ZIEGLER-NATTA CATALYSTS

1. Introduction

The origin of the Ziegler-Natta catalysis dates back to 1953 when Ziegler discovered, at Muelheim, that some transition-metal compounds, eg, $TiCl_4$, used in combination with aluminium alkyls, could polymerize ethylene into linear polyethylene under mild conditions of pressure and temperature. In 1954, Ziegler's concept was applied by Natta, at the Polytechnic of Milan, to the regio- and stereoselective polymerization of propylene into a partially crystalline and stereoregular, previously unknown and unexpected polymer: isotactic polypropylene. These scientific breakthroughs, which allowed Ziegler and Natta to share the Nobel Prize in 1963, were quickly translated into industrial realities by Hoechst in 1955 and Montecatini in 1957, with the manufacture and commercialization of high-density polyethylene and isotactic polypropylene, respectively. Since then, the development of catalysts related polymerization technologies and products has been relentless and is still in progress today. Over the years, the property envelope of polyolefins has been largely expanded by the generation of improved–innovative products that clearly outperform the previously available materials. For example, polypropylene modification with ethylene–propylene copolymers via sequential copolymerization of propylene and ethylene–propylene mixtures (*in situ* alloys) has led to the synthesis of multiphase copolymers offering an unprecedented balance between fluidity, rigidity, impact strength, transparency, etc. Starting from the initial few thousand tons, the production of polyolefins via Ziegler-Natta polymerization has grown exponentially in time, and today is approaching a global volume of 65 million tons. This is due not only to the intrinsic properties and performances of these materials but

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especially to the availability of ever more efficient, sophisticated and versatile catalyst systems, and resulting manufacturing processes. Following the initial (mid-1950s) studies on titanocenes (1), a family of homogeneous, single-site catalyst systems has more recently been developed, which are based on metallocenes (2–8) or late transition-metal complexes (9,10) that, in principle, offer a number of advantages over conventional Ziegler-Natta systems. However, despite this, heterogeneous Ziegler-Natta catalysts are still at the forefront of the scientific and, especially industrial, world since they still account for the majority of the global polyolefin market share.

2. Evolution of Ziegler-Natta Catalysts

Broadly speaking, a Ziegler-Natta catalyst system can be defined as a transition-metal compound bearing a metal–carbon bond able to promote a repeated insertion of olefin units and thus generate a macromolecular polyolefin chain. Usually, the catalyst system consists of the combination of two components: a transition-metal compound (most frequently a titanium halide) and a main group metal alkyl (generally an aluminium alkyl or alkyl halide), and can comprise additional components, eg, electron donors.

Starting from the discoveries of Ziegler and Natta concerning the ability of the $TiCl_4/AlR_3$ mixture to promote the polymerization of ethylene and of propylene, continuous research in the field, mainly driven by industrial requirements, has led to the development of various families and generations of catalysts having a level of sophistication and performances one could only dream about at the time of their first discovery.

The polyolefin industry, aimed at both continuous simplification of polymerization technologies and product optimization–innovation, has fixed a number of ambitious objectives for the catalyst to target over the years, most of which have been achieved by the latest generations of catalyst systems:

- Very high mileage (chlorine content in the exreactor product less than ∼50 ppm, preferably <10 ppm).
- Stereoregularity for polypropylene and the other 1-olefins (Isotactic Index, expressed as the polymer fraction insoluble in xylene at room temperature, higher than ∼97%).
- Control of the most important polymer parameters like molecular mass (MW), molecular mass distribution (MWD), and comonomer incorporation, when required.
- Complete morphology control over both catalyst and polymer particles.

These spectacular achievements have been obtained thanks to the exploitation of several scientific and technological breakthroughs, and, especially:

- The active form of magnesium chloride.
- The stereoregulating effect of electron donors.
- The chemical route to the active form of magnesium chloride.

- The control of the morphology of the catalyst particle and the exploitation of the polymer–catalyst replication phenomenon.

If we exclude the pseudo–homogeneous catalysts based on vanadium compounds, mainly used to prepare ethylene–propylene (EPM) or ethylene–propylene–diene (EPDM) rubbers, industrial Ziegler-Natta catalysts can be roughly classified into two families: the first family includes fundamentally $TiCl_3$, actually a $TiCl_3 \cdot 0.33\ AlCl_3$ solid mixture, which is obtained via reduction of $TiCl_4$ either by aluminium metal or aluminium alkyls or alkylhalides, and subsequent activation of the resulting solid; the second family is based on the discovery and exploitation, starting from the late 1960s, of the active form of $MgCl_2$ as a support for titanium compounds. In both cases, the solid catalyst or support needs to be activated and converted into the most active δ crystalline modification: In the case of aluminium-reduced $TiCl_3$, this was achieved via intensive dry milling whereas in the case of aluminium alkyl (alkylhalide) reduced $TiCl_3$, this was obtained via thermal treatments. No morphology control was possible in the first case, whereas control of the shape (spheroidal) of the catalyst particle could be obtained in the second case. Initially, intensive milling was also used to get the active form of $MgCl_2$. Today, activation of $MgCl_2$ is generally performed via chemical methods that not only allow the fine tuning of catalyst performances but also provide an unprecedented control over the morphology of the catalyst particles (see the section, The Growth of the Polymer Particle). The performances of $TiCl_3$, which was preferably used in combination with $AlEt_2Cl$ in the case of the stereospecific polymerization of propylene and with $AlEt_3$ in the case of the polymerization of ethylene, were rather poor in terms of both activity and, in the case of polypropylene, stereoselectivity. For these reasons, both a postpolymerization deashing step and an extraction step (polypropylene) were necessary in order to remove, respectively, the catalyst residues and the amorphous components from the polymer. An increase of catalyst stereospecificity (Isotactic Index from ∼88% to ∼95%), but not activity, was achieved via modification of the catalyst by third components, especially electron donors, like, eg, methyl metacrylate (19).

The poor activity of $TiCl_3$ was attributed to the fact that only a small fraction of Ti atoms, the ones located at the surface of the catalyst crystallites, are available as potential active sites. Efforts to increase the working surface of the catalyst led Solvay (20,21) to develop a more advanced, spheroidal catalyst for polypropylene, obtained via reduction of $TiCl_4$ with $AlEt_2Cl$ and subsequent treatments with electron donors like, eg, di-n-butyl or di-iso-amyl ethers, followed by a treatment with $TiCl_4$. With respect to first-generation $TiCl_3$, this second catalyst generation is characterized by much higher surface area, productivity, and isospecificity. Because of the increased isospecificity, the removal of the amorphous polymer fraction was not necessary anymore and the polymerization plants setup could be simplified accordingly. On the other hand, the productivity was not high enough to eliminate the deashing steps. Both targets, and others, were achieved with the discovery by Montedison (22) of $MgCl_2$ as support for titanium compounds and the resulting development of the next, more advanced, family of Ziegler-Natta catalyst systems. As in the case of the Solvay catalyst, the use of $MgCl_2$ as a support was based on the

assumption that the supportation, or "dilution" of Ti atoms on a high surface area carrier could largely improve catalyst efficiency because a large number of surface Ti atoms are available for polymerization. Actually, it has been indicated (17) that $MgCl_2$ is not a mere diluent for the transition-metal atoms, since not only the number of active centers, but also the relevant propagation constants increase. The first attempts to exploit Mg derivatives as supports dates back to the early 1960s using, eg, Mg(OH)Cl, hydroxylated MgO, or $MgSO_4$ (17), and then, in the late 1960s, milled $MgCl_2$ or reactive Mg compunds that lead to the formation of active $MgCl_2$ (see the section Preparation of $MgCL_2$– Supported Catalysts). These catalysts were very active for both polyethylene and polypropylene, but were not isospecific enough. The major breakthrough in the field was the discovery, by Giannini and co-workers (23) in the early 1970s, of the stereoregulating ability of electron donors. The most modern and advanced catalysts for polypropylene are exactly based on the combination of $MgCl_2$, a titanium compound, and electron donors. In particular, the solid catalyst particles comprise chemically activated $MgCl_2$, $TiCl_4$, and an "internal" electron donor (ID). In polymerization, they are usually used in combination with $AlEt_3$ as cocatalyst and an "external" donor (ED). The corresponding catalysts for polyethylene in principle do not require any donor, even though electron donors can be part of the catalyst system for the synthesis of special polymer grades.

Within the mentioned $MgCl_2$–$TiCl_4$ systems, several generations of catalysts for polypropylene have been developed over the years. These catalysts differ mainly in the nature of the internal–external donor couple: overall catalyst performances, especially activity and isospecificity have been largely improved, in the early 1980s, by replacing the first family of internal–external donors (ethylbenzoate–aromatic esters) with the couple diisobutyl phthalate–alkoxysilane (24) and, more recently, with diethers. These diethers are typically a 2,2-disubstituted -1,3-dimethoxypropane used without or in combination with an alkoxysilane (25–35). The above electron-donor couples define, respectively, the third, fourth, and fifth generation of Ziegler-Natta catalyst systems. The main properties of the various catalyst generations for polypropylene, including the early $TiCl_3$ systems are reported in Table 1. Starting from the fourth generation, not only the deashing step but also the removal of the atactic polymer fraction could be eliminated, with consequent enormous simplification of the polymerization processes. But the role of the electron donor goes beyond the control of yield and isospecificity, since it can affect several polymer properties like MW and MWD. For example, whereas the fourth catalyst generation provides both medium MW and MWD polymers, the fifth generation can provide very low MW and narrow MWD polymers and, in addition, high polymer isotacticity without the use of any external donors. Quite recently, a next generation of $MgCl_2$–$TiCl_4$ systems was developed (36–38), which is based on succinates as internal donors and that is able to provide both controlled polymer stereoregularity (either very high or low) and broad MWD.

An additional important peculiarity of $MgCl_2$–$TiCl_4$ systems is that, starting from $MgCl_2 \cdot n$EtOH supports, they can be shaped into perfectly spherical particles having control of size, size distribution, and porosity to fit any polymerization process and/or product requirements or constraints (see the section TECHNOLOGICAL IMPLICATIONS). Morphology control can also be achieved via deposition of

Table 1. **Generations of Ziegler-Natta Catalysts for the Polymerization of Propylene**[a]

Generation	Catalyst composition	Productivity	I.I[b]	mmmm	M_w/M_n
(year)		(kg_{pp}/g_{cat})	%	%	
First					
(1954)	δ-TiCl$_3 \cdot 0.33$AlCl$_3$ + AlEt$_2$Cl	2–4	90–94		
Second					
(1970)	δ-TiCl$_3$ + AlEt$_2$Cl	10–15	94–97		
(1968)	MgCl$_2$/TiCl$_4$ + AlR$_3$	15	40	50–60	
Third					
(1971)	MgCl$_2$/TiCl$_4$/benzoate + AlR$_3$/benzoate	15–30	95–97	90–94	8–10
Fourth					
(1980)	MgCl$_2$/TiCl$_4$/phthalate + AlR$_3$/silane	40–70	95–99	94–99	6.5–8
Fifth					
(1988)	MgCl$_2$/TiCl$_4$/diether + AlR$_3$	100–130	95–98	95–97	5–5.5
	MgCl$_2$/TiCl$_4$/diether + AlR$_3$/silane	70–100	98–99	97–99	4.5–5
"Next"					
(1999)	MgCl$_2$/TiCl$_4$/succinate + AlR$_3$/silane	40–70	95–99	95–99	10–15

[a](Polymerization conditions: liquid propylene, 70°C, H$_2$).
[b]Isotactic Index.

MgCl$_2$ precursors on inorganic supports like SiO$_2$. In this case, however, the degrees of freedom concerning both size and porosity control are more limited than in the case of pure MgCl$_2 \cdot n$EtOH supports.

The evolution of the catalysts for polyethylene, has paralleled, actually anticipated, the evolution of the catalysts for polypropylene. On the other hand, they can hardly be classified into comparable, well-defined generations. This does not mean that no progress has been made in this area. Since MgCl$_2$ supported catalysts for polyethylene proved to be very active since the beginning of their discovery and they do not need to be stereospecific, their development was mainly focused at continuously improving their control over polymer MW, MWD, and comonomer distribution. To the best of our knowledge the typical productivities of catalysts for polyethylene, based either on MgCl$_2$ or its precursors, range from ~10 kgPol/g Cat to ~40 kg Pol/g Cat (slurry, 0.7-MPa ethylene partial pressure, temperature 70–80°C, 2 h) and their MWD, expressed as M_w/M_n, can range from ~4 to ~25. As to the comonomer distribution in linear low-density polyethylenes (LLDPEs), a number of patents claim that the combination of suitable internal or external donors, eg, tetrahydrofuran (THF), especially in combination with trimethylaluminium or chlorinated Al-alkyls as cocatalysts, can substantially reduce the amount of polymer extractables and improve both the mechanical and optical properties of the resulting product (39–48).

Based on the above discussion, it is clear why the first generations of Ziegler-Natta catalysts based on TiCl$_3$ have been almost completely displaced and, nowadays, possess a mere historical significance. For this reason, and since they have been extensively covered elsewhere (11), the next sections will be dedicated exclusively to MgCl$_2$ supported systems, based either on pure MgCl$_2$ or its precursors.

3. Preparation of MgCl$_2$-Supported Catalysts

As already mentioned, the discovery of MgCl$_2$, or its precursors (any kind of Mg-derivative transforms into MgCl$_2$ during catalyst preparation) as supports for Ziegler-Natta catalysts can be considered a major breakthrough both from the scientific and industrial point of view.

The choice of MgCl$_2$ as the "election" support for TiCl$_4$- based heterogeneous catalysts was, at the beginning, the result of a serendipitous discovery. It was soon justified, even if *a posteriori*, based on a number of scientific considerations, and, in particular the similarity in the ionic radii of Mg^{2+} and Ti^{4+} ions (Pauling ionic radius: Mg^{2+} = 0.65 Å, Ti^{4+} = 0.68 Å) and the isomorphism of the crystalline structure of MgCl$_2$ (α and β forms) and the crystalline structure of TiCl$_3$ (γ and δ forms). More specifically, both Mg^{2+} and Ti^{3+} ions display the same octahedral coordination geometry and have comparable M$-$Cl bond lengths [Mg$-$Cl = 2.57 Å and Ti$-$Cl = 2.51 Å, see (17)], making it possible for the epitactic adsorption of TiCl$_4$ on the MgCl$_2$ surface.

Obviously, in order for the MgCl$_2$ support to exploit its maximum potential its surface area must be very high so as to maximize the amount and optimize the dispersion of active titanium sites, and hence the productivity of the resulting catalyst. This usually entails an *activation* process by which MgCl$_2$ is transformed into the active δ form. This form is characterized by very small crystallite dimensions and high structural disorder (49). Thus, all the methods used for the preparation of highly performing MgCl$_2$–TiCl$_4$ catalysts pass through a stage where δ-MgCl$_2$ is formed starting from either MgCl$_2$ itself or its precursors.

The synthesis of the active form of MgCl$_2$ can be performed according to two different approaches: either using a mechanical treatment (usually ball milling) or a chemical reaction, during which the other catalyst ingredients, either the titanium derivative or/and the Lewis base (LB), can be directly incorporated.

