ZIEGLER–NATTA CATALYSTS

Introduction

Ziegler–Natta catalysts have had enormous impact on the polymer industry in the past 50 years, with current world production of polyolefins using Ziegler–Natta catalysis amounting to more than 50 million tons per annum. The vast advances made during the past decades stem from breakthrough discoveries made by Karl Ziegler and Giulio Natta in the early 1950s. It was in 1953 that Ziegler and co-workers, at the Max Planck Institute in Mülheim, were investigating the “Aufbau” reaction in which triethylaluminum reacts with ethylene to give higher aluminum trialkyls (1). Unexpectedly, one experiment led not to the oligomerization of ethylene via the Aufbau reaction, but to the formation of 1-butene. It turned out that this dimerization reaction had been catalyzed by traces of nickel present as a contaminant in the reactor. Soon afterwards, a revolutionary breakthrough was achieved when combinations of transition-metal compounds and aluminum alkyls were found that could polymerize ethylene under mild conditions, yielding high density polyethylene (2,3). In 1954 Giulio Natta and co-workers at Milan Polytechnic succeeded not only in polymerizing propylene with the Ziegler catalyst combination TiCl₄/Al(C₂H₅)₃, but also in fractionating the resulting polymer to obtain and characterize isotactic polypropylene (4–6). This demonstration of stereoregular polymerization led to an explosive growth of new polymers and industrial applications as the full scope of Ziegler–Natta catalysis was realized (7–9); Ziegler and Natta were jointly awarded the Nobel Prize for Chemistry in 1963.

Ziegler–Natta catalysts for polyethylene and polypropylene have progressed from first-generation titanium trichloride catalysts, used in the manufacturing processes of the late 1950s and the 1960s, to the high activity magnesium chloride supported catalysts used today. Improvements in catalyst performance have
facilitated the development of efficient gas-phase and bulk processes for polyethylene and polypropylene, and at the same time have led to ever-increasing control over polymer composition and properties.

**Early Catalysts**

**Titanium Trichloride.** One of the first catalysts found by Ziegler to be effective in ethylene polymerization was the product of the reaction of titanium tetrachloride with triethylaluminum. At low Al/Ti ratios, this reaction yields titanium trichloride as a solid precipitate. TiCl$_3$ exists in four crystalline modifications, the $\alpha$, $\beta$, $\delta$, and $\gamma$ forms, of which the $\beta$-modification has a linear (chain-like) structure and the $\alpha$, $\delta$, and $\gamma$ forms have a layered structure (10,11). The reaction product of TiCl$_4$ and AlR$_3$ is $\beta$-TiCl$_3$, which can be converted to the $\gamma$ form by heating. The latter catalyst has much higher stereoregulating ability in propylene polymerization, while $\beta$-TiCl$_3$ is an effective catalyst for the production of cis-1,4-polysoprene. $\alpha$-TiCl$_3$ can be prepared by reduction of TiCl$_4$ with hydrogen or with aluminum powder. The $\delta$ form can be prepared by prolonged grinding of $\gamma$- or $\alpha$-TiCl$_3$ and has a more disordered structure as a result of sliding of Cl–Ti–Cl triple layers during mechanical activation (12).

The first-generation Ziegler–Natta catalysts used in early manufacturing processes for polypropylene (PP) comprised TiCl$_3$ and cocrystallized AlCl$_3$, resulting from reduction of TiCl$_4$ with Al or an aluminum alkyl. The cocatalyst used in the polymerization process was Al(C$_2$H$_5$)$_2$Cl (DEAC). Catalyst activity was relatively low, giving polymer yields of around 1 kg PP/g cat., necessitating removal (deashing) of catalyst residues from the polymer. In many cases, extractive removal of atactic polymer was also required.

**Other Early Developments.** In addition to the breakthrough by Ziegler, two other discoveries of ethylene polymerization catalysts were made in the early 1950s. A patent by Standard Oil of Indiana, filed in 1951, disclosed reduced molybdenum oxide or cobalt molybdate on alumina (13). At the same time, Phillips discovered supported chromium oxide catalysts, prepared by impregnation of a silica–alumina support with CrO$_3$ (14–16). Both the Phillips catalyst and titanium chloride based Ziegler catalysts are widely used in the production of high density polyethylene (HDPE).

The various discoveries made independently by different industrial research groups in the early 1950s resulted in intensive patent litigations (8,17,18), which in the case of PP continued up to the 1980s, when a composition of matter patent on PP was awarded in the United States to Phillips, because a fraction of crystalline PP was found to be present in a polymer prepared using a CrO$_3$/Al$_2$O$_3$/SiO$_2$ catalyst (19). However, despite the importance of the Phillips catalyst for HDPE, it was unsuitable for PP, which is produced entirely using Ziegler–Natta catalysts and (to a much smaller extent) metallocene-based catalysts.

