PROPYLENE POLYMERS

Introduction

The stereospecific polymerization of propylene by Giulio Natta in 1954 is one of the most commercially significant scientific breakthroughs in polymer chemistry. Natta’s discovery that a Ziegler catalyst could be used to produce highly isotactic polypropylene led to the first commercial processes for the production of this polymer by Montecatini in Italy and Hercules in the United States in 1957. The attractive properties and relatively low cost of polypropylene produced using this technology led to its rapid commercial acceptance. Consequently, Karl Ziegler and Giulio Natta were awarded the Nobel Prize in Chemistry in 1963. The commercial potential of olefin polymerization was recognized by many of the leading companies, leading to a tremendous amount of activity and the invention of a number of competing technologies in the early 1950s. These technologies were not economically competitive with those based on Ziegler–Natta catalysts. However, the competing claims of a number of companies led to a massive patent interference in the United States that continued for almost 30 years, eventually resulting in the award of a U.S. patent for the composition of matter of crystalline polypropylene to Hogan and Banks of Phillips Petroleum in 1983. Continued interest in olefin polymerization led to the invention of the supported high yield, high stereoregularity catalyst systems by Montedison and Mitsui Petrochemical. This led to the development of a number of low cost polymerization processes, spurring a dramatic increase in production capacity. Today, these catalyst systems are used to produce polypropylene in every major region of the world. The use of homogeneous organometallic (metallocene) olefin polymerization catalysts has led to the development of a number of unique propylene polymers. Currently, these polymers are produced in relatively limited amounts for a number of specialty applications.

Polypropylene is one of the most widely used polymers in the world because of the widespread availability and low cost of monomer, low manufacturing cost, and attractive polymer properties. These properties can be modified to be suitable for a wide variety of applications. Polypropylene can be processed by almost all commercial fabrication techniques. Approximately 30,000,000 ton was consumed worldwide in 2001.
Table 1. Physical Properties of Propylene

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>42.078</td>
<td>1</td>
</tr>
<tr>
<td>Boiling point at 101.3 kPa a, °C</td>
<td>−47.7</td>
<td>3</td>
</tr>
<tr>
<td>Melting point, °C</td>
<td>−185.3</td>
<td>3</td>
</tr>
<tr>
<td>Critical temperature, °C</td>
<td>92</td>
<td>1</td>
</tr>
<tr>
<td>Critical pressure, MPa b</td>
<td>4.65</td>
<td>1</td>
</tr>
<tr>
<td>Critical density, g/mL</td>
<td>0.233</td>
<td>2</td>
</tr>
<tr>
<td>Critical compressibility</td>
<td>0.275</td>
<td>3</td>
</tr>
<tr>
<td>Dipole moment, 10^{-30} C·m c</td>
<td>1.3</td>
<td>3</td>
</tr>
<tr>
<td>Refractive index, n D</td>
<td>1.3567</td>
<td>3</td>
</tr>
<tr>
<td>Explosion limit, % by volume in air</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lower</td>
<td>2.4</td>
<td>1</td>
</tr>
<tr>
<td>Upper</td>
<td>11.1</td>
<td>1</td>
</tr>
<tr>
<td>Autoignition temperature, °C</td>
<td>224</td>
<td>1</td>
</tr>
<tr>
<td>Solubility in water (at 20 °C, 101.3 kPa a)</td>
<td>44.6 mL</td>
<td>3</td>
</tr>
</tbody>
</table>

a To convert kPa to mm Hg, multiply by 7.5.
b To convert MPa to atm, multiply by 9.87.
c To convert C·m to D, divide by 3.336 x 10^{-30}.

Monomer

Properties. Propylene is an olefin hydrocarbon that is a gas under ambient conditions but is normally stored as a liquid under pressure. The physical properties of propylene are given in Table 1. Thermodynamic properties are widely reported in the literature. Vapor–liquid equilibria of mixtures of propylene with other hydrocarbons and hydrogen are accurately represented by correlations for hydrocarbon mixtures, such as the Chao–Seader correlation.

The reactivity of propylene is a result of the olefinic double bond in H₂C=CHCH₂, which gives rise to addition reactions. Consequently, propylene is used in the synthesis of many industrially important compounds, including propylene oxide, acrylonitrile, cumene, and isopropyl alcohol. The consumption of propylene in the production of polymers, however, is greater than the total for all other chemicals. Propylene is also used in alkylating feedstocks for gasoline.

Manufacture. The major commercial sources of propylene are processes for the cracking of hydrocarbons. Initially, these processes were designed for the manufacture of other products, and propylene was considered an undesirable by-product. Now, propylene is often an equally desirable co-product. Ethylene is produced by the steam cracking of hydrocarbons at high temperatures and very short residence times. The two most common feedstocks are naphtha and ethane. This process produces a variety of by-products; the ratio of ethylene to by-products is dependent on the type hydrocarbon feedstock and the reaction conditions. Propylene production is higher when naphtha is used as a feedstock rather than ethane. Catalytic cracking of hydrocarbons is often used to increase the production of gasoline in oil refining. Increasing consumption of gasoline in the United States has led refiners to increase the severity of the cracking process, resulting in an increase of the production of propylene as a by-product. Consequently, the ratio of
Table 2. Recommended Maximum Limits of Impurities in Propylene Used in Polymerization

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Maximum limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetylene, ppm vol</td>
<td>5</td>
</tr>
<tr>
<td>Methylacetylene, ppm vol</td>
<td>3</td>
</tr>
<tr>
<td>Propadiene, ppm vol</td>
<td>5</td>
</tr>
<tr>
<td>Butadiene, ppm vol</td>
<td>50</td>
</tr>
<tr>
<td>Green Oils (C6-C12), ppm vol</td>
<td>20</td>
</tr>
<tr>
<td>Oxygen, ppm vol</td>
<td>2</td>
</tr>
<tr>
<td>CO, ppm vol</td>
<td>0.03</td>
</tr>
<tr>
<td>CO₂, ppm vol</td>
<td>5</td>
</tr>
<tr>
<td>COS, ppm vol</td>
<td>0.02</td>
</tr>
<tr>
<td>Total sulphur, ppm wt</td>
<td>1</td>
</tr>
<tr>
<td>Methanol, ppm vol</td>
<td>5</td>
</tr>
<tr>
<td>Isopropanol, ppm vol</td>
<td>15</td>
</tr>
<tr>
<td>Water, ppm wt</td>
<td>2</td>
</tr>
<tr>
<td>Arsine, ppm vol</td>
<td>0.03</td>
</tr>
<tr>
<td>Phosphine, ppm vol</td>
<td>0.03</td>
</tr>
<tr>
<td>Ammonia, ppm wt</td>
<td>5</td>
</tr>
</tbody>
</table>

*Source: Basell.*

Propylene isolated from refineries to propylene from steam cracking is greater in the United States than in Western Europe and other parts of the world. The propylene isolated from the cracking processes is purified by distillation to remove propane and other impurities. Propylene is commercially available as chemical grade (approximately 95% propylene) and polymerization grade (>99.5% propylene) where propane is the major impurity. However, the suitability of propylene as polymerization monomer is dependent on the levels of trace impurities rather than on the propane content. Commonly occurring impurities are acetylenes, dienes, CO, COS, water, and alcohols. These impurities affect the activity and stereospecificity of propylene polymerization catalysts. Typical limits for the level of impurities acceptable in polymerization grade propylene are given in Table 2.

Propylene is also produced by the metathesis of butene and ethylene. Usually, this process is installed as an addition in a refinery or steam cracking facility to increase the production of propylene. The first commercial metathesis process for the production of propylene was developed by Phillips, and is now licensed by ABB Lummus.

The relative abundance of propane and other light hydrocarbons in certain locations has increased interest in the production of propylene by the catalytic dehydrogenation of propane. Currently only a few propane dehydrogenation plants are operating, producing a small fraction of the world supply of propylene; however, it is anticipated that propane dehydrogenation will be the major source of propylene in the Middle East. The two major processes available are the Catofin process originally developed by Houdry and now licensed by ABB Lummus and the Oleflex process licensed by UOP. Natural gas can be used as the feedstock for the production of propylene by adding a Lurgi MTP process facility to a conventional methanol plant.
Transportation, Storage, and Handling. Propylene is stored and transported as a liquid under pressure. The preferred method of transporting propylene is through pipelines. Commercial quantities of propylene are also shipped by tanker and rail. The most extensive pipeline system for the transportation of propylene is in the Gulf Coast region of the United States. This pipeline system is also connected to a series of underground brine caverns used for propylene storage. Pressure vessels are also used for the storage of propylene.

Propylene is a flammable gas under normal ambient conditions and is not hazardous at low concentrations, but is an asphyxiant, which is a concern in closed environments. Direct contact with liquid propylene can cause skin burns from freezing. Fire or explosion is the greatest potential hazard associated with the storage and handling of propylene. Care must be exercised to avoid creating an explosive atmosphere when disconnecting lines and unloading vessels containing propylene. Explosions of vapor clouds formed from large leaks of liquid or gaseous propylene are the greatest potential hazard. The fire and explosion hazards associated with propylene are similar to those of propane and liquified petroleum gas (LPG).

Molecular Structure

The unique feature of propylene polymerization, versus ethylene polymerization, is the symmetry of the monomer insertion into the growing polymer chain. It is the presence of the methyl group in the propylene monomer that is responsible for this difference. This gives the monomer insertion an orientation (the monomer has a “head” and a “tail”) and a stereochemical configuration with respect to the other units in the chain backbone. Regularity with respect to monomer orientation is termed the regiospecificity of the polymerization. Regularity of the methyl group placement relative to the other methyl groups along the chain backbone is termed the stereospecificity of the polymerization. The three limiting classifications of stereospecificity in polypropylene (PP) are illustrated in Figure 1. In isotactic polypropylene (iPP), all of the methyl groups have the same configuration with respect to the polymer backbone. In syndiotactic polypropylene (sPP), the methyl groups have an alternating configuration. Atactic polypropylene (aPP) has a random configuration. An additional configuration, hemi-isotactic polypropylene, is discussed elsewhere (4). iPP is overwhelmingly the most commercially significant form of PP. In practice, the degree of stereoregularity (and tacticity microstructure) can vary considerably within these general classifications. For the specific case of isotactic polymerization, Figure 2 shows three idealized limiting sample microstructures. Figure 2a shows a case where an isolated stereo error is immediately corrected along the growing chain. Figure 2b shows a case where a stereo error is propagated along the growing chain, and Figure 2c shows an iPP/aPP multiblock structure (5–7). Figure 2a is most common. Further discussions of stereo defects are available in the literature (4–22). In general terms, stereoregularity (or stereospecificity) refers to the content of defects that disrupt the regular placement of methyl groups. The intrachain defect content can also vary widely between chains (interchain distribution) (23) for different catalyst systems. The
control of stereoregularity by catalyst and polymerization process is a critical determinan of PP properties.

Kinetic arguments suggest that iPP polymerization shows a strong preference for primary “head-to-tail” insertion of monomer into the growing chain (24–26). Regioirregular insertion of monomer renders the active site kinetically dormant (24–30), and its incorporation in the growing polymer chain occurs infrequently. With Ziegler–Natta polymerization catalysts, regio misinsertion errors are generally not present in the isotactic fraction (30). Metallocene polymerization catalysts can show appreciable levels of regio misinsertion errors in chains of high stereospecificity (4,27,31–41) (see METALLOCENES; SINGLE-SITE CATALYSTS).
Fig. 2. Sample tacticity microstructures in isotactic polymerization: (a) isolated stereo error is corrected in growing chain; (b) stereo error is propagated in growing chain; (c) an iPP/aPP multi-block structure.

The stereo- and regioregularity of PP is best characterized by solution $^{13}$C NMR spectra (42). These spectra can also provide information on the polymerization mechanism (4,7,9,11,12,14–22,30), and have been modeled in terms of the interchain tacticity distribution (14,43–45). Infrared spectroscopy (IR) has also been used to characterize the stereospecificity of iPP. Commonly the ratio of the 998 and 973 cm$^{-1}$ band absorbance is used (46,47). The result is sensitive to thermal history (46). Solvent fractionation techniques are commonly used in industrial practice. These methods are based on the fact that chains with varying stereospecificity have different crystallinity and solubility in hydrocarbon solvents. In nominally isotactic PP, the atactic fractions of the interchain tacticity distribution are soluble, whereas the isotactic fractions are not. The isotactic index suggested by Natta represents the percentage of polymer insoluble in boiling $n$-heptane (48). Other procedures require preliminary total dissolution of the polymer in high boiling hydrocarbons such as xylene, and subsequent cooling in order to separate the precipitated crystalline portion (an example is ASTM D5492-94). The insoluble fraction is a measure of the stereospecificity. Often the term stereoblock is used to refer to fractions of the interchain distribution of intermediate solubility. Related solvent fractionation techniques include preparative and analytical temperature rising elution fractionation (TREF) (49). The use of pulsed proton solid-state NMR has been demonstrated as an alternative to solubility measurements of stereoregularity (50). Other secondary measurements which probe melting and/or crystallinity behavior can also be applied.

In addition to tacticity, important additional parameters of the PP chain which influence properties include the molecular weight, polydispersity, and composition and comonomer distribution in blends and copolymers. PP, like all synthetic and most natural polymers, consists of a distribution of macromolecules of different lengths. Therefore, the polymers exhibit a molecular weight
distribution. The number-average molecular weight ($M_n$) is determined by gel-permeation chromatography (GPC), more generally referred to as size-exclusion chromatography (51). Because of the strength of the GPC technique, the older techniques of osmometry (52,53), cryoscopy (54), and ebulliometry (54) are less commonly used today. For PP, the GPC method typically utilizes high temperatures (135–145°C) in solvents such as o-dichlorobenzene and trichlorobenzene. The weight-average molecular weight ($M_w$) can be obtained by light scattering (55) and GPC. Higher moments of the molecular weight distribution can also be obtained by GPC. The viscosity-average molecular weight $M_v$ can be obtained by measurement of the solution intrinsic viscosity $[\eta]_0$ (52). $M_v$ and $[\eta]_0$ are related by the Mark–Houwink equation:

$$[\eta]_0 = K(M_v)^a$$

Generally, values of $M_v$ lie between $M_n$ and $M_w$ values. Values of the constant $K$ and exponent $a$ are determined by calibration with homogeneous fractions of known molecular weight for specific solvent/temperature conditions. In practice, for polypropylene, homogeneous fractions are not available and values for some moment of the molecular weight distribution ($M_n$ or $M_w$) are used in equation 1 on an empirical basis to determine $K$ and $a$. This allows for the correlation of viscosity to molecular weight, though corrections need to be applied for samples with polydispersity much different from the correlation standards (56). Representative values using $M_w$ from relatively narrow polydispersity fractions in decalin at 135°C are $K = 2.38 \times 10^{-4}$, $a = 0.725$ (57) and $K = 1.0–1.10 \times 10^{-4}$, $a = 0.80$ (58,59), and in tetralin at 135°C are $K = 9.42 \times 10^{-5}$, $a = 0.784$ (60). A common industrial measure of molecular weight is the melt-flow rate (MFR) (ASTM D1238), which is related to the melt viscosity. The MFR technique measures the amount of molten polymer extruded by a standardized apparatus in 10 min. Higher MFR values are obtained for lower molecular weight polymer. The breadth of the molecular weight distribution (polydispersity) has a large effect on polymer properties. Rheological measurements, including the steady-state compliance, can be very sensitive to higher moment components (62) important in flow processes.

The molecular structure of PP can be further modified by the introduction of comonomers during the polymerization process, most commonly ethylene or butene. This comonomer incorporation greatly expands the property range of PP. Table 3 illustrates the broad range of copolymer microstructures possible for the specific case of propylene–ethylene copolymerization. Similar to the case of stereoregular defects in PP homopolymer, comonomer defects introduced into “random” PP copolymers (PP-RACO) can show an interchain composition distribution depending on the catalyst and process. In some cases it can be advantageous, in terms of quality and the process conditions, to achieve a homogeneous distribution of the comonomer molecules. Metallocene catalysts show a greater tendency for homogeneous comonomer incorporation (4). In this case, each chain, regardless of length, contains the same percentage of comonomer. Impact-modified
Table 3. Propylene–Ethylene Copolymerization Microstructure

<table>
<thead>
<tr>
<th>Microstructure</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPPPPPPPPPPPPPPP (PP)</td>
<td>Homopolymer polypropylene</td>
</tr>
<tr>
<td>PPPEPPPPPPPEPPPP (PP-RACO)</td>
<td>Polypropylene randomly modified with ethylene</td>
</tr>
<tr>
<td>PPPPPPPPP + EPEEPEP (PP-EPR)</td>
<td>Impact-resistant polypropylene</td>
</tr>
<tr>
<td>PPPPP + EPEP + EEEE (PP-EPR + PE)</td>
<td>Impact-resistant polypropylene (with polyethylene</td>
</tr>
<tr>
<td>EPEPPEEPEPEPEPE (EPR)</td>
<td>Ethylene–propylene rubber (elastomer)</td>
</tr>
<tr>
<td>EEEPEEEEEEEPEEEE (PE-RACO)</td>
<td>Polyethylene randomly modified with propylene</td>
</tr>
<tr>
<td>EEEEEEEEEEEEEEE (PE)</td>
<td>Homopolymer polyethylene</td>
</tr>
</tbody>
</table>

*P = propylene, E = ethylene.

