CHAPTER II

LITERATURE REVIEW

2.1 Introduction

In 1963 Karl Ziegler and Giulio Natta were awarded the Nobel Prize for Chemistry for their landmark discoveries of the polymerization catalysts named after them. The first Ziegler-Natta catalysts were discovered four decades ago. In 1953 Ziegler revealed that high density polyethylene was easily made at low pressure with binary mixture of metal alkyls and transition metal salts, and in the next year Natta demonstrated the ability of the same type of catalysts to form isotactic polymers from α-olefins. The discoveries changed polymer chemistry forever, and provoked a worldwide research and development effort that culminated in many new commercial plastics and elastomers. The Ziegler-Natta catalyst has now joined the ranks of conventional cationic, anionic and radical initiators as one of the major methods available to initiate polymerizations, and it is doubtful that it can be challenged by any other catalyst for its versatility. Ziegler-Natta catalysts became prominent in a special period in the history of polymer science, a period that not only produced many new commercial polymers but also enhanced our basic knowledge of polymer properties and structure as well as polymerization processes [9].

2.2 History and Development of Stereospecific Catalysts

Generally speaking, the Ziegler-Natta catalyst is a complex formed by reaction of a transition metal compound (halide, or alkoxide, or alkyl or aryl derivative) of group IV-VIII transition metals with a metal alkyl or alkyl halide of Group I-III base metals [10]. The former component is usually called the catalyst and the latter the cocatalyst. There are a very large number of patents involving every combination of pure or mixed metal alkyls with transition metal compounds, each claiming particular advantages. In practice, only a few group I-III metal alkyls are effective. Aluminum alkyls (such as $AlEt_3$, $Al\text{-}i\text{-}Bu_3$, $AlEt_2Cl$, $AlEtCl_2$ and $AlEt_2OR$) have been overwhelmingly preferred [11]. Also, transition metal compounds containing titanium

(Ti), vanadium (V), chromium (Cr) and, in special cases, molybdenum (Mo), cobalt (Co), rhodium (Rh) and nickel (Ni) are primarily used.

Not long after Ziegler-Natta catalysts were discovered, it was found that electron donors could greatly affect the catalyst's kinetic and stereochemical behavior. Electron donor compounds, such as amines, ethers and esters, have the potential of complexing and reacting with the components of the catalyst or the active centers. They have been used in controlled amounts in many Ziegler-Natta catalytic systems as a third component to increase catalyst activity and/or stereoselectivity [9].

2.2.1 First Generation Catalysts

The $TiCl_3/AlEt_3Cl$ catalyst used in the earlier industrial processes for PP manufacturing , in fact, showed a low productivity and stereospecificity, the Isotactic Index (II) (i.e., the fraction of isotactic polymer) being around only 90%. Consequently, both removal of the catalytic residues (deashing) and separation of the atactic polymer fraction were required [12].

The research carried out both in Natta's group and in other industrial laboratories led very soon to the discovery that catalysts obtained by prolonged ball milling of either Al-reduced $TiCl_3$ (thus containing co-crystallized $AlCl_3$) or mixtures of $TiCl_3$ and $AlCl_3$ were much more active than pure $TiCl_3$ [13,14]. A catalyst of this type, named AA-$TiCl_3$ (where AA stands for Al-reduced and activated), was made commercially available by Stauffer Chem. Co. in 1959 [15] and is usually considered as the first generation Ziegler-Natta catalyst for PP. AA-$TiCl_3$, together with similar catalysts prepared in different ways but having similar performance, has been used, in combination with $AlEt_2Cl$ (DEAC) as cocatalyst, for PP production by many companies, at least up to the mid '70s and is probably still used today by some minor PP producers.

Its productivity and stereospecificity, however, were still rather low, and the need for deashing and atactic removal, together with the poor polymer morphology, rendered the production process complicated and expensive [12]. Considering that in $TiCl_3$ only the surface Ti atoms, which represent only a small fraction of total Ti, were likely to be accessible to the Al-alkyl and thus available for making active polymerization sites [16,17], several efforts were soon started to improve the Ti efficiency.

2.2.2 Second Generation Catalysts

Efforts to increase accessibility to Ti atoms led to the development by Solvay [18,19], in the early '70s, of a $TiCl_3$ catalyst having a much higher surface area than the usually AA-$TiCl_3$ (150+ instead of 30 m^2/g to 40 m^2/g), a fivefold productivity and an isotactic index around 95%. This catalyst, usually referred to as "Solvay" $TiCl_3$, can be considered as the first example of the second generation catalysts for PP and, after several improvements [20], is still employed today, together with DEAC as cocatalyst, in some production processes. Many other catalysts of this type also referred to as "low-Al" catalysts, have been developed during the '70s and '80s by several companies.

