distortion temperature of the resin. Syndiotactic PB crystallizes to Form I very slowly, for 2 weeks at 20°C (17), but stretching the melt can increase the crystallization rate.

3.5. Transformations in the Solid State.   From the practical standpoint, the most important solid-state transformation of PB involves irreversible conversion of its meta-stable Form II developed during crystallization from the melt into the stable Form I. This transformation is affected by the molecular weight and stereoregularity of the polymer as well as by temperature and pressure, mechanical stress, and the presence of impurities and additives (25). At room temperature, half-times of the transformation range between 4 and 45 h, with an average half-time of 22–25 h (25). The process can be significantly accelerated by annealing articles made of PB at temperatures <90°C, by ultrasonic irradiation, or by additives. Conversion of Form II into I is slower in copolymers of 1-butene containing 7–8 mol.% of other α-olefins, both linear, such as 1-hexene, 1-octene, 1-nonene, 1-decene, and 1-dodecene, and branched, such as 3-methyl-1-butene and 4-methyl-1-pentene (25).

3.6. Mechanical Properties.   Mechanical properties of stereoregular polyolefins strongly depend on the type of a side group in a polymer chain. Polymers with long linear side groups have low crystallinity and exhibit mechanical behavior typical for elastomers or very viscous fluids. On the other hand, PB and most polymers with branched side groups are highly crystalline; their mechanical properties are similar or superior to those of isotactic polypropylene. Excellent mechanical, thermal, and optical properties contribute to the industrial importance of PB and PMP. Poly(3-methyl-1-butene) and poly(vinylcyclohexane) also exhibit good mechanical characteristics. However, their high melting points, poor oxidative stability, and brittleness still preclude industrial application.

Mechanical Properties of PB.   Strain–stress testing of crystalline isotactic PB shows that the resin does not have a sharp yield point, but undergoes uniform stretching followed by strain hardening (25). Mechanical properties of two

commercial grades of PB are listed in Tables 4 and 5. The resin's ultimate strength and modulus increase with crystallinity. The most important mechanical properties of PB are excellent creep resistance (25,26) and resistance to environmental stress cracking (25). Detailed data on morphological, mechanical, and thermomechanical properties and on environmental stress cracking resistance of different commercial grades of PB are given in Refs. (26) and (27).

Mechanical Properties of PMP. Physical, thermal, mechanical, and electrical properties of commercial crystalline PMP are given in Table 6. Poly-(4-methyl-1-pentene) resins are rigid plastics with a high tensile modulus and low elongation at break. The PMP homopolymer is brittle at low temperatures due to a relatively high T_g (Table 3). Introduction of 2–3 mol% of a linear α-olefin into PMP chains is required to reduce the brittleness (31). These copolymers have a lower mechanical modulus and a higher elongation at break, up to 80–120%. High temperature mechanical and creep properties of PMP are superior to those of polyethylene and polypropylene. Moreover, the impact strength of PMP is two to three times higher than the impact strength of other thermoplastics with comparably high light-transmission characteristics, such as polystyrene and acrylic plastics.

3.7. Electrical Properties. All polyolefins have low dielectric constants and can be used as insulators. In particular, the dielectric constant of PMP is the lowest among all synthetic resins. As a result, PMP has excellent dielectric properties and a low dielectric loss factor, surpassing those of other polyolefin resins and Teflon. These properties remain nearly constant over a wide temperature range. The dielectric characteristics of poly(vinylcyclohexane) are especially attractive: its dielectric loss remains constant between −180 and 160°C; this makes it a prospective high frequency dielectric material of high thermal stability.

3.8. Optical Properties of PMP. While all other polyolefins are opaque materials, isotactic PMP exhibits an outstanding feature: it has low haze, 1.2–1.5%, and high optical transparency, 90–92%, comparable to that of polystyrene, 88–92%, and acrylics, 90–92% (28). High transparency of PMP is a consequence of low optical anisotropy of PMP molecules in the helical conformation. The addition of a small amount of linear α-olefin units to PMP chains further reduces the haze (31). Light transmittance of PMP in the near ultraviolet (uv) region is also excellent, higher than for glass and inferior only to quartz. Optical clarity accounts for many applications of PMP.

3.9. Properties of Polycycloolefins. Polymers of monocyclic olefins, including cyclopentene and cyclooctene, are produced via the (ROMP) reaction. They are linear elastic materials of low crystallinity and their properties are similar to those of poly(*trans*-1,4-butadiene). Because the molecule of dicyclopentadiene has two double bonds, its ROMP polymer is a heavily cross-linked resin with high toughness, tensile strength and excellent impact strength, even at low temperatures. Table 7 lists some properties of poly(dicyclopentadiene).

Stereoregular polymers of cycloolefins produced with metallocene catalysts have linear structures with various cycloalkyl rings as parts of main chains (33). These polymers are highly crystalline, have densities >1.0 and have extremely high melting points (see Table 3), which exceed the range of their thermostability (19,33) and preclude their practical uses. Copolymers of the cycloolefins with

ethylene prepared with the same catalysts have much lower melting points or are completely amorphous. The amorphous copolymers are highly transparent plastics with high T_g values, which accounts for many of their commercial applications. Some physical properties of these copolymers are as follows:

Norbornene−Ethylene Copolymers.   The density of these copolymers is 1.02 g/cm^3, their refractive index is 1.53, light transmission is 92%, haze is <1%, dielectric constant at 60 Hz is 2.35, volume resistivity is >10^{16} Ω cm (35). The T_g value ranges from 70 to >200°C, depending on composition. The norbornene−ethylene copolymers have excellent mechanical properties: tensile strength of ∼65 MPa, elongation at break 3−10%, tensile modulus is 2600−3200 MPa, flexural modulus is 3.4×10^3 MPa, notched impact strength 1.7−2.6 kJ/m^2, Shore hardness 89D (35). A special type of these copolymers, an alternating norbornene−ethylene copolymer, contains 50 mol.% of norbornene. It is a crystalline material and has both high T_m, ∼320°C, and high T_g, ∼145°C.