“copolymers” (PP-EPR) are better described as polymer blends or alloys. The composition of the PP-EPR formulations varies over a wide range in industrial practice. However, a typical formulation would contain 60–90% homopolymer (or PP-RACO) and 10–40% ethylene–propylene copolymer rubber (EPR) with ethylene concentration of 30–60%. The EPR component has a lower glass-transition temperature ($T_g$), lower crystallinity, and typically exists as a separate phase. PP-EPR formulations were first produced by mechanical blending of two components. Today they are commonly synthesized directly in a multistage process to obtain better economics, and often better distribution of the elastomeric phase in the polypropylene matrix and thus better quality. In some cases polyethylene is present as a third phase. The characterization of PP copolymers is often complicated by the multiplicity of structural species present. An in-depth characterization requires knowledge of the distributions of molecular weight and composition. Different solvent fractionation techniques are combined, and each fraction is analyzed. Composition is most frequently determined by solution $^{13}$C NMR, by IR, or inferred from secondary measurements which probe melting behavior, crystallinity, or glass-transition temperature.

**Morphology**

**Crystallography and Polymorphism.** The stereochemistry of PP plays a critical role governing the packing of chains in the crystalline regions of the morphology. Figure 3 shows the wide-angle X-ray scattering (WAXS) patterns of iPP, sPP, and aPP (23). The regular molecular structure of iPP and sPP readily enables crystallization of the chains, leading to well-defined crystalline reflections differing in unit cell symmetry. aPP lacks a regular molecular structure, and does not crystallize. This leads to a very broad and diffuse scattering from X-rays. The iPP chain adopts a helical conformation in the crystalline unit cell, as shown in Figure 4 (63). The helix repeats itself after three monomeric units, with an identity period of 0.65 nm. Four helical arrangements are possible by right- or left-handed rotation about the central axis with unique (non-identical) “up” and “down” inclinations independent of the handedness (23,64,65). The dominant
crystallographic form for iPP is the $\alpha$-form. The elementary unit cell of $\alpha$-form iPP is monoclinic, containing 4 chains and 12 monomeric units with specific packing of helical arrangements. Crystallographic densities are generally in the range of 0.936–0.946 gm/cm$^3$. Representative cell constants are given in Table 4, and have been reviewed elsewhere (23). The helical conformation of sPP differs from that of iPP, and has an identity period of 0.74 nm. The elementary unit cell of the most stable crystallographic form of sPP is orthorhombic, containing 4 chains and 16 monomeric units with specific packing of helical arrangements (23,64,66–69). The crystallographic density is 0.930 gm/cm$^3$. Representative cell constants are given in Table 4 (69).

Table 4. Unit Cell Constants of Polypropylene

<table>
<thead>
<tr>
<th>Cell constants</th>
<th>Isotactic$^a$</th>
<th>Syndiotactic$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit cell</td>
<td>monoclinic</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>$a$, nm</td>
<td>0.664</td>
<td>1.45</td>
</tr>
<tr>
<td>$b$, nm</td>
<td>2.084</td>
<td>1.12</td>
</tr>
<tr>
<td>$c$, nm</td>
<td>0.651</td>
<td>0.74</td>
</tr>
<tr>
<td>$\beta$</td>
<td>99.0°</td>
<td>90°</td>
</tr>
</tbody>
</table>

$^a$Averages from literature compilation of P2$_1$/c space group symmetry refinements (23).

$^b$From Ref. 69.
Both iPP and sPP exhibit polymorphism, which is the tendency to crystallize into different crystallographic forms depending on crystallization conditions. In iPP, the dominant form is the $\alpha$-form. Other forms include the $\beta$-, $\gamma$-, and mesomorphic (smectic) forms. All of these crystalline forms maintain the same helical conformation with 0.65 nm repeat distance, but differ in unit cell symmetry, interchain packing, and structural disorder. The mesomorphic form is formed by rapid quenching conditions, and has important property implications, particularly in film and fiber applications. Crystallographically, the mesomorphic form has disordered interchain packing relative to the other polymorphic unit cell symmetries (65,70,71). The mesomorphic form converts rapidly to the $\alpha$-form on heating (23). Formation of the $\beta$-form results from the addition of specific nucleators and additives, specific crystallization conditions, crystallization under controlled temperature gradients, and in some cases crystallization under shear (20). The $\beta$-form has lower unit cell density, higher rate of crystallization, and lower apparent melting point relative to the $\alpha$-form which

Fig. 4. Chain conformation of isotactic polypropylene (iPP).
is due, in-part, to its unique crystallography (64,72,73). The \( \gamma \)-form is rarely observed in pure form in commercially significant homopolymer from Ziegler–Natta catalysts under typical processing conditions. A variety of conditions for \( \gamma \)-form formation are outlined below (23). The \( \gamma \)-form occurs in low molecular weight fractions, homopolymer from some homogeneous (metallocene) catalysts (74–76), random copolymers, random copolymer and metallocene homopolymer at high crystallization temperature (76), samples with high stereoblock content, and homopolymer crystallized at high pressure (77). Crystal structure refinements suggest that \( \gamma \)-form iPP has nonparallel chains (64,65,78–81), a conclusion not previously cited in polymeric crystal structure. Because of its importance, further discussion of iPP morphology is restricted to the \( \alpha \)-form of iPP.

\( \text{sPP} \) also exhibits polymorphism (23,64,66–69,82,83). Polymorphism is related to both the intrachain conformation and interchain packing. Crystallization at lower temperature can lead to defect structures relative to the unit cell symmetry of the dominant form (66–68,84–86). Other unit cell variations are formed from \( \text{sPP} \) with low syndiospecificity (87,88), as-polymerized \( \text{sPP} \) (89–92), \( \text{sPP} \) copolymers (92), oriented \( \text{sPP} \) (23,87,93), \( \text{sPP} \) crystallized at low temperature (94,95), and nonhelical structures associated with cold drawing (87,96) and exposure of cold drawn samples to solvent vapor (97).

**Crystallinity.** The degree of crystallinity varies between 0 for a completely amorphous material (such as \( \text{aPP} \)) and 1 for a completely crystalline material. As with most semicrystalline polymers (qv), the degree of crystallinity plays a critical role in determining properties of PP. Commonly measured properties such as modulus, yield stress, oxygen and moisture barrier resistance, and hardness, to name a few, all increase with increasing crystallinity. In iPP (and \( \text{sPP} \)) tacticity is a critical factor influencing the crystallinity (23,47,98). This is due to the role of stereo defects in disrupting the length of the crystallizable isotactic sequences. Details of the interchain tacticity distribution affect not only the crystallinity at room temperature, but also the partial melting behavior (and hence crystallinity) at elevated temperature, influencing hot drawing characteristics. Solvent fractionation techniques, which separate the interchain tacticity distribution of the whole iPP homopolymer into fractions of varying tacticity, show that the lower tacticity fractions have lower crystallinity (47). With metallocene catalysts (4,18,30), PP chain microstructure can now be varied continuously with decreasing isospecific sequencing from iPP (stiff thermoplastic) to \( \text{aPP} \) (very low modulus lacking dimensional integrity) to \( \text{sPP} \) (stiff thermoplastic) correlating to changes of either isotactic or syndiotactic crystallinity. The crystallinity of \( \text{sPP} \) is less than that of iPP with currently available catalysts. In addition to tacticity, crystallinity generally increases with decreasing molecular weight (increased chain mobility), and is promoted by slower cooling rates from the melt. It should be emphasized that the crystalline fraction of perfectly isotactic PP is still much less than unity because of the long-chain nature. Copolymerization (PP-RACO in Table 3) is also used to modify the polymer crystallinity in a controlled manner. In this case, the comonomer is the source of irregularity in the polypropylene chain. The introduction of comonomer decreases crystallinity, reduces stiffness and melting temperature, and increases impact resistance (99).
The degree of crystallinity is determined by a number of analytical techniques based on different criteria (see Crystallinity Determination). The most widely used are fractional solubilization (previously discussed), density determination, X-ray diffraction, and thermal analysis. The density of iPP in the α-form varies between the limit of 100% amorphous \((\rho_a=0.850 \text{ to } 0.855 \text{ g/cm}^3)\) and 100% crystalline \((\rho_c=0.936 \text{ to } 0.946 \text{ g/cm}^3)\) (20). In this way, the measured mass density \(\rho\) gives a measure of the crystallinity. Values of \(\rho\) are most often measured by the density gradient technique (ASTM D1505-85). Similarly, dilatometric methods are used to measure variations of density as a function of temperature (100). X-ray diffraction (101) is also widely used to determine PP crystallinity. Figure 3 shows the contributions of the crystalline scattering and amorphous scattering in the unoriented pattern of the α-form of iPP. The shaded region represents the area attributable to the noncrystalline fraction. From the relationship of the peak area to the total area, crystallinity can be evaluated by a number of numerical means (101). Orientation complicates the analysis (101). Differential scanning calorimetry (DSC) provides useful information on PP structure by the determination of related parameters, such as transition temperature, heat of fusion, crystallization temperature, and others. The crystalline fraction is given by the ratio of the measured heat of fusion to the value for 100% crystalline material (see Thermodynamic Properties of Polymers). The shape of the melting curve gives information on the melting distribution.

**Lamellar and Spherulitic Morphology.** The crystal habit of iPP quiescently crystallized from the melt, like other semicrystalline homopolymers, is that of folded chain lamellae (Fig. 5). The lamellar thickness \((\ell_c)\) increases with increasing crystallization temperature, and is generally in the range of 5–20 nm for iPP. iPP in the α-form exhibits a tendency, unique among semicrystalline polymers, to form a “cross-hatched” pattern (23,64). Radial lathlike lamellae coexist with “cross-hatched” tangential lamellae oriented nearly orthogonal to the radial direction. This homoepitaxy (102–107) is related to the relatively modest mismatch between the c- and a-axis unit cell parameters (Table 4), and the detailed molecular aspects have been reviewed (64). Spherulites are larger scale aggregates made up of the smaller scale lamellar building blocks. Depending on the...
crystallization conditions, the dimensions of spherulites can vary from a few micrometers to 100 \( \mu \text{m} \), or larger. In the \( \alpha \)-form of iPP, there is a strong link between lamellar and spherulitic morphologies. The \( \alpha \)-form iPP spherulites have been classified according to different optical characteristics in cross-polarized light (106,108,109). The optical characteristic is highly sensitive to crystallization temperature and resin type, and has been linked to the lamellar morphology through the balance of cross-hatched radial and tangential lamellae (23,103,104,106,109,110). Optical and mechanical properties depend on the dimension and number of spherulites, which can be modified with nucleating agents that act as crystallization centers. Optical properties (such as clarity) improve with decreasing spherulite size. The borders among spherulites can represent weak zones (111), with large spherulites adversely affecting properties such as impact. Unlike iPP, pronounced cross-hatched lamellar morphologies in bulk crystallized material appears limited in sPP (112,113). As with iPP, well-developed small-angle X-ray (SAXS) long spacings, characteristic of well-developed lamellar morphologies, are observed for sPP of high syndiospecificity (113–116). In general terms, spherulite formation in as-polymerized metallocene-based sPP tends to be more restricted than in iPP (117–119), and the spherulite-scale morphologies are generally smaller than in iPP in bulk-crystallized specimens. Spherulitic growth rate measurements have been summarized (120), with rates lower than those of Ziegler–Natta iPP (113). Unique morphologies (relative to iPP) are observed in sPP with special preparation procedures, including a transition from single-crystal-like entities to spherulitic structures on cooling (68,117–119).

**Macromorphology and Processing Relationships.** Other morphologies in iPP include the macroscopic phase morphologies in multiphase structures such as rubber-modified iPP (an example being PP-EPR in Table 3), and additional morphologies associated with the specific method of polymer processing. Unique morphologies and structure/processing relationships are associated with fiber, film, and injection molding processes to name a few. In parts formed by the injection molding process, pronounced morphological gradients exist in a processed part which can be crudely partitioned into highly oriented skin layers (near the mold surface) and less oriented core layers (near the part center). These layers can approach macroscopic dimensions (\( \sim \text{mm} \)) depending on the part geometry, resin, and molding conditions. The properties of moldings can often be correlated to the orientation and crystallinity of the part (23,121). A literature review of more detailed aspects of the morphology of iPP injection moldings is available (23). In mixtures of iPP homopolymer and EPR (PP-EPR in Table 3), the two components are generally immiscible in the melt. In the solid state, the rubber has low glass-transition temperature \( T_g \) and imparts impact resistance to the blend. The effectiveness of the rubber phase as an impact modifier depends critically on the dispersion (particle size). The dispersion is a complex function of (1) matrix and rubber phase composition, (2) viscosity ratio of matrix and dispersed phases, (3) compounding history, and (4) melt deformation history during fabrication of the final processed part (23). In impact-modified copolymers for injection molding applications, the dimension of the dispersed rubber phase in the core (reduced melt deformation) is typically on the order of 0.5–2 \( \mu \text{m} \) in formulations with optimal impact performance. Near the surface of moldings (high melt deformation), highly anisotropic dispersed phase morphologies can be observed.
depending on blend composition. Generally rubber phase dispersion worsens (increased phase size) with increasing melt temperature and melt time prior to molding due to coalescence.

High speed melt spinning of fibers represents another of the most common processing methods for iPP. The final morphology results from the complex interrelationships of polymer structure (polydispersity, molecular weight, tacticity) and processing conditions (melt temperature, melt throughput, spinnerette design, spin speed, cooling rate). For high spinning speeds, the orientation of melt-spun fibers greatly exceeds that of injection-molded parts. The orientation of crystalline regions is greater than the non-crystalline regions (122). As the spinning speed increases, orientation increases. The orientation can be further increased with post-spinning drawing operations (122). As with unoriented material, the as-spun fiber shows alternating crystalline and amorphous regions on lamellar size scales (10–30 nm), but generally smaller than hot-drawn articles. This periodicity is highly oriented along the fiber axis, and characterized by a high fraction of tie molecules (the same chain passing through several crystalline regions).

Drawn film, and more specifically biaxially oriented polypropylene (BOPP) film, is another of the most common fabrication methods (see Films, Manufacture; Films, Orientation). During BOPP film formation, a cast sheet of iPP is drawn below the melting point in two directions. This drawing process creates a film of useful dimension while imparting desired properties such as barrier and stiffness. These properties are related to the imposed orientation during drawing. During unidirectional drawing of semicrystalline polymers at elevated temperature, the initial spherulitic morphology of the cast sheet is transformed to an oriented fibrillar morphology (122–125). The yielding process, during which the lamellar crystallites are disrupted, is strongly correlated to the crystallinity at the draw temperature. As with melt-spun fibers, the orientation of the crystalline regions is greater than that of the noncrystalline regions (122). Orientation is generally much higher than in injection moldings. For BOPP, the molecular orientation is dominated by the transverse orientation stage for sequentially oriented film (126), and tends to be planar (126, 127) for both sequential and simultaneous oriented film. Generally, the lamellar crystals in the initial as-cast sheet are highly disrupted in the final BOPP film.

**Polymerization Particle Morphology.** Morphological control of as-polymerized polymer particles influences the polymerization process. Aspects of the particle morphology include the shape, size, size distribution, and porosity. Control of particle morphology is also a critical concern to technologies which utilize the as-polymerized particle in subsequent polymerization processes (128). Because of the replication phenomenon (129–137), the morphological characteristics are strictly dependent on the catalyst. The catalyst reproduces its shape in the polymer on an obviously greater scale according to its activity. The activity is the quantity of polymer produced by a unit of catalyst.

The replication phenomenon of iPP polymerization from magnesium chloride supported Ziegler–Natta catalysts is illustrated in Figure 6. The polymer particle has the same shape as the catalyst particle, although its diameter is approximately 20–100 times larger. The growth of the polymer particle during polymerization has been extensively modeled (129–137). In the multigrain model (131–135, 137), the
Fig. 6. Ziegler–Natta catalyst particle (a) and corresponding polymer particle (b).

catalyst undergoes fragmentation into microparticles evenly distributed within the macroscopic particle due to forces exerted by the growing polymer layers. In Ziegler–Natta catalysts, fragmentation occurs at very low polymer yields (137–139), which provides a large active surface from the beginning of polymerization. The growth of the macroparticle results from the cumulative uniform expansion of microparticle layers. Although the actual morphology of Ziegler–Natta polymerized particles shows a more complicated hierarchy than the “two-level” approach of the multigrain model, a key feature is the replication of the porous spherical catalyst morphology into a porous spherical polymer particle during polymerization. In practice, a careful morphological analysis of the polymerization particle requires, beyond microscopic investigations, analyses of particle size distribution (ASTM D1921-96), poured bulk density (ASTM D1895-96, Method A), and pourability (ASTM D1895-96, Method A).

Thermodynamic Properties

Melting. The melting point of \( \alpha \)-form iPP is strongly influenced by the stereoregularity (19,23,47,99,140–144) and regioregularity (4,33,34,145,146). Melting point increases with improved regularity. \( T_m^0 \) is the theoretical equilibrium melting point of a perfect and infinitely large crystal. This value exceeds experimentally observed melting points because of kinetic effects leading to small crystal size (23) (Fig. 5). The value of \( T_m^0 \) is sensitive to stereoregularity. However, the value for 100% isotactic material is not expected to differ significantly from that of highly isotactic commercial materials (23). For highly regular materials, literature summaries of \( T_m^0 \) suggest that values of 185–188°C seem reasonable (23), though there remains disagreement in the literature (147). Melting points in the 160–168°C range are typical for commercial homopolymer samples under normal analysis conditions. Introduction of comonomer (ethylene, butene, and higher \( \alpha \)-olefins) reduces the melting point, and can vanish at intermediate compositions.
as the material approaches an amorphous rubber (Table 3). Literature summaries of the heat of fusion of 100% crystalline material, $\Delta H^0$, generally lie in the range of 148–209 J/g (23). The most often applied values are clustered around 165 J/g (77,140,148,149) and 209 J/g (150,151).