2.2.3 Third Generation Catalysts

Attempts to develop supported catalysts started very early in the '60s by making use of conventional high surface supports bearing surface functional groups (mainly –OH) able to chemically anchor the transition metal compound (e.g., silica, alumina, Mg-hydroxides or Mg–hydroxychlorides). These attempts, however, though leading in some cases to highly active catalysts for polyethylene (PE), were not very successful for PP (because of the low activity) until the discovery in the late '60s [21] that catalysts based on "activated" $MgCl_2$ were highly active for PE and PP as well. Owing to their low stereospecificity (II < 50%) [22], the use of these catalysts was initially limited to PE (actually in 1972 Montedison started a plant for PE running with a high-yield catalyst based on comilled $MgCl_2/TiCl_4$). In a few years, however, this problem was overcome by the addition of appropriate Lewis bases [18] which made it possible to obtain highly active and stereospecific catalysts by comilling $MgCl_2$, $TiCl_4$, and Lewis base (LB), usually referred to as "internal donor" (ID), combined with an Al-trialkyl as cocatalyst and a second Lewis base, usually called "external donor" (ED).

Later, an improved version of this catalyst was developed [23] and used in a plant started by Montedison in Ferrara in 1978, in which the Lewis base were ethybenzoate (EB) as ID and methyl-p-toluate (MPT) as ED.

This $MgCl_2$-supported, donor-modified catalyst is the parent of a large family of catalysts which have been called the third generation. Though sufficiently active to avoid the need for deashing, these catalysts still required the removal of the atactic polymer which, depending on the conditions used, still constituted from 6% to 10% of the total. The research was thus focused on both more deficient routes for the catalyst synthesis and more efficient combinations of electron donors.

2.2.4 Fourth Generation Catalysts

Further research led to highly active and stereospecific catalysts, called by the inventors super high activity catalysts (SHAC), which, though still making use of benzoic acid esters as electron donors, were claimed to display a superior productivity and isotacticity [24-26]. The latter resulted, in the early '80s in the discovery of a new combination of electron donors, namely alkylphthalates as ID and alkoxysilanes (or silyl-esters) as ED, able to afford a much better productivity/isotacticity balance than benzoic acid esters [27].

The above catalyst systems, which are currently used in most of the modern industrial processes for PP manufacturing, were named "super-active third generation" by Galli *et al.* [28], but to avoid confusion with the SHAC above and also because they are based on a totally different electron donors pair.

2.2.5 Fifth Generation Catalysts

As described above, the complexity of $MgCl_2$-supported catalyst is derived from the chemical interactions between the Lewis acids ($MgCl_2$, $TiCl_4$, alkylaluminum) and bases (internal and external donors), mostly from the high reactivity of alkylaluminums towards Lewis bases used as internal and external donors. In the second half of the '80s, a new type of electron donors was discovered which, if used as internal components, provided extremely high activities and isotacticities without the need of any external Lewis base [29]. It was found that some hindered diethers like 2,2-diisobutyl-1,3-dimethoxypropane (DBDMP) and 2,2-dimethoxypropane (DMP) used as internal donor can improve the catalyst isospecificity to a great extent even without using any external donor. Iiskola *et al.* reported an interesting experimental result on this special catalyst system that DBDMP contained in the $MgCl_2$-supported catalyst is hardly removed by the treatment with a triethylaluminum [30].

2.2.6 Metallocenes-Sixth Generation Catalysts

At the same time, the approach to homogeneous stereospecific catalysts, which had proven disappointing for many years, began to advance with the discovery that stereorigid metallocenes of transition metals, such as Zr and Hf, when combined with methylaluminoxane (MAO), were able to provide highly stereoregular isotactic or syndiotactic PPs in extremely high yields [31-33]. This discovery aroused an enormous interest in both the industrial and the academic worlds, not only because of its scientific value but also because it appears to open the way to materials with unprecedented properties. The metallocene systems can, thus, be fully thought to represent the "sixth generation" of stereospecific catalysts for propylene polymerization, and they will probably undergo a great development in the near future.

Comparisons of the performance achievable with the different catalyst generations, up to the fourth on, have been often reported in the literature. Table 2.1 shows an updated comparison, based on data from Himont (now Montell) obtained under hexane slurry or bulk polymerization conditions, including all the above catalysts generations. Although the figures are only valid relative to one another, they clearly show the great progress in catalysts over forty years of undeashing research efforts.

Table 2.1 Performance of the different catalyst generations [34].

Generation	Composition	Productivity[a] (kg PP/g Cat)	II (wt%)	Morphology control	Process requirements
1st	δ-$TiCl_3$0.33$AlCl_3$ + DEAC	0.8-1.2	90-94	not possible[b]	Deashing + atactic removal
2nd	δ-$TiCl_3$ + DEAC	3-5 (10-15)	94-97	possible	Deashing
3rd	$TiCl_4$/Ester/$MgCl_2$ + AlR_3/Ester	5-10 (15-30)	90-95	possible	Atactic removal
4th	$TiCl_4$/Diester/$MgCl_2$ + TEA/Silane	10-25 (30-60)	95-99	possible	–
5th	$TiCl_4$/Diether/$MgCl_2$ + TEA	25-35 (70-120)	95-99	possible	–
6th	Zirconocene + MAO	($5\text{-}9.10^3$) (on Zr)[c]	90-99[d]	to be achieved	–

[a] Polymerization: hexane slurry, 70°C, 0.7 MPa, 4 h, H_2 for MW control (values in brackets are from bulk polymerization for 2 h at 70°C, with H_2)

[b] Only possible with Al-alkyl reduced $TiCl_3$, at 200-300 μm size level

[c] One hour polymerization time

[d] *mmmm*% (by ^{13}C NMR)

2.3 Catalyst preparation Methods

The discovery of active $MgCl_2$ as a support for $TiCl_4$ and its derivatives was a major achievement in the field of Ziegler-Natta catalysis for the polymerization of propylene [21] because it allows the realization of catalysts with highest activity and stereospecificity.