The synthetic procedures for catalyst preparation can thus be divided into three main classes: mechanical routes, chemical routes, and mixed mechanical–chemical routes.

1. Mechanical Routes. This approach is directly derived from the methods used for the activation of the early TiCl$_3$-based catalysts: it consists of a step in which the catalyst components (MgCl$_2$, TiCl$_4$ and, optionally, the Lewis base or internal donor) are milled together for several hours (23,50–56). A ball mill is usually employed. MgCl$_2$ can also be generated during the milling process by reacting a magnesium compound with a chlorinating agent (eg, SiCl$_4$).

2. Mechanical Plus Chemical Routes. There are two different approaches belonging to this type of catalyst synthesis.
   - Co-milling of MgCl$_2$ or a MgCl$_2$-precursor and, optionally, a Lewis base or internal donor. The resulting solid is then separately treated with an excess of TiCl$_4$ at a temperature usually higher than 80°C, and washed with hydrocarbons to remove all the unreacted TiCl$_4$ (57–69).

     The treatment with TiCl$_4$ has a double role: (*1*) binding itself to the MgCl$_2$ surface and, in particular to the vacant Mg coordination sites,

displacing part of the internal donor, if present; and (2) removal from the catalyst surface all the undesired by-products formed during the reaction. In some cases, $TiCl_4$ can be diluted in aromatic or halogenated compounds that are good solvents for the by-products.

- Co-milling of all the catalyst components, as described in the pure mechanical approach, followed by one or more washings with halogenated or aromatic solvents. This type of posttreatment of the solid increases the activity and the stereospecificity of the final catalyst (70–74).

3. Chemical Routes. In this class of preparation methods, both the formation of the active form of $MgCl_2$ and the incorporation of the other components (titanium derivative and, optionally, internal donor) are carried out by means of a chemical reaction.

The most common synthetic procedures can be divided into four families, according to both types of reagents and of reaction(s) involved.

- A complex of $MgCl_2$ with a Lewis base (eg, an alcohol) is treated with excess $TiCl_4$ in the presence of an internal donor at 80°C or higher temperature. The solid is then carefully washed with hydrocarbon solvents (75–83). Minor modifications of this approach are either the use of aromatic or halogenated solvents to dilute $TiCl_4$ or a separate treatment with $TiCl_4$ and the Lewis base. The $MgCl_2$–Lewis-base complex can be transformed into the active form of $MgCl_2$ before the treatment with $TiCl_4$ and the internal donor, by removing the Lewis base via either a chemical reaction (eg, with aluminum alkyls or $SiCl_4$) or via thermal decomposition.

- $MgCl_2$ is obtained *in situ* from the reaction of a precursor and $TiCl_4$ in the presence of the internal donor and an aromatic or halogenated solvent. Typical precursors can be $Mg(OR)_2$ and $Mg(OR)Cl$ [eg, obtained from a Grignard compound and $Si(OR)_4$] and the titanium alkoxides formed are removed during the treatment or in the final washings (84–96).

- Active $MgCl_2$ is obtained from the reaction of MgR_2 or $MgRCl$ and a chlorinating agent (eg, $SiCl_4$). In order to get morphology control, the magnesium compound can be dispersed on a support, eg, silica, alumina, or other inorganic carriers, before the reaction. The final step is the usual treatment with $TiCl_4$ and, when desired, the internal donor. In some cases, the active $MgCl_2$ is prereacted with some amounts of a Lewis base (eg, an alcohol) (97–107).

- Either $MgCl_2$ or a precursor [eg, $Mg(OR)_2$, $Mg(OCOR)_2$, MgR_2] is dissolved in a solvent (ROH, trialkyl-phosphate, titanium alkoxides, etc). The solution is treated with a chlorinating agent to precipitate the active $MgCl_2$. This can be reacted directly with $TiCl_4$ and the internal donor or treated according to the conditions described above (108–121).

Some parameters are critical for the control and, in particular, for the improvement of the catalyst performances in polymerization. In the case of catalysts obtained from mechanical or mixed (mechanical plus chemical) routes, the

main factors affecting the catalyst performances are the time and the efficiency of milling and the ratio between the components. For example, a longer milling time brings about an increase of catalyst activity.

For catalysts obtained from chemical routes, the purity of the reagents, their ratio, the order of mixing, the reaction time, and the treatment temperature are the main factors to be optimized in order to obtain high-performance catalysts. For example, during the treatment with $TiCl_4$ both temperature and reaction time must be carefully controlled to prevent the side reactions leading to the formation on the catalyst of complexes or by-products between $TiCl_4$, the ID, and $MgCl_2$ that are inactive in polymerization.

An important distinction between the former preparation method based on the milling of the catalyst components and the more recent, pure chemical routes, is the difference in the physical status of the solid catalyst precursor. In fact, supports obtained through a mechanical treatment of $MgCl_2$ appear as powders with no morphology control in terms of shape, size, and size distribution. On the contrary, catalysts prepared via pure chemical routes can be obtained as particles with controlled shape (either spherical or granular), size, and size distribution. This is the most attractive procedure to prepare advanced catalysts for the industrial production of polyolefins as they are able, thanks to the replication phenomenon (see the section THE GROWTH OF THE POLYMER PARTICLE), to generate polymer particles having, on a larger scale, the same features of the parent catalyst particles.

To obtain supports and catalysts having finely controlled morphology, different approaches have been developed. The most used are

- Controlled precipitation of the solid support.
- Spray-drying or -cooling of either dissolved or molten magnesium derivatives.
- Use of silica or other solid carriers having controlled shape to support $MgCl_2$ or $MgCl_2$ precursors.
- Fast cooling of an emulsion, eg, in paraffin oil, of $MgCl_2 \cdot n$ROH complexes.

The latter procedure not only allows us to obtain almost perfect spherical particles with narrow size distribution, but also to get a very fine control of the size of catalysts particles, at least in the range of $10-100$ μm.

In addition, the resulting $MgCl_2$ particles can be further "manipulated", eg, to alter their surface area and porosity. It has been demonstrated that, via controlled removal of the alcohol from the support (dealcoholation) it is possible to both improve the morphological stability and tune the porosity of the resulting catalyst particles, at least in the range $0.3-0.6$ cm^3/g.

The control of the porosity of the catalyst particles is particularly important for the synthesis of *in situ* polypropylene alloys (see the section MULTIPHASE COPOLYMERS).

The above reported general synthetic methods can be applied to catalysts for both polypropylene and polyethylene. The use of electron donors is mandatory for catalysts for isotactic polypropylene, whereas it is optional for catalysts for polyethylene. On the other hand, the best catalysts for the synthesis of LLDPE usually require the presence of donors (39–48).

4. Polymerization

4.1. Mechanism and Stereochemistry of Polymerization. As already mentioned, Ziegler-Natta catalysts usually comprise two components: a transition-metal derivative (catalyst or procatalyst, generally a titanium compound) and a nontransition organometallic derivative (cocatalyst, generally an aluminium alkyl). Over the years, many mechanisms have been proposed for the polymerization of olefins over Ziegler-Natta catalysts (11,122); the most widely accepted is the so-called monometallic mechanism proposed by Cossee and Arlman in the mid-1960s (123) for crystalline $TiCl_3$. The essential feature of Cossee's mechanism is that surface titanium atoms, in order to ensure the electroneutrality of the system, need to posses a coordination vacancy. In particular, the potential, isospecific active site is an octahedrally coordinated titanium ion having a vacant position. The role of the cocatalyst is to turn potential active sites into actual active centers through alkylation (formation of a Ti−C bond) and possible reduction of the transition-metal atom. Thus, the active center is a titanium atom bearing a vacancy and a Ti−C bond. The polymerization occurs in two steps: coordination of the olefin at the vacant coordination position, with the formation of a four-center activated complex, followed by cis opening of the double bond and insertion of the olefin into the Ti−C bond (Fig. 1).

Chain extension occurs through multiple insertions of the monomer according to the above mechanism. An additional feature of Cossee's mechanism is that, after each monomer insertion there is a interchange of the positions between the vacancy and the growing chain (chain migratory insertion). This mechanism also postulates that in order for the isospecific active center to maintain its original stereospecificity, the growing polymer chain, after each monomer insertion, should migrate back to its original position. Actually, based on the microstructure of the resulting polymer this mechanism of isomerization of the active
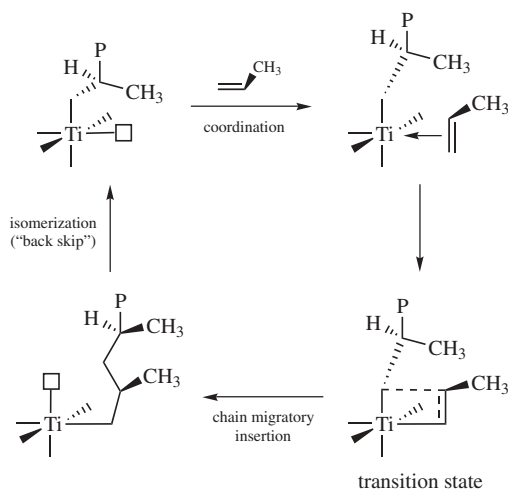

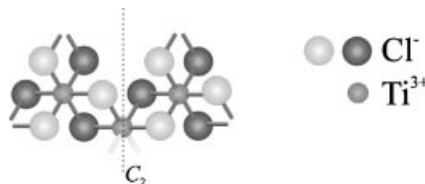**Fig. 1.**   Cossee's mechanism of Ziegler-Natta polymerization (propylene).

Fig. 2. Allegra's model for the C_2 symmetric isospecific active center.

centers (chain *back skip*) has been demonstrated to take place in the polymerization of propylene with syndiospecific metallocenes (124) and recently has been proposed to hold for heterogeneous Ziegler-Natta systems as well. This finding is based on the effect that the monomer pressure in polymerization has on the stereoregularity of the obtained polypropylenes (125). An alternative C_2 symmetric model of isospecific active centers in $TiCl_3$ was proposed by Allegra (126) that does not require chain *back skip* since the relative positions of the growing chain and the incoming monomer are equivalent (Fig. 2).

Perhaps Cossee's mechanism is still oversimplified but accounts for many features of olefin polymerization and, more important, has not been disproved yet by experimental facts.

As for the geometric aspects of Ziegler-Natta polymerization, one can distinguish the monomers according to their symmetry: ethylene is a monomer having a relatively high symmetry [D_{2h}, Fig. 3(**a**)] and both carbon atoms are equivalent, whereas propylene and other 1-olefins are prochiral molecules having lower symmetry [C_s, Fig. 3(**b**)].

Thus, whereas for polyethylene the orientation of the monomer during coordination at the active center has no impact on the microstructure of the resulting polymer, in the case of 1-olefins one must consider both the regioselectivity and stereoselectivity aspects of the polymerization. Actually, 1-olefins can coordinate and insert into the transition-metal–carbon bond in four different modes (see Fig. 4)

Thus, monomer insertion can occur via the formation of a bond between the metal atom and either the methylenic carbon (primary, or 1,2 insertion) or the methynic carbon (secondary, or 2,1 insertion). Poly-1-olefins derived from
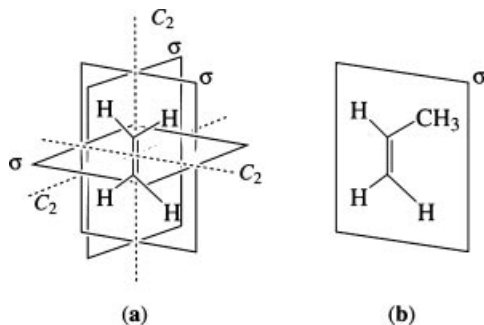

Fig. 3. Elements of symmetry in (**a**) ethylene and (**b**) propylenes molecules.

primary (1,2) propylene coordination

re-propene
(a)

si-propene
(b)

secondary (2,1) propylene coordination

re-propene
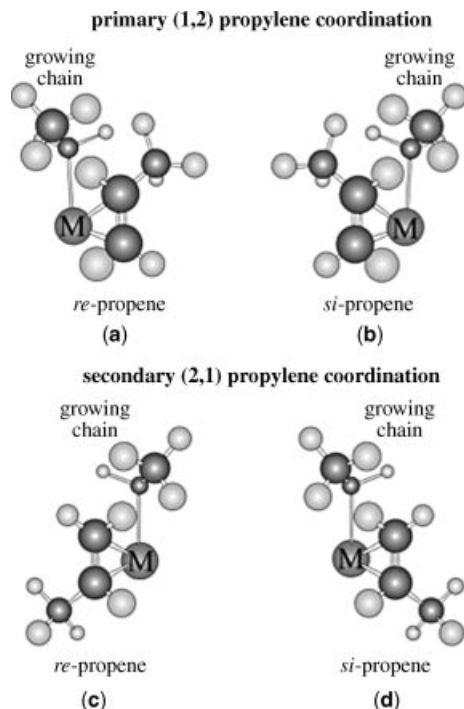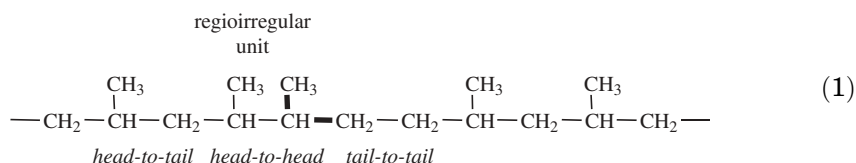**(c)**

si-propene
(d)

Fig. 4. Possible coordination modes of propylene.

regular, either exclusively 1,2 or 2,1 monomer insertions are called regioregular and the relevant catalyst is called regioselective.

The regioregularity of poly-1-olefins can be conveniently investigated via infrared (ir) or ^{13}C nmr spectroscopy. The presence of *head-to-head* or *tail-to-tail* enchainements of monomer units are indicative of regioirregularities (Eq. 1).

$$\begin{array}{c} \text{regioirregular} \\ \text{unit} \end{array}$$

$$\underset{\text{head-to-tail}}{\underset{}{}}\quad \underset{\text{head-to-head}}{\underset{}{}}\quad \underset{\text{tail-to-tail}}{\underset{}{}}$$

$$-CH_2-\underset{|}{\overset{CH_3}{CH}}-CH_2-\underset{|}{\overset{CH_3}{CH}}-\underset{|}{\overset{CH_3}{CH}}-CH_2-CH_2-\underset{|}{\overset{CH_3}{CH}}-CH_2-\underset{|}{\overset{CH_3}{CH}}-CH_2- \qquad (1)$$

Generally, heterogeneous Ziegler-Natta catalysts are highly regioselective and promote the polymerization of propylene into a regioregular polymer via 1,2 monomer addition.