As with iPP, the melting point of sPP is highly sensitive to stereoregularity. While comparison of $T_m^0$ for 100% syndiotactic sPP is ambiguous, with current catalysts and in current commercial sPP materials, the observed melting point is generally less than that of Ziegler–Natta iPP under practical crystallization conditions when compared at comparable stereospecificity (23). This difference is often of the order of 10–15 °C. Introduction of comonomer also reduces the melting point of sPP. Syndiospecific copolymerization with butene has the unique feature of being crystalline at all compositions because of the similarity of crystal structures of sPP and syndiotactic polybutene (152). Literature summaries of $\Delta H^0$ lie in the range of 105–190 J/gm (23). Values in the lower end of this range agree with extrapolated heats of fusion versus density (23) and X-ray crystallinity (116).

Glass-Transition Temperature. The value of the glass transition (qv) temperature ($T_g$) is dependent on the crystallinity of the polymer, the molecular weight, and the measurement techniques used. DSC measurements of $T_g$ for high molecular weight aPP and sPP are generally similar and usually close to 0 °C. The DSC glass-transition temperature in highly stereospecific iPP is often difficult to distinguish because of the high crystallinity. Transition temperatures are generally in the range of −13 to 0 °C. Other techniques, such as dynamic mechanical analysis, are often more sensitive to the $T_g$ of iPP. Copolymerization with ethylene reduces the glass-transition temperature. Figure 7 shows DSC measured $T_g$ values of propylene/ethylene copolymers prepared with an aspecific catalyst. In this case, all samples are noncrystalline and not affected by crystallinity. A similar trend is generally observed for isospecific and syndiospecific catalysts as well. Copolymerization with butene is less effective at lowering the $T_g$.

Heat Capacity and Thermal Expansion. Extensive tabulations of the extrapolated heat capacities of crystalline and amorphous iPP as a function of temperature are available (147). The specific volume (153) and heat capacity (154) of iPP in the melt as a function of temperature and pressure, and typical thermal expansion coefficients in the solid state as a function of temperature (151) are also reported.

Chemical Properties

iPP is soluble in high boiling aliphatic and aromatic hydrocarbons at high temperature. sPP shows solubility at lower temperature and in lower boiling hydrocarbons. aPP shows the highest solubility of the three forms. Extensive chemical resistance data is available for iPP (155). The high chemical resistance of iPP results in exceptional stain resistance, and has led to the use of iPP in automobile batteries (156). iPP has outstanding resistance to water and other inorganic environments (155). iPP resists most strong mineral acids and bases, but like other polyolefins is subject to attack by oxidizing agents including 98% sulfuric acid and 30% hydrochloric acid at high temperature (~100 °C), and fuming nitric acid (ambient temperature) (155). Inorganic chemicals produce little or no effect over
Fig. 7. Glass-transition temperature ($T_g$) versus ethylene concentration in propylene–ethylene random copolymer using aspecific catalyst (no crystallinity). Values were determined by differential scanning calorimetry (DSC).

a period of 6 months at temperatures up to 120°C (155). For organic media, absorption is greater for higher temperatures and decreased polarity, and is higher in copolymers than in homopolymer.

PP reacts with oxygen in several ways, causing chain scission and brittleness that is associated with the loss in molecular weight. This action is promoted by high temperatures, light, or mechanical stress. A wide variety of stabilization packages are added for protection, depending on the application (157).

The reactivity of iPP can also be usefully exploited. For example, treatment with peroxides has led to controlled rheology resins (61,158,159) with reduced molecular weight and narrow polydispersity relative to as-polymerized product from Ziegler–Natta catalysts. For a fixed final melt-flow rate (MFR), lower precursor MFR gives narrower polydispersity. These resins are used in some fiber-spinning and injection-molding applications. The creation of radical sites along the polymer backbone, most often through peroxide-based initiation, is also an essential condition for many functionalization/grafting chemistries. The functionalization chemistry of post-polymerized iPP has been extensively reviewed (160). The focus has been on the incorporation of polar functional groups into the polymer chain and/or the graft polymerization of monomers which are generally incompatible with Ziegler–Natta catalysts. The incorporation of polar functionality has been sought to improve paintability, printability, and metal adhesion characteristics (important to coatings); to act as coupling agents in composites such as glass-reinforced iPP; to improve oxygen barrier resistance; and to act as compatibilizers in polymer alloys. Recent advancements in metallocene and
related transition metal catalysts are showing promise for the direct copolymer-
ization of polar monomers with ethylene and propylene (161). Other chemical
modifications include plasma and acid treatment technologies.

Radiation chemistry of PP has been extensively reviewed (162). Under suit-
able conditions, radiation treatment can lead to desirable branching reactions
(163) with rheological characteristics favorable for thermoforming, foaming, blow
molding, and extrusion coating. Resistance to radiation sterilization is an impor-
tant requirement in some medical applications, and requires specialized formulation
and stabilization packages.

Physical Properties

A vast number of PP grades are sold in the United States, including homopolymers
with varying molecular weight (melt-flow rate) and tacticity, filled grades, grades
with varying stabilization packages, and grades which incorporate comonomers
with varying architecture (Table 3). The basic categories of iPP polymers are ho-
momomers, random copolymers, impact or heterophasic copolymers, and filled
polymers. A number of grades are approved for food contact (164). Many poly-
mers carry a UL94 flammability class HB rating (164), and some specialized for-
mulations have improved ratings. Additional specialty grades include nucleated
polymers for improved clarity and mechanical properties, radiation-resistant for-
mulations, chemically visbroken “controlled rheology” grades (61,158,159), high
melt strength grades, and a large number of formulations with specialized additive
functions including slip agents, antiblocking agents, antistats, and pigments
to name a few (157). Standardized test methods such as ASTM or ISO are used in
commercial specifications. The properties that distinguish iPP from high density
polyethylene are high heat distortion temperature, stiffness, hardness, and lower
density.

Properties of various homopolymer grades are given in Table 5. In this
table, polymer molecular weight and polydispersity is tailored to give the best
processing characteristics for each fabrication process. The polymers shown in
Table 5 are produced by direct polymerization. Higher melt flow grades, and
“controlled rheology” grades with narrow polydispersity, can be important in
other applications, including fibers. Narrow polydispersity resins can also be
produced by metallocene catalysts (4). These catalysts can also produce iPP
with a narrow interchain tacticity distribution and low levels of extractables.
High crystallinity (tacticity) grades, and high polydispersity grades, provide
additional stiffness and higher heat distortion temperature in injection molding
applications (23,120,166,167). Properties of selected random copolymer grades
are given in Table 6. These copolymers have ethylene as the comonomer,
although butene copolymerization is also possible. The stiffness of these poly-
mers is lower than that of homopolymers. The impact resistance is improved,
particularly at refrigeration temperatures. Clarity is also enhanced. The low
melting point allows the use of some copolymer grades as sealant layers in
PP films. Properties of impact-resistant, or heterophasic, copolymers are given
in Table 7. Much of this class of material is used in injection-molding applications,
Table 5. Properties of Polypropylene Homopolymers

<table>
<thead>
<tr>
<th>Melt flow, (g/10 min)</th>
<th>Tensile strength, Mpa&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Elongation, % (ASTM D638)</th>
<th>Flexural modulus 1% secant, Mpa&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Deflection temperature at 455 C, kPa&lt;sup&gt;d&lt;/sup&gt;</th>
<th>Notched Izod impact at 23 C, J/m&lt;sup&gt;e&lt;/sup&gt;</th>
<th>Rockwell hardness, R</th>
<th>Products/Applications</th>
</tr>
</thead>
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<tr>
<td>0.5</td>
<td>33</td>
<td>13</td>
<td>1200</td>
<td>96</td>
<td>81</td>
<td>86</td>
<td>Extrusion, sheet, profiles</td>
</tr>
<tr>
<td>4</td>
<td>34</td>
<td>12</td>
<td>1400</td>
<td>93</td>
<td>39</td>
<td>86</td>
<td>Injection molding, general-purpose</td>
</tr>
<tr>
<td>12</td>
<td>34</td>
<td>10</td>
<td>1400</td>
<td>92</td>
<td>35</td>
<td>88</td>
<td>Injection molding, general-purpose</td>
</tr>
<tr>
<td>22</td>
<td>36</td>
<td>10</td>
<td>1500</td>
<td>93</td>
<td>34</td>
<td>93</td>
<td>Injection molding, general-purpose, thin wall</td>
</tr>
<tr>
<td>35</td>
<td>32</td>
<td>12</td>
<td>1200</td>
<td>95</td>
<td>32</td>
<td>89</td>
<td>Controlled rheology injection molding, thin-wall</td>
</tr>
</tbody>
</table>

<sup>a</sup>Ref. 165.

<sup>b</sup>At yield.

<sup>c</sup>To convert Mpa to psi, multiply by 145.

<sup>d</sup>To convert kPa to psi, multiply by 0.145.

<sup>e</sup>To convert J/m to ft-lbf/in., divide by 53.38.
<table>
<thead>
<tr>
<th>Melt flow, (g/10 min) (ASTM D1238)</th>
<th>Tensile strength, $a$ (ASTM D638)</th>
<th>Elongation, $c$ (ASTM D638)</th>
<th>Flexural modulus $b$ (ASTM D790A)</th>
<th>Deflection temperature at 455 secant, @ C (ASTM D648)</th>
<th>Notched Izod Impact at 23 $^\circ$C (ASTM D256A)</th>
<th>Products/Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>28</td>
<td>13</td>
<td>940</td>
<td>79</td>
<td>330</td>
<td>High clarity blow molding, extrusion, thermoforming</td>
</tr>
<tr>
<td>6.5</td>
<td>28</td>
<td>13</td>
<td>920</td>
<td>76</td>
<td>56</td>
<td>High clarity cast film</td>
</tr>
<tr>
<td>11</td>
<td>30</td>
<td>13</td>
<td>1000</td>
<td>84</td>
<td>66</td>
<td>High clarity injection molding and injection-stretch blow molding</td>
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<tr>
<td>35</td>
<td>28</td>
<td>13</td>
<td>940</td>
<td>83</td>
<td>140</td>
<td>Controlled rheology high clarity injection molding</td>
</tr>
</tbody>
</table>

$^a$Ref. 165

$^b$Based on ethylene comonomer.

$^c$At yield.

$^d$To convert Mpa to psi, multiply by 145.

$^e$To convert kPa to psi, multiply by 0.145.

$^f$To convert J/m to ft-lbf/in, divide by 53.38.
<table>
<thead>
<tr>
<th>Melt flow, (g/10 min) ASTM D1238</th>
<th>Tensile strength, Mpa&lt;sup&gt;a&lt;/sup&gt; ASTM D638</th>
<th>Elongation, % ASTM D638</th>
<th>Flexural modulus 1% secant, Mpa&lt;sup&gt;b&lt;/sup&gt; ASTM D790A</th>
<th>Deflection temperature at 455 C, kPa&lt;sup&gt;c&lt;/sup&gt; ASTM D648</th>
<th>Notched Izod Impact at 23 °C, J/m&lt;sup&gt;e&lt;/sup&gt; ASTM D256A</th>
<th>Products/Applications</th>
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<td>1100</td>
<td>88</td>
<td>No break</td>
<td>Extrusion</td>
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<td>1200</td>
<td>90</td>
<td>270</td>
<td>Injection molding medium impact</td>
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<td>8</td>
<td>1200</td>
<td>90</td>
<td>110</td>
<td>Injection molding medium impact</td>
</tr>
<tr>
<td>35</td>
<td>27</td>
<td>6</td>
<td>1400</td>
<td>100</td>
<td>70</td>
<td>High flow injection molding and thin-wall medium impact</td>
</tr>
<tr>
<td>50</td>
<td>26</td>
<td>6</td>
<td>1200</td>
<td>107</td>
<td>42</td>
<td>High flow injection molding and thin-wall medium impact</td>
</tr>
<tr>
<td>4</td>
<td>21</td>
<td>8</td>
<td>1000</td>
<td>81</td>
<td>No break</td>
<td>Extrusion and injection molding high impact</td>
</tr>
<tr>
<td>8</td>
<td>26</td>
<td>8</td>
<td>1200</td>
<td>87</td>
<td>100</td>
<td>Blush-resistant injection molding medium impact</td>
</tr>
<tr>
<td>22</td>
<td>24</td>
<td>7</td>
<td>1000</td>
<td>83</td>
<td>100</td>
<td>Blush-resistant controlled rheology injection molding medium impact</td>
</tr>
<tr>
<td>12</td>
<td>22</td>
<td>8</td>
<td>900</td>
<td>82</td>
<td>340</td>
<td>Blush-resistant injection molding high impact</td>
</tr>
</tbody>
</table>

<sup>a</sup>Ref. 165
<sup>b</sup>Based on ethylene comonomer.
<sup>c</sup>At yield.
<sup>d</sup>To convert Mpa to psi, multiply by 145.
<sup>e</sup>To convert kPa to psi, multiply by 0.145.
<sup>f</sup>To convert J/m to ft·lbf/in, divide by 53.38.
providing impact resistance well below 0°C. Copolymers containing high flexible product. Mineral fillers, such as talc or calcium carbonate, and other reinforcements such as glass fiber or mica, increase the stiffness and heat-distortion temperature. Some properties of mineral-filled iPP are given in Table 8. Filled formulations based on impact copolymers (PP-EPR) are also common.

Catalysts for Polymerization

**TiCl₃-Based Catalyst.** Isotactic polypropylene was first synthesized by Natta in 1954 by employing a system consisting of TiCl₄ and Al(C₂H₅)₃ activator (169–174). It was based on Ziegler's catalyst system (175), which was used for the polymerization of ethylene. Only 30–40% of the polypropylene produced by Natta’s catalyst had the typical characteristics of isotactic polypropylene; for example, it was insoluble in boiling heptane and had a melting point of about 165°C. The remaining product was atactic with poor structural uniformity and a rubbery consistency. Natta quickly realized that the polymer isotacticity was directly connected to the uniformity of the catalyst surface. Thus for the polymerization of propylene, he employed solid crystalline TiCl₃ (obtained by the reduction of TiCl₄) (176) with Al(C₂H₅)₂Cl or Al(C₂H₅)₃ and obtained a higher percentage of isotactic product (see ZIEGLER-NATTA CATALYSTS).

The various TiCl₃ structural forms, α, β, γ, and δ, were identified in subsequent studies (177); the δ-form, in combination with Al(C₂H₅)₂Cl, gave the best results. The high polymer isotacticity (ca 90%) permitted a scaled-up industrial process by Montecatini, which had supported Natta's research at the Politechnic in Milan. This first plant (and subsequent others) contained a large section for the separation of the undesirable atactic fraction from the isotactic fraction and a section for the removal of catalyst residues that affected product quality. Substantial progress was achieved in a short time (178,179).

Hercules discovered the role of hydrogen as a molecular weight regulator (180). Esso improved performance by using AlCl₃ in TiCl₃ solid solution instead of pure TiCl₃ (181). Mitsubishi increased isotacticity to 92–94% by adding an electron donor, such as carboxylic acid ester, to the TiCl₃ (182).

The treatment of the TiCl₃ produced from the reaction between TiCl₄ and Al(C₂H₅)₂Cl, first with the electron donor, diisoamyl ether, and then with TiCl₄, gave a highly stereospecific catalyst. This catalyst system was four to five times more active than δ-TiCl₃ (183) and capable of producing a polymer with narrow particle size distribution. This system can be referred to as the second-generation catalyst (Table 9). However, the catalyst yield was still insufficient to reduce catalyst residues enough to eliminate the deashing step in the production process.

In the meantime it was established that only a small percentage of the titanium on the catalyst was actually active. The active titanium was located on the lateral faces and edges, and along the crystal defects (184). This led to the realization that much of the catalyst mass acted as the support (185). Decisive progress could be achieved by depositing the active Ti on a support whose residues, unlike those of TiCl₃ would not be detrimental to polymer properties.