For industrial perspective, it is utmost importance to find the simple routes for catalyst synthesis to realize a lower cost level. A further challenge was to gain access to $MgCl_2$ supports with the required particle morphology, which plays a key role in industrial processes because it influences reactor loading and reactor fouling.

Three main industrially viable synthetic routes have been followed to fulfill the requirements. A short description is given below.

2.3.1 Ball milling

An important additional landmark in the development of supported catalysts for propylene polymerization was the recognition that the ball milling of $MgCl_2$ in the presence of an internal donor such as ethylbenzoate followed by subsequent treatment with $TiCl_4$ could produce a highly active catalyst which, when used along with triethylaluminium and an external donor such as benzoate or toluate as the cocatalyst system, could produce polypropylene of high stereoregularity [21,35]. The primary effect of this procedure is to break the layered structure and to reduce the crystal size of $MgCl_2$. Thus, this method results in a significant increase in the specific surface area of the solid $MgCl_2$ which composed of very small crystallites. However, the most important disadvantage is the insufficient particle morphology which can not be manipulated as requested.

2.3.2 Recrystallization

A further development has been the use of an alcoholate of $MgCl_2$, allowing the preparation of spherically shaped support and hence catalyst particles [36]. This important advance resulted from the establishment of catalyst particle replication during polymerization [12,37] which is an important consideration both for slurry and gas phase commercial polymerization. The method consists of a chemical activation by reaction of crystalline $MgCl_2$ with alcohol to form $MgCl_2 \cdot n\mathrm{ROH}$ adducts, followed by a controlled regeneration of the active support through recrystallization by removing the added compound (quick cooling, solvent evaporation or titanation). In consequence, the assemblies of spherically fined $MgCl_2$ crystallites with highly distort and high number of uncoordinated magnesium sites is produced.

2.3.3 Chemical Conversion

Catalysts prepared from the reaction between $TiCl_4$ and magnesium alkoxides such as $Mg(OEt)_2$ show a very high activity for the polymerization of ethylene and propylene. Such catalysts were successfully developed for ethylene polymerization by Hoechst AG [21] and Solvay & Cie [38] during the late 1960s and early 1970s. Further advances have been achieved by the Toho Titanium Company [39] in the preparation of a high activity catalyst for the polymerization of propylene. Magnesium alkoxide compounds consist of crystals with layers of magnesium cations and alkoxy anions with loose layers of alkyl chains of the alkoxy groups in between [40]. Solvent can penetrate into these loose layers. These layers swell and the bonds are weakened. During the reaction with $TiCl_4$, hydrocarbon solvent are incorporated and a reaction with $TiCl_4$ takes place in this layer to form $MgCl_2$ and $TiCl_{4-n}(OEt)_n$ compounds. The in petrol suspended magnesium ethoxide is transformed into the $MgCl_2$ support and at the same time, $TiCl_4$ is absorbed. The soluble $TiCl_{4-n}(OEt)_n$ compounds are removed by washing with petrol. A catalyst particle with spherical shape, high porosity and high specific surface area is achieved.

2.4 Structure of $MgCl_2$

Two crystalline modifications are known for $MgCl_2$, the commercial α form and the less stable β form. Similar to the γ-$TiCl_3$, the α-form has a layer structure of the $CdCl_2$ type and shows a cubic close-packed stacking (ABC…ABC…) of double chlorine layers with interstitial Mg^{2+} ions in sixfold coordination [41]. The β-form, on the contrary, shows a hexagonal close packing like that of α-$TiCl_3$ [42]. The layer structure of α-$MgCl_2$ displays an X-ray diffraction spectrum with a strong (104) reflection at $d = 2.56$ Å as a result of the cubic close-packed arrangement of the Cl ions. The internal structures of hexagonal layers in both cases are almost equivalent since van der waals interaction between layers is weak.