The other source of isomerism in the polymerization of 1-olefins, ie, stereoselectivity, stems from the fact that the monomer, eg, propylene, can coordinate and insert via its *re* or *si* enantioface (Fig. 4). Multiple insertions of the same enantioface produce a polymer chain with pseudochiral centers (the tertiary carbon atom of the polymer chain) having the same configuration; multiple insertions of alternating enantiofaces produce a polymer chain with pseudo-chiral centers having alternating configuration, whereas random insertions of the
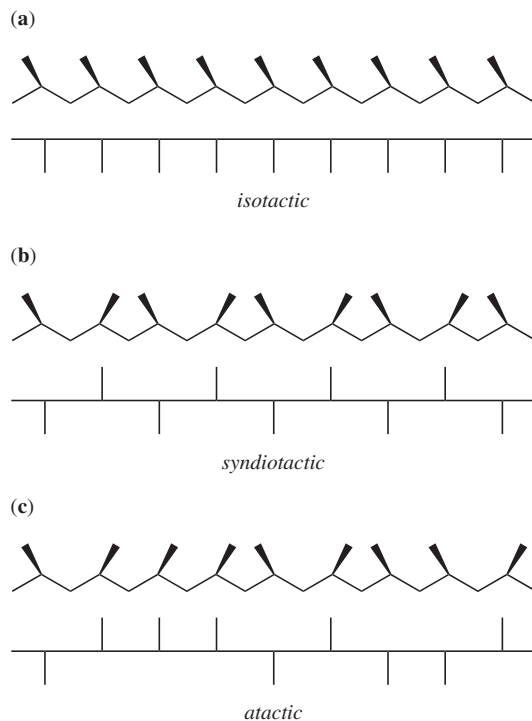
(a)

isotactic

(b)

syndiotactic

(c)

atactic

Fig. 5.   Regioregular poly-1-olefins.

enantiofaces produce a polymer chain without configurational regularity. Regioregular poly-1-olefins whose stereochemistry falls within one of the above mentioned three categories are, respectively, called isotactic (Fig. 5**a**), syndiotactic in Fig. 5**b** and atactic (Fig. 5**c**) and the relevant catalysts, according to their stereoselectivity, are defined isospecific, syndiospecific and aspecific.

The ability for the catalyst to select one of the two enantiofaces of the 1-olefin monomer is exactly the basis of stereospecificity in general, and isospecificity in particular, in Ziegler-Natta catalysis.

In principle, there are two possible sources of enantioface selectivity in 1-olefin insertion (Fig. 6): the first is the chirality of the active center itself,
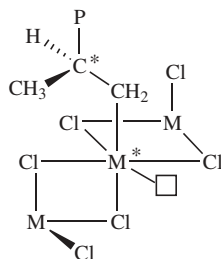
Fig. 6.   The two possible sources of propylene enantioface selectivity. C*: chiral carbon atom; M*: chiral catalytic site.
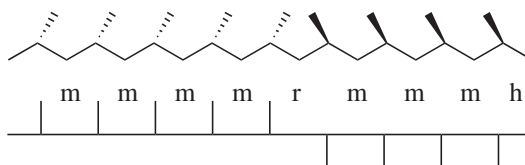
Fig. 7.   Isotactic stereoblock polymer.

including its ligand environment (*enantiomorphic site control*) and the second is
the growing chain itself. In particular, the chiral carbon atom of the last inserted
unit (*chain end control*).

These two possible mechanisms of stereocontrol can be discriminated on the
basis of the microstructure and, in particular, the types of stereodefects of the
resulting polymer chain [see (127) for a recent review on the use of ^{13}C nmr in
the study of polypropylene microstructure]. If the poly-1-olefin chain grows
under isospecific chain end control, after the possible insertion of the less
preferred enantioface, a chiral center is generated having opposite configuration
and thus enantioface selectivity. Consequently, an isotactic stereoblock polymer
chain is produced (error propagation, Fig. 7).

On the other hand, when the poly-1-olefin chain grows under enantio-
morphic site control, a possible insertion of the less favored monomer enantioface
does not change the chirality and the enantioface selectivity of the active center.
As a result, the successive monomer insertion occurs via the preferred "usual"
enantioface. Thus, the insertion defect appears as a single monomer unit having
an opposite configuration with respect to two adjacent isotactic blocks (error
correction, Fig. 8).

In the case of polypropylenes, which are obtained with isospecific
$MgCl_2$–$TiCl_4$ catalyst systems, ^{13}C nmr spectra exhibit signals from mrrm,
mmrr, and mmmr pentads in the ratio: mrrm/mmrr/mmmr = 1/2/2. This indi-
cates that polymer chain growth is under enantiomorphic site control. Further
experimental evidences for this stereocontrol mechanism are that the "usual"
propylene enantioface is selected even after the insertion of an ethylene "spacer"
to generate a Ti–CH_2–CH_2–CH_2–*CHR– group (the possible 1,3 steric asym-
metric induction between the incoming monomer and the chiral carbon atom
C* of the last inserted propylene units is eliminated) and that the first monomer
insertion into a Ti–CH_2–CH_3 bond, with no chiral carbon atoms in the alkyl
group, is isospecific (128,129).

4.2. Models of Active Centers.   According to the above discussion, it is
clear that isospecific polymerization requires the presence of a center of chirality
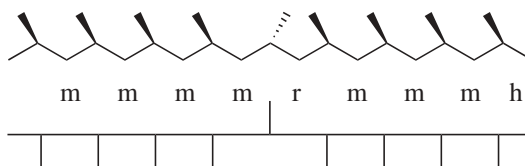

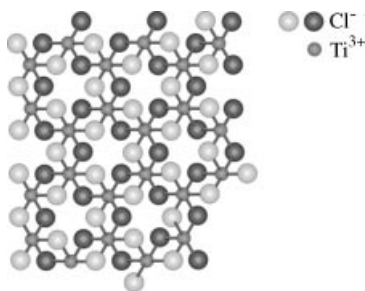**Fig. 8.**   Insertion defect appears as a single monomer.

Fig. 9. Model for a monolayer of a TiCl$_3$ crystal.

that, in the case of heterogeneous Ziegler-Natta catalysts, is very likely the active center itself. Based on the crystalline texture of TiCl$_3$, and especially on the structure of its lateral cuts where polymerization occurs, a number of models for active centers with the right chirality to be isospecific have been proposed (11,13,15). For example, according to Cossee and Arlman the active center is a coordinatively unsaturated octahedral Ti atom bonded to four Cl atoms, bridged in turn to two other Ti atoms, and to an alkyl group derived from the cocatalyst (Fig. 1).

The crystalline structure of MgCl$_2$ is very similar to that of TiCl$_3$; actually, the ionic radii of Mg^{2+} and Ti^{4+} ions are very close and MgCl$_2$ is isomorphous with TiCl$_3$ (Figs. 9 and 10). This allows, eg, via epitactic adsorption of TiCl$_4$ on the MgCl$_2$ surface, the formation of catalytic sites, which are analogous to those present on the surface of pure TiCl$_3$ (Fig. 11).

Incidentally, this sort of dilution of the potential catalytic species on a high surface area carrier is believed to be one of the reasons for the effectiveness of MgCl$_2$ in enhancing catalyst productivity. Moreover, upon supportation of TiCl$_4$ on MgCl$_2$, not only the fraction of active Ti atoms (especially the isospecific centers), but also their propagation constant increases (see the section Kinetics) with respect to pure TiCl$_3$. Thus, MgCl$_2$ seems also to affect the electronic state of the active Ti atoms, likely increasing their electrophilicity. Generally, either before or during supportation of the Ti derivative, MgCl$_2$ is transformed in its *active form*, either via mechanical or chemical methods (see the section PREPARATION OF MgCL$_2$ SUPPORTED CATALYSTS). This brings about the transformation of MgCl$_2$
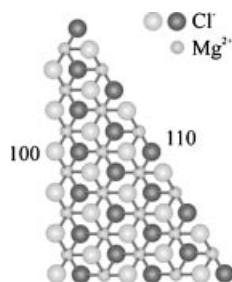

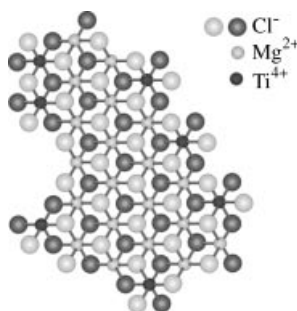**Fig. 10.** Model for a monolayer of a MgCl$_2$ crystal showing the most probable cleavage cuts.

Fig. 11.   Modes of epitactic adsorption of $TiCl_4$ species on $MgCl_2$.

into its δ crystalline form, characterized by higher disorder and surface area with respect to the nonmodified $MgCl_2$. According to Giannini (130), this activation process results in the cleavage of $MgCl_2$ crystal into its most probable cuts, the (100) and (110) crystallografic planes. These lateral cuts, in order for the $MgCl_2$ crystal to maintain its electroneutrality, bear coordinatively unsaturated Mg^{2+} ions with coordination number 4 or 5 on the (110) or (100) cuts, respectively (Fig. 10). It is exactly on these cuts that the epitactic adsorption of $TiCl_4$, according to the modes depicted in Figure 11, leads, after reduction of the Ti atoms, to the formation of the catalytic centers (131).

   According to Corradini (132), only bridged Ti_2Cl_8 dimers located on the (100) lateral cut have the right chirality (see below) to lead to the formation of isospecific active sites. In contrast, the monomeric $TiCl_4$ units present on either the (100) or (110) cuts do not have any intrinsic chirality and thus cannot form isospecific centers (Fig. 12). This is in agreement with the observation that donor-free $MgCl_2-TiCl_4$ catalysts exhibit a rather poor isospecificity in propylene polymerization (Isotactic Index $\sim$60%, see Table 1 and the section Role and Mechanism of Action of Electron Donors).

   Coming back to the similarities between $TiCl_3$ and $MgCl_2-TiCl_4$, it is worth mentioning that the structure of the dinuclear Ti_2Cl_8 species on the (100) cut of $MgCl_2$ looks very similar to that of the predicted chiral centers on $TiCl_3$.
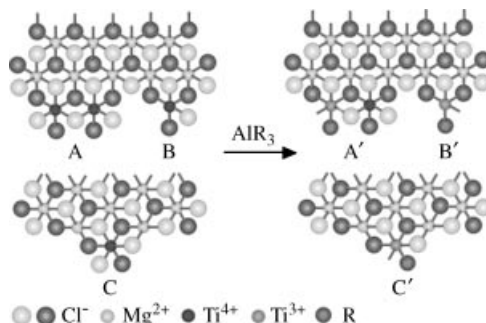

Fig. 12.   Possible $TiCl_4$ species on the most probable $MgCl_2$ lateral cuts, before and after activation by AlR_3. A, B, A', B': (100) cut; C, C': (110) cut. A': isospecific centers; B', C': nonspecific centers.
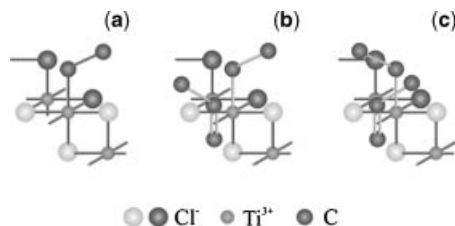
Fig. 13. Possible coordination modes of propylene for a primary insertion on an iso-specific active center (a). (b) Preferred enantioface (*si* face). (c) Unfavored enantioface (*re* face).

Actually, according to Corradini (132), based on molecular modeling and, in particular, on the calculation of nonbonded interaction energies, the driving force toward isospecificity is the same for both types of centers. In particular, the chirality of the active center controls the stereochemistry of monomer insertion in an indirect way: first it forces the growing polymer chain to assume a definite conformation and then the combined influence of Ti ligands and of chain conformation imposes the selection of one of the enantiofaces of the monomer. On the basis on nonbonded energy calculations, the preferred, and always preferred, enantioface is the one that forces its methyl group to be placed on the opposite side with respect to the β-carbon atom of the growing chain (Fig. 13).

More recently, new theoretical approaches have been developed to deepen our knowledge about the intimate structure of active centers. Cavallo and co-workers (133) studied the interaction of $TiCl_4$ or $TiCl_3$ fragments with the (110) and (100) lateral cuts of $MgCl_2$ using a computational approach based on the density functional theory (134,135). They found that either $TiCl_4$ or $TiCl_3$ monomeric species coordinate preferentially on (110) lateral cuts whereas, on the (100) cut, the dimeric Ti_2Cl_8 species are preferred with respect to the mono-meric species. Quite surprisingly, the reduced Ti_2Cl_6 species looks less stable than the monomeric $TiCl_3$ species. On the other hand, the formation of larger Ti_nCl_{3n} clusters ($n > 3$) on the (100) cut seems possible and energetically favored. In addition, it was observed that on the (110) cut the progressive filling of the two coordination positions at the two sides of the aspecific $TiCl_4$ units could generate sites with increasing isospecificity: an isotactoid and an isotactic polymer should be produced by the dimeric and trimeric species, respectively. This seems to be in agreement with Busico's results (136) concerning the microstructure (high-resolution ^{13}C nmr) of polypropylenes obtained with heterogeneous Ziegler-Natta catalysts: the polymer chain consists of stereoblocks comprising isotactic, isotactoid, and syndiotactic blocks whose proportion, but not nature, changes according to the catalyst type. From these experimental results, Busico proposed the existence of three, rapidly interconverting sites having different symmetry and stereospecificity (Fig. 14).

On the basis of the "ab initio molecular dynamics approach" developed by Car and Parrinello (137), Boero compared the energetics of the "classical" octahedral $TiCl_4$ unit and of a pentacoordinated $TiCl_4$ unit on the (110) $MgCl_2$ cut (138). Even if the pentacoordinated $TiCl_4$ species is less stable, it seems to
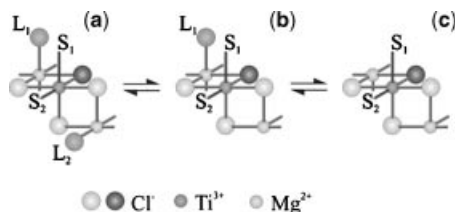
Fig. 14. Models for C_2-symmetric, isospecific (a); C_1-symmetric, isotactoid-specific (b), and syndiotactoid-specific (c) centers. L_1 and L_2 represent either chlorine atoms or electron donors. S_1 and S_2 are the two coordination positions available for bonding both the growing chain and the monomer. (see Fig. 10).

be a suitable catalytic site due to the lower activation energy and the large stabilization energy of the system during and after monomer insertion, respectively. In a following work, Boero also showed that this pentacoordinated Ti site can be isospecific (139).

Specific studies dedicated to the models of centers that are active for ethylene polymerization are surprisingly scarce. On the other hand, any of the above mentioned models of active species for polypropylene, both isospecific and nonspecific, can also in principle constitute active centers for polyethylene. In this case, it is likely that both the electronic and sterical environment of the active site play a role, apart from activity, on the molecular mass of the resulting polymer as well as on the microstructure of the resulting copolymers. In particular, it was postulated (17,140) that the more "open" centers, particularly those bearing two vacancies, are also more reactive toward comonomers, whereas overreduced Ti^{2+} centers give poor comonomer incorporation (17,141,142).