Tetracyclododecene−Ethylene Copolymers.   The density of these copolymers is 1.02−1.04 g/cm^3, refractive index is 1.54, light transmission is 90− 91%, haze is 2−4% (34). The T_g value of the copolymers is in a 70−135°C range, depending on composition,. These copolymers have tensile strength of 50−60 MPa; elongation at break 3−100%, depending on copolymer composition; flexural strength is 90−110 MPa; flexural modulus 2.4−3.2 $\times 10^3$ MPa.

3.10. Chemical Properties.   Chemical properties of most PO resemble those of polypropylene. The resins resist most inorganic and organic acids and bases below 90°C, as well as most salt solutions, solvents, soaps, and detergents. Properties of PO rapidly deteriorate in contact with strong oxidizing agents: fuming HNO$_3$, concentrated solutions of chromic acid, chlorine and bromine solutions. All PO undergo peroxidation, halogenation, and halosulfonation reactions (14).

Both commercially produced crystalline resins, PB and PMP, exhibit high stability to inorganic substances, including excellent resistance in nonoxidative inorganic environments, eg, aqueous solutions of inorganic salts, acids, and alkalis. The PMP polymer easily withstands prolonged boiling and autoclave treatment required for medical and pharmaceutical applications. However, prolonged exposure of the polymers under stress to some hydrocarbon solvents and aqueous detergent solutions can cause development of cracks and eventual failure. This phenomenon is usually referred to as "environmental stress cracking".

3.11. Thermal, Thermooxidative, and Photooxidative Degradation. Polymers of higher α-olefins have one or two tertiary C−H bonds in each monomer unit of a polymer chain. This makes such polymers quite susceptible both to thermal and to thermooxidative degradation. The degradation reaction is especially significant in the case of PO with branched alkyl side groups. For example, thermal decomposition of poly(3-methyl-1-butene) starts at ∼300°C and thermooxidative degradation at ∼100°C. Thermal degradation of PMP occurs above 280°C, eg, during polymer processing (18).

Under thermooxidative conditions, all PO undergo chain scission reactions (21). These reactions result in a decrease of molecular weight and the formation of gaseous products, eg, formaldehyde, acetone, and various alkanes (17,18). Amorphous polymers of higher α-olefins are more reactive in the thermooxidation reactions than their crystalline analogues, mostly because of a higher rate

of oxygen diffusion. High reactivity of PO in thermooxidative degradation reactions, especially at the high temperatures required for their processing, usually >260°C, and for many potential applications, represents the main obstacle for a widespread use of these materials. For example, thermooxidative degradation of PMP is noticeable even at 140−150°C (18,36). Due to high permeability to oxygen and abundance of tertiary C−H bonds, PMP is three times more susceptible to this type of degradation than polypropylene. As a result, durability of PMP decreases sharply with increasing temperature: 30,000 at 120°C, 20,000 at 130°C, 1000 h at 150°C, and 20 h at 200°C (28,36).

Photooxidative degradation of PMP, especially at wavelengths <400 nm, also proceeds at a relatively high rate, which limits some of its outdoor applications (29). Photodegradation reduces the molecular weight of PMP, it becomes brittle; develops polar groups in polymer chains (carboxylic, ketonic, etc); and produces low molecular weight compounds, methane, ethane, acetone, CO_2, and isobutane.

Thermooxidation and photooxidation of PO can be prevented through the use of the same antioxidants as those employed for stabilization of polypropylene, ie, alkylated phenols, polyphenols, thioesters, and organic phosphates, in the amount of 0.2−0.5% (36).

Poly (1-butene) can be cross-linked at ambient temperature in the absence of air by irradiation with γ-rays or high energy electrons. The performance of articles manufactured from PB is only slightly affected by ionizing radiation at doses <3 Mrad (37). The PMP polymer is also relatively stable to β- and γ-radiation employed in sterilization of medical supplies (31).

3.12. Solubility. None of highly crystalline isotactic PO is soluble in any organic solvent at room temperature. However, most amorphous PO and oligomers of α-olefins are easily soluble under these conditions in saturated and aromatic hydrocarbons. This difference in solubility is used to separate amorphous atactic components of PO from the crystalline isotactic material in crude PO mixtures. Although crystalline isotactic PMP is insoluble in any organic solvent at 20°C, it can absorb some aliphatic and aromatic hydrocarbons, esters, and halogenated hydrocarbons. The swelling causes loss of mechanical strength and clarity.

Above 100°C, most PO dissolve in many aliphatic and aromatic hydrocarbons and their halogenated derivatives. For example, PB dissolves in benzene, toluene, decalin, tetralin, chloroform, and chlorobenzenes. As with other PO, solubility of PB depends on temperature, molecular weight, and crystallinity.

3.13. Gas and Moisture Permeability. Moisture content and moisture permeability, as well as permeability to oxygen, are crucial for many applications of PO, especially for food packaging. Crystalline PMP is has a relatively high permeability to various organic and inorganic gases. Its permeability to oxygen, nitrogen and light hydrocarbons, C_1−C_4, is 20−30 times higher than that of polyethylene (20,22). High permeability of PMP to various gases is related to its low packing density. Water vapor transmission for 2.5−μm film at 38°C and relative humidity 90% is 61−69 μmol/(m^2 s) [95−107 g/(m^2 24 h)]. Both families of cyclo-olefin polymers and copolymers, those produced with ROMP and metallocene catalysts, have very low moisture permeability which, combined with high

dimensional stability and transparency, accounts for their application in food packaging and in packaging of drugs and medical equipment (35).

4. Catalysts for PO Production and Polymerization Processes

4.1. Polymerization of α-Olefins. *Ziegler−Natta Catalysts.* All isotactic polymers of higher α-olefins are produced with heterogeneous, titanium-based Ziegler−Natta catalyst systems of the same types that are used for the manufacture of isotactic polypropylene. The catalyst systems contain two components, a solid catalyst containing a titanium compound, and a cocatalyst, an organoaluminum compound (17,18,38). Both 1-butene and 4-methyl-1-pentene are ~three to four times less reactive in the polymerization reactions with the Ziegler−Natta catalysts compared to propylene (17,18,38). All modern highly active catalysts are supported on $MgCl_2$. Two types of the supported catalysts are used in industry. The catalysts of the first type are usually prepared by cogrinding anhydrous $MgCl_2$ and $TiCl_4$ in the presence of an aromatic ester such as ethyl benzoate (38). These catalysts are employed with cocatalyst mixtures containing $Al(C_2H_5)_3$ or $Al(i\text{-}C_4H_9)_3$ and aromatic esters, ethyl benzoate, or ethyl anisate. The supported catalysts of the second type use aromatic diesters, such as dialkyl phthalates, during cogrinding of $MgCl_2$ and $TiCl_4$. They employ mixtures of $Al(C_2H_5)_3$ and alkylalkoxysilanes, $R_xSi(OR')_{4-x}$, as cocatalysts (17,18,39). The PO resins produced with these Ziegler−Natta catalysts contain both highly isotactic crystalline polymers and amorphous atactic fractions. The yields of the isotactic fractions strongly depend on the catalytic system (38). Modern commercial $MgCl_2$-supported catalysts afford synthesis of polymers containing >95−98% of the isotactic material.