**Second-Generation Catalysts.** In the 1970s, an improved TiCl$_3$ catalyst for PP was developed by Solvay (20). Catalyst preparation involved reduction of TiCl$_4$ using DEAC, followed by treatment with an ether and TiCl$_4$. The ether treatment results in removal of AlCl$_3$ from TiCl$_3 \cdot n$AlCl$_3$, while treatment with TiCl$_4$ effects a phase transformation from $\beta$- to $\delta$-TiCl$_3$ at a relatively mild
Polymerization and Particle Growth

Polymer Chain Growth. The essential characteristic of Ziegler–Natta catalysis is the polymerization of an olefin or diene using a combination of a transition-metal compound and a base-metal alkyl cocatalyst, normally an aluminum alkyl. The function of the cocatalyst is to alkylate the transition metal, generating a transition-metal–carbon bond. It is also essential that the active center contains a coordination vacancy. Chain propagation takes place via the Cossee–Arlman mechanism (23), in which coordination of the olefin at the vacant coordination site is followed by chain migratory insertion into the metal–carbon bond, as illustrated in Figure 1.

Regulation of polyolefin molecular weight is effected by the use of hydrogen as chain-transfer agent. Chain transfer can also occur via β-hydrogen transfer from the growing chain to the transition metal or to the monomer, and to a lesser extent via alkyl exchange with the cocatalyst (Fig. 2).

In propylene polymerization using titanium chloride catalysts, chain propagation takes place via primary (1,2-) insertion of the monomer. For isospecific propagation, there must be only one coordination vacancy and the active site must be chiral. Corradini and co-workers have demonstrated that the asymmetric

\[
\begin{align*}
\text{Ti-CH}_2\text{-CH}_2\text{-Polymer} + \text{H}_2 & \rightarrow \text{Ti-H} + \text{CH}_3\text{-CH}_2\text{-Polymer} \\
\text{Ti-CH}_2\text{-CH}_2\text{-Polymer} + \text{CH}_3\text{═CH}_2 & \rightarrow \text{Ti-CH}_2\text{-CH}_3 + \text{CH}_2\text{═CH-Polymer} \\
\text{Ti-CH}_2\text{-CH}_2\text{-Polymer} + \text{AlR}_3 & \rightarrow \text{Ti-R} + \text{AlR}_2\text{-CH}_2\text{-CH}_2\text{-Polymer}
\end{align*}
\]

Fig. 1. Cossee–Arlman mechanism for polymerization.

Fig. 2. Chain transfer in ethylene polymerization.
Fig. 3. Model for stereospecific polymerization of propylene. The orientation of the growing chain is influenced by the chlorine atom marked with an asterisk.

The environment of the active site forces the growing chain to adopt a particular orientation so as to minimize steric interactions with (chlorine) ligands present on the catalyst surface (24). This in turn leads to one particular prochiral face of the incoming monomer being preferred, as illustrated in Figure 3, leading to isotactic polymer.

An elegant demonstration of the above mechanism has been provided by Zambelli and co-workers (25), who showed that the first insertion of propylene into a Ti–CH₃ bond generated by chain transfer with Al alkyl using the system TiCl₃/Al(CH₃)₃ is not stereospecific, whereas the second insertion (ie into Ti–isobutyl) is stereospecific. The importance of the combined effects of the steric bulk of the Ti–alkyl group and the halide ligand is apparent from the very high stereospecificity observed using TiI₃ (26). Particularly high stereospecificity (but low activity) was also found by Natta when TiCl₃ was used in combination with Al(C₂H₅)₂I (27).

In contrast to the isospecific titanium-based catalysts, vanadium-based catalysts give predominantly syndiotactic PP. At very low polymerization temperature (−78°C), living polymerization can be obtained using homogeneous catalysts obtained by reaction of a vanadium compound (eg VCl₄ or a V(III) β-diketonate) with R₂AlCl (28,29). With these catalysts, syndiospecific propagation occurs via secondary (2,1-) insertion of the monomer. The overall stereo- and regioregularity of the polymer is poor, comprising not only syndiotactic blocks resulting from secondary insertions but also short, atactic blocks arising from sequences of primary insertions. This polymer has not been developed commercially, but vanadium catalysts are used in ethylene (co)polymerization (outlined under Ziegler–Natta Catalysts for Ethylene (Co)polymerization).

Cs-symmetric metallocene catalysts (30) have been developed for the production of syndiotactic polypropylene having significantly higher chain regularity.

Polymer Particle Growth. A very important feature of any heterogeneous catalyst used in slurry and gas-phase processes for polyolefin production is particle morphology. Heterogeneous Ziegler–Natta catalysts are microporous solids, with particle sizes typically in the range 10–100 μm. Each particle comprises millions of primary crystallites with sizes of up to about 15 nm. On contacting the catalyst components, at the start of polymerization, cocatalyst and monomer diffuse through the catalyst particle and polymerization takes place on the surface of each primary crystallite within the particle. As solid, crystalline polymer is formed, the primary crystallites are pushed apart as the particle grows, analogous to the expanding universe. The particle shape is retained, and this phenomenon
Fig. 4. “Replication” phenomenon during polymerization.

is therefore referred to as replication (Fig. 4). Ideally, the catalyst particle should have spherical morphology and controllable porosity. It is important that the mechanical strength of the catalyst is high enough to prevent disintegration but low enough to allow progressive expansion as polymerization proceeds (31). Further implications of particle morphology and porosity are discussed under Ziegler–Natta Catalysts for Ethylene (Co)polymerization and also under Reactor Granule Technology.