4.3. Role and Mechanism of Action of Electron Donors. As already mentioned, donor-free $MgCl_2-TiCl_4$ catalysts are suitable for ethylene polymerization but are not isospecific enough to produce isotactic polypropylene. The major breakthrough in this field was the discovery and the exploitation of the stereoregulating effect of the electron donors (23) and, in particular, of the internal—external donor pair (see the section, Evolution of Ziegler-Natta Catalysts).

At the very beginning, it was thought that the major role of the donor was the selective and preferential deactivation of the nonspecific centers, but it was soon realized that donors play a much more complex role since, according to their nature and concentration, they can also impact on the following parameters: catalyst productivity, kinetic profile and hydrogen response, and polymer MW and MWD (15). Many papers have been dedicated to the role of donors as well as to their mechanism of action (143–150). Due to the complexity of the matter and to the fact that it is still far from being fully understood and rationalized, we will report here just on some general concepts.

In principle, electron donors can interact with both the $MgCl_2$ or $MgCl_2-TiCl_4$ surface and the other Lewis acids of the system, eg, the AlR_3 cocatalyst and $TiCl_4$ leading, in this case, to undesired by-products. It is probable that, in both the third and the fourth generation catalysts, the main function

of the external donor is to replace, to a significant extent, the internal donor, thereby compensating for the loss of the internal donor on contacting the catalyst and cocatalyst.

From the mechanistic point of view, the function of the internal donor is at least twofold: stabilization of the crystallites of $MgCl_2$ and control of the distribution of $TiCl_4$ on the possible $MgCl_2$ cuts (see below). On the other hand, it has recently been observed (151) that the nature of the internal donor also has a considerable impact on the size of the $MgCl_2$ crystallites and thus on the *working surface* and the productivity of the resulting catalyst.

As for the stereoregulating role of donors, at least two hypotheses have to be taken into account:

1. Selective poisoning of the nonspecific centers as they are believed to be more acid than the isospecific centers (152).
2. Ability to compete with $TiCl_4$ for the adsorption on the $MgCl_2$ cuts and, in particular, to prevent the formation of those Ti species that, according to Corradini's model, would produce nonstereospecific sites (153), as the monomeric Ti species on the (110) lateral cut (Fig. 15).

Both hypotheses, however, are insufficient to explain some experimental evidences, eg, the increase in the productivity of isotactic polypropylene in the presence of electron donors (147,149); the dependence of polymer MW and MWD, and of the stereochemistry of the first insertion step on the nature of the donor (154). In order to account for these findings, at least two hypotheses have been proposed that do not involve a direct interaction (coordination) of the donor with the transition metal of the active center:

1. The donor could coordinate to Mg ions adjacent to aspecific sites, imparting them the right chirality (155).
2. The donor could be able to shift the equilibrium between monomeric (aspecific) and dimeric (isospecific) titanium species toward the dimeric ones (153).
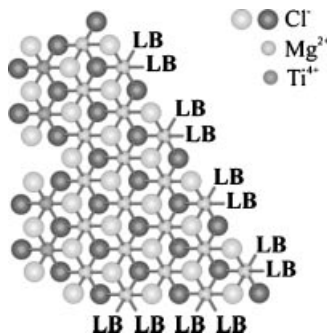

Fig. 15. Competition between $TiCl_4$ species and Lewis bases for the adsorption on the lateral cuts of $MgCl_2$.

As a result, additional active isospecific, somewhat donor-associate species are generated that can have different sterical–electronic environment with respect to the "normal" ones. This can justify both the enhancement of the productivity of the isotactic polymer fraction and the variation of the molecular properties of the polymer in the presence of donors.

On the other hand, one cannot exclude a direct interaction of donors with the transition-metal atom of the active center or the presence of donors molecules bridging titanium and magnesium atoms (156).

Recently, based on the stereoblock structure of the polypropylenes obtained with $MgCl_2$–$TiCl_4$–Donor systems, Busico and co-workers (136) proposed the presence of three active species: a C_2 symmetric, isospecific center, a C_1 symmetric isotactoid center and a syndiotactoid center (Fig. 11). A temporary loss of steric hindrance, eg, loss of a coordinated donor molecule, from one side of the isospecific active species with local C_2 symmetry, can result in the transformation of highly isospecific sites into moderately isospecific sites. Thus, in this case the Lewis base would modify the nature of the active center via direct interaction with the transition-metal atom.

Having said that, and considering that the search for the most appropriate couple of donors is still proceding on a semiempirical basis, some general selection rules exist, mainly dictated by the nature of the internal donor. In particular, it should (157,158):

- Be firmly bound to the $MgCl_2$ surface.
- Be stable and not form complexes or by products with AlR_3, $TiCl_4$, and Ti−C and Ti−H bonds of the polymerization centers.
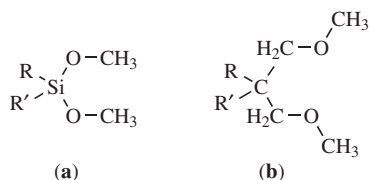
In this respect, internal donors, eg, phthalates, diethers and, more recently, succinates, and external donors, eg, dialkoxysilanes, proved to be much more effective than the initial internal–external donor couple based on aromatic esters. In particular, dimethoxy silanes having bulky alkyl groups on the silicon atom, eg, cyclohexyl or cyclopentyl, are the preferred ones (see structure A in Scheme 5).

The first general reason is that these donors are bidentate and thus tend to be more firmly bound to the $MgCl_2$ surface. The second is that they have the right oxygen–oxygen distance in their functional groups to form strong chelating complexes with the "right" $MgCl_2$ face [tetracoordinated Mg ions located on the (110) cut].

On the other hand, phthalates tend to react with the AlR_3 cocatalyst during polymerization and thus are easily displaced from the solid catalyst surface, whereas silanes tend to react with $TiCl_4$ during catalyst preparation and thus can only be used as external donors.

In contrast, diethers having the general formula (**b**) reported (see below) can satisfy all the requirements for the ideal donor (25−35): polyfunctionality, suitable conformation to give a distance between their oxygen atoms in the 2.5−3.3 Å, capability to coordinate $MgCl_2$ also in the presence of $TiCl_4$ and AlR_3 and, finally, no side reaction with $TiCl_4$ during the catalyst synthesis and with Al−C, Ti−C, and Ti−H bonds during polymerization. For these reasons, diethers are able to produce isotactic polypropylene even in the absence of any

external donors.

$$
\begin{array}{cc}
\underset{(\mathbf{a})}{
\begin{array}{c}
R \\
\diagdown \\
R' ~ \diagup ~ Si
\end{array}
\begin{array}{c}
O-CH_3 \\
\diagup \\
\diagdown \\
O-CH_3
\end{array}
}
&
\underset{(\mathbf{b})}{
\begin{array}{c}
R \\
\diagdown \\
R' ~ \diagup ~ C
\end{array}
\begin{array}{c}
H_2C-O \\
\diagup \\
\diagdown \\
H_2C-O
\end{array}
\begin{array}{c}
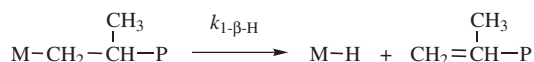CH_3 \\
\\
CH_3
\end{array}
}
\end{array}
$$

As for succinates, they are a very new family of donors, whose mechanism of action is still under investigation.

Electron donors can also be used as components in catalysts for polyethylene. In this case, of course, their role should be different from the one played in propylene polymerization. Studies on the effect of donors in ethylene (co)polymerization are almost nonexisting in the open literature. On the other hand, the patent literature teaches (39–48) that donors can alter the performances of $MgCl_2$- based catalyst for polyethylene and, in particular, tend to improve the quality of LLDPEs, thanks to a better intramolecular and intermolecular comonomer distribution, probably due to a selective deactivation of some active centers.
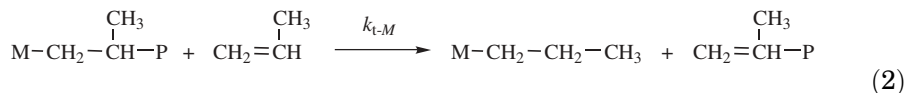
4.4. Kinetics. In addition to the monomer coordination, insertion, and chain propagation steps, Ziegler-Natta polymerization is characterized by a number of reactions that lead to chain termination but not deactivation of the active centers (This does not mean that the active centers that are generated via chain transfer have the same kinetic behavior as the "original" ones, see, eg, the "hydrogen effect.") as well as by some, less well defined reactions that lead to the deactivation of the active centers.

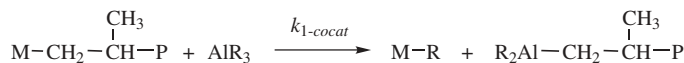Polymer chain termination/transfer can occur through the steps shown in (Eq. 2) (15).

β-*hydride elimination*

$$
M-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{CH}-P \quad \xrightarrow{k_{1\text{-}\beta\text{-H}}} \quad M-H \;+\; CH_2=\overset{\overset{\displaystyle CH_3}{|}}{C}-P
$$

chain transfer with monomer

$$
M-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{CH}-P \;+\; CH_2=\overset{\overset{\displaystyle CH_3}{|}}{CH} \quad \xrightarrow{k_{\text{t-}M}} \quad M-CH_2-CH_2-CH_3 \;+\; CH_2=\overset{\overset{\displaystyle CH_3}{|}}{C}-P
$$

chain transfer with cocatalyst

$$
M-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{CH}-P \;+\; AlR_3 \quad \xrightarrow{k_{1\text{-}cocat}} \quad M-R \;+\; R_2Al-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{CH}-P
$$

chain transfer with hydrogen

$$
M-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{CH}-P \;+\; H_2 \quad \xrightarrow{k_{\text{t-}H_2}} \quad M-H \;+\; CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-P
$$

$$(2)$$
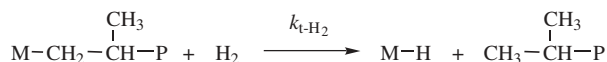
In general, under normal polymerization conditions, chain transfer with hydrogen is the most effective process. This is the reason why molecular hydrogen is normally used to control polymer MW either in the lab or in industrial

scale polymerization of olefins. Chain transfer with hydrogen leads to chain termination via formation of saturated end groups. Hydrogen hardly affects polymer MWD but it can have a considerable effect on catalyst performances: it tends to enhance catalyst activity in propylene polymerization whereas it tends to depress catalyst activity in ethylene polymerization (see below).

In the absence of hydrogen, the most important reaction is β-hydride transfer with monomer, producing vinylidene end groups. Chain transfer with the cocatalyst is of minor importance, unless diethyl zinc is used as cocatalyst. In this case, and in the absence of hydrogen, chain transfer with the cocatalysts becomes the most important reaction.

Finally, β-hydride elimination is unlikely to take place with heterogeneous Ziegler-Natta systems, whereas it can occur with some metallocene-based catalysts.

The kinetics of Ziegler-Natta polymerization has been treated in several excellent books and reviews (12,159−162); in particular, a very exhaustive mechanistic model of the polymerization, including all the reaction steps involved in Ziegler-Natta catalysis, has been reported by Boehm (163). The polymerization of propylene over $MgCl_2-TiCl_4-$Donor systems, especially in slurry, is so complicated that it has been quoted by Keii (164) as a still unsolved problem.

Many equations, either simple or rather complex, have been proposed to express the instantaneous polymerization rate $R_p = dm_p/M_m dt$ (where m_p is the mass of polymer produced, M_m is the molecular mass of the monomer, t is the polymerization time) as a function of the number of active centers n^*, the relevant overall propagation constant k_p and the monomer concentration [M].

In its simpler form, Rp is given by

$$R_p = k_p\, n^*[M]^\alpha$$

Where [M] is the monomer concentration at the active center (not necessarily the same as that in the bulk).

However, even considering the above simplified equation, polymerization kinetics is complicated by many factors that impact on both k_p, n^*, [M] and the relevant exponent α, which is usually, but not necessarily, equal to 1. The major peculiarity of Ziegler-Natta catalysts is that they comprise a multiplicity of active centers, each of them characterized by its own kinetic constants, including the relevant decay constant k_d, which defines the stability of the active species as a function of time and temperature. For example, based on the microstructure of the resulting polymers as well as the deconvolution of the relevant GPC and/or TREF curves, at least three to four and five to six families of active centers have been proposed, respectively, for the polymerization of propylene or ethylene over $MgCl_2-TiCl_4$ catalysts (165−170). In particular, according to Busico and co-workers (136), based on the stereoblock nature of polypropylenes obtained with $MgCl_2-TiCl_4-$Donor systems, each active species can rapidly interconvert between three different propagating species that produce either isotactic, isotactoid, or syndiotactic chain segments. Different active species give different proportions of each segment in the polymer chain. According to Kissin (168,169), catalysts for polyethylene of the $SiO_2/MgCl_2-TiCl_4$ type contain at least five families of active species differing in kinetic parameters,

including the reaction order and the hydrogen sensitivity, stability, and reactivity toward the comonomer.

This multiplicity of active centers, even if individually they obey the most probable distribution ($M_w/M_n = 2$), not only accounts for the spread in the MWD of the resulting polymer in general (167,171) and in the chemical composition distribution of copolymers (170), but also accounts for the complexity of the kinetic profiles of the polymerization reaction (rate vs polymerization time curves). For example, the overall kinetic profile of ethylene polymerization over the above mentioned $SiO_2/MgCl_2-TiCl_4$ catalyst results from the contributions of five families of active centers, some of which deactivate rapidly whereas others remain active for many hours (168,169).

In addition, Ziegler-Natta polymerization can also be affected by transfer limitation of both mass and energy.

Whereas energy-transfer phenomena can impact on the real temperature the active center "feels" and thus on the relevant k_p and k_d constants, mass-transfer phenomena can impact on both n^* and [M]. For example, both n^* and [M] can change in time due, respectively, to alterations in the working surface of the catalyst grain or diffusion limitations of the monomer from the bulk to the active center (see the section THE GROWTH OF THE POLYMER PARTICLE).

For these reasons, the above simplified equation should be applied to any of the active center families that are fixed on the solid catalyst particle and also should take into account the mentioned diffusion limitations, if any.