The polymerization reactions with Ziegler−Natta catalysts are carried out at 40−80°C in pure monomers or in their mixtures with aliphatic solvents, including hexane, cyclohexane, or heptane. Molecular weights of polymers are controlled by the addition of hydrogen, an effective chain transfer agent. Some Ziegler−Natta catalysts polymerize linear α-olefins, such as 1-hexene or 1-decene, into linear polymers with ultrahigh molecular weights (19,40), which find application as drag-reducing agents for a hydrocarbon flow (41,42).

In the presence of Ziegler−Natta catalysts, all higher α-olefins easily copolymerize with other α-olefins and with ethylene (17-19,38). In these reactions, higher α-olefins are all less reactive than ethylene and propylene (17-19). Their reactivities in the copolymerization reactions depend on the size and the branching degree of their alkyl groups (38).

4.2. Polymerization Processes. Isotactic PB and PMP are produced commercially in slurry processes in liquid monomers or monomer mixtures with light inert hydrocarbons at 50−80°C (17,18,25). The catalysts most suitable for these processes are ester- or diester-modified supported $TiCl_4/MgCl_2$ catalysts. The process scheme for PB is relatively simple (43): liquid 1-butene and the catalyst system are contacted in two reactors connected in series, then solution of the polymer in unconverted 1-butene is removed from the reactor, the monomer is recovered from the mixture, and molten PB is made into pellets (44). Poly (1-butene) can be also manufactured in the gas-phase process.

4.3. Metallocene Catalysts.   Higher α-olefins can be polymerized with catalyst systems based on metallocene complexes containing either two or one cyclopendadienyl ring (17-19). The first catalysts of this type, usually called Kaminsky catalysts, include common bis (metallocene) complexes of zirconium (zirconocene complexes), such as bis (cyclopentadienylzirconium dichloride). These complexes are activated with a special organoaluminum compound, methylaluminoxane. The catalysts polymerize α-olefins with the formation of amorphous atactic polymers. Polymers with high molecular weights are produced at decreased temperatures; they have rubber-like properties (17-45). When the polymerization reactions with the same catalysts are carried out at increased temperatures, 70–100°C, oligomers with low molecular weights are produced; they can be used as components of synthetic lubricating oils (46).

Zirconocene complexes containing two indenyl or tetrahydroindenyl groups bridged with short links, such as $-CH_2-CH_2-$ or $-Si(CH_3)_2-$, produce isotactic polymers of higher α-olefins (17-19,45). To synthesize syndiotactic PO, bridged zirconocene complexes with rings of two different types are required, one cyclopentadienyl and another 1-fluorenyl. These complexes are used for the synthesis of syndiotactic PB (2,3,17,45) and PMP (3,18).

4.4. Cationic Polymerization.   α-Olefins with linear and branched alkyl groups can be readily polymerized with cationic initiators. For example, olefins containing linear alkyl groups, 1-pentene, 1-hexene, 1-octene, and 1-decene, as well as their mixtures, are oligomerized at low temperatures using BF_3, mixtures of BF_3 and alcohols, $AlCl_3$, or $AlBr_3-HBr$ systems with the formation of lowmolecular weight oils of an irregular structure (4,47). These oligomers are used as basestocks for synthetic lubricating oils (4).

4.5. Polymerization of Cycloolefins.   Depending on catalyst, polymerization of cycloolefins proceeds either through ring opening or via the double-bond opening with preservation of the ring.

4.6. Ring-Opening Polymerization.   Ring-opening polymerization of cycloolefins in the presence of tungsten-, ruthenium-, or molybdenum-based catalysts proceeds via the metathesis mechanism (5,48-50):

$$(CH_2)_n - R - (CH_2)_m - CH = CH \rightarrow [-(CH_2)_n - R - (CH_2)_m - = CH-]_x$$
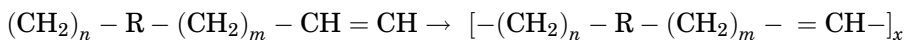
where R=0 in cycloolefins, $-CH=CH-$ in cyclodiolefins, or another cyclic group in dicyclopentadiene and norbornene. A number of commercially useful polymers, including polymers of cyclopentene and cyclooctene, were produced with such catalysts as WCl_6 activated by organometallic compounds (51), molybdenum-based catalysts, and organoruthenium catalysts (52,53). Ruthenium-based catalysts such as $[P(cyclohexyl)_3]_2Cl_2Ru=CHC_6H_5$ are most effective in these reactions (49-51). The reactions produce mixtures of linear polymers and macrocycles, up to 25% of all macromolecules. The polymers have varying [trans]/[cis] double-bond ratios; the trans unit content ranges from 60 to 85%, depending on reaction conditions. Polymers of cyclooctene (usually called polyoctenamers) with the highest *trans*$-C=C$ bond content melt at 50–60°C and the materials with the *trans*-C=C bond content of ∼60% melt at 30–35°C. Properties of two marketed polyoctenamer grades are shown in Table 8.

The same ROMP catalysts are used for the synthesis of poly(norbornene) with a high molecular weight, up to 2×10^6 (51). The ROMP poly(norbornene) is an amorphous polymer with high thermal stability, optical transparency and a low dielectric constant.