Ziegler–Natta Catalysts for Ethylene (Co)polymerization

Ziegler–Natta catalysts are widely used in the production of high density and linear low density polyethylene (HDPE and LLDPE). More than half the world production of HDPE is based on Ziegler–Natta catalysts, chromium catalysts also being widely used. Less than 1% of HDPE production utilizes metallocene or other single-site catalysts. In LLDPE production, Ziegler–Natta catalysts occupy a dominant position, accounting for more than 90% of the total production. Single-site catalysts currently account for less than 10% of this market, but increased use of such catalysts is expected throughout the next decade.

The most important titanium-based catalysts for HDPE and LLDPE are those comprising a titanium component on magnesium chloride or on a magnesium chloride containing support. Toward the end of the 1960s, catalysts obtained by reaction of TiCl₄ or a derivative thereof with a magnesium compound such as Mg(OH)Cl, Mg(OH)₂, or MgCl₂ were found to give very high activity in ethylene polymerization, eliminating the need for deashing of the polymer (31,32). The most effective support was found to be active magnesium chloride, prepared by co-milling of MgCl₂ and titanium halides or by chlorination of organomagnesium compounds (32). Numerous catalyst systems and methods of preparation have been disclosed (33), and the characteristics of magnesium chloride as a support for Ziegler–Natta catalysts are discussed in depth under Ziegler–Natta Catalysts for Polypropylene. Magnesium chloride can also be used in combination with a silica support, for example by impregnation of the porous support with a solution of MgCl₂ and TiCl₄ in tetrahydrofuran (34).
An important manufacturing process for HDPE that makes use of high mileage catalysts is the cascade process, in which polymerization reactors in series are used to give reactor blends with improved properties for film and pipe applications (35). Broad molecular weight distribution (MWD) can be obtained by the use of different hydrogen concentrations in each reactor. In addition, the process can be designed to give low molecular weight homopolymer in the first reactor and a high molecular weight copolymer in the second. The high molecular weight copolymer chains function as tie molecules linking the crystalline, homopolymer domains, thereby leading to high stress crack resistance of the polymer. This process allows an “inverse” comonomer distribution to be obtained, in the sense that the comonomer is in the high molecular weight fraction, counteracting the general tendency of Ziegler–Natta catalysts to incorporate the comonomer mainly in the low molecular weight chains. The latter feature is an important consideration in Ziegler–Natta catalyst design for LLDPE. Comonomer incorporation is highest at the most open catalytic centers, whereas sterically hindered centers will tend to give polyethylene chains with little or no comonomer. The best catalysts for LLDPE are therefore those that have relatively uniform active center distribution, lacking excessively hindered or unhindered active sites.

Vanadium catalysts have also been developed for polyethylene and ethylene-based copolymers, particularly ethylene–propylene–diene rubbers (EPDM). Homogeneous (soluble) vanadium catalysts produce relatively narrow MWD polyethylene, whereas supported vandium catalysts give broad MWD (36). Polymerization activity is strongly enhanced by the use of a halogenated hydrocarbon as promoter in combination with a vanadium catalyst and aluminum alkyl cocatalyst (36,37).

Ethylene polymerization, in contrast to the polymerization of propylene and other alpha-olefins, is often affected by diffusion limitations, which occur if the monomer reactivity in polymerization is high relative to diffusivity through the catalyst particle. This can result in the formation of an “onion” particle structure as polymerization first takes place at the external surface of the particle, particle growth occurring step by step as the monomer reaches the inner parts of the catalyst particle. This mechanism of particle growth is associated with a kinetic profile in which an initial induction period is followed by an acceleration period, after which, in the absence of chemical deactivation, a stationary rate is obtained.

Ziegler–Natta Catalysts for Polypropylene

Worldwide manufacture of PP, currently around 30 million tons per annum, is dominated by high activity MgCl₂-supported Ziegler–Natta catalysts. The first- and second-generation TiCl₃ catalysts have all but disappeared, and the recently developed metallocene catalysts still account for less than 1% of all PP produced, although they are likely to grow in importance. The development and implementation of MgCl₂-supported catalysts in bulk (liquid monomer) and gas-phase processes has led to the advent of simple, low-cost (nondeashing, nonextracting) manufacturing processes for PP (18).

The basis for the development of the high activity supported catalysts lay in the discovery, in the late 1960s, of “activated” MgCl₂ able to support TiCl₄ and give
high catalyst activity, and the subsequent discovery, in the mid-1970s, of electron donors (Lewis bases) capable of increasing the stereospecificity of the catalyst so that (highly) isotactic PP could be obtained (32,38,39). A further feature that has contributed greatly to the commercial success of MgCl₂-supported catalysts is the development of spherical catalysts with controlled particle size and porosity (40), which not only replicate their morphology during polymerization as the polymer particle grows, but which have now opened the way to a broad range of homopolymers and multiphase polymer alloys via what has been termed Reactor Granule Technology (41).

**Catalyst Structure and Composition.** In the early stages of MgCl₂-supported catalyst development, activated magnesium chloride was prepared by ball milling in the presence of ethyl benzoate, leading to the formation of very small (≤3 nm thick) primary crystallites within each particle (21). Nowadays, however, the activated support is prepared by chemical means such as complex formation of MgCl₂ and an alcohol or by reaction of a magnesium alkyl or alkoxide with a chlorinating agent or TiCl₄. Many of these approaches are also effective for the preparation of catalysts having controlled particle size and morphology. For example, the cooling of emulsions of molten MgCl₂·nC₂H₅OH in paraffin oil gives almost perfectly spherical supports, which are then converted into the catalysts (18). A typical catalyst preparation involves reaction of the MgCl₂·nC₂H₅OH support with excess TiCl₄ in the presence of an “internal” electron donor. Temperatures of at least 80°C and at least two TiCl₄ treatment steps are normally used, in order to obtain high performance catalysts in which the titanium is mainly present as TiCl₄ rather than the TiCl₃OC₂H₅ generated in the initial reaction with the support. Catalysts obtained via chemical routes generally have a BET surface area of around 300 m²/g and pore volumes in the range 0.3–0.4 cm³/g (18).