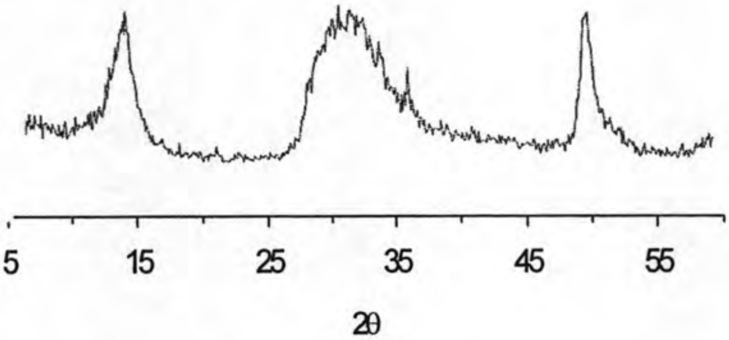


Figure 2.1 Powder X-ray diffraction pattern of δ-$MgCl_2$ [43].

The key ingredient of the catalysts is the "activated" or δ-$MgCl_2$, which exhibits a disordered structure arising from the translation and rotation of the structural Cl-Mg-Cl layers with respect to one another that destroy the crystal order in the stacking direction [44]. In consequence, the X-ray spectrum shows a gradual disappearance of the (104) reflection and its replacement by a broad "halo" centered at d = 2.65 Å. As shown in the Figure 2.1, the structurally disordered δ-$MgCl_2$ exhibited broad bands centered at $2\theta = 15$, 32 and 50.5°. Moreover, it is believed that the outstanding success of $MgCl_2$ is because δ-$MgCl_2$ and δ-$TiCl_3$ have the same crystal structure and the nearly identical ionic radii and lattice distances (see Table 2.2). Such a dramatic increase in activity was revealed to be caused by marked increases in the propagation rate constant (k_p) as well as the number of active species [C*] [44]. The latter effect is easily understood in terms of a high dispersion of the active titanium species on the large surface of $MgCl_2$.

Table 2.2 Crystallographic data for δ-$MgCl_2$ and δ-$TiCl_3$ [45]

δ-$MgCl_2$	δ-$TiCl_3$
hexagonal close packing of the Cl ions	
a = b = 3.63Å	a = b = 3.54Å
c = 5.93Å	c = 5.86Å
Cation coordination: octahedral	
Mg–Cl = 1.23Å	Ti–Cl = 1.25Å
Mg^{2+} = 0.65Å	Ti^{4+} = 0.68Å
	Ti^{3+} = 0.76Å

Experimental data suggest that preferential lateral cuts correspond to the (100) and (110) planes [44], and theoretical calculations of the lattice electrostatic energies give a lower energy for the (110). The activation processes (mechanical or chemical) of the $MgCl_2$ increase the portion of (100) and (110) surfaces on the $MgCl_2$ surface [34]. These two lateral cuts contain coordinatively unsaturated Mg^{2+} ions, with coordination number 4 on the (110) cut and 5 on the (100) cut, as shown in Figure 2.2 [46]. That is to say, the magnesium atoms are coordinated with 4 or 5 chlorine atoms, as opposed to 6 chlorine atoms in the bulk of the crystal.

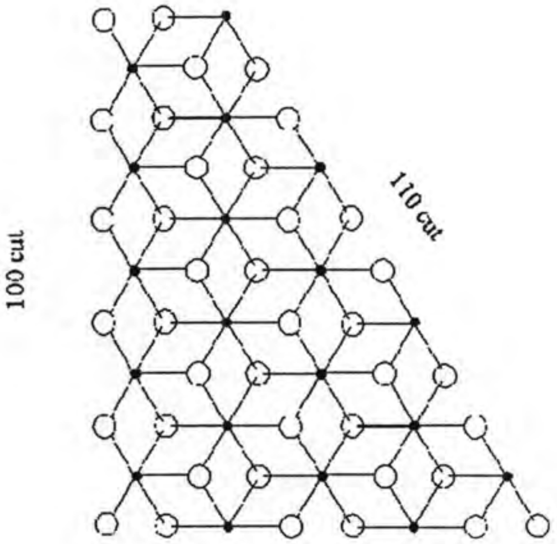


Figure 2.2 Model of $MgCl_2$ layer showing the (100) and (110) cuts [46].

The situation on crystal edges and corners could present additional differences, so that the presence on the $MgCl_2$ surface of Lewis acidic sites with different acid strength and steric requirements is likely to occur and actually has been verified through interaction with Lewis bases of different strength and steric hindrance. The "activated" $MgCl_2$ support, as it exists in the catalyst, can thus be envisaged as an agglomerate of very small crystallites (primary units) bearing on their side surfaces a variety of exposed Mg^{2+} ions with different degrees of unsaturation, Lewis acidic strength and steric hindrance, and thus potentially able to coordinate with the other catalytic components.

2.5 Catalyst Chemistry

It is well known that neither $TiCl_4$ nor the internal donor can be easily removed from the catalyst unless severe thermal treatments or strongly coordinating solvents are used. Thus, it seems that the catalyst components lose their identity and become strongly linked together, forming new complexes. A considerably amount of work has been aimed at elucidating the nature of this bonding mainly by means of spectroscopic observations (IR, NMR) and thermogravimetric (TG) analyses carried out on both the true catalyst and model combinations of its components (i.e., $MgCl_2$/ID, $TiCl_4$/ ID, $TiCl_4$/$MgCl_2$, $TiCl_4$/ID/$MgCl_2$ complexes or comilled mixtures).