Dicyclopentadiene is polymerized with tungsten-based catalysts. Because the polymerization reaction produces heavily cross-linked resins, the polymers are manufactured in a special process named reactive injection molding (RIM). All catalyst components and resin modifiers are slurried in two batches of the monomer. The first batch contains a catalyst, which is a mixture of WCl_6 and $WOCl_4$, nonylphenol, acetylacetone, additives and fillers, and the second batch contains the cocatalyst, a combination of an alkylaluminum compound and a Lewis base such as ether, as well as antioxidants, and elastomeric fillers that are added for better moldability (32). Mixing two liquids in a 1:1 volume ratio in a mold at room temperature and at low injection pressure, 1–3 atm, results in a rapid exothermic polymerization reaction. Its rate is controlled by the ratio between the amounts of the cocatalyst and the Lewis base. The solidification time of the reaction mixture varies from 2 s to 60 min, depending on catalyst composition, and a typical overall cycle time is 4–6 min. Low viscosity of the liquid components allows the molding of very large parts with a surface area of up to 12–15 m^2 and thickness up to 30 cm. Such items can weigh several hundred kilograms. Similar catalyst systems are used for polymerization of norbornene and for its copolymerization with ethylidene norbornene.

A different type of ROMP catalyst produces linear poly(dicyclopentadiene) with very attractive properties (54): an amorphous plastic with T_g of ~140°C, excellent transparency (light transmittance 92%), high chemical resistance, and very low water absorption, <0.01%. This polymer found application in the optical industry and, due to a very low catalyst residual content, in the biotechnical industry, which requires low fluorescence and high uv transmission.

4.7. Polymerization with Metallocene Catalysts. Polymerization of cycloolefins with Kaminsky catalysts, combinations of metallocene complexes and methylaluminoxane, produces materials with a completely different structure. The reaction proceeds via the double-bond opening in cycloolefins and the formation of C−C bonds between adjacent cycles (19,33). If the metallocene complexes contain bridged substituted cyclopentadienyl rings, such as ethylene(bisindenyl)zirconium dichloride, the polymers are stereoregular, they have the cisdiisotactic structure and are highly crystalline.

5. Processing of PO

5.1. Rheology. Both molten PB and molten PMP exhibit strong non-Newtonian behavior: Their apparent melt viscosity decreases with an increase in shear stress (20,31). Melt viscosities of both resins also strongly depends on temperature (29,31). The activation energy for the PB viscous flow is 46 kJ/mol (11 kcal/mol) (25) and for the PMP melt it is 77 kJ/mol (18.4 kcal/mol) (20). The equipment used for polypropylene processing is usually suitable for PB and PMP processing as well; however, adjustments in processing conditions must be made to account for differences in melting temperatures and rheology.

5.2. Extrusion.   Extrusion is a fabrication method in which an article is shaped by forcing a molten polymer through a die. Main applications of extrusion include production of film, sheet, pipe, and tubing, as well as wire insulation. Extrusion temperatures and pressures are selected depending on the resin's T_m and melt viscosity. This resin is usually extruded using the same equipment, single- or twin-screw extruders, as that used for polypropylene, at melt and die temperatures of 170–190°C. The PMP polymer is processed on extruders with a high length/diameter ratio, >25, at temperatures of 240–300°C and at compression ratios of 2.5–3.5.

5.3. Pipe Manufacture.   Pipe and tubing from PB are fabricated at melt temperatures from 145 to 195°C using single-screw extruders equipped with vacuum- or pressure-calibration devises (44,55). Properties of pipe-grade PB are given in Table 4. Immediately after exiting the die, the tube of molten resin is cooled in two steps, first by a water spray and then by passing through a water well. After that, the pipe is vacuum-calibrated and, after sizing and cooling, it passes through a puller and then is coiled or cut into straight lengths. Soon after manufacture, PB pipe shrinks ~2% due to the onset of the crystal transformation from Form II to Form I. The pipe should be stored 7–10 days to bring the transformation to completion. The PB pipes are joined by thermal fusion (socket or butt fusion) or by mechanical fittings (crimp, compression, flare, etc).

5.4. Injection Molding.   In this technique, resin pellets are melted in a single-screw extruder and the molten resin is injected through a nozzle into a steel mold. The mold consists of a fixed and a movable platen tightly held together. After the mold is filled with the resin melt, it is cooled and opened to remove the article. The duration of the molding cycle depends on melt viscosity of a polymer and on the rate of polymer crystallization. Molds usually accommodate several articles formed in a single shot. Injection molding of PB is carried out at 145–190°C under conditions similar those for polypropylene. Injection molding of PMP is carried out at melt temperatures of 260–330°C, mold temperatures of 60–90°C, injection pressures of from 30 to 100 MPa (300–1000 atm), and at relatively low injection rates; molded parts shrink 1.5–2.0%.

5.5. Film Manufacture.   The blown-film technique is most commonly used in the production of PB film (44). The film is fabricated from resins with melt indexes from 0.3 to 10 g/10 min at a melt temperature of 200–215°C using conventional equipment for the manufacture of polyethylene film and cooling the film with chilled air. The polymer is melted in an extruder and the melt exits upward through a die with a thin circular gap to form a thin-walled tube of a molten resin. After exiting the die, the tube is mechanically stretched about five times in the machine direction and then expanded in the transverse direction by air pressure inside the tube. The blow-up ratio of the film, the ratio of the final film bubble diameter to the die diameter, ranges from 2.5 to 3.0 (56). To achieve a necessary level of melt plastification, the preferred extruders have single- or two-stage mixing screws with a compression ratio of 2.5:7 and a length/diameter ratio of at least 24:1 (44). Mechanical properties of blown PB film depend on the degree of orientation in the film and other film processing parameters. Some of the film properties are listed in Table 5. The PB film can be sealed at 160–220°C, both on-line, when the polymer in Form II, and after the transformation from Form II to Form I. Another technique for the PB film

production consists of film casting from the melt on a polished chilled roll and coextrusion or lamination with other films. Blends of 1-butene–ethylene copolymers with polypropylene enhance the processability and properties of PB film (22).

The PMP polymer is also manufactured into film using the casting method. The thickness of the film varies from 30 to 100 μm; its width can be as high as 1.5 m. The film is manufactured with a gloss finish without plasticizers, stabilizers or other processing aids. It offers a clean surface for laminate manufacturing and can be corona-treated for better adhesion and printing.