**MgCl₂-Supported Catalysts.** Magnesium chloride, in the active form as a support (186,187), increases catalyst yield and allows for the simplification of the
Table 8. Properties of Filled Homopolymer*

<table>
<thead>
<tr>
<th>Melt flow, g/10 min</th>
<th>Tensile strength, b Mpa</th>
<th>Elongation, b % (ASTM D638)</th>
<th>Flexural modulus, 1% secant, Mpa</th>
<th>Deflection temperature at 455 C, kPa</th>
<th>Izod Impact at 23 C, J/m</th>
<th>Rockwell hardness, R</th>
<th>Products/Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>34</td>
<td>12</td>
<td>1400</td>
<td>93</td>
<td>39</td>
<td>86</td>
<td>Injection molding homopolymer, general-purpose</td>
</tr>
<tr>
<td>3</td>
<td>83</td>
<td>—</td>
<td>4500</td>
<td>157</td>
<td>85</td>
<td>—</td>
<td>20% glass filled homopolymer</td>
</tr>
<tr>
<td>4</td>
<td>31</td>
<td>4</td>
<td>1900</td>
<td>109</td>
<td>37</td>
<td>84</td>
<td>20% talc filled homopolymer</td>
</tr>
<tr>
<td>4</td>
<td>29</td>
<td>4</td>
<td>2900</td>
<td>125</td>
<td>27</td>
<td>94</td>
<td>40% talc filled homopolymer</td>
</tr>
<tr>
<td>4</td>
<td>30</td>
<td>7</td>
<td>1500</td>
<td>96</td>
<td>37</td>
<td>89</td>
<td>20% calcium carbonate filled homopolymer</td>
</tr>
</tbody>
</table>

*aRef. 168.

bAt yield.

cTo convert Mpa to psi, multiply by 145.

dTo convert kPa to psi, multiply by 0.145.

eTo convert J/m to ft·lbf/in, divide by 53.38.

fTangent method.
Table 9. Different Ziegler–Natta Catalyst Generations—Composition, Performance, Morphology and Process Requirements

<table>
<thead>
<tr>
<th>Generation</th>
<th>Composition</th>
<th>Productivity, kg of PP/g of catalyst</th>
<th>Isotactic index</th>
<th>Morphology control</th>
<th>Process requirements</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\delta$-TiCl$_3$·0.33AlCl$_3$ + AlEt$_2$Cl</td>
<td>0.8–1.2</td>
<td>90–94</td>
<td>Not possible</td>
<td>Deashing and atactic removal</td>
</tr>
<tr>
<td>2</td>
<td>$\delta$-TiCl$_3$ + AlEt$_2$Cl</td>
<td>3–5 (10–15)</td>
<td>94–97</td>
<td>Possible</td>
<td>Deashing</td>
</tr>
<tr>
<td>3</td>
<td>TiCl$_4$/ester/MgCl$_2$ + AlR$_2$/ester</td>
<td>5–10 (15–30)</td>
<td>90–95</td>
<td>Possible</td>
<td>None</td>
</tr>
<tr>
<td>4</td>
<td>TiCl$_4$/diester/MgCl$_2$ + AlEt$_3$/silane</td>
<td>10–25 (30–60)</td>
<td>95–99</td>
<td>Possible</td>
<td>None</td>
</tr>
<tr>
<td>5</td>
<td>TiCl$_4$/diether/MgCl$_2$ + AlEt$_3$</td>
<td>25–35 (70–120)</td>
<td>95–99</td>
<td>Possible</td>
<td>None</td>
</tr>
</tbody>
</table>

*Polymerization productivity: hexane slurry, 70 °C, 0.7 MPa, 4 h, with hydrogen for molecular weight control. Values in parentheses are polymerizations performed in liquid propylene at 70 °C for 2 h with hydrogen.

*Only possible with alkyl aluminum reduced TiCl$_3$ to produce a catalyst within a 200–300 µm size.

polymerization process in hydrocarbon slurry with the elimination of the costly deashing step. This discovery and further improvements led to the development of the superactive, third-generation catalysts (188–193) (Table 9). Better yield, higher stereospecificity, and morphology control resulted in simplified processes in which the monomer is the polymerization medium.

Other catalyst systems that are usually soluble in the reaction medium are of high scientific importance but not used industrially. Among these is the system consisting of the product of the reaction of AlR$_2$Cl and Al$_2$R$_2$Cl$_4$ with vanadium compounds. This system is utilized in the production of syndiotactic polypropylene at very low temperature (194,195).

Isotactic polypropylene has been obtained, although with very low yields, from Ti and Zr benzyl compounds (196) and allylic derivatives (197).

Other highly active catalyst systems are based on single-site catalyst, for example ($\eta$-$^5$C$_5$H$_5$)$_2$M(CH$_3$)$_2$; (M = Ti, Zr). These systems will be discussed in more detail in the Homogeneous Catalyst section.

**Heterogeneous Catalyst Preparation.**

*TiCl$_3$-Based Catalysts.* First-generation catalysts are prepared by the reduction of TiCl$_3$ with metallic aluminum in aromatic solvent between 100 and 200 °C (198,199). A solid solution with the composition of AlCl$_3$·3TiCl$_3$ (200) is formed. Milling converts the crystalline TiCl$_3$ from the $\alpha$- to the $\delta$-form, increasing its surface area and radically improving its performance (201); Al(C$_2$H$_5$)$_2$Cl is the best activator. Hydrogen and Zn(C$_2$H$_5$)$_2$ are the molecular weight regulators, but diethyl zinc is rarely used. Typical performance for this type of catalyst is reported in Table 9. Milling produces a catalyst, and thus a polymer, with broad particle size distribution.

A second-generation catalyst (183) is prepared by reducing TiCl$_4$ with Al(C$_2$H$_5$)$_2$Cl in a hydrocarbon at 0 °C. The 3TiCl$_3$·AlCl$_3$ product with surface area
around 1 m²/g thus obtained is washed at 35° C with diisoamyl ether to remove most of the AlCl₃. The product is then treated with TiCl₄ at 65° C and washed with hydrocarbons. The catalyst has a high surface area (up to 150 m²/g). In polymerization with Al(C₂H₅)₂Cl and hydrogen, it gives the average performance shown in Table 9. The polymer has regular shaped, compact particles and narrow particle size distribution, with an average diameter around 300–400 µm. Catalyst activity is maintained by storage under refrigeration.

**MgCl₂-Supported Catalysts.** The scientific and patent literature reports several methods for the preparation of the MgCl₂-supported catalysts of third and superactive third generations. They can be classified as follows:

1. Catalysts obtained by milling mixtures of anhydrous MgCl₂ with an electron donor and a titanium compound (186,187)
2. Catalysts obtained by milling anhydrous MgCl₂ with an electron donor and treated with a titanium compound (TiCl₄) above 80° C, followed by washing with hydrocarbons (188–192)
3. Catalysts obtained by treatment of “active” MgCl₂ with an electron donor and a titanium compound (TiCl₄) under conditions similar to those of the previous case (202)

The second method gives the average results reported in Table 9 with regard to third-generation catalysts. In practice, anhydrous MgCl₂ and an aromatic ester, usually ethyl benzoate (EB) in molar ratios between 2 and 15, are shaken in a vibrating mill containing steel spheres for 20–100 h. The MgCl₂ is activated; that is, it is converted from the crystalline ordered form to the disordered δ-form while the crystallite size is reduced.

The product is treated twice with an excess of TiCl₄ between 80 and 130° C, washed repeatedly with hydrocarbons, and dried. During the treatment with TiCl₄, the base is partially extracted, and TiCl₄ enters the support. The final composition of the solid includes 0.5–3.0 wt% Ti and 5–15% EB; the remainder is MgCl₂. The surface area is in excess of 100 m²/g. The active or δ-form of MgCl₂ resembles the δ-form of TiCl₃ (203). It can also be obtained by direct contact of anhydrous MgCl₂ with Lewis base or by chlorination of magnesium organic compounds (188–192). The degree of activation can be determined by X-ray diffraction (203), where the passage from α to δ gives rise to a widening and lowering of the diffraction peaks. The active form, because of the corners, edges, and surface defects of the crystallites, binds the titanium compound strongly, and repeated washing or treatment under vacuum cannot remove it. This strong binding is attributed to the closeness of the Mg and Ti ionic radii (204) and to the similarity among the crystallographic forms of their halogens. The Ti atoms located in exposed sites give rise to polymerization active centers (205–208). Magnesium chloride may easily interact with electron donors, probably affecting the stereospecificity of the active site. It can be easily transformed into particles with controlled morphology because of the low melting point of its adducts with alcohols or water. These catalysts are used with aluminum trialkyl alone or in blends with chlorinated aluminum alkyls and with a second electron donor, which can be equal to or different from that contained in the solid catalyst.
Heterogeneous Catalyst Evaluation. To evaluate a catalyst system, the following characteristics must be known: yield or productivity, which is the amount of polymer produced per unit of total catalyst or single component; the polymerization kinetics, or yield development with time; stereospecificity; sensitivity to the molecular weight regulator; the molecular weight distribution of the polymer produced; the microtacticity of the resulting polymer; ability to copolymerize; and the final polymer morphology.

To forecast the behavior of a catalyst system in an industrial continuous polymerization, these characteristics should be determined within a wide range of conditions; eg, temperature, concentration, and ratios of the various components (activator, external donor, solid catalyst, etc). A laboratory batch-scale test can provide most of this information. A small, simple reactor suitable for these studies is shown in Figure 8. The polymerization can be carried out in a hydrocarbon or liquid propylene. In some cases the polymerization test can be performed in the gas phase, provided the reactor is prepared with a suitable heat transfer and catalyst dispersing bed (eg, a salt bed).

The stainless steel reactor is provided with a jacket for temperature control in the range ±0.5°C using a steam and chilled water mixture. The reactor contents are agitated by a magnetic stirrer (500–900 rpm). The consumption of the propylene is followed by weighing the vessel from time to time or through gas flow meters.

A test using hexane as diluent is the simplest to perform because it does not require the safety measures required for tests in liquid propylene. It can be carried out as follows.

Fig. 8. Lab-scale polymerization reactor.
The reactor is kept under nitrogen at 40–50°C to exclude oxygen and moisture. Anhydrous, deaerated hexane is introduced followed by a fixed amount of catalyst. The reactor is closed and heated to 60–70°C, and hydrogen and propylene are fed at the desired concentrations. These feeds are maintained for a certain time. Data on the polymerization kinetics are obtained from the mass of propylene fed over time. At the end of the test the temperature is reduced, the reactor degassed, and the slurry (hexane/polypropylene) discharged from the reactor (either through a dip tube or a bottom valve). The polymer is separated from the hexane by filtration or by evaporation. The polymer is dried at 60°C under nitrogen, weighed, and analyzed.

Typical graphs follow which represent the performance of a superactive, third-generation catalyst system as a function of processing variables. The activity is expressed as kilograms polymer per gram catalyst, and the isotacticity as polymer percentage residue from a boiling heptane extraction in a modified Soxhlet extractor for 12 h.

Figure 9 shows the trend of activity for polymerizations in hexane with a propylene concentration of 14% at 70°C; Figure 10 shows the isotactic index. Polymerization temperature, as reported in Figure 11, influences performance; an increase from 50 to 80°C increases both activity and isotacticity. Isotacticity should be between 94 and 98% to meet various application requirements. The ratio between aluminum and electron donor controls stereospecificity. At very high levels of electron donor the activity will be reduced, as shown in Figure 12 (209).

The aluminum compound alkylates the transition metal and can act as a transfer agent. It also removes impurities from the reaction medium (eg, water, CO₂, alcohols), thereby avoiding catalyst poisoning. In addition, aluminum alkyl reduces the transition metal to lower valence, thus affecting its activity (210). In the case of supported catalysts, aluminum alkyl plays a fundamental role by complexing the electron donors (204).

![Fig. 9. Activity vs polymerization time.](image-url)
Polymerization Reaction Mechanisms

The rate $R_p$ of the primary propagation step of monomer to polymer in Ziegler–Natta catalysis is represented by

$$R_p = k_p[C^*][M]$$

where $k_p$ is the propagation constant, $[C^*]$ the concentration of active sites, and $[M]$ the monomer concentration.
Fig. 12. Activity and isotactic index vs Al:donor ratio.

The global polymerization rate changes with time. A period of increasing rate is usually followed by a decline and eventually by a stationary state. The rate decay is often attributed to the change in concentration of active sites in the context of the above noted expression. The initial increase may be due to the progressive activation of new active centers. The deactivation, particularly evident in supported catalysts (211,212), is attributed to variations in both number and chemical nature of the centers (213).

Global polymerization rate and rate of primary propagation are affected by the catalyst system and polymerization conditions (203,214). Effects are due to the chemical and physical structure of the catalyst as well as to the nature of the activator. Important parameters include the ratio between catalyst and activator, and their concentrations, hydrogen concentration, temperature, stirring rate, and type and amount of Lewis base. The effects vary with the polymerization medium; i.e., diluent or the monomer in liquid or gas phase (215–218).

The complexity of the catalyst systems and their heterogeneous nature make an accurate analysis of the parameters associated with the primary propagation step difficult. This is one reason why literature analyses are rarely in agreement; also, the data are obtained by methods and under conditions that are rarely comparable. A typical example is the determination of the concentration of the active sites and the propagation constant, which can be carried out by various methods (chemical, radiochemical) that are not completely reliable. Nonetheless the parameters are valuable in determining catalyst potential and performance.

The same uncertainty is involved in the determination of the activation energy of the propagation reaction and the average lifetime of the polymer chain. A value of 23 kJ/mol (5.5 kcal/mol) for TiCl₃-based catalysts is reported for the former (219). For the latter, values of 360–600 s (220) and 160 s (219) for TiCl₃-based catalysts are reported at 70°C and 5 s (221) for MgCl₂-supported catalysts at 45°C.

A short time after the discovery of Ziegler–Natta catalysts, it was suggested (222,223) that chain propagation occurred by monomer insertion into a Ti–carbon
bond of the catalyst. This bond was considered to be polarized, with a weak negative charge on the carbon atom; this hypothesis is still widely supported today. It was confirmed by IR analysis of chain terminal groups (224) as well as by $^{13}$C enriched aluminum alkyls (225).

In an attempt to provide a model to explain the growth of the polymer chain satisfactorily, several hypotheses have been suggested. In Boor’s book on Ziegler–Natta catalysis (179), he exhaustively reviewed the literature and addressed four mechanisms for chain growth. The four mechanisms are based on the description of the center where chain growth takes place:

1. transition metal–carbon bond,
2. activator metal–carbon bond,
3. bound radical center, and
4. bound anion center.

Of these four, the majority of the research tends to support the transition metal–carbon center model, as the mechanistic scheme of choice. Using a homogeneous catalyst (Cp$_2$TiEt$_2$) as a model, Breslow and Newburg proposed that polymerization growth occurred at the Ti–C center. Somewhat later, Cossee extended this concept into a more elaborate mechanism for supported catalysts, which he substantiated with molecular orbital calculations (see Ref. 179, Chapt. 13).

According to this widely accepted model (226–230) for the surface site and surface coordination environment, the active site is a titanium atom with octahedral shape and a vacant position (the other positions being occupied by an alkyl group derived from the alkylation by the aluminum alkyl and the remaining chloride atoms). In total the active site is made up of four ligands, which, in the case of TiCl$_3$, are chlorine atoms, the alkyl group, and the vacant site.

Monomer insertion occurs through a first step of monomer coordination to the transition metal, with formation of a $\pi$-complex, subsequent weakening of

![Diagram of polymerization process]
the Ti–C bond, and finally insertion of the monomer coordinated between the transition metal and the C atom. Because the two positions are not equivalent in the crystal lattice of the catalyst, the vacancy and the growing chain exchange positions. These phases are repeated at the insertion of each monomer unit. On the basis of molecular orbital theory, a semiquantitative interpretation of the mechanism was provided by assuming weakening of the metal–carbon bond during olefin complexation in the case of metal ions with 0–3 d-electrons (as in Ti, V, Cr), and with more difficulty when the number of d-electrons is greater. This mechanism is called monometallic; it requires only the participation of the transition metal, attributing to the aluminum compound the role of forming the active center by alkylating the titanium atom. The aluminum compound is also involved, as demonstrated by the different effects that various aluminum alkyls have on the performance of these catalyst systems.

Some researchers believe that the active metal (aluminum) directly participates in directing of the incoming monomer, in which case this system would be considered a bi metallic site. However, Boor makes a convincing argument that because of the size of the polypropylene helix, there is no room at the active site for the aluminum to participate. The titanium site occupies roughly 0.16 nm² (diameter ∼0.45 nm) and the cross-sectional area of a polypropylene helix is about 0.35 nm² (diameter ∼0.7 nm). This would eliminate the titanium and aluminum from sharing a common chloride bridge and thus preclude aluminum from directly participating in directing the incoming monomer (179). It has been suggested that the effect the different aluminum alkyls have on polymer microstructure and molecular weight is due to the way in which the alkyl aluminum sets up the titanium chloride surface. These differences in polymer microtacticity and molecular weight could be due to the fact that the activator may be generating different isotactic sites.

The basic concept of monomer insertion has now been discussed and for the polymerization of ethylene this simple description of a monometallic, transition metal–carbon centered active site would be sufficient to describe the polymerization. However, with α-olefins the matter of stereo- and regio-chemistry must be addressed and will be done in the next section.

**Stereo- and Regiochemistry of Monomer Insertion.** For substituted α-olefins a number of issues concerning monomer coordination/insertion must be considered. The way in which the monomer inserts itself into the polymer chain determines the microstructure of the polymer and subsequently the properties. Does the methyl group on the propylene end up towards the chain or away? What is the position of the methyl group on the propylene molecule with respect to coordination site of the metal and the polymer chain, cis versus trans? The way in which the propylene molecule may be inserted in the polymer chain by various mechanisms can give rise to complex phenomena of structural and steric isomerism.

Two possible regio-insertion mechanisms for α-olefins exist—primary and secondary. In a primary insertion the unsubstituted end (methylene group) of the monomer attaches to titanium center. This is also known as a 1,2-insertion. In a secondary insertion the substituted end of the monomer attaches the titanium. This is also called a 2,1-insertion.
The experimental evidence indicates that for the production of isotactic polypropylene the primary insertion mechanism is predominant. This is substantiated via end group analysis by the presence of isopropyl groups as the end groups after chain transfer by hydrogen. The regioselectivity of Ziegler–Natta catalysts is very high as have been proved by NMR analyses (231,232). Syndiotactic polypropylene can be prepared by the low temperature polymerization of propylene using a vanadium catalyst. In this case the secondary insertion mechanism is operative (233,234).