High activity Ziegler–Natta catalysts comprising MgCl₂, TiCl₄, and an internal donor are typically used in combination with an aluminum alkyl cocatalyst such as Al(C₂H₅)₃ and an “external” electron donor added in polymerization. The first catalyst systems containing ethyl benzoate as internal donor were used in combination with a second aromatic ester such as methyl p-toluate as external donor (39). These were followed by catalysts containing a diester (eg diisobutyl phthalate) as internal donor, used in combination with an alkoxy silane external donor of type RR′Si(OCH₃)₂ or RSi(OCH₃)₃ (42). The combination MgCl₂/TiCl₄/phthalate ester–AlR₃–alkoxy silane is currently the most widely used catalyst system in PP manufacture. The most effective alkoxy silane donors for high isospecificity are methoxy silanes containing relatively bulky alkyl groups branched at the position alpha to the silicon atom (43–46). Typical examples include cyclohexyl(methyl)dimethoxy silane and dicyclopentyl dimethoxy silane (47). Of these, the latter gives particularly high stereospecificity (48) and broader MWD (49). High PP stereoregularity and broad MWD have also been obtained by the use of dimethoxy silanes containing polycyclic amino groups (50,51).

The function of the internal donor in MgCl₂-supported catalysts is twofold. One function is to stabilize small primary crystallites of magnesium chloride; the other is to control the amount and distribution of TiCl₄ in the final catalyst. Activated magnesium chloride has a disordered structure comprising very small lamellae. Giannini (32) has indicated that, on preferential lateral cleavage surfaces, the magnesium atoms are coordinated with four or five chlorine atoms, as
opposed to six chlorine atoms in the bulk of the crystal. These lateral cuts correspond to (110) and (100) faces of MgCl₂, as shown in Figure 5.

It has been proposed that bridged, dinuclear Ti₂Cl₈ species can coordinate to the (100) face of MgCl₂ and give rise to the formation of chiral, isospecific active species (Fig. 6), it being pointed out that Ti₂Cl₆ species formed by reduction on contact with Al(C₂H₅)₃ would resemble analogous species in TiCl₃ catalysts (52, 53). Accordingly, it has been suggested (18) that a possible function of the internal donor is preferential coordination on the more acidic (110) face of MgCl₂, such that this face is prevailingly occupied by donor and the (100) face is prevailingly occupied by Ti₂Cl₈ dimers.

Analytical studies (54) have indicated that a monoester internal donor such as ethyl benzoate is coordinated to MgCl₂ and not to TiCl₄. In the search for donors giving catalysts having improved performance, it was considered (55) that bidentate donors should be able to form strong chelating complexes with tetracoordinate Mg atoms on the (110) face of MgCl₂, or binuclear complexes with two pentacoordinate Mg atoms on the (100) face. This led to the development of the MgCl₂/TiCl₄/phthalate ester catalysts, used as indicated above in combination with an alkoxysilane as external donor. The requirement for an external donor when using catalysts containing a benzoate or phthalate ester is due to
the fact that, when the catalyst is brought into contact with the cocatalyst, a large proportion of the internal donor is lost as a result of alkylation and/or complexation reactions. In the absence of an external donor, this leads to poor stereospecificity because of increased mobility of the titanium species on the catalyst surface. When the external donor is present, contact of the catalyst components leads to replacement of the internal donor by the external donor, as has been shown (56,57) with MgCl₂/TiCl₄/ethyl benzoate–Al(C₂H₅)₃–methyl p-toluate and with MgCl₂/TiCl₄/dibutyl phthalate–Al(C₂H₅)₃–C₆H₅Si(OC₂H₅)₃. The most active and stereospecific systems were those which allowed the highest incorporation of external donor (58), the effectiveness of a catalyst system depending more on the combination of donors rather than on the individual internal or external donor. For example, the use of a monoester rather than an alkoxysilane as external donor with a phthalate-containing system is ineffective (59), as in this case very little of the external donor is adsorbed (58). Further studies (60,61) showed that a phthalate-containing catalyst adsorbed alkoxysilanes to a greater extent than a catalyst without internal donor.