5.6. Processing of Polycycloolefins.   Poly(cyclooctene) prepared with ROMP catalysts has very low melt viscosity for a polymer. This feature accounts for its many applications, as an admixture to various rubbers during their processing. This polymer is vulcanized with the same agents as natural rubber: sulfur, peroxides, curing polymers. The polymer is compatible with virtually all rubbers, irrespective of their chemical structure or polarity (53). Copolymers of cycloolefins and ethylene produced with metallocene catalysts are amorphous materials with high T_g values. They are processed by all methods suitable for thermoplastic resins in general: injection molding, film, sheet and profile extrusion, blow molding (34,35). The film can be biaxially stretched for the use in capacitors or monoaxially stretched for shrink-wrapping applications.

6. Analytical Methods and Quality Control

Analytical and test methods for the characterization of polyethylene and polypropylene are also used of characterization of PB, PMP, and polymers of other higher α-olefins. The ^{13}C nmr (carbon-13 nuclear magnetic resonance) method, as well as ir and Raman spectroscopic methods, are used to study the chemical structure and stereoregularity of PO resins. In industry, PO stereoregularity is usually estimated by the solvent-extraction method similar to that used for isotactic polypropylene. Intrinsic viscosity measurements of dilute solutions in decalin and tetralin at elevated temperatures provide the basis for the molecular weight estimation of PB and PMP with the Mark–Houwink equation, $[\eta] = K \cdot M_w{}^{\alpha}$. The constants K and α for different PO are given in Refs. (17-19).

Tables 4-6 list ASTM methods used for the characterization of PB and PMP. A number of specialized methods have been developed for testing particular articles manufactured from PO. Several tests characterize the performance of PB and PMP film. They include the measurement of the dart impact strength of the film and the film tear strength, which reflects its resistance to tear propagation. The dart impact strength is measured by dropping a heavy dart with a round tip on a piece of stretched film. Tear resistance is measured with an Elmendorf tear–testing apparatus. Two values for the tear strength are usually reported; one determines the tear propagation in the machine direction of the film and the second one in the transverse direction. Pipes manufactured of PB are tested by internally pressurizing them with water. The standard test method for haze and luminous transmittance (ASTM D1003) is used for the measurement of PMP optical characteristics.

7. Commercial Aspects

Linear higher α-olefins with even carbon numbers, 1-butene, 1-hexene, 1-octene, 1-decene, etc, are produced commercially by Ethyl, Shell, Chevron, Spolana, Idemitsu, Mitsubishi, and Sasol. The latter company also produces 1-pentene. The global annual production of these products is ∼2 million tons. The annual growth of the olefin production during the 1990–2000 period was ∼6%. Over 30% of the olefins are used to produce linear low density polyethylene (LLDPE) resins. Most of α-olefins with branched alkyl groups are produced as by-products of petroleum refining or specially synthesized. Their prices are usually higher than those of linear α-olefins. The most commercially important of the branched olefins, 4-methyl-1-pentene, is manufactured by propylene dimerization by Mitsui Petrochemical Company in a 22,700-ton/year volume and by British Petroleum Company, 25,000 ton/year. Dicyclopentadiene is recovered as a by-product from off-stream of ethylene crackers by Dow Chemical, ExxonMobil, BP Shell, and other companies.

The first commercial manufacture of PB started in Europe in 1964 by Chemische Werke HÜLS in Germany and in 1968 by Mobil Oil Company in the United States. Until 2002, Shell Chemical Company produced PB in the United States in a ∼25×10^3-ton/year volume. At a present time, crystalline isotactic PB is manufactured in Europe, Japan, and China. Basell Company produces 27,000 ton/year of PB in the Netherlands. Several grades of different isotacticity, from 90 to >99%, and with different molecular weights are marketed, including extrusion resins for hot- and cold-water pipe and other purposes, film resins, and hot-melt adhesives. Some applications require manufacture of 1-butene–ethylene copolymers with ethylene contents from 5 to 8 wt%. The copolymers have lower softening points and are more flexible and resistant to environmental stress cracking. The flexural modulus of the copolymers is >500 MPa. In Japan, PB is manufactured by Mitsui Chemicals under the trade name Beaulon. The world production of PB is expected to increase to 50,000 tons in 2006.

Mitsui Chemicals Company manufactures crystalline PMP in Japan under the trade name of TPX at a 13,000-ton/year volume. The resin, a copolymer of 4-methyl-1-pentene and a linear C_{10}–C_{16} α-olefin, is produced in six different grades that differ in molecular weight, copolymer composition, crystallinity, and T_m (57). The resins are used for injection molding, blow molding, and extrusion. Filling of PMP with fiberglass and mica, with a filler concentration from 10 to 35–40 wt.%, improves rigidity and increases the thermal deflection temperature of the resin to 130–140°C.

Degussa manufactures polyoctenamer [poly(cyclooctene)] in Europe in a 12,000-ton/year volume under the trade name of Vestenamer (52,53). Two grades of the polymer, TOR 8012 (53) and TOR 6213 (52), have similar molecular weights, ∼100,000, but different contents of trans-double bonds, 80 and 60%, respectively, and, as a result, different crystallinity, 30 versus 10%; different densities, 0.910 versus 0.890 kg/m^3; and different T_m, 55 versus 35°C.

Several companies in Japan and Europe (Zeon Chemicals, Total, CdF Chemie, etc) manufacture poly(norbornene) under the trade name Norsorex.

Components for the manufacture of poly(dicyclopentadiene), a liquid molding resin, are produced in the United States (Hercules, 13,600 ton/year), Japan (Teijin, 3,000 ton/year) and Europe (Shell) under the trade name of Metton, and by Goodrich (trade name Telene) in the United States and Japan. Optically transparent poly(dicyclopentadiene) prepared with ROMP catalysts is manufactured in Japan by Nippon Zeon; its two trade names are Zeonex and Zeonor.

Several grades of copolymers of norbornene and ethylene are produced using metallocene catalysts in Germany by Ticona-Celanese under the trade name Topas in a 30,000-tons/year volume. Tetracyclododecene–ethylene copolymers are manufactured by Mitsui in Japan under the trade name Apel (34).

Prices for PO/kg are PB film \$3.10; pipe for hot and cold water \$4.50; general-purpose, adhesives \$2.00–2.50; PMP \$3.50–4.50. The COC resins are priced at \$4–7/kg, depending on type.