For stereoregular insertion there are two modes to consider—cis insertion and trans insertion. For both isotactic and syndiotactic production, the cis mechanism has been determined to be in operation. This was established by polymerizing with cis- and trans-1-deuteriopropylene or related monomers. The expected stereochimistry was demonstrated when deuteriopropylene was polymerized. The cis monomers produce erythro monomer units whereas the trans monomer yields the threo units when cis- and trans-1-d-propylene is polymerized. In some cases the nomenclature appearing in the literature can be confusing and contradictory, but all indicate cis insertion. To be specific, as defined below, stereochemical structures from cis and trans addition to the double bond of cis-(1-d) and trans-(1-d)-propylene to isotactic polypropylene are as follows (229):
Two potential mechanisms have been proposed as governing factors regulating the stereochemistry of the isotactic insertion, the first being the asymmetric structure of the active site (enantiomeric site control) and the second being the asymmetric carbon atom of the last chain-inserted monomer unit (chain end control). It has been proved experimentally that the regulating factor is the active center (enantiomeric site control) because the steric order is transferred also through ethylene units and because an occasional error is not perpetuated in the chains (231,232). This mechanism is valid for Ziegler–Natta catalysts and many (if not most) homogeneous metallocene catalysts. In addition it has been shown (235–240) how, in the polymerization of racemic \( \alpha \)-olefins, a mixture of optically active polymer can be obtained with an asymmetric catalyst.

Examination of the crystalline structure of the catalyst components reveals the asymmetric structure of the active center. In TiCl\(_3\) six chlorine atoms at the vertices of an octahedron surround each titanium atom. These six chlorine atoms are then chelated, by pairs, to three other titanium atoms. This creates two enantiomorphic structures.

The next section will discuss some of the concepts associated with models for the catalytic sites.

**Ziegler–Natta Active Site Models**

An important characteristic of a polymerization catalyst is its morphology or structural architecture. Titanium chloride exhibits four different crystalline modifications: \( \alpha, \beta, \gamma \) and \( \delta \) forms depending upon the method of preparation. In each
case the titanium atom is octahedrally coordinated, except at various defects and edges. The violet \( \alpha \)-form, and the \( \gamma \) and \( \delta \) forms consist of regular stacking of \( \text{Cl} - \text{Ti} - \text{Cl} \) layers containing titanium atoms between two layers of chloride ions. The \( \alpha \)-\( \text{TiCl}_3 \) form, which will be discussed, is hexagonally close packed.

Stereospecific behavior of the catalyst site is related to the chirality of the surface sites of the solid \( \text{TiCl}_3 \). Models by Corradini can explain a number of observations—the type of tacticity errors along a predominantly isotactic chain, stereospecificity of the initiation reaction, and the maintenance of isotacticity after the insertion of ethylene monomer in the chain (241). Furthermore, since violet \( \text{TiCl}_3 \) and \( \text{MgCl}_2 \) solid-state crystal structures are similar, Corradini’s model relates well to both \( \text{TiCl}_3 \) and \( \text{MgCl}_2 \)-supported catalysts.

The structure of titanium trichloride and other Ziegler–Natta catalysts consisting of transition metal halides (\( \text{VCl}_3 \), \( \text{CrCl}_3 \), etc) is comprised of layers of close-packed chlorine atoms. The crystalline modifications are based on the different ways in which the layers are stacked on top of one another. Within each layer the metal atoms reside in an ordered arrangement. The metal atoms occupy two thirds of the octahedral positions. The adjacent metal atoms, which are bridged by two chlorine atoms, have opposite chirality. The chirality of these metal atoms is designated \( \Lambda \) and \( \Delta \) according to the International Union of Pure and Applied Chemistry (IUPAC) nomenclature (242). In the \( \text{MgCl}_2 \) structure there are no vacancies in the lattice and every octahedral position is occupied by a magnesium atom; however, it can be seen that the gross structures of \( \text{TiCl}_3 \) and \( \text{MgCl}_2 \) are similar. This similarity in structure between \( \text{TiCl}_3 \) and \( \text{MgCl}_2 \) is what makes magnesium chloride a suitable substrate for the deposition of titanium chloride to form active sites. It was determined early on that only a small portion of the titanium on \( \text{TiCl}_3 \) catalysts was active; the rest was essentially acting as a support. The bulk of the titanium chloride was the culprit in causing polymer instability and degradation problems. When using \( \text{MgCl}_2 \) as a support the yield of polymer per weight of catalyst is much greater. Along with the fact that the magnesium chloride is practically inert, this produced a polymer that was inherently more stable.

A diagram of the \( \text{TiCl}_3 \) structure of the (110) cut and the (100) cut of \( \text{MgCl}_2 \) is shown in Figure 13; the chloride atoms are omitted for clarity.

Magnesium chloride can be treated either chemically or physically (ball milling) to achieve activation. Activated \( \text{MgCl}_2 \) has a very disordered structure, which consists of very small lamellae. In the bulk, magnesium atoms are coordinated to six chlorine atoms, but at the lateral edges or cleaved surfaces the coordination is with 4 or 5 chorine atoms. These lateral cuts correspond to the (110) and (100) faces respectively for magnesium chloride. Upon treatment of activated \( \text{MgCl}_2 \) with \( \text{TiCl}_4 \), the bridged dinuclear \( \text{Ti}_2\text{Cl}_8 \) species coordinate on the (100) surface while the single \( \text{TiCl}_4 \) species usually prefer the (110) faces. Treatment of the catalyst by aluminum alkyls will reduce the \( \text{Ti}_2\text{Cl}_8 \) to \( \text{Ti}_2\text{Cl}_6 \) species and alkylate the titanium. This will generate both \( \text{TiCl}_3 \) and \( \text{Ti}_2\text{Cl}_6 \) species on the \( \text{MgCl}_2 \) support. The placement of these \( \text{Ti}_2\text{Cl}_6 \) units on the (100) lateral surface of \( \text{MgCl}_2 \) produces sites very similar to those on the (110) surface of \( \text{TiCl}_3 \) catalysts. These \( \text{Ti}_2\text{Cl}_6 \) sites are chiral and stereospecific. Coordination of the \( \text{TiCl}_4 \) species on the (110) faces and reduction by aluminum alkyls produce \( \text{TiCl}_3 \) sites, which lack chirality and are nonstereospecific producing sites for propylene polymerization. In Figure 14, is shown both the \( \text{TiCl}_3 \) catalyst and \( \text{MgCl}_2/\text{TiCl}_4 \) catalyst after
reduction with AlR₃. Now with the basics of the active centers and structures described, the details of the polymerization mechanism can be discussed.

As mentioned previously, a two-stage reaction mechanism for the polymerization of propylene was proposed which consists of a coordination stage of the olefin then followed by an insertion step of the monomer into the Ti–polymer bond. Although this picture (Fig. 15) reveals the basic mechanism of monomer coordination and then insertion, it does not provide any insight into the mechanism for stereocontrol of the propylene monomer. This is addressed by chirality considerations.

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Fig. 13. Comparison of the structures of α-TiCl₃ and MgCl₂.

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Fig. 14. Crystal structures of α-TiCl₃ and MgCl₂ with Ti₂Cl₆ clusters. Chlorine atoms are shown at the catalyst sites, and substrate chlorine atoms are omitted for clarity.
As discussed previously the active sites on TiCl₃-based catalysts or MgCl₂-supported catalysts are chiral. In all, there are three elements of chirality that are considered with respect to the polymerization of α-olefins and stereospecificity of the polymer:

1. α or δ chirality of the titanium atoms
2. The si or re chirality of the coordinated propylene monomer
3. The chirality of the tertiary carbon atoms of the growing polymer chain

For this discussion the bridged dimers of Ti₂Cl₆ on the lateral face of a MgCl₂ crystal will be considered. If Figure 16 (below) is studied in detail, it can be seen that at one of titanium atoms of the Ti₂Cl₆ cluster there are two positions that are available to the growing polymer chain and the coordinating monomer. One position can be considered outside or away from the bulk of the crystal and the other can be considered inside, or towards the bulk of the crystal lattice. These two positions are not sterically equivalent. Through computer modeling calculations, Corradini and co-workers demonstrated that the most favorable energy position for the growing chain was at the inside position (241).

If the most favorable energetic position for the chain is at the inward position, then the monomer must occupy the outside location. For the Δ titanium site, the si outward coordination of propylene is favored (re for the outward Δ titanium site). In this model the production of stereospecific polypropylene can be explained.

For syndiotactic propagation it was proved that the steric control of the insertion comes from the last inserted monomer unit, whose hindrance affects the
insertion of the subsequent unit in such a way as to prevent a monomer molecule with the same configuration of the previous molecule from entering (243,244). Recall that syndiotactic polymerization from Ziegler–Natta vanadium catalysts differs from this isotactic polymerization monomer insertion. For the vanadium syndiotactic catalysts secondary or 2,1-insertion is operative (233,234). More recently developed homogeneous syndiotactic catalysts follow 1,2-insertion.

Summarizing, isotactic and syndiotactic propagation highlights the catalyst site as the entity controlling stereoregularity for iPP and the last monomer unit of growing chain for syndiotactic propagation with vanadium catalysts. The monomer insertion type is primary (1,2) for isotactic and secondary (2,1) for this latter syndiotactic catalyst.

**Electron Donors**

There are two classifications of electron donors, internal and external. Electron donors are thus named for their ability to act as Lewis bases and donate electrons to Lewis acid sites. For the TiCl₃ type catalyst, the electron donors are traditionally referred to as just donors and are generally amines, esters, ethers, alcohols, etc. Their roles range from modifying the catalyst site and structure of the TiCl₃ substrate to complexing with the alkyl aluminum either during catalyst preparation or catalyst activation.

For MgCl₂-supported catalysts (the third- and fourth-generation types; see Table 9 the electron donors are classified as internal and external based on their sequence of addition during catalyst preparation or during activation, respectively. For the preparation of the MgCl₂-supported catalyst an electron donor is added
during the process of adding the TiCl$_4$ (titanation of the support) to the activated MgCl$_2$-support; this is referred to as the internal donor. At the stage of activation of the MgCl$_2$-supported catalyst, another donor is added during the addition of the alkyl aluminum; this donor is referred to as the external donor. For the third-generation MgCl$_2$-supported catalyst, the internal donors are usually phthalates and the external donors are alkyl alkoxy silanes. For the fifth-generation type catalysts, the internal donors are diethers and the external donor (alkyl alkoxy silane) may or may not be used. In most cases electron donors are used to increase the activity and stereospecificity of the catalyst system.

Donors work in a variety of ways and the roles of both internal and external donors as they relate to the MgCl$_2$-supported catalysts will be discussed in this section. As mentioned previously, MgCl$_2$ can be activated through mechanical or chemical means. The process of activating magnesium chloride through mechanical means can be achieved by ball milling. This process usually involves co-milling the magnesium chloride with a Lewis base (233). The preparation of the catalyst is followed by treatment of the activated magnesium chloride with TiCl$_4$ and heat. The subsequent treatment of the MgCl$_2$/internal donor support with TiCl$_4$ usually removes some of the internal donor. In other cases the activated MgCl$_2$-support can be treated with TiCl$_4$ and the Lewis base at the same time, and then given a heat treatment. The internal donor helps structurally stabilize the activated magnesium chloride, prepare sites for the TiCl$_4$, and possibly block certain sites on the MgCl$_2$ surface, thus making them unavailable for titanium chloride.

Whereas third-generation Ziegler–Natta catalysts use an ester (ethyl benzoate, EB) as internal donors and another ester as the external donor (methyl para-toluate, MPT), the fourth-generation catalysts use a phthalate (usually di-isobutylphthalate, DIBP) as the internal donor and an alkyl alkoxy silane (e.g., phenyl triethoxy silane, PES) as an external donor (233). In both cases the internal and external donors play similar roles. The internal donors stabilize the MgCl$_2$ support and set up positions for the TiCl$_4$ complex. The purpose of employing an external donor in both the third- and fourth-generation catalyst systems is that without them, the stereospecificity of the catalyst would be very poor for the polymerization of propylene. This is due to the fact that activation of the catalyst with the alkyl aluminum extracts a portion of the internal donor out of the catalyst. The external donor is added during the activation of the catalyst for the purpose of occupying the site left vacant by the extracted internal donor (233).

From the discovery of the high yield MgCl$_2$-supported catalysts it was apparent that the presence of both an internal and external donor was a necessary condition for a highly active, highly stereospecific catalyst. Soon after, it was learned that an interrelationship existed between the two donors and, furthermore, specific donor pairs gave optimum results. However, with the advent of the fifth-generation catalysts, those employing diethers, there was no need for the addition of an external silane donor (234). These catalysts, MgCl$_2$/TiCl$_4$/diether, did not lose the internal donor during activation with the alkyl aluminum and consequently maintained relatively good stereocontrol and excellent activities (2 to 3 times that of the conventional MgCl$_2$-supported/phthalate catalysts) (245,246) (see Table 9). Interestingly enough, these diether donors can also be used as external donors in the more traditional MgCl$_2$-supported/phthalate/TiCl$_4$ catalyst systems and they produce the same type of homopolymer. This supports the theory that there is a phthalate/external donor exchange during activation where
the external donor (diether) occupies the site left vacant by the phthalate, very
similar to the phthalate/alkoxy silane exchange. In general the following model
best describes the interactions between the internal and external donors with the
catalyst and activator (246,247):

\[
\text{Cat} \cdot \text{ID} + \text{AlR}_3 \rightleftharpoons \text{Cat} + \text{AlR}_3 \cdot \text{ID}
\]  

\(1\)

\[
\text{AlR}_3 + \text{ED} \rightleftharpoons \text{AlR}_3 \cdot \text{ED}
\]  

\(2\)

\[
\text{Cat} + \text{ED} \rightleftharpoons \text{Cat} \cdot \text{ED}
\]  

\(3\)

\[
\text{Cat} + \text{AlR}_3 \cdot \text{ED} \rightleftharpoons \text{Cat} \cdot \text{AlR}_3 \cdot \text{ED}
\]  

\(4\)

\[
\text{Cat} + \text{AlR}_3 \cdot \text{ED} \rightleftharpoons \text{Cat} \cdot \text{ED} + \text{AlR}_3
\]  

\(5\)

As previously mentioned, the alkyl activator will extract internal donor from the
catalyst; therefore equilibrium 1 is always present even in the absence of an exter-
nal donor. Depending upon the location of the titanium site on the magnesium chlo-
ride support, the free site (Cat-□) could be isospecific or aspecific. Equilibrium 2
is also present because of the propensity of the external donor and AlR₃ to form
acid/base adducts. These ED·AlR₃ adducts may also form exchange products (248).
In fact, these exchange products are important because they reduce the concen-
tration of free external donor present in the system, which also acts as a poison. In
the presence of excess aluminum, there should be very little free external donor
present in the system; therefore equilibrium 3, (the interaction of catalyst with
free external donor) can be neglected. For the external donor to interact with
the free titanium site there are two possibilities—through the ED·AlR₃ complex
(equilibrium 4) and through the ED·AlR₃ complex initially as a carrier for the
ED (equilibrium 5). In equilibrium 5, the ED·AlR₃ complex releases the ED to
the vacant titanium site. Experimental results indicate equilibrium 5 as the most
likely case. The alkyl aluminum activates the titanium and removes the internal
donor but does not participate in the actual stereochemical regulation of the
polymerization of propylene (246).

To recap, there are two types of donors, internal and external. For the third-
generation catalysts the internal/external pair is an ester/ester pair, while for
the fourth-generation it is the phthalate/alkoxy silane pair. The fifth-generation
Ziegler–Natta catalysts are comprised of an internal donor, which is a diether
compound and may be used with or without the additional external donor
(see Table 9).

There has been a large effort towards elucidating the roles of the external
donor in the polymerization of propylene. Some of this work has centered on the
structural considerations of the external donor. Since the MgCl₂/TiCl₄/phthalate–
alcohol silane/AlR₃ catalyst system is the most widely used commercial catalyst
system for polymerization of propylene, the focus in the next section will be on the
alcohol silane as the external donor.

**Structural Considerations of Electron Donors.** The most effective
alcohol silanes used in the polymerization of propylene give the greatest activity
along with the highest selectivity. These types of silanes are of the general for-
mula R¹R²Si(OR)₂ and R¹Si(OR)₃, with R = methoxy or ethoxy (any larger alkoxy
group is ineffective). Early on, PhSi(OEt)₃ was used; however, the more effective
silanes for catalyst performance are those that contain methoxy groups (R = OMe).
Interestingly enough, silanes with only one alkoxy group were poor performers,
producing polypropylene with low isotacticity. The best activity/selectivity balance
was found for silanes having two methoxy groups and two alkyl groups (R¹ and R²)
that are relatively large—in other words, sterically bulky. The importance of steric
volume was investigated by Okano and co-workers (249). They correlated silane
molecular volume and electron density (calculated by molecular modeling) with
polymerization performance (activity) and stereocontrol (isotactic index). In their
study they found a straight-line correlation with silane volume and isotacticity.
Both Okano’s group and Härkönen (250) found a decrease in atactic polymer for-
mation with an increase in electron density.

In addition to affecting polymer stereoregularity and catalyst activity, silane
donors influence other aspects of propylene polymerization. It was also found
that external silane donors influenced molecular weight of the polymer via the
use of hydrogen as a chain-transfer agent. When using hydrogen to decrease the
molecular weight of the polymer, there was also an increase in activity when us-
ing an external alkoxy silane with the MgCl₂/TiCl₄/phthalate ester catalyst sys-
tem (251–254). While hydrogen is used as a molecular weight control agent, this
level of control varies from external donor to external donor. In some cases, un-
der the same hydrogen charge, two different donors will give polypropylene with
two very different molecular weights (255). These differences between donors in
molecular weight control are not unlike the differences observed in stereocontrol.
Some donors are better at stereocontrol than others. The general observation is
that donors with good stereocontrol or high selectivity (usually those containing
bulky hydrocarbon groups) are usually poor at effectively using hydrogen to lower
the molecular weight of the polymer. Donors with poor regio- or stereocontrol
exhibit good hydrogen response. Chadwick and co-workers have explained this
phenomenon by the process of chain transfer after a regioirregular insertion of
propylene (256). With a 2,1-insertion it is harder for the next propylene unit to
insert into the Ti—CH(CH₃)CH₂—polymer bond; however, there is a probability
of hydrogen inserting to affect a chain transfer. Therefore those donors with low
regio-control permit more 2,1-insertions, thus making chain transfer with hydro-
gen easier. Donors with good regio-control make far fewer 2,1-insertions, thus
denying an easy path and an opportunity towards chain transfer with hydrogen.