Recently, research on MgCl₂-supported catalysts has led to systems not requiring the use of an external donor. This required the identification of bidentate internal donors that not only had the right oxygen–oxygen distance for effective coordination with MgCl₂ but that, unlike phthalate esters, were not removed from the support on contact with Al(C₂H₅)₃ and that were unreactive with TiCl₄ during catalyst preparation. It was found (55,62–64) that certain 2,2-disubstituted 1,3-dimethoxypropanes met all these criteria. The best performance was obtained when bulky substituents in the 2-position resulted in the diether having a most probable conformation (65) with an oxygen–oxygen distance in the range 2.8–3.2 Å. The successive “generations” of high activity MgCl₂-supported catalyst systems for PP are summarized below:

1. MgCl₂/TiCl₄/ethyl benzoate–AlR₃–aromatic ester
2. MgCl₂/TiCl₄/phthalate ester–AlR₃–alkoxysilane
3. MgCl₂/TiCl₄/diether–AlR₃

Catalyst performance has improved considerably with each generation. The PP yield obtained under typical polymerization conditions (liquid monomer, in the presence of hydrogen, 70°C, 1–2 h) has increased from 15–30 kg/g cat. for
the third-generation ethyl benzoate containing catalysts to 30–80 kg/g cat. for the fourth-generation phthalate-based catalysts. With the recently developed fifth-generation catalysts containing a diether as internal donor, yields of 80–160 kg/g cat. can be achieved. These different catalysts also display different kinetic profiles in propylene polymerization. The catalysts containing a diether as internal donor exhibit very stable activities during polymerization. A low rate of catalyst decay during polymerization is also obtained with the catalyst system MgCl₂/TiCl₄/phthalate ester–AlR₃–alkoxysilane, whereas the system MgCl₂/TiCl₄/ethyl benzoate–AlR₃–aromatic ester has a very high initial polymerization activity but also a high decay rate, limiting the final polymer yield. The rapid decay in activity can at least partially be ascribed to the use of an ester as external as well as internal donor, the ester being able to react with titanium–hydrogen bonds formed in chain transfer with hydrogen, generating Ti–O bonds inactive for chain propagation (66).

Most recently, a further family of MgCl₂-supported catalysts has been developed (67,68), in which the internal donor is a succinate rather than a phthalate ester. As is the case with the phthalate-based catalysts, an alkoxysilane is used as external donor. The essential difference between these catalysts is that the succinate-based systems produce PP having much broader MWD (discussed under Catalyst/Polymer Relationship).

Mechanistic Aspects. It is well established that effective external donors not only increase the isotactic index of the polymer (the proportion of polymer insoluble in boiling heptane or in xylene at 25°C), but can also increase in absolute terms the amount of isotactic polymer formed. This has been demonstrated by Kashiwa (69) for the catalyst system MgCl₂/TiCl₄–Al(C₂H₅)₃. An increase in the molecular weight and stereoregularity of the isotactic fraction was also noted. Similar trends are apparent with catalyst systems of type MgCl₂/TiCl₄/phthalate ester–AlR₃–alkoxysilane (70). Kakugo (71) has used elution fractionation to demonstrate that the external donor not only decreases “atactics” formation but also increases the degree of steric control at isospecific sites. Soga has reported that an almost aspecific MgCl₂/TiCl₃ catalyst, with a very low content of (probably isolated, monomeric) Ti species, could be rendered isospecific by the addition of ethyl benzoate as external donor (72) or by using Cp₂Ti(CH₃)₂ as cocatalyst (73). It was suggested (74) that in both cases aspecific sites having two coordination vacancies could be converted to isospecific sites by blocking one of the two vacancies.

A powerful technique to study the effects of electron donors on site selectivity in Ziegler–Natta catalysts is the determination of the stereoregularity of the first insertion step in propylene polymerization. Sacchi and co-workers (60,75) have investigated the effect of Lewis bases on the first-step stereoregularity resulting from propylene insertion into a Ti–C₃H₅ bond formed via chain transfer with ¹³C-enriched Al(C₂H₅)₃. First-step stereoregularity is particularly sensitive to the steric environment of the active center, because the stereospecificity of the first monomer insertion is always lower than that of the following propagation steps. For example, with a MgCl₂/TiCl₄/diisobutyl phthalate catalyst it was found (60) that the mole fraction of erythro (isotactic) placement in the isotactic polymer fraction was 0.67 with no external donor, 0.82 with CH₃Si(OC₂H₅)₃, and 0.92 with C₆H₅(OC₂H₅)₃. It could be concluded that the alkoxysilane external donor
was present in the environment of at least part of the isospecific centers (Fig. 7). Subsequent studies (76,77) indicated that similar considerations apply to diether donors.

Recently, significant advances have been made in understanding the fundamental factors determining the performance of state-of-the-art MgCl₂-supported catalysts. Studies by Busico and co-workers (78) have shown that the chain irregularities in isotactic PP prepared using heterogeneous catalysts are not randomly distributed along the chain but are clustered. The chain can therefore contain, in addition to highly isotactic blocks, sequences that can be attributed to weakly isotactic (isotactoid) and to syndiotactic (syndiotactoid) blocks. This implies that the active site can isomerize very rapidly (during the growth time of a single polymer chain, i.e., in less than a second) between three different propagating species. The same sequences are present, but in different amounts, in both the soluble and the insoluble fractions. The polymer can therefore be considered to have a stereoblock structure in which highly isotactic sequences alternate with defective isotactoid and with syndiotactoid sequences. A mechanistic model has been formulated in which the relative contributions of these sequences can be related to site transformations involving the presence or absence of steric hindrance in the vicinity of the active species. ¹³C NMR studies have indicated (79) the presence of C₁-symmetric active species in MgCl₂-supported catalysts, with a mechanism of isotactic propagation which is analogous to that for certain C₁-symmetric metallocenes, in the sense that propylene insertion at a highly enantioselective site tends to be followed by chain “back-skip” rather than a less regio- and stereoselective insertion when the chain is in the coordination position previously occupied by the monomer. The probability of chain “back-skip” will increase with decreasing monomer concentration, and it has indeed been confirmed that increased polymer isotacticity is obtained at low monomer concentration. It is proposed (78) that a (temporary) loss of steric hindrance from one side of an active species with local C₂-symmetry, giving a C₁-symmetric species, may result in a transition from highly isospecific to moderately isospecific propagation. Loss of steric hindrance on both sides can lead to syndiospecific propagation in which chain-end control becomes operative. The model is illustrated in Figure 8.