8. Health and Safety Factors

Polymers of higher α-olefins are not toxic. In particular, PB and PMP are inert materials; they represent no health hazard (57). The PMP polymer is employed extensively for a number of medical and food packaging applications. Several grades conform to FDA regulations and to the health standards of other countries. Polymers and copolymers of cycloolefins are also widely used in medical applications. The main potential health hazards of PO are associated with residual monomers, antioxidants, and catalyst residues. Another health-related factor: smoke, fumes, and toxic decomposition products are formed during combustion or pyrolysis of PO. When PB burns, it gives off irritating decomposition and oxidation products in very low concentrations, such as lachrymatory aldehydes, formaldehyde and acrolein. Flammability of PO resins is equal to that of polypropylene and polyethylene, $\sim$2.5 cm/min (ASTM D635).

9. Applications

9.1. Uses of PB.   The largest share of commercially produced crystalline PB is used to manufacture pipe and tubing with diameters from 0.1 to 1.2 m (44). Advantages of PB in pipe applications include high flexibility, toughness, and high resistance to creep, environmental stress cracking, wet abrasion, and to many chemicals. Pipes manufactured from PB retain their properties at temperatures up to 85°C. Properties of pipe-grade PB are listed in Table 4. Black-pigmented grades are suitable for outdoor use. The pipe is widely used in Europe and Asia in residential and commercial hot- and cold-water plumbing, including chlorine-containing hot water, both above the ground and underground. (This type of piping is not currently used in the United States for legal reasons). The PB pipe is also used in water wells, water manifolds, for waste and recycled water, piping in ships, for fire sprinklers, for the manufacture of domestic water heaters, etc (44).

Blown film manufactured from PB has high tensile strength and resistance to tear, impact, and puncture (44). The film exhibits a "hard-elastic" behavior: it

completely recovers the original length even after large stretching. Some properties of PB film are given in Table 5. The film is widely used for packaging of food products, such as cereal and delicatessen packaging, and for sterilizable packaging (44). The PB polymer is also used for modification of other polyolefin resins, such as high density polyethylene and polypropylene. Blending a small fraction of PB with these materials increases their strength and toughness, improves their processability, and improves their end-use features such as higher flexibility and softness.

A relatively low crystallization and recrystallization rate of PB are beneficial when this resin is used as a component in hot melt adhesives, in particular, for nonwoven fibers.

9.2. Uses of PMP. Most PMP applications capitalize on high optical transparency of the resin, its excellent dielectric characteristics, high thermal stability, and chemical resistance (58). Manufacture of medical equipment consumes ∼40% of PMP production. The articles include hypodermic syringes, needle hubs, tubing connectors, breast pumps, equipment for blood collection and transfusion, parts of pacemakers, cells for blood analysis, and respiration equipment. Articles made of PMP can be subjected to all sterilization procedures, such as autoclave sterilization, uv irradiation, dry heat treatment, β- and γ-irradiation, and ethylene oxide treatment. The second important area of the PMP use is chemical and biomedical laboratory equipment: cells for spectroscopic and optical analysis, laboratory ware, and animal cages. Other applications encompass a variety of injection-molded articles, such as caps for enclosures, ink cartridges for printers, light covers, tableware, cosmetic and household containers, and sight-glasses. The PMP polymer is suitable for microwave oven cookware and service. In many applications, PMP replaces stainless steel trays and is used for thermal insulating floats, barriers for hot sulfuric acid and hydrochloric acid pools and acid washing tanks, and packing rings in gas-scrubbing towers. This material is also utilized for wire and cable coating, especially in oil well and communication cables, and for film and paper coatings with good release properties (58).

Due to excellent optical properties, PMP can be fashioned into optical windows and lenses used in equipment for both the far-infrared (ir) and visible parts of the spectrum, eg, allowing cotransmission of a He-Ne laser alignment beam.

Melt-spun fiber is produced from PMP at 280°C and is drawn in air at 95°C about three times. The fiber has a 2−3 g/denier strength and ∼30% elongation. Melt-spun hollow fibers are also manufactured. The PMP polymer has one of the highest permeabilities for gases, and many of its uses utilize this property.

Poly (4-methyl-1-pentene) film has good release properties for up to 180°C, low density, and excellent clarity. It is used for fabrication of composite products that perform at temperatures up to 180°C. The composites are used in such products as golf club shafts, aircraft lavatory components, and printed circuit boards, both rigid and flexible. The PMP film is also used for applications involving the curing of rubber films and sheets, and in food packaging (57).

9.3. Synthetic Lubricating Oils. Liquid oligomers of higher linear α-olefins, such as 1-decene, are produced with cationic initiators. These viscous liquids are usually called poly-α-olefins (PAO). These oligomers are the most

versatile of all synthetic lubricants. They combine good lubricating properties over a broad temperature range, including excellent low temperature properties, high frictional, and oxidative stability, and low volatility. They are miscible with all mineral oils and most other synthetic lubricants. For these reasons, PAO have found wide application as synthetic base oils in the formulation of various lubricants. They include lubricating oils for cars, transformer oils, transmission and crankcase fluids, as well as hydraulic fluids and compressor oils (47). ExxonMobil Chemical Company uses a large volume of PAO as the basestock for industrial oils and lubricating oils for cars, truck, diesel, marine and gas engines under the trade name Mobil 1. Chevron, Ethyl Corporation, Neste Chemical and Uniroyal manufacture similar synthetic lubricants.

9.4. Uses of Polymers of Cycloolefins. Polyoctenamer elastomers produced with ROMP catalysts are mostly used as components in rubber, PVC- and PS-based compositions. Compounding of polyoctenamer with natural rubber and polyisoprene reduces the energy requirement during rubber processing, improves plasticity during resin mixing, facilitates blending of different elastomers, eg, natural rubber and EPDM, and significantly increases the green strength of tire components (53,59). Small amounts of polyoctenamer, 4–5 wt.%, are added to ground recycled rubber, and the mixture is used as a component in rubber articles or in high grade asphalt with greatly improved properties (53). Pure polyoctenamer is processed by extrusion, injection molding, and calendering into hoses, rubber coatings and tire components.