Having said that, we should not be surprised at that the kinetic profiles of Ziegler-Natta polymerization look rather complex. From the phenomenological point of view, the occurrence of steady-state kinetic profiles is almost nonexisting. Actually, the experimental rate–time plots generally show a variation of polymerization rate as a function of time. Usually, polymerization of propylene over $MgCl_2$ supported systems shows a very rapid acceleration period followed by a decay period (Fig. 16). Polymerization of ethylene, however, is generally characterized by a relatively long acceleration period, followed by a pseudo-stationary or a slow decay period (Fig. 17).
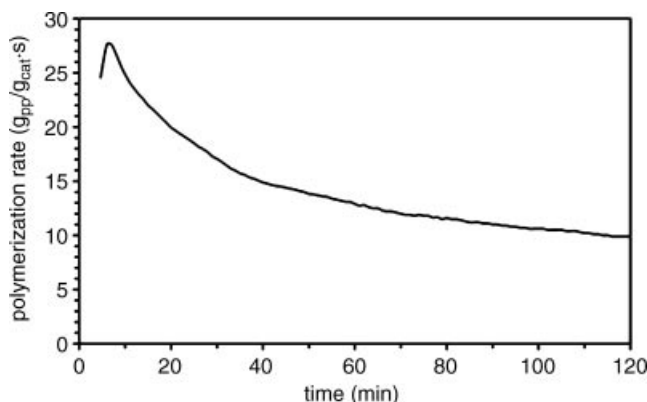

Fig. 16. Typical rate–time profile for propylene polymerization on $MgCl_2$–phthalate–$TiCl_4$/AlR_3–silane catalysts. Polymerization conditions: liquid propylene, 70°C.
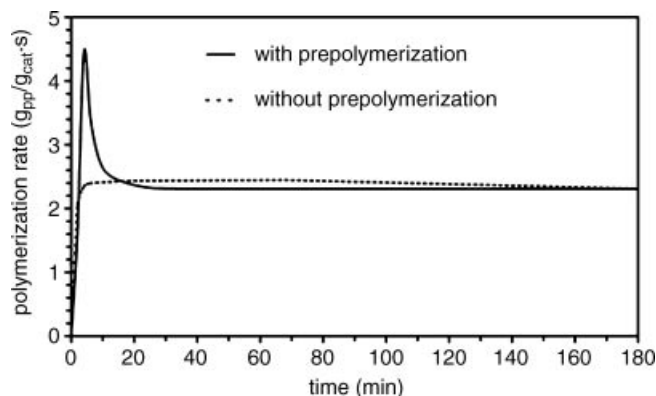
Fig. 17. Typical rate–time profile for ethylene polymerization on $MgCl_2$–$TiCl_4$ catalysts, either without or with prepolymerization with propylene (∼50 g PP/g Cat). Polymerization conditons: propane slurry, 75°C, ethylene partial pressure 0.7 MPa.

There is no evidence of mass-transfer limitation in the case of propylene polymerization (172); thus, the relevant kinetic profile has been attributed to a rapid formation, followed by a more or less rapid deactivation of active centers and thus a decrease of n^* with time. Both first- and second-order deactivation mechanisms of active centers have been proposed (173), but the mechanism of deactivation, though generally attributed to chemical factors, has not yet been rationalized and is still under debate. In our opinion, the values of the deactivation constants as well as their activation energies, obtained from the experimental rate–time profiles, have a limited scientific significance since they represent just values averaged over many different species.

As opposed to propylene, ethylene polymerization can be affected by transfer limitations. For example, Cecchin (174) attributes the induction and/or slow acceleration periods, observed during ethylene polymerization over spherical $MgCl_2$–$TiCl_4$ systems, coupled with the "onion" morphology of the resulting polymer particles, to the fact the monomer, due to its high reactivity to diffusion ratio, tends to react first only at the exterior of the catalyst particle. At this point, the polymerization rate is minimum since just the external catalyst surface is available for the reaction. As the first polymer shell reaches a given critical volume, the mechanical stresses generated by the growing polymer mass are able to fragment the corresponding catalyst shell and the next catalyst shell is made available to the monomer. The polymerization rate thus increases because the first catalyst shell continues to be active and an additional shell supports the reaction. Catalyst fragmentation proceeds step by step and the polymerization rate continues to increase to reach a maximum value when the fragmentation process has gone to completion and thus all the potential catalyst working surface is made available. If no chemical deactivation of active centers occurs, this maximum also corresponds, as frequently observed, to a stationary polymerization rate. This mechanism is supported not only by the profile of polymerization kinetics but also by the fact that prepolymerization of the catalyst grain with either propylene or other 1-olefins, not only suppress the induction period but also greatly enhances the initial polymerization rate (Fig. 17).

The reason is that the prepolymerization step with the above monomers provides an early breaking of the catalyst particle and thus promotes ready access of the monomer even into the catalyst bulk since the beginning of the polymerization (175).

Additional and quite general kinetic peculiarities of $MgCl_2$ supported systems are the hydrogen effect in both propylene and ethylene polymerization and the comonomer effect in ethylene-1-olefin copolymerization.

Hydrogen is universally used as a chain-transfer agent in Ziegler-Natta polymerization but, in addition to this role it has other effects. For example, hydrogen tends to enhance polymerization rate in the case of propylene (176), whereas it tends to reduce polymerization rate in the case of ethylene polymerization. The first phenomenon has been recently rationalized by Chadwick, and co-workers (177−179) by assuming that, in propylene polymerization, even the most isospecific centers are not totally regiospecific: an occasional 2,1 insertion of the monomer leads to the formation of a "dormant" catalytic site that has limited activity due to sterical reasons. Chain transfer with hydrogen removes this sterical constraint with the generation of a Ti−H species on which the monomer can be readily inserted (Eq. 3)

$$(3)$$
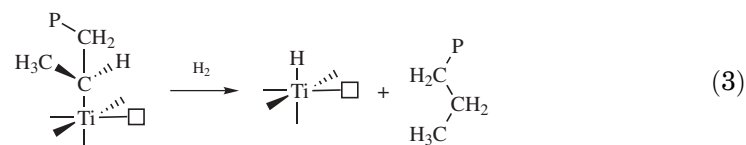
The second phenomenon is likely connected with the formation of Ti−H species as well. However, in this case the insertion of an ethylene unit into a Ti−H bond leads to the formation of a $Ti−CH_2−CH_3$ species that, according to Kissin (168), is scarcely reactive because it is stabilized by the β-agostic interaction between the Ti atom and the methyl hydrogen (Eq. 4).

$$(4)$$
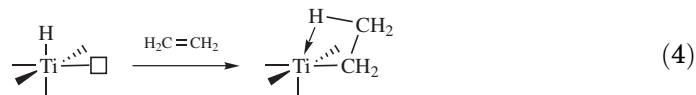
Concerning the comonomer effect in ethylene−1-olefin copolymerization, it has long been known that the polymerization of ethylene in the presence of an 1-olefin, contrary to what is expected based on the classical copolymerization mechanism (1-olefins are less reactive than ethylene), considerably enhances the ethylene consumption rate and can also suppress the induction period. This phenomenon has been attributed to a number of physical or chemical factors (180), eg, early breaking of the catalyst particle and formation of new active centers (175), reduction of the crystallinity of the growing polymer particle and thus better access of the monomer to the particle bulk (181), or reactions involving the active sites.

In view of the strong effects of diffusion limitations in ethylene homopolymerization (see also the section The Growth of the Polymer Particle), the possible role of the comonomer in reducing this phenomenon can be particularly

important. On the other hand, according to Kissin and co-workers (168,169) the activation effect of the 1-olefin could be explained on the basis of purely kinetic reasons: the homopolymerization of ethylene is surprisingly slow based on its intrinsic reactivity; this is because of the formation of the above mentioned β-agostic dormant species; the insertion of the 1-olefin into the Ti−H bond bypasses the formation of the above "sleeping" Ti−CH$_2$−CH$_3$ group and thus greatly enhances polymerization rate. More specifically, 1-hexene accelerates the formation of some centers without affecting their decomposition rate and reduces the reactivity of the remaining centers, in line with the copolymerization reaction theory.

As for the values of n^* and k_p, there are so many and contrasting methods for their determination (182−187) that we believe a clear picture has not emerged yet. Whereas for the first generation catalysts based on TiCl$_3$ the proportion of active Ti atoms and the value of the propagation constant at 70°C are, respectively, in the 0.2−1% range and ∼100 L/mol·s, in the case of MgCl$_2$−TiCl$_4$ catalysts for polypropylene at the same temperature, the proportion of the active titanium atoms has been reported to range from 0.2 to 10%. The relevant propagation constants span a range between ∼500 and 2000 L/mol·s (isospecific centers) and between ∼300 and 800 L/mol·s (aspecific centers) (188). In the case of catalysts for polyethylene derived from Mg(OEt)$_2$ and TiCl$_4$, Boehm (189) reported that at 85°C, up to 75% of titanium is active in polymerization with a k_p value of ∼80 L/mol·s. On the other hand, according to Baulin and co-workers (190), in the case of MgO−TiCl$_4$ catalysts, the proportion of active titanium and the k_p values at 70°C are ∼20% and 2200 L/mol·s, respectively. According to the majority of authors (188) the efficiency of MgCl$_2$ supported systems, as compared with TiCl$_3$, is due to both the increased number of active centers and the value of their propagation constant. According to others (191), it is solely due to the increased number of active centers. Frankly speaking, the situation is very complicated, not only because of lack of a universally accepted methodology for the determination of n^* and k_p, but also because of the intrinsic complexity of the catalyst system and its possible evolution in time. Actually, the catalyst grain bears titanium species that can differ in their sterical and chemical environment and their oxidation state, species that can evolve in time via exchange of ligands or can either be activated or deactivated, species that have different stereospecificity, activity, sensitivity to hydrogen, stability, reactivity and reactivity ratios toward comonomers, etc. Attempts to determine the number of any specific catalytic species and their relevant propagation constants have been made, but likely they are biased by the same limitations that have prevented, to date, the exact determination of the overall kinetic parameters.

As expected, temperature has a significant effect on polymerization kinetics. The kinetic parameters that are mainly involved are the propagation constant and the deactivation constant of the various active centers. Since the values of both parameters tend to increase with temperature, it is not unusual, especially for catalysts for polypropylene, to exhibit a maximum in both productivity and isospecificity as a function of temperature, generally in the 70−80°C range (192). In the case of catalysts for polyethylene, a convenient polymerization temperature can be in the 75−95°C range.

4.5. The Growth of the Polymer Particle. *Background.* The growth of the polymer particle over Ziegler-Natta catalysts has been, and still is, an area

of intensive investigation in both academic and industrial laboratories. Actually, on the one hand, the knowledge of this phenomenon is a fundamental step toward the comprehension of the intimate mechanism of Ziegler-Natta catalysis and polymerization, while on the other hand its rationalization and control can constitute the scientific platform for the optimization of the existing polymerization technologies and the implementation of new processes and products.

It is generally accepted that the solid polymer particle that grows in slurry, bulk, or gas-phase processes, constitutes a completely segregated system that behaves like a microreactor characterized by its own kinetics and balances of mass and energy (193). It has also been long known that heterogeneous Ziegler-Natta catalysts can replicate their morphology into the morphology of the resulting polymer particles (replication phenomenon) in terms of shape, size distribution, surface area, porosity, and bulk density (11).

The first generation polymerization processes had usually to face a lot of troubles and limitations because the catalyst was only able to generate polymer particles having irregular and uncontrolled shape and size, and a considerable and variable amount of fines. The most modern and advanced polymerization technologies are exactly based on the capability of controlling and fine-tuning the morphology of the catalyst particles, and thus of the polymer particles, according to any process and product needs. For example, starting from controlled morphology $MgCl_2$ supported catalysts, it is possible to generate polymer particles having high bulk density, regular, generally spherical shape, narrow size distribution and any kind of size from ~0.1 to ~3 mm. This in turn translates into many advantages, eg, high plant throughput, because of the corresponding high polymer content, excellent plant operability, because of the good flow properties of the particles and no tendency for them to stick to each other or the reactor walls; and finally, excellent quality and consistency of the product, because of the optimal control of mass and energy transfer within the polymer particles. For some specific application, like the *in situ* synthesis of polypropylene-based heterophasic copolymers, especially those containing large amounts of ethylene–propylene copolymers, it is also possible to alter the porosity of the catalyst particle in order for the resulting polymer particle to incorporate large amounts of rubbery material without sticking problems. All this was achieved thanks to our ability to understand and controll the mechanism of growth of the polymer particle and to the ability to design and tune the architecture of the catalyst particle according to any process and product requirements.

Mechanism.   Probably the first attempt to rationalize the mechanism of growth of the polymer particle over Ziegler-Natta catalysts dates back to 1959, when Natta and Pasquon (194), based on kinetic considerations, hypothesized a progressive fragmentation of the catalyst particle due to the mechanical stresses generated by the growing polymer. By the end of the 1960s, many key features of the mechanism of polymer particle growth had already been well recognized. In particular, (195−198) the multiparticle texture of the catalyst grain, the capability of the growing polymer to fragment the catalyst down to the so-called primary particles or even beyond, the capability for the growing polymer to reproduce the shape of the catalyst particle, and finally, the possible occurrence of diffusion limitations within the polymer mass. Over the years, many physical as well as conceptual models have been proposed to explain the

mechanism of polymer particle growth, including a number of elegant simulations aimed at predicting both heat and mass-transfer effects as well the kinetic profile of the polymerization reaction and some polymer properties (199–213).

In this section, we will deal with physical rather than mathematical models of polymer growth and will mainly focus on the mechanism of particle growth over $MgCl_2$ supported catalyst systems. On the other hand, it could be useful to recall some conceptual models that, though being unable to provide an exhaustive description of the particle growth mechanism have their own merits, either because of historical reasons or because they can constitute the starting point for more sophisticated models that, in our opinion, better depict the physical reality.

Four models were proposed by Schmeal and Street (214) in the early 1970s. Among these, it is worth considering the following limiting cases: the "solid core" model, according to which the polymer accumulates at the surface of a nonfriable catalyst sphere; and the "flow model" according to which the polymer particle is considered as an expanding universe where the active centers move with the velocity of the growing polymer mass and, under particular conditions, tend to accumulate at the surface of the polymer particle.

The "multigrain model" developed by Ray's group (215) assumes that the catalyst particle (macroparticle) is made up of several much smaller fragments (microparticles), all of which are immediately accessible to the monomer. The monomer diffuses readily into the catalyst bulk and forms a polymer shell around each microparticle, causing a progressive expansion of the catalyst–polymer particle as polymerization proceeds.

Laurence and Chiovetta (216) proposed a model that is very similar to the previous one, but with an important difference: The fragmentation of the catalyst, instead of being instantaneous, may have a duration of at least the same order of magnitude as the critical monomer diffusion.

In principle, the above two models might just be discriminated according to the nature of the monomer: eg, whereas polypropylene growth could obey Ray's model, polyethylene growth could be better described by Chiovetta's model, since ethylene polymerization is characterized by much higher reactivity/diffusivity ratios.

On the other hand, based on a number of experimental evidence, it is likely that none of the above reported models is able to account for the mechanism of polymer particle growth over "real" Ziegler-Natta catalysts. To begin with, the micromorphology of the catalyst particle, or macroparticle, is much more complex than that depicted in the multigrain model, since both $TiCl_3$ (217,218) and $MgCl_2$ supported systems (219,220) display at least a dual morphological texture consisting of microparticles, or primary particles, and larger microparticle agglomerates (subparticles). This led Bukatov and co-workers (217,218) to propose the so-termed "double grain" model for polypropylene growth over $TiCl_3$, which is characterized by the fact that the polymer particles reflect the dual morphological hierarchy of the catalyst particles, forming microglobules around each catalyst microparticle and larger agglomerates, or subglobules. However, this relatively complex model is not able to account for the observed morphology of polypropylene-based heterophasic copolymers obtained by sequential copolymerization of propylene and ethylene–propylene mixtures over $MgCl_2/TiCl_4$ systems. Actually, by means of accurate scanning electron microscopy

(sem) and transmission electron microscopy (tem) investigations of the resulting polymer particles, Kakugo and co-workers (219,220) first found that the rubbery ethylene–propylene copolymer phase is located around globular agglomerates that make up the host polypropylene matrix and tends to fill the pores that are in between. In order to account for this morphological evidence, Kakugo and co-workers (219,220) proposed a polymer growth mechanism that implies the migration of at least part of the catalyst primary particles, from the bulk to the surface of the polypropylene globules, where they sustain the ethylene–propylene polymerization. According to Kakugo and co-workers, these microparticles might consist of catalyst fragments that are active for ethylene but not for propylene.