**Molecular Weight and Molecular Weight Distribution Effects of
Electron Donors.** The production of broad molecular weight distributed
polypropylene is a function of the multiplicity of active centers, which differ in
stereo- and regiospecificity, and the propagation rate. Lewis bases in general, and
external alkoxy silane donors in particular can influence the molecular weight
distribution of polypropylene by associating with these multiple active centers (245,257,258). The regio- and stereoselectivity of the external donors affects the molecular weight distribution of the polymer indirectly. Normally the atactic fraction of polypropylene has a lower molecular weight. This is in part due to regioirregular insertions of the monomer, which in turn leads to the easier pathway of hydrogen complexation and subsequent chain transfer (259). It has been shown that the different fractions of homopolypropylene separated by temperature rising elution fractionation (TREF) not only differ in microtacticity but also by molecular weight (245). For the MgCl2/TiCl4/diether based catalyst, Chadwick and co-workers found that the higher temperature eluting fractions also had higher molecular weights. Not unexpectedly, each fraction from TREF exhibited a narrow molecular weight distribution (259).

Microtacticity Considerations. In the early days of Ziegler–Natta polymerization of propylene, two concerns were activity of the catalyst and the stereospecificity of the polymer. Stereospecificity or stereoregularity of the polymer was measured by the amount of insolubles produced versus the amount of solubles. However, another important feature affecting the performance of polypropylene is the microtacticity of the polymer chain. Nowadays, with the aid of TREF and 13C NMR spectroscopy, the overall stereospecificity of polypropylene can be further defined by observing stereoirregular and regioirregular insertions. The type and quantity of these disruptions in the chain lead to differences in the physical properties and processing performances.

Chadwick and co-workers demonstrated that the quantities of the three major fractions derived from TREF vary with different donors (256). The fraction of polymer that elutes from 26 to 95°C, normally referred to as the stereoblock fraction, can vary from as little as 4% up to 21% by weight of the total polypropylene sample (260). The differences in homopolymer made with two different donors can be seen by looking at the "mmm" pentads, via 13C NMR spectroscopy, of the TREF fraction eluting from 96 to 125°C.

In summary, donors, both internal and external (alkoxy silanes and diethers), affect catalyst performance and polypropylene properties in the following ways:

1. The internal donors restrict the placement of titanium on the (110) face of MgCl2.
2. The internal donors shift the equilibrium between the aspecific monomeric species (TiCl3) to the stereospecific dimeric species (Ti2Cl6) on the (100) face of the MgCl2.
3. The external donors transform nonstereospecific sites into isospecific sites by blocking open coordination sites near the titanium active centers.
4. External donors control the path of the incoming monomer to varying degrees:
   a. Little control produces stereo- and regioirregularities that result in microtacticity changes; this in turn affects crystallinity and thus the solubles levels.
   b. Lack of monomer insertion control also affects regioirregular insertions (2,1-insertions), which leads to chain transfer by hydrogen and lower molecular weight.
Metallocenes

Metallocene catalysts for the polymerizations of olefins have been known since early 1957 when Natta and co-workers first reacted triethyl aluminum (AlEt₃) and bis(cyclopentadienyl) titanium dichloride ($\eta^5$-C₅H₅)₂TiCl₂ to form a complex that polymerized ethylene. The structure of this complex was described and the polymerization results reported. With ethylene they reported to have made 7 g of crystalline polyethylene in about 8 h at 95°C with 40 atm ethylene pressure in $n$-heptane. Later in the same year, Breslow and co-workers repeated Natta’s experiments. They found that the blue complex described by Natta was a somewhat poor catalyst (in agreement with Natta’s findings), but discovered that small amounts of oxygen in the ethylene boosted polymerization activity. When compared to the heterogeneous Ziegler–Natta catalyst system, these metallocene catalysts were poor with respect to polymerization activity. They were used essentially for mechanistic studies because of their simplicity and ease of structure elucidation.

In 1975 Kaminsky found that a slight amount of water added to a mixture of bicuscopentadienyl titanium dimethyl and trimethyl aluminum rapidly polymerized ethylene. Eventually it was determined that the addition of water produced methylaluminoxane (MAO), which was responsible for the boost in activity (261). Although these Cp₂MX₃/MAO catalyst systems rapidly polymerized ethylene and copolymerized other monomers with ethylene, they were less effective for the polymerization of propylene. There were several critical shortcomings with these early metallocene catalysts toward the polymerization of propylene: low activity, poor stereospecificity, and low molecular weight polypropylene production.

Because these metallocene catalysts are discrete, single molecules, their structures can easily be determined by X-ray crystallography. This allows the catalyst chemist to begin the process of relating the structure of the metallocene catalyst to polymer properties (molecular weight, stereoregularity, stereospecificity, etc) and polymerization activity. This ability to relate catalyst structure to polymer properties allows the process of elucidating polymerization mechanisms and designing catalysts to tailor make polymers and copolymers. This is a big advantage over the traditional Ziegler–Natta catalysts, which contain multiple sites (see Metallocenes; Single-Site Catalysts).

General Description of Structures. A brief description of metallocene catalyst structures is necessary before going any further in discussions concerning these systems. In their most basic form these metallocenes consist of a Group IV metal (M = Ti, Zr, Hf), two π-bonded cyclopentadienyl rings, and two sigma-bonded groups (these rings are also referred to as carbocyclic π-ligands while all the groups attached to the metal are generally referred to as ligands). Because of the nature of the π-bonding between the metal atom and the carbocyclic π-ligands, there is free rotation of these ring groups about their metal-to-ring centroid axes. This free rotation makes these metallocenes nonstereorigid and produces atactic polypropylene.

A bridged metallocene contains a linking unit (usually CH₂, —CH₂CH₂—, or SiR₂) between the two carbocyclic ligands. These bridged metallocenes are stereorigid, but will not necessarily produce stereospecific polypropylene.
Furthermore, these bridged metallocenes can become more complicated structurally with more substitutions on the carbocyclic \( \pi \)-ligands. In fact, the more complicated bridged metallocenes are of commercial interest because they provide for the production of isotactic and syndiotactic forms of polypropylene at high molecular weights. Because of the carbocyclic \( \pi \)-ligand's complexity, catalyst stereochemistry will be addressed in the next few paragraphs.

Bridged metallocenes can be further classified based on their stereochemistry. Using an ethylene-bridged bis-indenyl metallocene \((\text{CH}_2\text{CH}_2[\text{Ind}]_2\text{MX}_2)\) as an example, one can follow the spatial relationships between the ligands and their effects on monomer insertion mechanisms and polymer properties. The \(\text{CH}_2\text{CH}_2[\text{Ind}]_2\text{MX}_2\) metallocene can exist in two forms, mesomeric and racemic (\(\text{meso}\) and \(\text{rac}\)). The \(\text{meso-CH}_2\text{CH}_2[\text{Ind}]_2\text{MX}_2\) catalyst has a mirror plane and is nonstereospecific in the polymerization of propylene; it is designated as \(C_s\)-symmetric. The \(\text{rac-CH}_2\text{CH}_2[\text{Ind}]_2\text{MX}_2\) catalyst has a nonsuperimposable mirror image and, to a certain degree, each enantiomer is a stereospecific catalyst site; it is labeled as \(C_2\)-symmetric.

Finally, two other structural types of metallocenes need to be mentioned. One type consists of carbocyclic \( \pi \)-ligands, which are not identical but each possessing a plane of symmetry (orthogonal to the ring plane). These types of metallocenes are labeled as \(C_s\)-symmetric. The other type of metallocene contains two nonidentical carbocyclic ligands, one symmetrical and one asymmetrical. These types of
Implications of Metallocene Catalyst Structure on Polypropylene Structure. The previous section gave a brief description of the various types of metallocenes. In this section a general relationship between metallocene structure and type of polypropylene produced will be made. It is important to note that these are generalizations. While the stereochemistry of the metallocene plays an important role in mechanism of monomer insertion and ultimately the stereo- and regiospecificity of the polymer, the substituents and location of the substituents on the carbocyclic $\pi$-ligands also effect the microstructure of the polymer.

In general, metallocenes that are either bridged or nonbridged and possess $C_{2v}$ symmetry (eg, $\text{Cp}_2\text{TiCl}_2$ or $\text{Me}_2\text{Si(fluorenyl)}_2\text{ZrCl}_2$) will produce atactic polypropylene. This is because these types of catalysts have low stereocontrol. The only stereocontrol mechanism operating in these systems is chain end control from the polymer. Consequently the polymer is predominately atactic at normal polymerization temperatures. In fact, these metallocenes are the best source for producing high molecular weight, high atactic polypropylene (very low to almost zero crystalline polymer).

To produce highly isotactic polypropylene the metallocene catalyst should be a bridged chiral metallocene (preferably containing zirconium) having $C_2$ symmetry with some alkyl substitution in the ring (262). However, with the right substitution others have shown that a $C_{1}$-symmetric metallocene can also produce highly isotactic polypropylene with high $T_m$ ($161^\circ C$) (263).

Early metallocenes were less than desirable polypropylene catalysts because they produced polymer with low stereocontrol and low molecular weight. Recently there has been much progress in making high molecular weight, high stereo- and regioregular polypropylene with relatively high melting points. In general, all these metallocenes are structurally complicated and the reader should refer to references cited.

Advantages of Metallocenes. Because they are discreet molecules, one of the important features of metallocenes is that their structures are easily deduced. This allows almost direct correlation between the catalyst’s structure and the microstructure of the polymer produced. This fact allows for a rather rapid evolution of focused catalyst design to tailor polymer properties to specific needs. For example, one of the early successful metallocenes used in the isospecific polymerization of propylene was $[\text{Et(Ind)}_2\text{ZrCl}_2]$. By structurally characterizing this compound and making some changes in the bridging group, a new metallocene was prepared $[\text{Me}_2\text{Si(Ind)}_2\text{ZrCl}_2]$ which produced a higher molecular
weight polypropylene with high isotacticity and, consequently, a higher melting point. The evolution of the carbocyclic ligand and subsequent improvement in isotactic polypropylene properties can be seen in Table 10.

From the standpoint of monomer insertion control, judicious choice of groups and location on the carbocyclic π-ligand produce polypropylene with higher isotacticity, greater molecular weight, and higher melting points.

**Polymer Property Advantages.** Metallocene catalysts, through variation of catalyst structure, can produce a broad spectrum of polymer microstructures leading to a very wide property envelope which is potentially accessible. Because of the defined molecular structure of the catalyst, once a catalyst is chosen for a given application, the properties can be precisely controlled.

Some of the property advantages and types of polypropylene and copolymers of propylene that can be realized with metallocenes are as follows:

1. Highly tunable tacticity microstructure (isotactic, syndiotactic, atactic, isoblock/stereoblock, regiospecific microstructures)
2. Narrow molecular weight distribution
3. Absence of oligomers and extractables
4. Improved melting point/extractable balance
5. Narrow interchain composition distribution in copolymers
6. Polypropylene with vinyl end groups
7. Polymerization of expanded comonomer types (including dienes and cyclo-olefins)

**Activators/Cocatalysts.** As in conventional Ziegler–Natta catalysts, metallocene catalysts must be activated before polymerization of olefins can proceed. Methyl aluminoxane (MAO) has been the activator of choice since its discovery by Kaminsky in 1975 (261). MAO is prepared by the controlled hydrolysis of trimethyl aluminum. The product is a relatively difficult species to characterize. It consists of oligomers, both linear and cyclic. The composition of the numerous oligomer structures varies depending upon the preparation methods, concentration of the reactants, temperature, and time. The two simplified linear and cyclic oligomeric alumoxane structures (with a general allyl group) are shown in Figure 17.
The role of MAO in the activation of a metallocene is essentially the same as in the traditional Ziegler–Natta catalyst that is to alkylate the halogenated metal center. The MAO forms a cationic complex with the metallocene and a dispersed anionic charge on the aluminoxane. An excess of MAO will lead to dialkylation of the metallocene metal center. One of the main disadvantages of aluminoxane activators is the high aluminum concentration level needed; typical AlZr ratios are over 1000:1. The basic mechanism for the alkylation and activation of a Cp₂ZrCl₂ is shown in Figure 18.

Other cocatalysts can be used to activate single-site catalysts. Some other typical activators, in addition to other alumoxanes, include tetraphenylborate [(C₆H₅)₄B⁻], tetra(perfluorophenyl)borate [(C₆F₅)₄B⁻], and carborane (C₂B₉H₁₂⁻).

**Supportation of Single-Site Catalysts.** Without the ability to support single-site catalysts, the commercial use of these systems would be eliminated in the numerous bulk and gas-phase polymerization facilities used today. In essence, they would be restricted to a limited number of slurry processes. The strategy of supporting a single-site catalyst for an industrial process is much the same as that for the heterogeneous Ziegler–Natta catalysts. The target is a morphologically uniform catalyst particle that is easy to feed into a slurry, bulk-monomer, or gas-phase process, which produces a polymer that is roughly the same shape as the catalyst particle but that is 20 to 200 times in volume. In addition the catalyst particle should be robust and not easily fractured during polymerization. Fracturing of the polymer particle during polymerization produces fines that foul the process.

There are a number of materials suitable for supporting single-site or metallocene catalysts. These are inorganic oxides, metal halides, and polymers. Among the inorganic oxides, silica or silica gels have been the supports most widely used because of their wide range of particle sizes, porosities, etc. More about
silica supports will be discussed later. Other types of supports, which will not be discussed in detail, are the other types of inorganic oxides such as aluminas (zeolites type materials), MgO, etc. However, it should be noted that zeolites have shown some promise as supports because of their ordered structures and precisely known pore sizes. Other support materials are polymers which include polystyrene, derivatized polystyrenes, polysiloxanes, and various polyolefins (porous types of polyethylene and polypropylene) and copolymers. The following discussions will be predominately focused on silica gel since it is the most widely used support for metallocenes.

There are essentially three methods in which to make a supported-metallocene catalyst:

1. Supporting the metallocene, then treating with an activator
2. Supporting the activator, then treating with the metallocene
3. Preparing the metallocene/activator complex in solution, then treating the support with the complex

**Supporting the Metalloocene, then Treating with the Activator.** Because of their method of preparation, silicas have a high concentration of surface hydroxyl groups and complexed water. Normally both hydroxyl groups and water will promote decomposition of a metallocene or metallocene/activator complex. Therefore it is necessary to remove the water either by thermal or chemical dehydration. Full dehydration of silica can occur at 150°C. At this point the silica gel will have a surface that is fully hydroxylated. Even these hydroxyl groups can decompose some types of metallocenes. In most cases the silica gel can be further dehydrated at 400°C (see Fig. 19).

Much work has been reported in the literature on the preparation of silica at various temperatures and under various conditions. Needless to say, the calcination conditions play a large part in preparing the silica support for the metallocene.

As far as the actual mechanism of how the metallocene is supported, various theories abound. However, the metallocene can be “connected” in two ways to

![Fig. 19. The steps to the dehydration of silica gel.](image-url)
Fig. 20. Methods of attachment of a metallocene to silica.

the support: (1) through bonding to the metal and the oxygen of the Si—O to create the Si—O—Metal complex, or (2) by connection of the metallocene to the support via a linkage through the carbocyclic ligand moiety (Fig. 20). Tethering the metallocene to the support through the ring system is the method of choice, but requires preparing specialized carbocyclic ligands, which have spacers with groups that are able to react with residual OH groups on the silica. In this case it is necessary to have some remaining hydroxyl groups on the silica.

Supporting the Activator, then treating with the Metallocene. Supporting the alumoxane on the silica support first and then treating with the metallocene was one of the first methods used for supporting metallocenes. Many methods of silica treatment, prior to contacting with the MAO, have been reported. In addition, treatment of the silica gel with solutions of MAO at various temperatures and pressures, heating with dry MAO, etc, have been reported. All of these methods have advantages and disadvantages depending on the metallocene, monomers polymerized, and polymerization conditions used.

Supporting the Metallocene/Activator Complex. The last method to discuss is the supportation of the Metallocene/MAO complex. In this method the metallocene and the MAO are reacted in solution to form a complex. The silica is then treated with the metallocene/MAO solution. The solvent is then evaporated from the silica support to leave a dry, free-flowing catalyst. In some cases the support is held under low pressure while treated with the metallocene/MAO solution to assist in the impregnation of the catalyst complex into the pores of the silica. Other methods have been developed which improve the impregnation of the metallocene/MAO complex into the interstitial pores of the support. Concentrating the catalytic complex into the interior of the support rather than on the surface improves flowability of the supported catalyst system, decreases fouling, and improves the final polymer morphology. While much is known about the structure of the single-site catalyst and the properties of the resulting polymers, much of this changes upon supportation.