High molecular weight poly(norbornene) produced with ROMP catalysts is a powder with very high affinity to hydrocarbon liquids: one volume of the polymer can absorb up to 15 volumes of the liquids. This property makes the polymer useful in cleaning oil spills on land and on the surface of water. This polymer is also fabricated into dense porous sheets with exceptional vibration and sound dampening properties. These materials are used for vibration prevention in engine mountings, shockproof bumpers, flexible coupling and in loudspeakers. Cross-linked poly(norbornene) is a deformation-resistant elastomer that can be molded into soft seals, gaskets, shoe soles, etc (51).

Cured liquid-molding resins based on poly(dicyclopentadiene) with trade names Metton and Telene have high strength and rigidity, excellent low temperature impact resistance up to $-40°C$, low moisture absorption, light weight, high chemical resistance, and a glossy surface finish. Main applications of these resins are in the manufacture of automotive parts for trucks, snowmobiles, wheel loaders, recreational vehicles, etc, and in other areas that require toughness and good all-weather impact resistance such as hopper-car lids, electrical housing, and large-size housing for electrochemical cells.

Different grades of optically transparent ROMP poly(dicyclopentadiene) manufactured by Nippon Zeon under trade names of Zeonex and Zeonor are used for optical applications such as lenses for laser printers and optical parts of photographic cameras. The polymers are also used in medicine and biotechnical industry due to their ultra-high purity and high uv transmission. These materials have a very low dielectric constant and are used as insulating components in electrical products. This type of poly(dicyclopentadiene) is also a multipurpose transparent engineering plastic with a wide range of heat resistance,

70–160°C, and high chemical resistance. It is used in light guide plates, automotive parts, cosmetic bottles, and diagnostics parts.

Copolymers of norbornene and ethylene produced with metallocene catalysts under the trade name Topas are amorphous materials with high T_g, 70–180°C, depending on copolymer composition (35). They are melt-processed into foils, tubes, pipes, and fibers. Their high transparency and high refractive indexes, similar to that of glass, make them suited for many optical applications such as lenses, prisms, carrier plates and foils for optical data storage, DVD disks, medical containers, etc. These resins withstand steam sterilization at 120°C. The film of these resins is used for food and drug packaging and for the manufacture of capacitors (35). Copolymers of tetracyclododecene and ethylene produced with metallocene catalysts under the trade name Apel are amorphous materials with high T_g, 70–145°C (34). They are melt processed into sheet, film, bottles, medical package, optical and industrial parts using injection molding, blow molding, extrusion, and vacuum molding processes. They have excellent optical properties (high transparency, low haze, low birefringence), low moisture permeability and high chemical resistance. Their main uses are in medical applications, such as bottles, syringes, and drug packaging; in optical applications, including lenses for optical disks and sensors; and as shrink film (34).

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Table 1. **Physical Properties of 1-Butene[a] and 4-Methyl-1-pentene[b]**

Property	1-Butene	4-Methyl-1-pentene
flash point, °C	−150	−7.0
boiling point, °C	−6.25	53.86
T_m, °C	−185.35	−153.64
density, kg/m^3	601.4 (15°C)	663.7 (20°C)
n_D	1.3962 (25°C)	1.3827 (20°C)
critical temperature, °C	147.4	
critical pressure, MPa	4.056	
vapor pressure, kPa	415.7 (38°C)	29.47 (20°C), 89.34 (50°C)
heat capacity, liquid, at 25°C, J/(mol K)	89.33	184.4
heat of vaporization at bp, J/mol	20.38	27.11
viscosity, mPa·s (=cP)		0.288 (20°C)

[a]Refs. 14,15.
[b]Refs. 15,16.

Table 2. **Properties of Other Higher Olefins**[a]

Monomer	Molecular weight	Boiling point, °C	T_m, °C	Density,[b] g/cm^3	Refractive index, n_D^{20}
Linear Olefins					
1-pentene	70.1	29.96	−165.22	0.6405	1.3715
3-methyl-1-butene	70.1	20.05	−168.49	0.6272	1.3643
1-hexene	84.2	63.48	−139.83	0.6732	1.3879
3-methyl-1-pentene	84.2	54.17	−153.0	0.6674	1.3842
4-Methyl-1-pentene	84.2	53.86	−153.64	0.6637	1.3827
1-heptene	98.2	93.64	−118.88	0.7013	1.3998
4-methyl-1-hexene	98.2	86.73	−141.46	0.6985	1.4000
5-methyl-1-hexene	98.2	85.31		0.6920	1.3967
1-octene	112.2	121.29	−101.72	0.7149	1.4087
5-methyl-1-heptene	112.2	113.3		0.7164	1.4094
vinylcyclohexane	110.2	128		0.8060	1.4458
1-decene	140.3	170.60	−66.28	0.7408	1.4215
1-dodecene		213.36	−35.23	0.7584	1.4300
Cycloolefins					
cyclopentene	68.1	44.2	−135.08	0.7720	1.4225
cyclopentadiene	66.1	40.0	−97.2	0.8021	1.4440
cyclooctene	110.2	146	−16	0.846	1.4690
norbornene[c]	94.6	96.0	44−46		
dicyclopentadiene	132.2	170	−1	0.986	1.511

[a]Ref. 16.
[b]At 20°C.
[c]Bicyclo[2.2.1]-2-heptene.

Table 3.   **Properties of Polyolefins**[a]

Polymer	T_m, °C	Crystal type	Helix type	Density,[b] g/cm^3	T_g, °C
Polymers of α-Olefins					
iso-poly(1-butene)					
form I	138–142	hexagonal	3_1	0.951	−25 to −50
form II	130	tetragonal	11_3	0.902	
form III	107–109	orthorhombic	4_1	0.905	
syndio-poly(1-butene)					
form I	50–55	orthorhombic	$(2_1)_2$		−18
form II	∼50		$(5_3)_2$		−18
iso-poly(1-pentene)					
form I	105–115	monoclinic	3_1	0.923	−40 to −55
form II	75–80	pseudoortho-rhombic	4_1	0.907	
syndio-poly(1-pentene)	42				−23 to −27
iso-poly(3-methyl-1-Butene)	360	monoclinic	4_1	0.93	50
iso-poly(1-hexene)	<20	monoclinic	7_2	0.726	−50 to −55
syndio-poly(1-hexene)	amor-phous				−32
iso-poly(3-methyl-1-pentene)	360		7_2	0.87	20–50
iso-poly(4-methyl-1-pentene)					
form I	245	tetragonal	7_2	0.813	50
form II	235–240	tetragonal	4_1		
syndio-(4-methyl-1-pentene)	197	tetragonal	$(12_7)_2$		
iso-poly(1-heptene)	∼35				−40
iso-poly(3-methyl-1-hexene	285				
iso-poly(4-methyl-1-hexene)	215	tetragonal	7_2	0.845	
syndio-poly(4-methyl-1-hexene)	166		$(2/1)_2$		
iso-poly(5-methyl-1-hexene)	130	monoclinic	3_1	0.84	
iso-poly(1-octene)	∼20		3_1	0.726	−60 to −65
iso-poly(5-methyl-1-heptene)	130	tetragonal	3_1		−15
iso-polyvinyl-cyclohexane	376–385	tetragonal	4_1	0.95	80–90
syndio-polyvinyl-cyclohexane	amor-phous				−2
iso-poly(1-decene)	22–27	side chain			33–26
Linear Polymers of Cycloolefins					
diiso-poly(cyclobutene)	485				
diiso-poly(cyclopen-tene)	395			1.104	
poly(norbornene)	>600				