Whereas Kakugo's mechanism provides an excellent picture of the morphology of polypropylene-based heterophasic copolymers, in principle it might be biased by the nature of the ethylene–propylene rubbery fraction. Actually, this fraction could grow inside the polypropylene globules and then, because of its intrinsic mobility, flow away and occupy the available space constituted by the interglobular pores of the host polypropylene matrix, as suggested by Popov and co-workers (221). On the other hand, Kagugo's model was supported and generalized by Cecchin and co-workers (222) who, using spherical $MgCl_2/TiCl_4$ catalysts, confirmed that the catalyst particle has at least a dual morphological texture, which is reflected by the dual morphology of the nascent polypropylene particle, which consists of microglobules and subglobules. They also found that, during propylene polymerization, the catalyst primary particles or microparticles tend to break into smaller catalyst fragments as polymerization proceeds. In addition, they observed that the particles of heterophasic copolymers prepared by sequential copolymerization of propylene and either ethylene or 1-butene to form crystalline "motionless" polyethylene or polybutene domains, respectively, display the same morphological features as that observed on heterophasic copolymers based on propylene and ethylene–propylene. Indeed, this proves that the polymerization front is located at the surface of polypropylene subglobules, where catalyst microparticles or microparticle fragments, and not just those that are only active for ethylene, tend to migrate, accumulate, and sustain the reaction. The fragmentation of the catalyst microparticle and their migration from the bulk to the surface of polypropylene globules has been directly observed quite recently by Weickert and co-workers (223), using a different $MgCl_2/TiCl_4$ catalyst. Thus, migration and surface accumulation of any kind of catalyst microparticles or smaller catalyst fragments, within the globular units that make up the polymer macroparticle, seems to be a general feature of propylene polymerization over $MgCl_2/TiCl_4$ catalysts. Based on the above findings, Cecchin and co-workers (222) recently proposed the following mechanism of growth of polypropylene particles over spherical $MgCl_2/TiCl_4$ catalyst systems (Fig. 18): The catalyst macroparticle displays a dual morphological texture, consisting of microparticles, or primary particles and larger microparticle aggomerates or subparticles.

The major contribution to the porosity of the catalyst macroparticle is provided by the interstitial voids between subparticles. The active centers are located on the surface of the microparticles, which are homogeneously distributed within the catalyst subparticles. The monomer diffuses readily into the
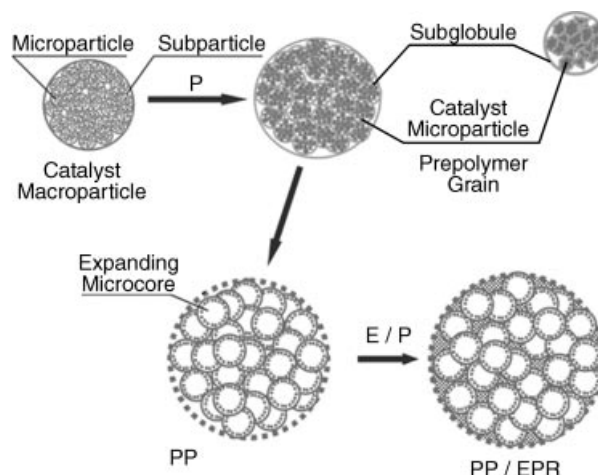
Fig. 18. Mechanism of propylene particle growth on $MgCl_2$-$TiCl_4$–donor catalysts. PP: polypropylene homopolymer; PP/EPM: heterophasic copolymer obtained via sequential copolymerization of propylene and ethylene–propylene mixtures.

catalyst bulk and forms a polymer shell (microglobule) around each microparticle, causing a progressive expansion of the catalyst macroparticle. As the polymerization proceeds, the catalyst microparticles likely fragment into smaller particles; the polymer microglobules tend to lose their identity and merge into larger and dense agglomerates (subglobules). Polymer subglobules behave as a continuum in which, as polymerization proceeds, the catalyst fragments are rejected from the interior to the surface, where they tend to accumulate and thus sustain the reaction. It can be readily recognized that this mechanism results from a combination of the simpler models mentioned earlier. Thus, at the very beginning of the polymerization (prepolymerization), polymer microglobules and subglobules can be assimilated, respectively, to the "solid core" entity described by Schmeal and Street (214) and the multigrain model by Ray and co-workers (215), whereas the polymer macroparticle behaves like Bukatov's double grain (218). As polymerization goes on, polymer subglobules tend to turn into a sort of "microcore" that reflects exactly the behavior of the polymeric flow model with surface accumulation of catalyst fragments, depicted by Schmeal and Street. The whole system can thus be described as a double grain model with expanding "microcore". This model may still be oversimplified, but not only does it account for the experimental facts like the macro- and micromorphology of the particles of polypropylene and its heterophasic copolymers, it also explains the replication phenomenon.

As for the mechanism of growth of polyethylene particles over Ziegler-Natta catalysts, it looks rather complex and it is far from being fully understood. As an example of this complexity we have observed that the surface of a polyethylene particle, grown over $MgCl_2/TiCl_4$ systems can consist of a number of different micromorphological textures eg, microglobules, worms, and cobwebs (Figure 19), as previously found with different Ziegler-Natta catalysts (224,225).

It has also long been recognized that the macromorphology of nascent polyethylene particles can develop into what has been termed "onion" structure (18).

Fig. 19. Scanning electron microscopy (SEM) micrograph of the surface of a polyethylene particle formed on a MgCl$_2$-supported catalyst.

This, in our opinion, is an indication that ethylene polymerization can be complicated by diffusion limitations which, in principle, involve both the whole growing particle or portions of it. The occurrence of monomer diffusion limitation in ethylene polymerization can be easily accounted for if one considers that this monomer is characterized by a high reactivity/diffusivity ratio (an order of magnitude larger than that of propylene). On the other hand, ethylene polymerization can also be complicated by additional diffusion limitations; eg, the diffusion of the cocatalyst, if bulky enough, can constitute the rate-limiting factor (226). Under this limitation of mass transfer, the mechanism of growth of the polymer particle is likely close to that proposed by Laurence and Chiovetta (216): The monomer tends to react first at the external surface of the catalyst particle, then, after the first polymer shell reaches a given critical volume, the mechanical stresses generated by the growing polymer mass are able to fragment the corresponding catalyst shell and make available the subsequent one. Thus, catalyst fragmentation proceeds step by step yielding the well-know onion morphology of the polymer particle. As a result, the polymerization rate should be minimum at the beginning and should increase with the polymer/catalyst ratio, until it reaches a maximum when the catalyst fragmentation is completed and the whole catalyst surface is available for the reaction. In the absence of chemical deactivation of active centers, this maximum should also correspond to a stationary state of polymerization. Both the morphology of the polymer particle and the kinetic profile of the polymerization tend to support this growth mechanism, at least in the case of spherical MgCl$_2$/TiCl$_4$ systems. As a matter of fact, the polymer particles tend to show the already mentioned onion structure, whereas the kinetic profile is generally characterized by an induction period, followed by an acceleration period. It has also been demonstrated that the induction period can be almost completely suppressed by prepolymerizing the catalyst particle with small amounts of polypropylene (see also the section KINETICS). This finding, because propylene has a rate of diffusion that is slower than the rate of
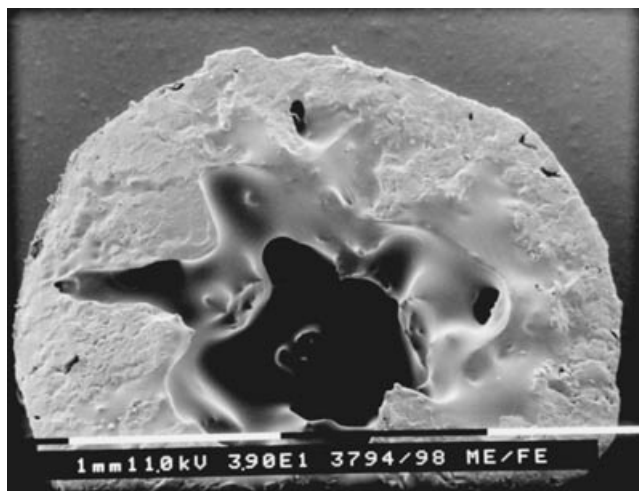
Fig. 20. SEM micrograph of the section of a PE/EPM sequential copolymer particle formed on a MgCl$_2$-supported catalyst.

polymerization, allows the early breaking of the catalyst particle and the exposure of all the working catalyst surface and thus the maximum number of active centers since the beginning of the reaction. In addition, we observed (174) that heterophasic copolymers prepared by sequential copolymerization of ethylene and rubbery ethylene–propylene copolymers, display a core-shell morphology in which the core and the shell are constituted mainly of polyethylene and ethylene–propylene phases, respectively (Fig. 20). This indicates that polyethylene grows over and exploits only part (the exterior) of the catalyst surface, and the ethylene–propylene copolymer grows over the remaining catalyst surface. Thus, without pretending to explain all the fine morphological details, the proposed model at least accounts well for the macromorphology of the polymer particle as well as for the kinetic profile of the polymerization reaction. According to Graff and co-workers (225), the formation of the cobweb texture often observed on the surface of polyethylene particles is due to the fact that ethylene first polymerizes at the surface of the catalyst particles and then in the interior. This leads to volume increase, and thus drawing of the initially formed polymer crust. The occurrence of different micromorphological details, as the mentioned worms, microglobules, and cobwebs in the same catalyst particle, is likely due to local differences in mass transfer.

Technological Implications.   The above proposed mechanism of polymer particle growth not only explains and accounts for the experimental facts but also can teach how and what the catalyst "architecture" should be in order to fully exploit the replication phenomenon. Actually, based on this model the polymer particle tends to reproduce both the shape, the dual structural hierarchy, and the porosity of the parent catalyst particle, enlarging, of course, its size as polymerization yield increases. Thus shape, size, and porosity of the catalyst particle can be predicted, designed, and tailored to meet any specific product and/or process requirements. In this respect, considering that a controlled, preferably spherical shape and a narrow particle size distribution can generally fit any

purpose, both particle size and, especially porosity, need fine tuning in order to both optimize plant operability and drive product innovation. The optimal size of polymer particles needs to be designed according to any reactor type and the relevant design criteria; the critical process parameters can be, eg, mixing of particles suspension (slurry or bulk stirred vessel reactors), particles transport capability (slurry−loop reactors), fluidization velocity (gas-phase fluidized-bed reactors), and mechanical mixing (gas-phase stirred-bed reactors). In addition, the size of polymer particles can also impact on the recovery and finishing sections of the polymerization plant. To the best of our knowledge (227), the optimum polymer particle size as a function of the most common reactor technologies is in the following ranges: 100−900 μm for slurry or bulk stirred vessel reactors, or gas-phase stirred-bed reactors; 600−900 μm for slurry loop, and 600−3000 μm for bulk loop reactors, respectively. As for gas-phase fluidized-bed reactors, the preferred particle size is in the 400−3000-μm range.

For homopolymers in general, in order to maximize the output of the polymerization reactors, the bulk density of the polymer particle should be as high as possible (228). Thus catalyst particles with low porosity should be utilized. In contrast, when the homopolymer particle, as is the case for heterophasic copolymers of polypropylene, is used as a bed for further ethylene−propylene polymerization to get a rubbery heterophase, the porosity of the catalyst should be finely tailored. In particular, the level of porosity needs to be proportional to the amount of rubber one wants to incorporate in the host homopolymer particle, and the size and distribution of pores needs to be designed so as to guarantee the optimal size and predistribution of the rubbery domains. The exploitation of the porosity control (229) has been the technical and scientific platform for the *in situ* synthesis of a family of previously unavailable and unachievable polyolefin materials eg, supersoft polypropylene products consisting of >70 wt% of propylene-rich ethylene−propylene rubbers (230) (see also the section MULTI-PHASE COPOLYMERS).

An additional implication of the proposed mechanism, as well as of the most quoted models, is that for some catalysts, especially when highly active and relatively large catalyst particles are used under severe polymerization conditions, it might be convenient to expose the catalyst system to the monomer under mild conditions of temperature and pressure before it enters the main reactor. This step (prepolymerization or encapsulation) not only preserves the polymer−catalyst particle from uncontrolled disintegration but also prevents overheating and possible partial melting of the polymer particles, which can result in particle agglomeration, reactor fouling, and, eventually, shutdown (201,203,208−210,213).

In the case of growth of the polymer particle under diffusion limitation, as can be the case of ethylene polymerization over $MgCl_2/TiCl_4$ systems, a prepolymerization step with propylene, can also lead to an increased catalyst mileage due to the suppression of the induction period.

5. Application of Ziegler-Natta Catalysts (Polyolefin Products)

Soon after their discovery, Ziegler-Natta catalysts were applied not only to the hopolymerization and copolymerization of ethylene and propylene, but also

to the polymerization of linear 1-olefins like 1-butene, branched 1-olefins like 4-methyl-1-pentene, other monomers like styrene, diolefins or more exotic monomers into a large variety of products (11). Only some of these products have been industrialized. This section is dedicated to the application of Ziegler-Natta catalysts to the synthesis of those materials that, owing to their outstanding performance-cost balance, versatility in end use applications as well as favorable environmental impact, have found wide commercial acceptance, eg, polypropylene, polyethylene, and their copolymers.

Today, nearly 33 million tons of polypropylene products and 32 million tons of polyethylene products, including both high-density polyethylene (HDPE) and LLDPE, are produced via Ziegler-Natta catalysis in >45 countries throughout the world (some additional 6 million tons of polyethylene, almost exclusively HDPE, are produced using chromium compounds supported on silica). In addition, 45 years after their discovery, polyolefins also show the highest growth rate among plastic materials.

In general, polymer optimization and innovation is the result of the synergistic concurrence of three major factors: catalyst science, polymer science, and polymerization technology. There is no doubt that, in the case of olefin polymerization, the catalyst system plays a major role, since it is not only able to tune the structure of the polymer chain, but also to provide the desired degree of freedom in both polymer and process design.

Actually, by selecting the most appropriate catalyst-process combination, it is possible to prepare a whole class of reactor-grade polyolefin homopolymers, copolymers, and alloys ranging from superstiff to supersoft materials and all the products that are in between to cover an extremely wide spectrum of applications, eg, fibers, tapes, films, pipes and sheets, articles for rigid and flexible packaging, houseware, toys, luggage, interior and exterior trims and bumpers for automotive industry, crates, bottles, small and large containers, membranes for roofing and landfills, materials for wire and cable coatings, etc.