Commercialization Aspects of Metallocene/Single-Site Catalysts. While metallocenes have been known to polymerize olefins since the 1950s, only in the last 10 years have they been introduced commercially. Exxon introduced its first generation metallocene in 1989 for the limited production of polyethylene. This was a homogeneous catalyst used in solution. Other companies have followed with their own metallocene catalyst technologies, which are supported and are used in solution, gas phase, and supercondensed phases and processes.
Table 11. Metallocene/Single–Site Technologies

<table>
<thead>
<tr>
<th>Company</th>
<th>Technology Name</th>
<th>Type of Polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exxon/Mobil</td>
<td>Univation (Exxpol/Unipol)</td>
<td>iPP, impact co-PP (commercial)</td>
</tr>
<tr>
<td>Basell</td>
<td>Metocene</td>
<td>iPP, impact co-PP (in development)</td>
</tr>
<tr>
<td>Dow</td>
<td>INSPiRE</td>
<td>iPP (in development)</td>
</tr>
<tr>
<td>Borealis</td>
<td>Borecene</td>
<td>iPP, impact co-PP (commercial)</td>
</tr>
<tr>
<td>JPC/Mitsubishi</td>
<td>Proprietary use&lt;sup&gt;a&lt;/sup&gt;</td>
<td>iPP, impact co-PP (in development)</td>
</tr>
<tr>
<td>TotalFina</td>
<td>Proprietary use&lt;sup&gt;a&lt;/sup&gt;</td>
<td>iPP (commercial)</td>
</tr>
<tr>
<td>Mitsui</td>
<td>Proprietary use&lt;sup&gt;a&lt;/sup&gt;</td>
<td>sPP (in development)</td>
</tr>
<tr>
<td>Chisso</td>
<td>Proprietary use&lt;sup&gt;a&lt;/sup&gt;</td>
<td>iPP, sPP (in development)</td>
</tr>
<tr>
<td>BP Amoco</td>
<td>Proprietary use&lt;sup&gt;a&lt;/sup&gt;</td>
<td>EPP (in development)</td>
</tr>
</tbody>
</table>

<sup>a</sup>Implies that technology is not commercially available, but the polymer may be commercially available.

The nonsupported metallocenes are used only in solution processes. The strategies for market penetration run from targeting commodities to specialty grades.

In the infancy of metallocene catalysis, many companies spent considerable research dollars on metallocene preparations and understanding the structure of the metallocene in relation to the polymer properties. In addition to these research dollars, large expenditures were also made to establish strong patent positions. In an effort to recoup these expenses for this budding technology, to be competitive, and to fill voids in their technology portfolios, many have established cooperative alliances or have consolidated.

At the time of this writing a number of metallocene/single-site catalyst technologies are available with which to produce polypropylene (see Table 11). Metallocene-based polypropylenes are commercially available and even catalyst licenses are available (264).

**Manufacturing Processes**

The first commercial processes for the production of polypropylene were batch polymerization processes using TiCl<sub>3</sub> catalysts activated by Al(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cl in a hydrocarbon medium. The hydrocarbon, usually hexane or kerosene, maintained the isotactic polypropylene in suspension and dissolved the undesirable atactic fraction. After polymerization, the suspension is treated with alcohol to deactivate and solubilize the catalyst residues, and filtered to separate the residues and atactic fraction from the desirable polymer, which is then dried. The alcohol and diluent are recovered by multiple distillations, and the atactic fraction is sold as a by-product. As the demand for polypropylene increased, these batch polymerization processes were rapidly replaced by continuous ones, such as the Hercules process shown in Figure 21. In this process, typical of those used throughout the 1960s and 1970s, a suspension of TiCl<sub>3</sub> catalyst in Al(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cl and kerosene diluent is continuously fed to the first of a series of continuous stirred overflow reactors. Monomer is fed to the first reactors and allowed to react out in the later ones, obviating the requirement for monomer recycle. Typical polymerization temperatures were in the range of 55–70°C and maximum pressures as high as 0.5 MPa (75 psig).
Fig. 21. Hercules slurry process for polypropylene.

Other similar processes, such as Montedison’s, operated at pressures as high as 1.3 MPa (200 psig) with monomer recycle (265). Hydrogen is added to the reactors as required to achieve the desired polymer molecular weight (266). Following polymerization, the slurry is contacted with isopropyl alcohol, then aqueous caustic to decompose and neutralize catalyst residues. The aqueous phase containing the alcohol and catalyst residues is separated from hydrocarbon, polymer slurry phase. The suspended isotactic polymer is separated from the diluent containing the atactic polymer by continuous filtration or centrifugation, then dried. The alcohol and kerosene are each purified by a series of distillations, then recycled. Atactic polymer is dried using a thin-film evaporator and sold as by-product. The aqueous stream containing catalyst residues is treated prior to disposal of wastewater and inorganic solids. The products available from this technology were limited to homopolymers with relatively high molecular weights (MFR < 15 dg/min), random copolymers containing low amounts of ethylene, and impact-resistant copolymers of high molecular weight and low rubber content. Excessive production of soluble polymer causing fouling of heat-transfer surfaces, was the primary cause of this limitation, more so than the loss of monomer to the production of less valuable by-products. This limitation, and the high energy cost of recycling
diluent and alcohol, led to the development of processes that eliminated the need for diluent.

Polymerization in liquid monomer was pioneered by Rexall Drug and Chemical and Phillips Petroleum. In the Rexall process, liquid propylene is polymerized in a stirred reactor to form a polymer slurry. This suspension is transferred to a cyclone to separate the polymer from gaseous monomer under atmospheric pressure. The gaseous monomer is then compressed, condensed and recycled to the polymerizer (267). In the Phillips process, polymerization occurs in loop reactors, increasing the ratio of available heat-transfer surface to reactor volume (268). In both of these processes, high catalyst residues necessitate post-reactor treatment of the polymer.

Gas-phase polymerization of propylene was pioneered by BASF, who developed the Novolen process, using stirred-bed reactors (269). Unreacted monomer is condensed and recycled to the polymerizer, providing effective removal of the heat of reaction. As in the early liquid-phase systems, post-reactor treatment of the polymer is required to remove catalyst residues (270). The high content of atactic polymer in the final product limits its usefulness in many markets.

In the 1970s, Solvay introduced an advanced TiCl₃ catalyst with high activity and stereoregularity (271). The level of atactic polymer was sufficiently low so that its removal from the product was not required. When this catalyst was used in liquid monomer processes, residues were sufficiently reduced so that simplified systems for post-reactor treatment were acceptable. Montedison and Mitsui Petrochemical introduced MgCl₂-supported high yield catalysts in 1975 (272). Use of these catalyst systems reduced the level of corrosive catalyst residues to the extent that neutralization or removal from the polymer was not required. Stereospecificity, however, was insufficient to eliminate the requirement for removal of the atactic polymer fraction. These catalysts were used in the Montedison high yield slurry process, which does not contain the sections required for alcohol treatment, neutralization, and diluent purification in older slurry processes (265).

Current Processes. Introduction of high yield, high stereoregularity catalysts by Montedison and Mitsui in 1983 enabled the development of processes in which removal of catalyst and atactic polymer is unnecessary. This enabled the widespread use of processes in which monomer is the polymerization medium replacing slurry processes using an inert diluent. Investment and operating costs were dramatically reduced because of the elimination of the sections of the plant required for handling and purifying diluent and alcohol, removing catalyst and separating atactic polymer. Consequently, many companies invested in new plants either increasing capacity or replacing plants using the older, now obsolete processes. Almost all of the plants built in the past 15 years use one of the simplified processes. Moreover, the production capacity of a newer plant using these processes is often many times greater than those of earlier plants. Single line production capacities of 250 kt/y are no longer unusual, and plants with higher production capacities have been announced. The most widely used processes are Spheripol, licensed by Basell; Unipol, licensed by Univation; and Novolen, licensed by Novolen GmbH.

The Spheripol process consists of one or more loop reactors for production of homopolymer and random copolymer, and one or more fluid bed gas-phase reactors for the production of the rubber phase for impact-resistant copolymers (Fig. 22).
When producing impact-resistant copolymers, monomer and catalyst components are fed to the loop reactor for homopolymerization. The use of spherical form catalyst, with a narrow particle size distribution, coupled with high liquid velocities, minimizes reactor fouling maintaining effective heat transfer and enabling specific outputs in excess of 400 kg PP/h·m³. After polymerization in the loop reactors, the polymer is separated from the liquid monomer by flashing at a pressure sufficient to allow condensation and recycle of the liquid monomer without recompression. The polymer is then transferred to the gas-phase reactors for the production of the rubber phase of impact-resistant copolymers. Ethylene and propylene are fed to the fluid bed reactor to produce ethylene–propylene rubber of the desired composition. Unreacted monomer is recycled and cooled using an external heat exchanger. The polymer is then separated from the unreacted monomer at a pressure slightly above 1 atm, and then contacted with steam for complete removal of residual monomer and termination of polymerization (273).

Liquid monomer is polymerized in continuous stirred tank reactors in a number of processes. The Hypol process, developed by Mitsui Petrochemical, uses a cascaded series of stirred reactors for homopolymerization, followed by fluidized bed gas-phase reactors for copolymerization (274). El Paso (now Huntsman) converted the Rexall liquid monomer process to use high yield catalysts eliminating the sections required for deashing and removal of atactic material (275). Shell (now Basell) developed the LIPP process to produce homopolymers and random copolymers, using their high yield catalysts.

The Unipol PP process developed by Union Carbide (now Dow) and licensed by Univation, uses a large gas phase fluidized bed reactor for the production of homopolymer and random copolymer. A second, smaller fluidized bed reactor is used in series to produce the rubber required for impact copolymers. The heat of reaction is removed by cooling the monomer through an external heat exchanger (Fig. 23). The heat removal capacity of this heat exchanger and, consequently, the
production capacity of the plant is increased by facilitating condensation of hydrocarbon. This “condensing mode” technology has enabled this process to be used in very large single line polymerization plants (patent). Use of high yield catalysts in the Novolen process (Fig. 24), developed by BASF and licensed by Novolen Gmbh, has eliminated the problems associated with the use of first-generation catalysts. These catalysts enable the plants to achieve high capacity and improve product quality by minimizing catalyst residues and atactic polymer. This process uses a single vertical stirred bed reactor for the production of homopolymer and random copolymer and a second, similar reactor for the production of impact copolymers. Amoco (now BP) developed a horizontal stirred bed gas-phase reactor that acts as a series of polymerization stages in a single reactor vessel. This facilitates the production of homopolymers with broad molecular weight distribution. As in other processes, a second reactor can be used in series for the production of impact

Fig. 23. The Unipol process.
copolymers. Basell produces specialty propylene copolymers in the multistage gas-phase Catalloy process (276).

The Borstar PP process developed by Borealis can operate at temperatures above the critical temperature of the reaction medium. This process uses a loop reactor and gas-phase reactor in series for the production of homopolymer. Additional gas-phase reactors are required for the production of impact copolymers. The first commercial scale plant using this process started in 2000. Basell has announced the development of the Spherizone process using a recirculating gas-phase reactor (Covezzi paper). The reactor contains two zones that can be operated under different conditions, enabling the production of multiphase specialty copolymers in a single reactor. This reactor was first used in a commercial scale plant in 2002.

**Processing**

PP structure can be tailored for use in most polymer processing technologies. The physical and mechanical properties of PP in the end use product are a function of both the molecular structure and the processing conditions. The most commonly used processes for iPP are discussed in the following.

**Injection Molding.** In the injection molding (qv) process, molten polymer is injected into a cold mold cavity. During mold filling, the melt is oriented by a combination of shear and elongational flow (277). Crystallization partially freezes in this orientation history. Injection-molded iPP articles are made from homopolymers, random and impact copolymers, and filled polymers. Melt flow rates lower
than 4 dg/min and as high as 100 dg/min in some impact copolymers can be used, depending on the mold geometry, part thickness, and cycle time desired. Processing conditions vary over a wide range because of the differences in polymer types. Since iPP melts exhibit shear-thinning properties, high injection pressures and high shear rates are used to promote the filling of the mold. Higher melt flow (lower molecular weight) polymers provide more uniform flow and low cycle times in parts with thin sections. Lower melt flow (higher molecular weight) polymers are employed when toughness is required, and can be used in parts that have thicker cross sections. Melt temperature varies with the melt-flow rate of the polymer and the mold shape. Higher temperatures reduce the melt viscosity and facilitate mold filling; however, the cycle time is increased. Melt temperatures as low as 200°C can be used with high melt-flow polymers; higher melt temperatures are required with low melt-flow polymers. Mold temperatures typically range from 20 to 50°C. Lower mold temperatures reduce the cycle time, but may produce a rough or low gloss surface. Orientation is an important determinant of properties and related to the skin layer thickness (see MORPHOLOGY). Melt temperature, melt-flow rate (MFR), polydispersity, and proximity to the mold gate influence skin thickness (120,278–286). Lower values result from higher melt temperature and MFR, and lower polydispersity. Regions far from the gate also have lower values. Molds should be designed to minimize localized stresses and ensure mold filling. When nonuniform wall thickness is required, it should decrease gradually in the flow direction. Like all crystalline thermoplastics, iPP is sensitive to failure at notches, and smooth radii are recommended at all sharp angles, corners, or ribs. Mold shrinkage varies with thickness from 1 to 2.5%. Thicker sections shrink more than thinner sections.

Fiber.

Melt Spinning. Melt spinning produces a broad range of iPP fibers, ranging from short staple fiber to continuous filament (CF) or bulked/textured continuous filaments (BCF) (see OLEFIN FIBERS). The tex per filament of the as-spun filaments, where tex is the mass of fiber (g) per 1000 m of length, is typically in the range of 0.14–7.78 tex (1.3–70 dpf). The lower end of this range corresponds to fine filaments of ~15-µm diameter. Noncircular cross sections can be used to modify fiber appearance.

Melt spinning of iPP typically involves forcing molten polymer through a spinnerette (a collection of small-diameter orifices) and collecting it, typically on a take-up reel, some distance from the spinnerette at a velocity exceeding the orifice velocity. The tension provided by the take-up reel (melt drawing) provides partial orientation which greatly influences the final properties of the fiber. Yarns are collections of individual filaments, and can range from monofilaments to several thousand filaments depending on the process. Spinning speeds can approach 3000 m/min or higher in some cases. The iPP melt expands upon exiting the holes, a phenomenon known as extrudate die swell (287). The diameter of the extruded filament just after the die plate can typically increase on the order of 30–100% relative to the spinnerette hole depending on resin structure (melt flow rate, polydispersity). The swelling increases as the size of the die holes is reduced. This factor, and most often more importantly the maximum sustainable spin speed, determines the minimum diameter of melt-spun iPP fibers. During the spinning process, a fluid element experiences an acceleration (increase of velocity), decreasing temperature
due to a high rate of cooling, and decreasing diameter with increasing distance along the spin line (288). Large vertical air-cooling chambers, or chimneys, as high as 15 m can be required to cool the molten filament and allow adequate time for crystallization under the applied extensional force. Short spin processes generally use low spinning speeds to minimize the space required for quenching.

Fiber properties depend on the complex interrelationship of polymer structure (polydispersity, molecular weight, tacticity), processing conditions (melt temperature, melt throughput, spinnerette design, spin speed, cooling rate), and equipment design. Both material and processing variables influence the die swell, extensional melt rheology, maximum spin speed, crystallization/nucleation characteristics along the spin-line, and fiber orientation. Controlled rheology resins with narrow polydispersity are often used to improve the balance of spinning performance and fiber properties. Metallocene iPP resins have been introduced as an alternative technology (289,290). The tenacity (ultimate stress) of individual as-spun filaments is generally in the range of 0.088–0.353 N/tex (1–4 g/den). Break elongation decreases and tenacity increases with increasing spin speed due to increasing orientation. Post-drawing of filaments in the solid state below the polymer melting point, either via in-line continuous or off-line batch processes, further increases the tenacity of the fibers by improving fiber orientation. Drawing is generally carried out at temperatures exceeding 70°C, with draw ratios in the 2–10 range. The drawability is a function of the starting morphology, polymer structure, draw rate, and draw temperature. The ultimate tenacity of perfectly oriented iPP fibers has been estimated to be 1.32 N/tex (15 g/den) (121), though most commercial drawn fibers have tenacities of 0.353–0.794 N/tex (4–9 g/den). A heat setting, or annealing process below the polymer melting point, can minimize fiber shrinkage.

**Melt Blowing.** The melt-blowing process uses very high melt-flow rate (low molecular weight) iPP, sometimes in excess of 400–1500 dg/min. These melt-flow rates are much higher than for melt-spinning operations. The flow of molten, low viscosity polymer, extruded through a small die is disrupted by high velocity hot air. A large volume of cooling air fed near the die exit quenches the fibers and deposits them on a collecting screen as a mat of entangled fibers. Processing conditions and polymer structure can be varied to alter the filament diameter, characteristics of the collected mat, and undesirable large “shots,” or polymer particles. Very fine fibers, less than 5 μm in diameter, can be produced. The fiber entanglement is sufficient to maintain the integrity of the web, and thermal bonding is not necessary. Fabrics produced by this process are very soft because of the small fiber diameter. Because the fibers are not highly oriented or bonded, meltblown fabrics usually have low tensile strength. Meltblown fabrics have improved barrier properties to aqueous liquids relative to spun-bonded fabrics.

**Spun Bonded Fabrics.** Spun bonded fabrics are produced by depositing extruded, spun filaments onto a collecting belt in a uniform randomized manner, followed by thermal bonding of the filaments. Polymers with melt-flow rates above 20 dg/min and narrow polydispersity improve stability during fiber formation and adequate melt throughput. The fibers are separated during the web-laying process by air jets and the collecting belt is usually perforated to prevent the air stream from deflecting and carrying the fibers in an uncontrolled manner. Thermal bonding, using heated embossing rolls or hot needles, imparts strength to the web
by fusing some of the fibers. This process can be combined with the melt-blowing process to produce soft, multilayer fabrics with good tensile properties. In these multilayer structures the meltblown fabric provides barrier resistance and the spun bonded fabric imparts strength.