If it is considered that the steric hindrance in the vicinity of the active species can result from the presence of a donor molecule, and that the coordination of such a donor is reversible, the above model provides us with an explanation for the fact that strongly coordinating, stereorigid donors typically give stereoregular polymers in which the highly isotactic sequences predominate. Several types of active species in which the presence of a donor in the vicinity of the active Ti atom is necessary for high isospecificity have been proposed (80), although the exact structure of the active species is still by no means resolved. Isospecific active
species not requiring the presence of a donor for high stereospecificity have also been proposed (81).

In PP production, hydrogen is used as a chain-transfer agent for polymer molecular weight (melt-flow rate) control. The effect of hydrogen (concentration) on polymer molecular weight is dependent on the catalyst system. An advantage of catalysts containing a diether donor, in addition to very high activity, is high sensitivity to hydrogen, so that relatively little hydrogen is required for molecular weight control. This effect can be ascribed to chain transfer after the occasional secondary (2,1-) rather than the usual primary (1,2-) insertion, a 2,1-insertion slowing down a subsequent monomer insertion and therefore increasing the probability of chain transfer (82). Reactivation of “dormant” (2,1-inserted) species via chain transfer with hydrogen also explains the frequently observed activating effect of hydrogen in propylene polymerization, giving yields which may be around three times those observed in the complete absence of hydrogen. These conclusions have been based on the $^{13}$C NMR determination of the relative proportions of $i$-$C_4H_9$ and $n$-$C_4H_9$ terminated chains, resulting from chain transfer with hydrogen after primary and secondary insertion respectively:

\[
\text{Ti} \rightarrow \text{CH}_2 \rightarrow \text{CH(CH}_3)_2 \rightarrow [\text{CH}_2 \rightarrow \text{CH(CH}_3)_2]_n \text{Pr} + H_2 \rightarrow \text{Ti} \rightarrow H + i- \text{C}_4\text{H}_9 \rightarrow \text{CH(CH}_3)_2[\text{CH}_2(\text{CH}_3)_2]_{n-1} \text{Pr}
\]

\[
\text{Ti} \rightarrow \text{CH(CH}_3)_2 \rightarrow [\text{CH}_2 \rightarrow \text{CH(CH}_3)_2]_n \text{Pr} + H_2 \rightarrow \text{Ti} \rightarrow H + n- \text{C}_4\text{H}_9 \rightarrow \text{CH(CH}_3)_2[\text{CH}_2(\text{CH}_3)_2]_{n-1} \text{Pr}
\]

Other studies have demonstrated that chain transfer is dependent not only on regio- but also on stereoselectivity (48). This is in keeping with the tendency that, with catalyst systems of type MgCl$_2$/TiCl$_4$/phthalate ester–AlR$_3$–alkoxyxilane, the silanes that give the most stereoregular isotactic polymer also give relatively low hydrogen response.

**Catalyst/Polymer Relationship.** By varying the catalyst composition, and in particular the nature of the electron donors (esters, silanes, diethers) present in the catalyst system, it is possible to control the PP tacticity, molecular weight, and MWD to produce a range of polymers having the processing and end-use properties required for very different applications. Ziegler–Natta catalysts typically give broader MWDs than are obtained with homogeneous
(metallocene) catalysts. This is because Ziegler–Natta catalysts contain a range of different active centers, each center giving different relative rates of chain propagation and chain transfer. Each individual site produces a Schulz–Flory distribution with $M_w/M_n = 2$ and $M_z/M_w = 1.5$, and the overall polymer MWD represents a combination of these individual distributions. The dominant effect of active center distribution has been demonstrated by the use of stopped-flow polymerization (83), where the polymer MWD was shown to be unaffected by the polymerization time. Stopped-flow polymerization has also been used to determine active site concentration ($C^*$) and propagation rate constants, $k_p$. For MgCl$_2$-supported catalysts, $C^*$ values of around 4% (of total Ti present) have been obtained from stopped-flow experiments (84). $C^*$ values obtained by other techniques, notably $^{14}$CO quenching of propylene polymerization, have ranged from 1% or less (85) to more than 20% (86). Clearly, there are large differences in $C^*$ values obtained by different groups, but it is consistently found that the major proportion of the Ti present in Ziegler–Natta catalysts is inactive. The $k_p$ values for isospecific active sites are around an order of magnitude greater than those for weakly specific sites (85,86). The value of $k_p$ increases significantly in the presence of hydrogen (87), in accordance with the reactivation of “dormant” (2,1-inserted) centers by chain transfer.

Recent work by Terano and co-workers (88) has shown that, under stopped-flow conditions, hydrogen is only effective as chain-transfer agent when catalyst and cocatalyst have been precontacted. These and subsequent (89,90) results indicated that effective chain transfer with hydrogen requires the presence of species able to promote the dissociation of H$_2$ to atomic hydrogen.