Without pretending to deal with all of the above product mix, we will focus on how catalyst attributes, resulting from its chemistry and/or architecture, have been or are instrumental in driving polyolefin product optimization and innovation via control of polymer design.

The polymer parameters that are under the catalyst's control and that affect both polymer design and properties are essentially MW, MWD and, in the case of polypropylene and the other 1-olefins, regio- and stereoregularity of the macromolecular chain. Regio- and stereoregularity in poly-1-olefins are the key parameters that control crystallinity, and thus stiffness. MW and MWD mainly affect product rheology in terms of fluidity and processability, but they also have a considerable impact on mechanical properties. For example, it is well known that low MW and narrow MWD bring about superior processing characteristics in applications, eg, high-speed melt spinning of very thin fibers, high-speed extrusion of thin films, and injection moulding of thin-wall articles. High MW and broad MWD are in turn able to provide high-melt strength coupled with optimal processability and thus are the key parameters for applications like extrusion of pipes and sheets, blow moulding, and thermoforming. But it is also well recognized that the various molecular weight averages and their distributions impact on many important mechanical properties, eg, brittleness,

environmental stress cracking resistance (ESCR) and creep, tenacity, tensile strength, elongation, and stiffness–impact. In particular, a broad MWD is known to optimize stiffness–impact because it not only promotes fast end effective nucleation but also tends to increase the concentration of tie molecules (231).

For copolymers in general, the incorporation of a comonomer along the chain, according to its nature, amount, and distribution (232–236), promotes the interruption of the length of the crystallizable homosequences (237) and thus a reduction of degree of crystallinity and perfection of lamellae, an increase of the amount of the amorphous phase, and of the number of tie molecules linking the crystalline domains (238–241). As a result, random copolymers are characterized by reduced density, stiffness, melting point, and improved ductility and optical properties with respect to the corresponding homopolymers. The main role of the catalyst here is to optimize comonomer incorporation, and intra- and intermolecular distribution along the chain.

In the case of *in situ* multiphase copolymers, eg, those prepared via sequential copolymerization of propylene and ethylene–propylene mixtures, an additional important catalyst attribute becomes more and more important: The architecture of the catalyst particle and, in particular, its porosity. Actually, according to the mechanism depicted in the section The Growth of the Polymer Particle, the rubbery phase grows inside and tends to fill the pores that are within the subglobules of the host homopolymer matrix. Since the homopolymer particle replicates the porosity of the catalyst particle, catalyst porosity needs accurate control and, in particular, should be proportional to the amount of rubber one wants to incorporate in the matrix. If the porosity of the catalyst–homopolymer system is not large enough, the rubbery phase first tend to occupy all the available internal space, and then, because of its fluidity, tends to migrate to the surface. Consequently, the polymer particles tend to stick to each other and to the reactor walls, leading to reactor fouling and, eventually shut-down.

5.1. Polypropylene Products. *Homopolymers.* Optimization and innovation in polypropylene homopolymers is essentially related to the control of polymer regio- and stereoregularity, MW and MWD (242).

Thus, eg, if the optimization of properties like stiffness, hardness, and heat distortion temperature (HDT) is sought, as is often the case of medium-fluidity injection moulded articles, the catalyst system has to be able to provide the maximum sterical purity of the macromolecular chain, coupled, preferably, with a broad MWD (230,242), see Table 2.

Actually, the desired properties are not only related to the Isotactic Index (wt% insoluble in xylene at 25°C) of the polymer and to its sterical purity (mmmm% of the isotactic fraction) as expected, but also show a more subtle, but significant dependence on its MWD. In particular, it has been found that when sterical purity of the polymer is the same, a broad MWD brings about a considerable increase in its stiffness. It has been demostrated that this is the result of an acceleration of the nucleation rate, and thus of the overall crystallization rate of the material. A broad MWD is thus able to translate the potential crystallinity provided by the sterical purity into actual crystallinity. The increase in nucleation rate has been attributed to the possibility of some very high MW polymer tails to survive during the melting process and to act as crystallization nuclei during subsequent cooling and solidification (self-nucleation).

Table 2. **Physicomechanical Properties of Isotactic Polypropylenes Obtained with Different ZN Catalytic Systems as a Function of Sterical Purity and Molecular Weight Distribution**

Catalyst type		Fourth generation catalyst monomodal[a]	Fourth generation catalyst monomodal	Fourth generation catalyst bimodal	Next generation catalyst monomodal	Next generation catalyst bimodal
melt flow rate	dg/min	17	20	20	22	16
polydispersity index[b]		4.2	4.3	6	6	12
Isotactic Index	(wt%)	98	98.5	98.4	98.2	98.4
mmmm[c]	(%)	96.8	98.7	98.6	98.4	98.2
melting point	(°C)	164.2	164.5	164.4	164.2	164.3
flexural modulus[d]	(Mpa)	1600	2000	2250	2280	2380
stress at yield[e]	(MPa)	41	39	40	40	41
stress at break[e]	(MPa)	35	34	35	34	33
elongation at break[e]	(%)	12	10	11	10	10

[a]Less efficient stereoregulating external donor.
[b]Rheological measurement of molecular weight distribution.
[c]From ^{13}C nmr of the xylene insoluble fraction.
[d]ASTM D790.
[e]ASTM D238.

A broad MWD, coupled with high MW and stereoregularity, is also beneficial for the extrusion of rigid pipes and sheets in order to achieve the best balance between zero-shear viscosity (melt strength) and shear sensitivity (processability). Again, a broad MWD, coupled, respectively, with high MW or medium MW, is required for the fabrication of blown films (bubble stability), or cast and biaxially oriented films (processability). However, in this case a high sterical purity is not always mandatory. Actually, a minimum content of stereoblocks (technically defined as the polymer fraction soluble in xylene at 100°C) is generally demanded, especially for biaxially oriented polypropylene (BOPP), in order to improve stretchability. On the other hand, injection moulding of both thin-wall articles and fibers require both low or very low MW (high fluidity, MFR up to 1500 g/10 min. for melt-blown fibres) and narrow MWD. However, whereas thin-wall injection moulded articles demand high rigidity and thus stereoregularity, this property is less important for fibres, where spinning speed and continuity, minimum achievable denier (diameter) and strength are the key factors.

5.2. Random Copolymers. From the industrial–commercial point of view, random copolymers of propylene are defined as partially crystalline, thermoplastic materials containing up to ~10 wt% of one or more comonomers, generally ethylene, 1-butene and, less frequently, 1-hexene.

With respect to the homopolymers, random copolymers are substantially characterized by reduced rate of crystallization and level of crystallinity, and thus lower stiffness and melting point and improved optical properties (haze and gloss). The major application areas of these materials are in the field of cast and blown films, injection and blow-moulding, and, to a lesser extent, extruded pipes and fibers.

A particularly critical, catalyst-related application of random copolymers is the fabrication of films used as sealing layer between BOPP films. These films should guarantee a sealing initiation temperature as low as possible, usually in the range $100-120°C$ or even lower, and thus should possess a corresponding low-melting temperature. The role of the catalyst–comonomer(s) combination here is to provide the maximum depression of the melting point, compatible with the constraints arising from both plant operability and FDA issues, all related to the presence of a maximum tolerable amount of extractables in the raw copolymer. Theoretically (237), this would imply the use of a single-center catalyst having the lowest product of the reactivity ratios. On the other hand, Ziegler-Natta catalysts are composed of a multiplicity of active species having different kinetic profile, stability, hydrogen response, reactivity, and reactivity ratios toward the comonomers. As a result, the copolymer generally consists of different fractions that can be separated, eg, via temperature rising elution fractionation (TREF) or cystallization analysis fractionation (Crystaf) (243,244). These fractions differ in both comonomer content and /or distribution, MW, and MWD. The same is true for ethylene copolymers like LLDPEs (see also the section, Kinetics). In particular, the product usually contains a certain quantity of highly modified, low MW, generally amorphous and sticky fractions, which tends to increase when the overall comonomer content increases. It is exactly the maximum tolerable amount of these fractions that sets the upper limits for both plant operability and compliance with FDA regulations. Thus, in principle, for this application Ziegler-Natta catalysts look inferior to their single-site counterparts, eg, metallocenes. On the other hand, even metallocenes, because of their single-site nature, apparently suffer from some limitations in this field: first, they cannot provide, either in gas-phase or slurry processes, random copolymers having a comonomer content higher than $\sim7-10$ wt%, because beyond this limit the copolymer tends to become mostly amorphous. Second, they tend to generate copolymers having a melting range that is too narrow to be easily managed in the mentioned sealing application. In this respect, copolymers from Ziegler-Natta catalysis are superior in that, because of the broader melting range and thus broader processability window they can offer, they can be processed more safely and consistently with the commonly used tranformation equipments. This does not mean that there is no room for improvement in Ziegler-Natta catalysis. The improvements should especially focus on the suppression of those active species that are responsible for the generation of the low MW, highly modified copolymer tails. These materials not only cause the above mentioned plant operability and FDA issues but also, because they tend to migrate to the surface of the finished article, also tend to deteriorate its optical properties and to cause (especially for films) sticking or blocking problems.

Multiphase Copolymers. Polypropylene-based multiphase (or heterophase copolymers) generally consist of a homopolymer (or a slightly modified homopolymer phase) and a rubbery ethylene–propylene or ethylene-1-butene phase, whose relative amount as well as nature (composition and MW) have to be modulated according to the desired properties and end-use application of the resulting materials. These materials constitute a family of polyolefin products spanning a wide range of properties, or better, balance of properties that can be, eg, the optimum stiffness–HDT–impact balance (impact copolymers) or the

optimum stiffness−impact−stress-withening (low-blush copolymers), or the optimum clarity−stiffness−impact (clear-impact copolymers); or, again, the optimum softness−elasticity (soft or supersoft copolymers). In this respect, polymer design plays a fundamental role as well as the catalyst. It is largely accepted that because of the extremely short lifetime of the polymer chain, especially under industrial conditions, it is impossible to obtain true block copolymers via sequential or multistage copolymerization by Ziegler-Natta catalysts (11,12). On the other hand, the catalyst has to be able to provide the desired amount and quality of the "building blocks" that make up the final material under many process constraints. It is exactly in the *in situ* synthesis of multiphase copolymers that the catalyst shows its maximum versatility and is asked to make the most from its chemical and morphological attributes.

It has long been recognized that the incorporation of an ethylene−propylene rubbery fraction into a polypropylene matrix, either via mechanical blending or sequential copolymerization (245), dramatically improves the impact properties of the resulting material, even at low temperatures, without excessive deterioration of its rigidity or heat distortion temperature.

The morphology of the impact copolymers exreactor is in agreement with the mechanism of particle growth depicted in the section The Growth of the Polymer Particle. However, after transformation it turns into the well-known morphological basis for this kind of materials: a multiphase texture consisting of spherical rubber domains embedded in a semicrystalline polypropylene matrix (245). The matrix provides stiffness, whereas the rubbery heterophase provides impact resistance by dissipating the impact energy, possibly via both crazing and shear yielding mechanisms. It is known that for these products the optimum rubber composition is in the range of 40−60 wt% ethylene, its amount ranges from ∼5 wt% to ∼30 wt% and the diameter of the rubber domains is ∼1 μm. It is also known that the rubbery phase, as a result of the multicenter nature of Ziegler-Natta catalysts, is heterogeneous in composition and not totally amorphous. For this reason, the rubber droplets usually display a shell-core morphology where the core is constituted by the partially crystalline ethylene-rich fractions and the shell by the generally amorphous propylene-rich fractions (13,246). This morphology of the rubbery domains could not be the best one in absolute terms for impact, but it is likely the most effective to get the optimum stiffness−impact balance. On the other hand, the major progresses in this field have been achieved by acting on the matrix rather than on the rubber fraction. In particular, by exploiting the same tools that proved to be effective in maximizing the stiffness of homopolymers: high sterical purity of the polypropylene chain coupled with a broad MWD (230,242), see Table 3.

A particular family of impact copolymers, commercially known as low-blush copolymers, are those that are required to be resistant to stress-withening under impact. In this case, a third fraction, usually constituted by polyethylene, is polymerized into an impact copolymer backbone. Kinetic profile is an important catalyst property in this case, since the catalyst needs to be active enough so as to incorporate the desired amount of an additional polymer fraction within a given residence time.

Clear/impact copolymers exploit the same toughening concepts and show the same morphological features as impact copolymers but, in this case, polymer

Table 3. Physicomechanical Properties of Heterophasic Propylene Copolymers Obtained with Different Zn Catalytic Systems as a Function of Molecular Weight Distribution and Rubber Content

Catalyst type		Fourth generation catalyst				Next generation catalyst	
matrix type		polypropylene monomodal		polypropylene bimodal		polypropylene monomodal	polypropylene bimodal
polydispersity index[a] (matrix)		*4.3*	*6.0*	*7.8*	*12*	*6*	*6.6*
heterophase[b]	(wt%)	16	10	14	16	17	12
melt flow rate	dg/min	13	17	15	12	11	23
flexural modulus[c]	(MPa)	1380	1780	1640	1800	1600	2020
IZOD + 23°C[d]	(kJ/m²)	9.3	5.3	5.6	5.8	9.1	5
IZOD − 20°C[d]	(kJ/m²)	5.5	3.1	3.6	4.5	5.7	3.5
break energy at −10°C[e]	(J)	9	5.8	4	8	10	7.4
break energy at −20°C[e]	(J)	8.1	5.5	3	8	9.1	7
ductile/brittle transition temperature[e]	(°C)	−50	−45	−45	−45	−45	−40

[a]Rheological measurement of molecular weight distribution.
[b]Ethylene–propylene copolymer (ethylene–propylene = 50/50 wt/wt).
[c]ASTM D790.
[d]ASTM D256.
[e]ASTM D3763.

design plays the major role since both composition and/or molecular weight of the phases need particularly accurate control. Actually, according to the well-known criteria to get transparency, the dimensions of the dispersed rubberlike droplets should be below the wavelength of light and the refractive indexes of the matrix and the dispersed phase should be as close as possible. The best compromise between transparency, stiffness, and impact, at least to the best of our knowledge, has been achieved in this area by using, as a dispersed phase, an ethylene-rich ethylene-1-butene copolymer (247). Apparently, these copolymers are more effective with respect to their ethylene–propylene counterparts because they are able to provide a toughening phase that matches, or at least approaches, the refractive index of the matrix still maintaining a relatively low T_g.

Whereas for the above mentioned product families stiffness is one of the key properties, for the so called soft or supersoft copolymers the key property is softness (flexural modulus $\sim$100 MPa, Shore hardness D in the range from 30 to 35), coupled with high elongation ($>$100%), reasonable tension set ($\sim$35−40% at room temperature and 100% elongation) and relatively high-melting points (145−155°C). Also in this case polymer design proved to be the key factor since it was demonstrated that in order to get the desired properties, both amount and composition of the rubber phase had to be outside the conventionally explored ranges. Actually, the targeted product performances were only obtained by incorporating $\sim$70 wt% of a substantially amorphous, propylene-rich ethylene–propylene copolymer into a polypropylene or slightly modified polypropylene matrix to get a cocontinuous morphological texture (230). In the case of supersoft materials, as opposed to the previous ones, catalyst stereoselectivity is logically not so important, whereas its architecture is the key factor. Actually, if starting from impact copolymers, catalyst porosity needs adequate control in order for the polymer particle to accommodate the desired amount of rubberlike material while maintaining the optimum plant operability and throughput, it is exactly with supersoft copolymers that this morphological catalyst attribute has found its most challenging exploitation: The conciliation of two largely contrasting principles such as incorporation of very large amounts of rubber and plant operability.