A great deal of IR data is available for catalysts containing ethylbenzoate (EB) as internal donor [12,47,48] for which a shift of the C=O stretching frequency from 1725 cm^{-1} in the free ester to 1680 cm^{-1} to 1700 cm^{-1} is most commonly observed in both the catalyst and the comilled EB/$MgCl_2$ mixtures. This result has been interpreted as an indication that a complexation of EB through the carbonyl oxygen takes place to Mg and not to Ti. The concomitant broadening of the C=O absorption band has been attributed to the presence of a variety of coordination complexes with different bond strengths [49].

Solid state CP MAS (cross polarization with magic angle spinning) ^{13}C NMR investigations on both the catalyst [50,51] and model $TiCl_4$·EB complexes or EB/$MgCl_2$ comilled mixtures also led to the conclusion that EB is prevailingly complexed to $MgCl_2$. Possible structures for EB complexed to the (100) and (110) faces of $MgCl_2$ have been proposed by Chien *et al.* [50] and are shown in Figure 2.3.

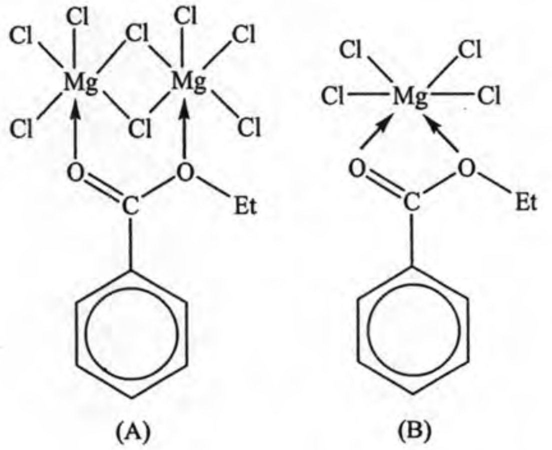


Figure 2.3 Possible models for EB coordination on the (100) (A) and (110) (B) faces of $MgCl_2$ [50].

According to some authors [33,52], however, a slight difference can be noticed in the infrared C=O absorption frequency of the catalyst (~1680 cm^{-1}) and that of the EB/$MgCl_2$ mixture (~1690 cm^{-1}) and this would suggest that in the former, EB is in some way complexed to both Mg and Ti. On the other hand, from electron spin resonance (ESR) analysis of the catalyst after interaction with TEA, some evidence for the presence of small amounts of EB or phthalates complexed to Ti^{3+} has been reported as well [53,54].

The information concerning bifunctional donors (phthalates, diethers) is not as abundant. For phthalic acid esters, however, IR observations show a shift of the C=O stretching frequency from ~1730 cm^{-1} in the free ester to 1685 cm^{-1} to 1700 cm^{-1} in both the catalyst and the $MgCl_2$/ester complex. Similarly, the C–O stretching frequency of diethers (1113 cm^{-1}) is shifted to a doublet at 1059 cm^{-1} and 1024 cm^{-1} in both the catalyst and the $MgCl_2$/diether mixture, with no bands from the $TiCl_4$·diether complex being detectable in the former [55]. The same indication is provided by ^{13}C NMR observations on catalyst containing either diethers [55] or phthalates [56], though in the latter case a considerable line narrowing observed in binary ester/$MgCl_2$ mixture after treatment with $TiCl_4$ would suggest, according to the Sormunen [56], that a separate crystalline phase is formed on the support surface.

From all the above, it seems possible to conclude that both monofunctional and bifunctional donors are essentially complexed to Mg rather than to Ti. The structure of the complexes could, however, be different for the different donor types. As a matter of fact, bifunctional Lewis bases could form either 1:1 chelate complexes with tetracoordinated Mg ions on the (100) face [55].

As far as the $TiCl_4$ bonding is concerned, the most widely accepted models, supported by energy calculations, are those based on epitaxial adsorption on the different $MgCl_2$ faces. According to Corradini and his group [57,58], for instance, the (100) cut is more basic than the (110) one as far as $TiCl_4$ coordination is concerned. Also, calculations suggest that $TiCl_4$ coordination as a Ti_2Cl_8 dimer on the former face and as a monomer on the latter are energetically favored. Similar models were proposed by Chien [59] who, however, assumed the presence of tetracoordinated rather than hexacoordinated monomeric species on the (110) face, both in clusters and in isolated form. As a consequence of the presence of $TiCl_4$ to coordinate on the (100) face, the situation in the catalyst, before and after reduction with the Al-alkyl, can be roughly represented as in Figure 2.4, with the (100) face being prevailingly occupied by Ti_2Cl_8 dimers and the (110) face by the Lewis base.