**Slit and Split Films.** Thick industrial-grade yarns are often produced by slitting films, providing a less expensive alternative to direct extrusion. Cast film is slit in the machine direction by parallel rotary knives. The resulting tape can then be cold drawn in an oven below the polymer melting point, in a manner similar to drawn melt spun fibers, to produce the final fiber. Draw ratios of 4–11 are common. Higher draw ratios produce higher tenacity. The width of the slit tapes depends on the spacing between knives and the draw ratio. Knife spacings as low as 1 mm are sometimes used to produce textile fibers, although spacings of 10–35 mm are more common. Tapes produced by slitting a fully drawn film are wider than those oriented after slitting because of the physical limitations on minimum knife spacing. An alternative approach is to directly extrude the tapes prior to drawing. The tapes are annealed to minimize shrinkage. Fibers from split or fibrillated films are formed by the drawing of polypropylene film to the degree that it splits into numerous fiber-like interconnected tapes. In some processes the draw-induced splitting is mechanically augmented by gears, rollers, or gas jets (291).

**Film.**

**Cast Film.** The first commercial iPP films were produced by extrusion casting. Polymer is extruded through a slit or a tubular die and quenched by cooling on chill rolls or in a water bath. Cast film is not highly oriented and consequently does not have the stiffness of oriented films. Resins are typical iPP homopolymer or random copolymers. Random copolymers have improved clarity, and somewhat improved impact resistance. Rapid quenching often results in conversion to the mesomorphic form, which can be advantageous for film clarity. This tendency is greater in random copolymers than in homopolymer. High chill roll temperatures can result in hazy films, while chill roll temperatures which are too low (below the dew point of the ambient air) can result in water condensation on the film. Additives such as antiblock and slip agents are often added for improved handling of the film rolls.

**Biaxially Oriented Polypropylene.** Orientation improves the strength of iPP films. Biaxially oriented polypropylene (BOPP) films have higher strength and stiffness than cast films and consequently can often be used in much thinner gauges. Homopolymers are used almost exclusively to provide maximum stiffness and water-vapor barrier. Oriented films are produced by the tenter frame and tubular blown or double bubble methods. Most of the newly installed capacity has utilized the tenter frame process, taking advantage of the economics of the large, high capacity units available. The trend is to ever increasing line speeds, with 300 m/min not uncommon. In the tenter frame process, iPP is melt extruded through a slot die to form a sheet after quenching onto a cast roll. The cast sheet is heated to a temperature below the melting point, and drawn. In the case of sequential orientation, the softened cast sheet is drawn by a series of rolls to the desired draw ratio in the machine (longitudinal) direction, and subsequently clamped by a series of clips and conveyed into a tenter oven where it is subsequently drawn in the transverse direction to the desired draw ratio by the divergent chain clips. In the bubble process, a tube is extruded, quenched, and radially expanded by
inflation with air to provide transverse orientation. Axial orientation is provided by extension in the machine direction through a series of nip rolls. The tube is then flattened and slit into flat film. Orientation in both processes is provided by stretching below the melting point. The drawing process is strongly correlated to the crystallinity at the draw temperature which is closely related to the stereoregularity of the resin. Generally there is a trade-off between processability and final film mechanical and barrier properties. Heat aging under slight tension at a temperature above the orientation temperature but below the melting point minimizes subsequent shrinkage. Opaque films are produced by introducing microvoids into the film during the orientation by introducing small particles during extrusion. During orientation, microvoids are created as the polymer expands from the inelastic solid. Untreated oriented iPP films are not easily heat sealed. Consequently, lower melting random copolymers and terpolymers are often coextruded with the homopolymer to form a heat sealing layer.

**Blow Molding.** Low melt flow polymers are used in blow molding (qv) to provide the melt strength required to maintain stability of the parison, ie, a molten, thick-walled tube of melt. High density polyethylene has been more commonly used to form large parts because of its greater stability; however, a number of improved polypropylene grades are suitable for these applications (292). In extrusion blow molding, the extruded parison hangs freely before entering the mold, and low melt temperatures (between 205 and 215°C) are preferred. In injection blow molding, a preform is injection-molded on a steel rod, transferred to a blow molding mold, and blown. Consequently, the melt strength requirements of extrusion molding is alleviated to some extent, and higher melt temperatures can be used. Injection stretch blow molding produces a biaxially oriented part with higher stiffness, lower temperature impact strength, and greater clarity. The parison is cooled after it is formed by extrusion or injection molding, reheated to the desired orientation temperature, mechanically stretched, and then formed into the desired shape by blowing. Random copolymers of intermediate melt-flow rate (~10 MFR) have improved processing characteristics.

**Extrusion and Thermoforming.** iPP is extruded into sheet, usually for subsequent stamping or thermoforming (qv), or into pipes and profiles (see Extrusion). Low melt flow rate resins are used to provide the melt strength required to maintain uniformity. The choice of resin can often be dictated by subsequent forming operations. High melt strength polymers, produced by post-polymerization modification of conventional iPP, improve uniformity. Care must be taken for profiles of complicated geometry due to dimensional changes on crystallization, and variable cooling rate for regions differing in thickness. Good mixing of the melt during the extrusion process is important. Melt temperatures which are too high can promote degradation, leading to loss of properties, discoloration, and *plate out* which is the migration of additives and/or low molecular weight polymer to the surface of the sheet or profile. Lower temperatures reduce throughput and uniformity and lead to higher levels of orientation detrimental to subsequent forming.

In the thermoforming process, the sheet is extruded either in-line or off-line and formed, either in melt phase or solid phase, into a part of desired shape. Sheet uniformity is important. Historically, iPP has not been used in conventional melt-phase thermoforming equipment because of its narrow forming temperature range and the tendency of the melt to sag. Controlling the sag is particularly important
for large parts or multiple cavities. The introduction of newer iPP grades with higher melt strength and improved sag resistance has increased the use of iPP in conventional melt-phase thermoforming equipment (293). Processes such as Shell’s solid-phase pressure forming (294) were developed to overcome problems associated with melt forming. The iPP article is formed at temperatures close to but below the crystalline melting point, by stretching the sheet into the mold cavity with a shaped plug. The part is forced against the mold surface by cold air to obtain the desired shape. Manufacturers of thermoforming equipment have also modified their processes to effectively utilize iPP (295).

**Stabilization.** Polypropylene is subject to attack by oxygen, radiation, and excessive heat causing a loss of molecular weight and physical properties. Stabilizers are added to the polymer to minimize these effects. Small quantities of hindered phenolic antioxidants (qv) are added in the polymerization plant, usually in the drying section, to protect the polymer against degradation (qv) during short-term storage. Typically 2,6-di-tert-butyl-p-cresol (BHT) and octadecyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate (Irganox 1076) are used. The bulk of the stabilizer is added during pelletization or fabrication to protect the polymer during processing or in the final application. Typical stabilization formulations include a hindered phenolic antioxidant, possibly with a thiodipropionate synergist, a phosphate to provide high temperature melt stabilization, and an acid scavenger such as calcium stearate or dihydrotalcite (296). Hindered phenols limit the propagation of alkyl radicals and the resulting chain scission. Thiodipropionic acid esters act to decompose peroxides formed by polypropylene oxidation. More importantly, the sulfonic acid intermediate of thiodipropionate oxidation acts as a scavenger for the free radicals formed by the decompositon of phenols, increasing the effectiveness of the phenolic antioxidant (297). Phosphites also act to decompose peroxides and are most effective at the temperatures usually encountered in processing. The acid scavenger acts to prevent the reactions between hindered phenols and metal chlorides that can form colored titanium phenolates, as well as minimize equipment corrosion. Protection against ultraviolet radiation is usually provided by a hindered amine light stabilizer (HALS), such as Tinuvin 770 (see UV STABILIZERS). Stabilization (qv) of polypropylene has been reviewed (157).

**Economic Aspects**

Polypropylene consumption continues to increase more rapidly than the economy and most other thermoplastics. Although the comparative growth in polypropylene consumption has slowed from that in the 1970s and 1980s, the relative share of polypropylene use in North America has increased from 17% to 20% of all thermoplastics during the 1990s (298). The annual increase in consumption of polypropylene in North America averaged about 7% through the same period (299). Consumption in Western Europe has also increased at a similar rate. Growth in Japan has been much slower than in other countries, in part because of the protracted Japanese recession in the late 1990s, but also because of competition from the emerging economies in East Asia. The rapid growth of the Asia/Pacific region has been the major economic story of the past decade, and the growth in polypropylene consumption and production has been phenomenal. This region is
Table 12. World Consumption of Polypropylene, $10^3$ ton$^{a,b}$

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<td>1026</td>
<td>1194</td>
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$^a$Ref. 300.
$^b$U.S. consumption in 2002 was $7748 \times 10^3$ t (301).

now the world’s largest market for polypropylene, accounting for almost 40% of supply and demand (302). China has developed as one the world’s major markets for polypropylene and other thermoplastics, and is the leading importer of plastics, despite a significant increase in its production capacity. World consumption data for polypropylene are listed in Table 12. Malaysia, South Korea, India, and Thailand have joined Taiwan as significant producers, with the construction of modern, world-scale manufacturing plants. Brazil, the largest market in Latin America, has also grown at a rapid pace.

This increase in consumption has, however, been more than matched by a larger increase in production capacity, fostering a situation of oversupply and low capacity utilization. New plants often have production capacities of 250 kt/y to capitalize on the economy of large-scale facilities. In North America, where refinery propylene is the source for most monomer, the decision to invest in polypropylene capacity is often related to the need to market propylene. Arco Products (now part of BP) and Tosco (now owned by Phillips) both decided to produce polypropylene as the most cost-effective way to eliminate regulatory problems caused by excess propylene production at their refineries. Arco/Tosco capacity increased by 23% from 1998 to 2001; however, consumption only increased by 17% over the same period. Capacity utilization dropped to the lowest levels since 1989. Producers’ profit margins have decreased dramatically as the polymer prices have fallen relative to the cost of production. These profit margins are highly dependent upon the difference between the price of polymer and the price of propylene monomer. Monomer prices are related to oil prices; however, polymer prices are related to supply and demand. This difference has decreased consistently through the past decade, as some producers have been willing to supply at the lower prices. It has been estimated that a significant number of producers have been operating at a loss (303). Consequently, producers reduced capacity by closing or idling plants. Table 13 gives world production data, and Table 14 gives world capacity information and Table 15 gives U.S. production and capacity for the years 2000–2002. The 4% decrease in polypropylene capacity in 2002 is unprecedented in North America. Excess capacity and low profit margins characterize the polypropylene industry throughout the world, not just in North America, as the industry has become globalized. The market situation in Asia can dramatically affect prices in North America and Europe as imports into that region increase or decrease.
To combat the decrease in profitability major producers have chosen to reduce costs through mergers. Royal Dutch/Shell and BASF have merged their polyolefin activities, formerly Montell, Elenac and Targor, to form Basell, which is the world’s largest producer of polypropylene. This company contains facilities that were once part of BASF, Hercules, Hoechst, ICI, Montedison, and Shell. Borealis, one of the largest European producers and the result of a merger between the polyolefin businesses of Statoil and Neste, acquired PCD and OMV, two smaller producers. Major mergers of large petroleum companies, such as Exxon and Mobil (ExxonMobil), BP, Amoco and ARCO (BP), and Total, Elf Aquitane and Fina (TotalFina) have also resulted in the combination of their polymer operations. The Dow Chemical Co. purchased Union Carbide, combining the polypropylene businesses of the two companies. Japanese producers affiliated with Mitsui have
Table 16. Distribution of Polypropylene by Principal North American Market, 10^3 ton

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</tr>
<tr>
<td>Electrical/electronic</td>
<td>147</td>
<td>162</td>
<td>180</td>
<td>193</td>
<td>207</td>
<td>185</td>
<td>155</td>
<td>156</td>
<td>0.038</td>
<td>164</td>
<td>0.039</td>
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<tr>
<td>Furniture and furnishings</td>
<td>766</td>
<td>1035</td>
<td>1003</td>
<td>1078</td>
<td>834</td>
<td>913</td>
<td>829</td>
<td>923</td>
<td>0.034</td>
<td>923</td>
<td>0.041</td>
</tr>
<tr>
<td>Consumer and institutional</td>
<td>1091</td>
<td>1215</td>
<td>1237</td>
<td>1373</td>
<td>1476</td>
<td>1538</td>
<td>1497</td>
<td>1510</td>
<td>0.075</td>
<td>1661</td>
<td>0.077</td>
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<tr>
<td>All other</td>
<td>892</td>
<td>904</td>
<td>1200</td>
<td>1285</td>
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<td>1784</td>
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<td>1784</td>
<td>0.104</td>
<td>1878</td>
<td>0.099</td>
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<tr>
<td>Exports</td>
<td>297</td>
<td>332</td>
<td>463</td>
<td>565</td>
<td>489</td>
<td>539</td>
<td>629</td>
<td>856</td>
<td>0.016</td>
<td>758</td>
<td>0.004</td>
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<td><strong>Total</strong></td>
<td>4511</td>
<td>4857</td>
<td>5497</td>
<td>5952</td>
<td>6278</td>
<td>7000</td>
<td>7067</td>
<td>7317</td>
<td>0.068</td>
<td>7748</td>
<td>0.068</td>
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merged operations to form Grand Polymers and those affiliated with Mitsubishi have formed Japan Polychem. Mitsui and Sumituomo have announced a merger of their chemicals businesses, and included polypropylene. At the end of 2001, the largest producers of polypropylene in order of capacity are Basell, BP, Atofina, ExxonMobil, and Dow Chemical (305). In Europe, the largest producers are Basell, Borealis, Atofina, Sabic, and BP, respectively.

The principal market applications of polypropylene in North America are shown in Table 16. The use of polypropylene in packaging has grown more rapidly than other areas because of its increased use in injection-molded containers and packaging films. The consumer and institutional products sector is the largest market for polypropylene. This sector is the most diverse and includes nonwoven polypropylene fabrics in baby diapers as well as injection-molded toys and houseware. This market has also grown considerably in the past decade. The consumption of polypropylene in furniture and furnishings, which includes carpet fiber, continues to be one of the major applications, but is growing more slowly than overall consumption. The use of polypropylene in transportation, primarily automobiles, is not growing as fast as other areas. Consumption of polypropylene in injection-molded transportation applications has declined in recent years, as shown in Table 17. Polypropylene is most commonly extruded into fibers or films, or injection molded. Other fabrication processes are not used as frequently.

### Table 17. Consumption of Polypropylene by Use in North America, 10^3 ton

<table>
<thead>
<tr>
<th></th>
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<tr>
<td>Injection molding</td>
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<td>1665</td>
<td>1765</td>
<td>1655</td>
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<td>2108</td>
<td>2068</td>
<td>2158</td>
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<td>Appliances</td>
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<td>129</td>
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<td>116</td>
<td>134</td>
<td>150</td>
<td>113</td>
<td>118</td>
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<tr>
<td>Consumer products</td>
<td>598</td>
<td>539</td>
<td>611</td>
<td>695</td>
<td>768</td>
<td>923</td>
<td>898</td>
<td>938</td>
</tr>
<tr>
<td>Rigid packaging</td>
<td>390</td>
<td>438</td>
<td>484</td>
<td>545</td>
<td>609</td>
<td>674</td>
<td>712</td>
<td>795</td>
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<tr>
<td>Transportation</td>
<td>229</td>
<td>281</td>
<td>262</td>
<td>185</td>
<td>215</td>
<td>251</td>
<td>259</td>
<td>244</td>
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<tr>
<td>Other</td>
<td>162</td>
<td>278</td>
<td>266</td>
<td>109</td>
<td>93</td>
<td>110</td>
<td>86</td>
<td>63</td>
</tr>
<tr>
<td>Blow molding</td>
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<td>80</td>
<td>78</td>
<td>78</td>
<td>81</td>
<td>84</td>
<td>66</td>
<td>81</td>
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<tr>
<td>Extrusion</td>
<td>1834</td>
<td>2048</td>
<td>2184</td>
<td>2209</td>
<td>2382</td>
<td>2546</td>
<td>2587</td>
<td>2478</td>
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<tr>
<td>Film</td>
<td>420</td>
<td>488</td>
<td>514</td>
<td>525</td>
<td>548</td>
<td>598</td>
<td>609</td>
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<tr>
<td>Sheet</td>
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<td>108</td>
<td>104</td>
<td>108</td>
<td>116</td>
<td>141</td>
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<td>1499</td>
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<tr>
<td>All other</td>
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<td>63</td>
<td>77</td>
<td>73</td>
<td>77</td>
<td>96</td>
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<tr>
<td>Other End Use</td>
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<td>732</td>
<td>1006</td>
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<td><strong>Total</strong></td>
<td>4214</td>
<td>4525</td>
<td>5034</td>
<td>5387</td>
<td>5789</td>
<td>6461</td>
<td>6439</td>
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Basell R&D Center
CONSTANTINE STEWART

PROTEIN FOLDING. See Volume 7.

PSA. See PRESSURE SENSITIVE ADHESIVES.

PULTRUSION. See COMPOSITES, FABRICATION.

PVC. See VINYL CHLORIDE POLYMERS.

PVDC. See VINYLIDENE CHLORIDE POLYMERS.

PVF. See VINYL FLUORIDE POLYMERS.

PVK. See VINYL CARBAZOLE POLYMERS.

PVP. See VINYL AMIDE POLYMERS.