The donors present in the catalyst system play an active role in the formation or modification of isospecific sites, and the polymer MWD depends on the relative contribution and hydrogen response (ie sensitivity to chain transfer with hydrogen) of each type of active site. The incorporation of an external donor into the catalyst system generally leads to an increase in molecular weight, the magnitude of the MW increase depending on the nature of the donor. The characteristics of different catalyst systems with regard to PP MWD are as follows (68):

<table>
<thead>
<tr>
<th>Internal donor</th>
<th>External donor</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diether</td>
<td>—</td>
<td>5–5.5</td>
</tr>
<tr>
<td>Phthalate</td>
<td>Alkoxy silane</td>
<td>6.5–8</td>
</tr>
<tr>
<td>Succinate</td>
<td>Alkoxy silane</td>
<td>10–15</td>
</tr>
</tbody>
</table>

It can be seen that the diether-based catalysts give relatively narrow MWD. A narrow MWD, and relatively low molecular weight, is advantageous in fiber spinning applications. In contrast, extrusion of pipes and thick sheets requires high melt strength, and therefore relatively high molecular weight and broad MWD. A broad MWD, along with high isotactic stereoregularity, is also beneficial for high crystallinity and therefore high rigidity. The new succinate-based catalysts enable very broad MWD PP homopolymers to be produced in a single reactor and are also of interest for the production of heterophasic copolymers having an improved balance of stiffness and impact strength, taking into account that the incorporation
of a rubbery (ethylene/propylene) copolymer phase into a PP homopolymer matrix increases impact strength but leads at the same time to decreased stiffness.

The relatively narrow PP molecular weight distributions obtained using diether-based catalysts can be attributed to the fact that in these systems even the most highly stereospecific active sites are not totally regiospecific. A proportion of approximately one secondary insertion for every 2000 primary insertions at highly isospecific sites has been noted for the system MgCl₂/TiCl₄/diether–AlR₃ (82). The probability of chain transfer with hydrogen after a secondary insertion is such that this is sufficient to prevent the formation of very high molecular weight chains, taking into account that the highest molecular weight fraction of the polymer is formed on the active species having the highest isospecificity. The broader MWDs obtained with catalysts containing ester internal donors are likely to be due to the presence of (some) isospecific active sites having very high regiospecificity and therefore lower hydrogen sensitivity. Such results illustrate the profound effect of catalyst regio- and stereospecificity distribution on both molecular weight control and polymer MWD and properties.

Reactor Granule Technology. As indicated in the section Polymer Particle Growth, particle morphology and porosity are very important features of a Ziegler–Natta catalyst used in modern bulk (liquid monomer or gas-phase) polymerization processes. Under appropriate polymerization conditions, polymer particles can be obtained that have an internal morphology that can range from a compact to a porous structure (91). In what is termed Reactor Granule Technology (RGT), porous polymer particles can be produced, which can then function as a microreactor for the polymerization of other monomers within the solid matrix. A polypropylene skin encloses the second polymer phase, thereby preventing coalescence of particles in which the second phase is an amorphous, low-melting material (92). RGT has been defined as “controlled, reproducible polymerization of olefinic monomers on an active MgCl₂-supported catalyst, to give a growing, spherical granule that provides a porous reaction bed within which other monomers can be introduced and polymerized to form a polyolefin alloy” (93).

Today, RGT is able to provide products ranging from superstiff, high fluidity PP homopolymers to stiff/impact or clear/impact heterophase copolymers and supersoft alloys, produced using the Catalloy process (31,68). The feasibility of producing heterophase alloys containing up to 70% of multimonomer copolymers arises from the use of a controlled porosity catalyst and the ability to control the porosity of the growing polymer particle during the early stages of polymerization. Prepolymerization is applied to give the particles sufficient heat capacity to withstand injection into a gas-phase polymerization step.

Several models have been put forward to explain the mechanism of particle growth during polymerization. One of the most popular models is the “multigrain model,” put forward by Ray and co-workers (94), in which the monomer diffuses into the catalyst macroparticle and polymerizes on the surface of the microparticles within, causing the macroparticle to expand progressively as polymerization proceeds. An investigation by Kakugo and co-workers (95) of nascent polymer morphology obtained using a TiCl₃ catalyst showed that the polymer particle comprised numerous globules, each of which contained some tens of much smaller primary particles. Recently, a model for particle growth with MgCl₂-supported catalysts has been proposed by Cecchin (68,96), who has also provided evidence for
polymer “subglobule” formation within the growing particle. Again, these subglobules originate from clusters of primary crystallites, but the crystallites themselves are pushed to the surface of each subglobule as the polymer forms. This model, illustrated in Figure 9, explains the fact that, in the preparation of heterophase copolymers via propylene homopolymerization followed by ethylene/propylene copolymerization, the rubbery ethylene/propylene copolymer is formed at the surface of the homopolymer subglobules, gradually filling up the pores within the particle. Clearly, the higher the porosity of the homopolymer matrix, the greater the proportion of (rubbery) copolymer that can be incorporated into the particle without running into problems of stickiness if the rubber phase blooms to the surface. Evidence for drifting of catalyst microparticles to the surface of polymer (sub)globules has been provided by scanning electron microscopy studies of prepolymerized catalyst particles (97).