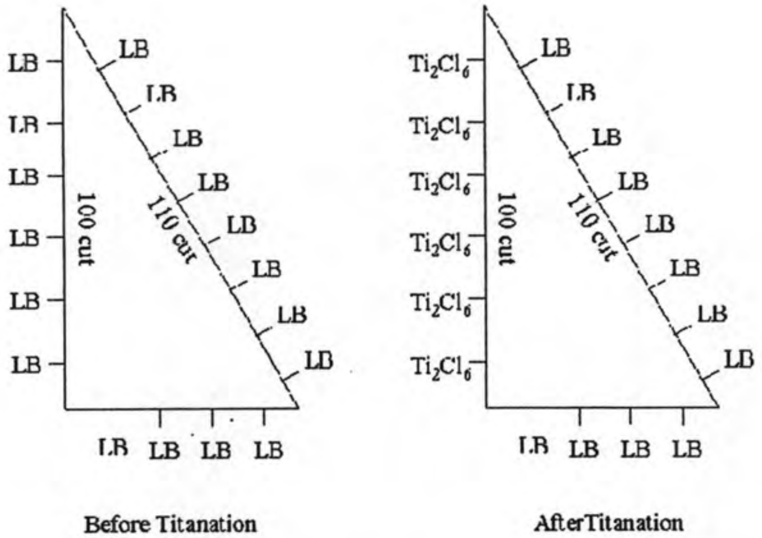


Figure 2.4 Schematic drawing of the Lewis base and Ti halide distribution on the (110) and (100) cuts MgCl$_2$: (left) = support, (right) = catalyst activated with the Al-alkyl [60].

However, recent spectroscopic studies using FT-Raman have provided evidence for strong adsorption of TiCl$_4$ on the (110) lateral cut of MgCl$_2$, giving a monomeric species with octahedrally coordinated titanium, which can be the precursor for active and stereospecific sites [61,62] as shown in Figure 2.5.

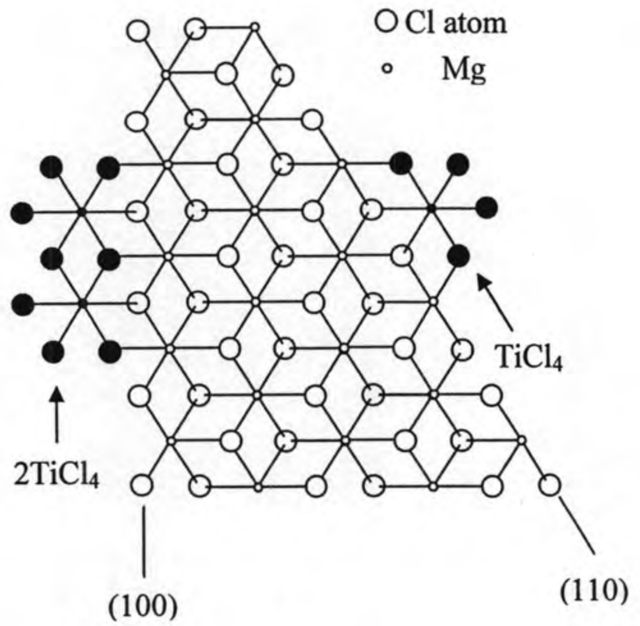


Figure 2.5 Epitaxial binding of TiCl$_4$ on to the surface of δ-MgCl$_2$ [61].

2.6 Cocatalyst Chemistry

The cocatalysts used with $MgCl_2$-supported catalysts are invariably Al-trialkyls, triethyl aluminium (TEA) and triisobuthyl aluminium (TIBA) being by far the most preferred ones. Al-alkyl-chlorides, in fact, afford a much poorer performance and can be used only in combination with trialkyls [63].

On the other hand, the external donor which can be used appears to be dependent on the type of internal donor. If ID is an aromatic monoester (EB is the most usual), esters of the same type are normally required, such as methyl-*p*-tolulate (MPT), ethylanisate (EA), *p*-ethoxy-ethylbenzoate (PEEB) and the like, whereas alkoxysilanes are required with phthalates (or diethers). Hindered piperidines, such as 2,2,6,6-tetramethylpiperidine (TMP), on the other hand, seem to work well with diethers, but not as well with monoesters. Whichever is the external donor, however, owing to its basic nature and the acidic nature of the AlR_3, a more or less complex interaction between the two components takes place.

Most of the literature deals with the interaction between TEA or TIBA and aromatic monoesters, whose chemistry has recently been reviewed by several authors. According to most of the findings, the interaction involves first the formation of an acid-base complex through the carbonyl oxygen, as demonstrated by the shift of the infrared C=O stretching frequency from ~1725 cm^{-1} in the free ester to 1655 cm^{-1} to 1670 cm^{-1} in the AlR_3/ED mixture. The complex is most often assumed to exist in a 1:1 ratio, but on the basis of spectroscopic evidence [64] and calorimetric studies [49], complexes involving two moles of AlR_3 per mole of ED also have been hypothesized. Structures such as those represented in Figure 2.6 have been proposed by Spitz *et al.* [64], while not very different structures were assumed by Chien *et al.* [65] and Tashiro *et al.* [66]. The complex formation is very fast even at low temperature and in dilute solutions.