5.3. Polyethylene Products.   Historically, polyethylene products are characterized by three major parameters: density (which determines mechanical and optical properties), MW and MWD (which define both rheology, and thus processability, and, again mechanical properties). Since ethylene lacks those stereochemical features that in general are typical for polypropylene and 1-olefins, polyethylene products could appear, at first sight, to be simpler to prepare with respect to their polypropylene counterparts. Actually, this is not true since polymer optimization and innovation in polyethylene requires a degree of sophistication, in both catalyst and polymer design, that is not inferior to that of polypropylene. In general, stereoregularity excluded, the catalyst, as in the case for polypropylene, should be able to provide excellent morphogical control of polymer particles, fine tuning of polymer properties like MW, MWD and, for modified polymers, good comonomer incorporation and distribution. The catalyst also needs control of its kinetic profile, which is usually finer with respect to propylene polymerization: Since ethylene polymerization is more affected by heat and mass-transfer limitations, a smooth start is usually preferred in order to prevent

the occurrence of overheating phenomena and the formation of hot spots during reaction. An additional requirement of Ziegler-Natta catalysts for polyethylene is that they should exhibit excellent hydrogen sensitivity while still maintaining high activity and kinetic stability, especially for the synthesis of advanced reactor alloys. This attribute is one of the key requirements characterizing the potential of the catalyst and it is not as trivial as it might appear based on propylene polymerization, since ethylene polymerization is generally characterized by a strong deactivating effect of hydrogen (see the section KINETICS).

High-Density Polyethylene. High-density polyethylenes are defined as those polymers having densities in the $0.940-0.965$-g/cm^3 range. According to their application areas, the most critical parameters to control in HDPEs are MW and MWD. For example, for injection moulding applications HDPE requires high fluidity (low MW) coupled with narrow MWD, HDPE for tapes and monofilaments medium fluidity, and MWD, whereas HDPE for films, large containers, and pipes demands low fluidity and broad to very broad MWD (248−250).

One of the most critical applications of HDPE is in the area of high-performance pipes (251), since these materials need to satisfy a number of severe specifications in terms of stiffness, impact strength, and especially, short- and long-term ESCR and creep resistance. Now, polymer science teaches that stiffness is related to crystallinity, whereas both short- and long-term mechanical resistance is related to the concentration of tie molecules linking the crystalline domains (248,252−255). It is also known that the concentration of tie molecules can be increased either by increasing polymer MW or/and by incorporating a suitable amount of comonomer along the polymer chain. On the other hand, both of these tools are known to bring about a decrease in the crystallinity degree and thus rigidity. Now, polymer design has demonstrated (256,257) that an optimum balance between stiffness, impact resistance, and ESCR can be achieved through a delicate combination of low and high MW polymer fractions to get a broad, even bimodal, MWD coupled with an inverse comonomer incorporation (only in the high MW polymer tails). The term "inverse" stems from the fact that Ziegler-Natta catalysts tend to incorporate the comonomer mainly in the low MW polymer tails. This optimum polymer configuration can easily be achieved by using at least two reactors in series, of which the first one usually generates the low MW polymer fraction and the second the high MW polymer fraction, preferably modified with a suitable amount of comonomer, eg, 1-butene or 1-hexene (cascade process technology). In this respect, as already mentioned polymer design, and process technology play the major role. For example, cascade technology (258) is unique in its versatility since it offers the possibility to change the MWD from narrow to broad, from uni- to bimodal in combination with the inverse comonomer incorporation to get polymer alloys having the components mixed at a molecular level. But the catalyst still plays a considerable role since it has to be characterized by both high hydrogen response and activity, steady kinetic profile, good comonomer incorporation and distribution. Its capability to generate broad MWD is not as important in this case, since this polymer property is provided by the technology. Actually, catalysts providing an intrinsically narrow MWD can be advantageously used, especially if they are also able to provide a good comonomer distribution. Quite recently, new catalyst systems have been claimed that provide broad MWD HDPE in a single reactor

(259,260), however, our opinion is that these systems are unlikely to match the level of sophistication and versatility the cascade technology can offer in terms of product portfolio and properties.

Linear Low Density Polyethylene. These LLDPEs are a family of polyethylene products obtained via copolymerization of ethylene with 1-butene or 1-hexene and, less frequently, 1-octene, and are characterized by densities in the range between 0.915 and 0.930 g/cm^3 (copolymers having densities in the 0.926–0.940 g/cm^3 are usually defined as medium density polyethylenes). As in the case of random copolymers of propylene, here the role of comonomer is to reduce the length of crystallizable ethylene sequences and thus the degree of crystallinity and density of the resin (261). The role of the catalyst is to guarantee a good comonomer incorporation and distribution along the macromolecular chain. It is necessary that the comonomer be evenly distributed, both intra- and intermolecularly, especially for the fabrication of films having good optical properties (haze and gloss), mechanical properties, eg, puncture and tear resistance, impact and tensile strength, and low blocking force, in addition to the control of the various MW averages and distributions (262). According to Hosoda and coworkers (263), the better mechanical properties exhibited by LLDPEs having narrow chemical composition distribution (CCD) can be attributed to both a higher concentration of tie molecules and of "effective" tie molecules. Apart from the unsatisfactory mechanical properties, an additional drawback of LLDPEs having broad CCD is that they usually contain a highly modified fraction having low MW. This fraction tends to impair both optical properties and blocking behavior, and causes both plant operability and FDA issues. The intramolecular inhomogeneity of LLDPE is clearly reflected by the typical TREF profile depicted in Figure 21, and, also in this case, can be related to the multicenter nature of Ziegler-Natta systems (243).

For example, according to Kissin (169), catalyst systems of the type MgCl$_2$/TiCl$_4$ supported on silica, are characterized by the presence of at least five families of active centers having different kinetic profile, reactivity, and reactivity ratios toward the monomers and hydrogen response. It is likely (17,140) that these centers can be differentiated according to their sterical environment: the most "open" centers are relatively more reactive toward the
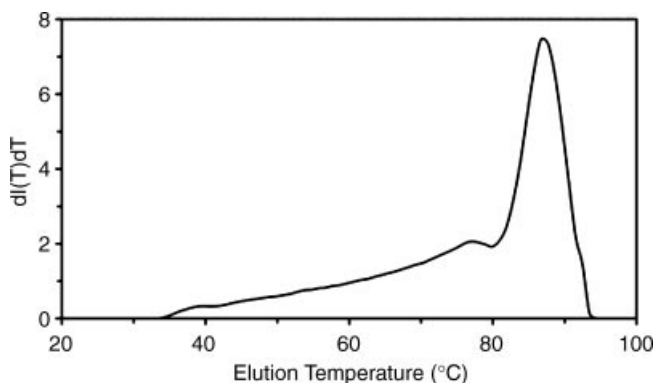

Fig. 21. Typical TREF profile for a LLDPE containing ∼8 wt% 1-butene.

comonomer, whereas the most "closed" centers are almost only reactive toward ethylene (see HDPE peak in the TREF profile). On the other hand, according to some authors (17,141,142), it is the oxidation state of the transition metal that plays the major role: Ti^{3+} would be reactive to both ethylene and the comonomer, whereas Ti^{2+} would be reactive only to ethylene, and thus less prone to comonomer incorporation. Many attempts to alleviate the problem have been reported, mainly in the patent literature: The use of specific Al-alkyls optionally coupled with suitable electron donors would allow a substantial reduction in the amount of extractables, and thus a considerable improvement of the quality of the resulting LLDPEs (39−48).

5.4. Catalyst Selection. Based on the above selected examples, it is now relatively easy to sort out the best catalyst system to meet each specific product target. In particular, the catalysts should provide:

- Very narrow MWD, high/very high fluidity and medium isotacticity for polypropylene fibers.
- Narrow MWD, both high fluidity and isotacticity for thin-wall injection molded polypropylene articles.
- Broad MWD, low fluidity, and high isotacticity for extruded polypropylene pipes and sheets.
- Broad MWD, medium fluidity, and very high isotacticity for rigid injection moulded polypropylene articles.
- Broad MWD and relatively low isotacticity for biaxially oriented polypropylene films.
- Same performances as above, without the necessity of sterical control, for polyethylene products.
- Good comonomer incorporation and distribution, both inter- and intramolecular, for polypropylene random copolymers or LLDPE.
- Excellent hydrogen response coupled with good activity for bimodal polyethylenes.
- Controlled particle size and narrow size distribution for optimum plant operability.
- Minimum particle porosity−maximum bulk density for maximum plant throughput.
- Tuned degree of particle porosity, up to very high levels, compatible with its mechanical integrity for the *in situ* synthesis of polypropylene heterophasic copolymers and supersoft alloys.

In addition, since catalysts behave very differently in different process systems (any technology requires its own particle size, kinetic profile etc), it is clear that a considerable degree of customization is needed to optimize catalyst performances with respect to both plant operability−throughput and to the desired product portfolio. As a result, even if we limit ourselves to polypropylene or to polyethylene and consider that process technology can help achieve some polymer properties (eg, broadening of MWD via multistage, or cascade polymerization) it can be safely stated that a unique, ideal catalyst system that can fit any purpose does not and can not exist.

However, in this respect the discovery and exploitation of $MgCl_2$ supported systems can be considered revolutionary in its significance due to the unprecedented control they can offer over both polymer and process design. This is not only due to the extremely high catalyst mileage, which led to the removal of many sections of the polymerization plants, but also to the versatility obtained in the overall catalyst performances as the result of the sophistication achieved in fine-tuning both the catalyst chemistry and architecture (see the section EVOLUTION OF ZIEGLER-NATTA CATALYSTS). Thus, the versatility of $MgCl_2$/$TiCl_4$ systems is such that the majority of the present and, maybe, future polypropylene product and process needs can be addressed and targeted just by acting on the nature of the electron donors and on the macro- and micromorphology of the support. In particular, phthalate-based catalysts can be regarded as a family of general-purpose systems with which it is possible to cover the majority of product properties and application. Both diether- and succinate-based catalysts can be considered as specialized systems that cover, respectively, the high fluidity, controlled rheology areas of applications demanding very narrow MWD, or the medium-low fluidity areas of applications demanding broad MWD. Until recently, MWD broadening was achieved via multistage, or cascade polymerization. It is worth stressing that the succinate-based systems can provide broad polymer MWD in a single stage, leading either to a considerable process simplification or to the manufacturing of products that could not be achieved based on single-reactor technologies. As for architecture-related attributes, the peculiarity of $MgCl_2$ supports is that they can be shaped into perfectly spherical particles having controlled and narrow size distribution via controlled emulsification of $MgCl_2 \cdot n$EtOH melts. The surface area and porosity of the resulting catalysts can be altered, when desired, via controlled dealcoholation of the corresponding solid supports. In particular, today it is possible, by using spherical $MgCl_2$/$TiCl_4$ catalyst systems having porosity of $\sim$50% vol (mercury porosimeter), to incorporate *in situ* (gas-phase polymerization processes) into spherical polypropylene particles, up to $\sim$80 wt% of rubbery copolymers without particle agglomeration or reactor fouling.

Based on the above considerations, it is now clear why controlled-morphology $MgCl_2$-supported catalysts today account for the majority of polypropylene production volume.

As for the manufacturing of polyethylene products, a considerable share is constituted by catalyst systems that, though still generally containing $MgCl_2$ as a main component can be obtained either through precipitation, starting, eg, from $Mg(OEt)_2$, or through support of $MgCl_2$ complexes or its precursors on inorganic carriers, eg, SiO_2, when fine morphology control is needed. These catalyst can be used either without or, for same specific applications like the synthesis of LLDPE, in combination with electron donors (39–48).

6. Future Trends in Ziegler-Natta Catalysis

Ziegler-Natta catalysts are robust, well-established versatile systems with which it is possible to synthesize a wide family of polyolefins, including both commodity and specialty products.

Among the positive attributes of Ziegler-Natta catalysts one can at least mention the following: low cost of both catalyst and cocatalyst; very high mileage; possibility to be used as drop-in components in all the existing polymerization technologies; possibility to control polymer MW and MWD in a broad range; tunable isospecificity, either very high or very low; complete control over morphology in terms of shape, size, surface area, and porosity of both catalyst and polymer particles.

Having said that, why do we need and what should we do to improve the performances of the existing Ziegler-Natta catalysts? So far, we have listed the pros of these systems; in order to answer the question we should also consider their cons, which substantially derive from their multisite nature. This means, eg, relatively broad MWD for both homo- and copolymers and, in particular, relatively poor intermolecular homogeneity of copolymers. This, eg, prevents the synthesis via heterogeneous Ziegler-Natta of very narrow MWD polypropylenes for fiber application or high-quality LLDPEs, propylene-based random copolymers, and ethylene–propylene rubbers.

Single-site catalysts can in principle overcome all these drawbacks but, on the other hand suffer, up to now, from several limitations: high cost of both catalyst and cocatalyst and lack of complete morphology control.

Considerable progress has been made in both catalyst families to alleviate their relevant limitations. For example, diether-based Ziegler-Natta catalysts are able to provide polypropylenes having quite narrow MWD (see the section Evolution of Ziegler-Natta Catalysts); catalysts for LLDPE have been developed, based on the combination of specific electron donors and cocatalysts, which give products endowed with better optical–mechanical properties and reduced amount of oligomers. As for single-site catalysts, their economics as well as morphology control are continuously improving, but both attributes still look too far from approaching those of heterogeneous systems.

We believe that future research on Ziegler-Natta catalysts should concentrate on solving their drawbacks while preserving their properties. In other words, one should combine the best of both Ziegler-Natta and single-site catalysts, aiming at the development of a very new family of "single-center" heterogeneous Ziegler-Natta systems.

The probability of success in this area depends on a number of factors and, especially, on our ability to better understand the intimate nature of the active centers, either via modeling or direct analytical tools. Then, one should operate at the support level and, based on what we know of molecular modeling, try to force $MgCl_2$, or alternative supports, to develop only the preferred crystal surface. A complementary approach should focus on the role of electron donors and, in particular, on the exploitation of their capability to selectively block the undesired active centers. We recognize that this ambitious target is easier to discuss than to achieve, but it should represent what a long-term and far-seeing research on Ziegler-Natta catalysis should focus on in the future.

Until quite recently, it was thought that homogeneous catalysts could not be highly isospecific; this statement was first disproved by Ewen (264) and by Kaminsky and Brintzinger (265). In Ziegler-Natta catalysis, many breakthroughs have been achieved over the years that even the most optimistic scientists could hardly envision. Long-term vision into Ziegler-Natta research should,

in our opinion, focus on disproving the generally accepted notion that heterogeneous catalysts cannot be single center.

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