Polymerization of Other Monomers Using Ziegler–Natta Catalysts

In addition to their widespread use in the production of polyethylene and polypropylene, Ziegler–Natta catalysts play an important role in the production of poly-1-butene and are also widely used in the manufacture of synthetic rubbers such as cis-1,4-polybutadiene and cis-1,4-polyisoprene, the synthetic equivalent of natural rubber. Ziegler–Natta catalysts for the manufacture of butadiene rubber, based on titanium, cobalt, nickel, or neodymium systems, are described elsewhere (see BUTADIENE POLYMERS). Isoprene rubber is produced using β-TiCl₃ (98), typically prepared by reaction of approximately equimolar quantities of TiCl₄ and Al-i-(C₄H₉)₃ in the presence of a small quantity of an ether. Increased catalyst activity can be obtained by incorporation of a sterically hindered phenoxyaluminum cocatalyst component (99). The latter component also gives increased activity in propene polymerization using TiCl₃ (100); in both cases the improvement
in catalyst performance can be attributed to selective complexation of the catalyst poison RAlCl₂. In addition to aluminum alkyls, poly(N-alkylaluminoxanes) have been found to be effective cocatalysts in isoprene polymerization (101). These components have cage structures (e.g. [HAlN-i-C₃H₇]₆) in which both Al and N atoms are tetracoordinated (102).

Cis-1,4-polymerization of conjugated dienes requires the presence of two coordination vacancies on the transition-metal atom, allowing bidentate coordination of the diene. β-TiCl₃ has a fiber-like structure in which the titanium atoms in the lattice are octahedrally coordinated to six chlorine atoms. The terminal titanium atoms are, however, incompletely coordinated and are linked to four or five chlorine atoms. Alkylation of the tetracoordinated titanium atoms will generate the double-vacancy species active in isoprene polymerization. Stereospecificity in diene polymerization can change dramatically if one of the coordination vacancies is blocked by a Lewis base. An interesting illustration of this (103) is that the addition of an external donor in isoprene polymerization with TiCl₄–Al(C₂H₅)₃ or MgCl₂/TiCl₄–Al(C₂H₅)₃ changes the catalyst stereospecificity to give mainly trans-1,4- rather than cis-1,4-polysoprene. At the same time, a notable increase in isospecificity in propylene polymerization is observed.

TiCl₃-based and MgCl₂-supported catalysts have been developed for the production of poly-1-butene. TiCl₃ catalysts are used with dialkylaluminum halide cocatalysts, Al(C₂H₅)₂I giving higher isotacticity than Al(C₂H₅)₂Cl (104). Very high isotacticity has been obtained using TiCl₃ in combination with Cp₂Ti(CH₃)₂ (105). Much higher polymerization activity, as well as high isotacticity and broad MWD, is obtained using MgCl₂-supported catalysts, for example the catalyst system MgCl₂/TiCl₄/diisobutyl phthalate–Al(C₂H₅)₃–alkoxysilane (106).

Ziegler–Natta catalysts have also been developed for the polymerization of 4-methyl-1-pentene (107) and higher alpha-olefins. Polymerization activity decreases with increasing steric bulk of the monomer. For example, with the catalyst system MgCl₂/TiCl₄/ethyl benzoate–Al(C₂H₅)₃–ethyl benzoate the relative activities in propylene, 1-butene, and 4-methyl-1-pentene polymerization were 100:80:15 (108). For catalyst systems of type MgCl₂/TiCl₄/phthalate ester–AlR₃–alkoxysilane, the type of silane required is dependent on the steric bulk of the monomer. An active center having high stereospecificity in propylene polymerization may be too sterically hindered for effective polymerization of a bulkier monomer, propylene/1-butene copolymerization studies having shown (109) that the incorporation of 1-butene into the polymer chain decreases with increasing site stereospecificity. This phenomenon is also illustrated by the fact that nonbulky alkoxysilanes such as (CH₃)₃SiOCH₃ are effective donors in 4-methyl-1-pentene polymerization (110), whereas such donors are relatively ineffective in propylene polymerization.

**Concluding Remarks**

The dominant position of Ziegler–Natta catalysts in the manufacture of polyolefins, in particular PP, is likely to continue for a considerable length of time, despite the many developments taking place in the field of metallocene and other single-site catalysis. Indeed, the range of polymer types and grades is so varied
that there is ample scope for further development and implementation of both Ziegler–Natta and single-site catalysts.

It will be clear that the composition and characteristics of a Ziegler–Natta catalyst must be tailored such that the required polymer molecular structure and properties are obtained. Different catalysts are required for different polymer applications, and the recent development and implementation of MgCl₂-supported catalysts containing diether and succinate donors, for the production of narrow and broad MWD PP respectively, illustrates the ongoing activity in Ziegler–Natta catalyst research. The ability to control catalyst particle size, morphology, and porosity has allowed the development of advanced and versatile polymerization process technologies, so that the characteristics of the catalyst can be tuned to both process and product requirements.

Ziegler–Natta catalysts are complex systems and are still by no means fully understood, but significant advances in basic understanding have recently been made. This will continue, with both experimental and molecular modeling studies providing additional mechanistic insight, which in turn can be applied in the further development and implementation of these catalysts.

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