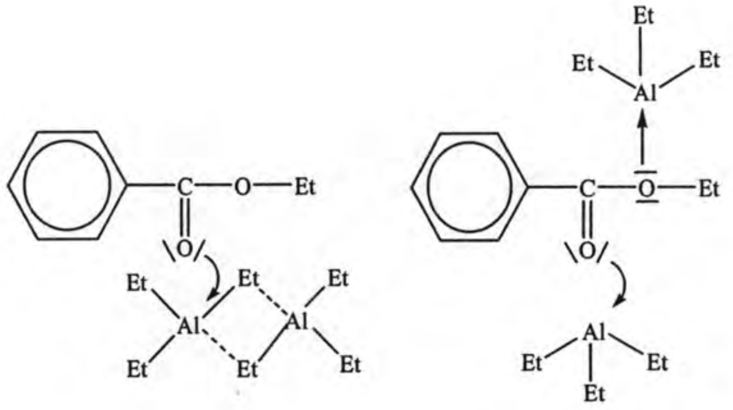
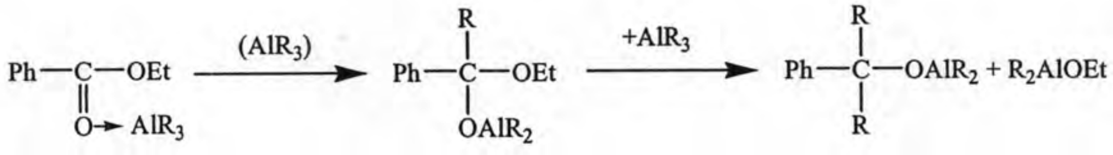


Figure 2.6 possible structures of 1:2 EB/TEA complexes [64].

As regards alkoxysilanes, the formation of a 1:1 complex between TEA and phenyltriethyoxysilane (PES) has been indicated by means of ^{13}C NMR spectroscopy, at least at relatively high TEA concentrations (0.5 mol/L) [67]. The complex seems to involve the O atom from only one OR group, irrespective of the number of OR groups attached to Si.

The above complexes can undergo a further reaction, especially in the presence of excess AlR_3 as is usual for polymerization. In the case of aromatic monoesters, such as EB, a nucleophilic attack of free AlR_3 on the carbonyl group complexed with AlR_3 has been postulated. The reaction leads finally to the formation of two moles of dialkylaluminium alkoxide per one mole of ester, according to the Figure 2.7 [63,68,69].



$$\underset{O \rightarrow AlR_3}{Ph-\overset{\|}{C}-OEt} \xrightarrow{(AlR_3)} Ph-\underset{OAlR_2}{\overset{R}{C}}-OEt \xrightarrow{+AlR_3} Ph-\underset{R}{\overset{R}{C}}-OAlR_2 + R_2AlOEt$$

Figure 2.7 The formation of EB and AlR_3 complexation [63].

Reduction of the C=O group, rather than alkylation, prevails with TIBA with the concomitant elimination of isobutene. The reaction rate is higher for TEA than TIBA and is greatly enhanced in concentrated solutions. Even at the mild conditions used in the polymerization and in the presence of the monomer, however, the reaction proceeds to a considerable extent.

Silyl ethers, in turn, can undergo an exchange reaction with the Al-alkyl, with the formation of alkylated silylethers and dialkyl-Al-alkoxides. The reaction rate is appreciable for silanes containing three or four OR groups and at high concentrations of the Al-alkyl. Starting from $PhSi(OMe)_3$ and TEA, for instance, the reaction at 75°C can proceed up to the formation of $PhEt_2SiOMe$, according to the scheme of Figure 2.8 [67].