[a]Refs. 3,17–22.
[b]Density of crystalline polymer.

Table 4. **Properties of Pipe-Grade PB Resin (Crystalline Form I)**[a]

Property	ASTM test method	Value
molecular weight, M_w		70,000–75,000
molecular weight distribution, M_w/M_n		10–11
melt index, g/10 min	D1238(cond. E)	0.4
crystallinity (Form I), %		48–55
density, kg/cm^3	D792	930–940
Mechanical		
tensile properties:		
yield strength, MPa	D638	16–18
break strength, MPa	D638	32–35
elongation to break, %	D638	275–320
modulus, MPa	D638	290–295
flexural modulus, MPa	D790	350–380
flexural strength at break, MPa	D790	14–16
elongation at break, %	638	300–380
notched Izod impact strength, J/m	D256	640–800
hardness, Shore	D2240	D55–65
Thermal		
brittleness temperature, °C	D746	−18
T_m, °C	D3418	124–130
T_g, °C		−18
vicat softening point, °C	D1525	112–114
heat deflection temperature, °C		
at 1.82 MPa	D648	55–60
at 0.46 MPa	D648	102–113
linear coefficient of thermal expansion, m/m/°C	D696	0.00013
thermal conductivity, W/(mK)	C177	0.217–0.220
UL flammability	UL94	HB
Electrical		
dielectric constant, 10^3–10^6 Hz	D150	2.53
dissipation factor, 10^3–10^6 Hz	D150	0.0005
water absorption, in 24 h, %	D570	<0.03

[a]Ref. 25.

Table 5.   **Properties of PB Film**[a]

Property	ASTM test method	Value
Resin (Form I) properties		
melt index, g/10 min	D1238	1.0
density, kg/m^3	D1505	910
cystallinity (Form I), %		46−52
T_m, °C	D3418	118−120
Film properties (50.8-μm film)		
tensile properties		
break strength, MPa		
machine direction	D882	44.8
transverse direction	D882	37.9
elongation at break, %	D882	300−320
dart drop strength, g	D1709	350
Elmendorf tear strength, kg/cm		
machine direction	D1922	433
transverse direction	D1922	394
optical properties		
haze, %	D1003	16
clarity, %	D1003	1.5
gloss, %	D2457	~70
sealing temperatures, °C		155−210

[a]Grade DP 1710, Ref. 25.

Table 6. **Properties of Crystalline PMP**[a]

Property	ASTM test method	Value
Physical		
density at 20°C, kg/m^3	D792	830–835
water absorption, at saturation, %	D570	0.01
refractive index, $N_D{}^{20}$		1.463
Thermal		
T_m, °C		235–240
heat of fusion, J/g		61.65
vicat softening point, °C	D1525	173–180
T_g, °C		
homopolymer		∼50
copolymer		∼30
deflection temperature under flexural load, °C		
at 0.46 MPa	D648	∼150
at 1.82 MPa	D648	∼100–120
coefficient of linear expansion, cm/cm·°C	D696	1.17×10^{-4}
thermal conductivity, W/(m K)	C177	0.167–0.172
specific heat capacity, J/(g K)	C351	2.18
maximum service temperature, in air, °C		∼175
linear mold shrinkage, %	D955	1.7–2.1
Electrical		
dielectric constant at 25°C, 10^2–10^6 Hz	D150	2.12
volume resistivity, O cm	D257	$>10^{16}$
dielectric strength, kV/mm	D149	63–65
dissipation factor at 10 MHz	D150	1.5×10^{-4}
Arc resistance, s		120
Optical		
transparency, %	D1476	91–92
haze, %	D1476	1.5–2.0
Mechanical		
tensile yield strength, MPa	D638	20–24 (200–240 kg/cm^2)
tensile break strength, MPa	D638	17–24 (170–200 kg/cm^2)
elongation at break, %	D638	10–25
bending strength, MPa	D790	25–36 (250–360 kg/cm^2)
tensile modulus, GPa	D638	1.3–2.0 (1.3×10^4–2.0×10^4 kg/cm^2)
flexural modulus, GPa	D790	1.3–1.8 (1.3×10^4–1.8×10^4 kg/cm^2)
compression modulus, MPa	D695	800–1200
notch-impact strength, kJ/m	D256	200–500
rockwell hardness	D7852	L80–L93
stiffness (Olsen)	D747	800–1000 (8.0×10^3–1.0×10^4 kg/cm^2)

[a]Refs. 20,28–30.

Table 7.   **Properties of Poly(dicyclopentadiene)**[a]

Property	Unfilled resin	20% Glass powder
density, kg/m^3	1050–1200	
flexural modulus, MPa	1800–2100	2600–2900
tensile strength, MPa	45–50	30–32
tensile modulus, GPa	1.9–2.0	
tensile elongation, %	80	25
impact strength, J		
at 23°C	13–16	11–13
at −29°C	11–13	11–13
compression strength, MPa	58–60	
T_g, °C	125–140	127
hardness	R114	

[a]Ref. 32.

Table 8.

Mol. Wt	[trans]/[cis] C=C ratio	Crystallinity, %	Density, kg/m^3	T_m, °C	T_g, °C
90,000	4.0	30	0.910	55	−65
110,000	1.5	10	0.890	∼35	−75