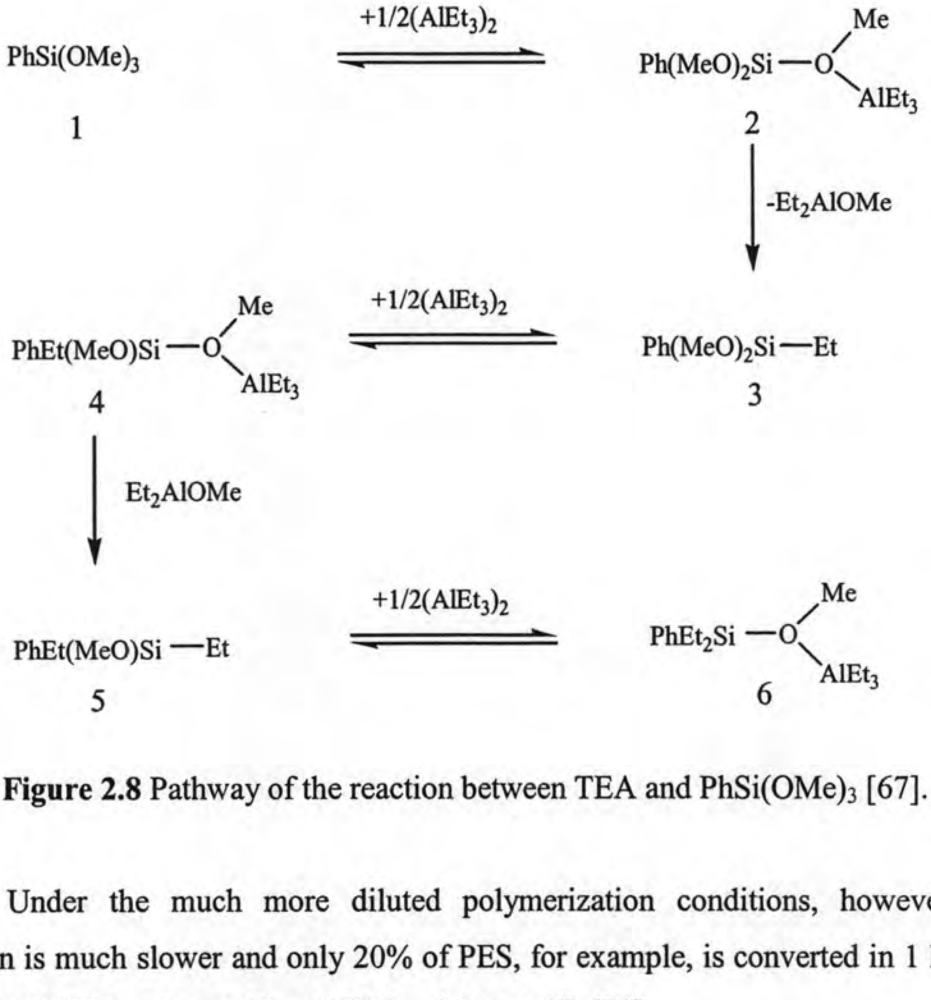


Figure 2.8 Pathway of the reaction between TEA and $PhSi(OMe)_3$ [67].

Under the much more diluted polymerization conditions, however, the reaction is much slower and only 20% of PES, for example, is converted in 1 hour at 70°C, with TEA = 5 mmol/L and PES = 0.5 mmol/L [70].

The reaction is even slower, and sometimes absent for dialkoxysilanes and practically absent at all for monoalkoxysilanes [67]. On the other hand, in the case of trialkoxysilanes the main reaction product besides the Al-alkoxide is a dialkoxy-Si derivative which, differently from the aromatic ester derivatives, still behaves as a good stereoregulating agent.

In conclusion, it can be stated that all types of external donor easily form complexes with the AlR_3 cocatalyst. These complexes are rather stable for silanes, whereas in the case of aromatic esters, they further react, leading to the partial destruction of the ester and its replacement with significantly less stereoregulating products. The true cocatalyst is, in this case, a mixture including free AlR_3, unconverted AlR_3/ester complex, and a mixture of Al-alkoxides of different bulkiness. Some free ED also can be present if the Al/ED ratio is very low.

2.7 Ti Oxidation State

$MgCl_2$-supported catalyst are much more complex systems than the $TiCl_3$-based ones, not only because of the presence of Lewis base, which can interact with both the catalyst and the cocatalyst, but also owing to the different type of Ti compound used, which is normally in a tetravalent state and prone to undergo reduction upon interaction with the Al-alkyl. On the other hand, the latter is normally a trialkyl and thus possesses a higher reducing power than DEAC used along with the earlier generation catalysts.

Because the oxidation state of the transition metal of the active center significantly affects the structure of that center, much work has been done to establish its value for different Ziegler-Natta catalysts. It is, however, important to distinguish between the measured average oxidation state of the whole catalyst and the oxidation state or states of the individual centers. The first can usually be determined easily, but a direct assignment of oxidation state of the active centers is more difficult. First of all, the fraction of the total transition metal atoms that are active centers is small, about 1% or less. Suggestions that traces of the transition metal in an unmeasured oxidation state actually form the active centers in some catalysts cannot be lightly dismissed.

The role in the transition metal oxidation state reduction has been widely demonstrated through both physical analysis and chemical measurements. Using techniques such as electron spin resonance spectrometry (ESR) [71], photometry [72], chemical ionization-mass spectrometry (CI-MS) [73], X-ray absorption spectroscopy [74], and chemical titration methods [60], the occurrence of oxidation state reduction upon the mixing of catalyst and cocatalyst has been confirmed.

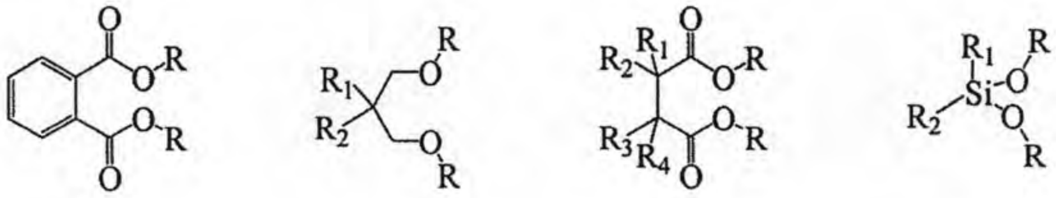
The literature shows different procedures and methods to determine the concentrations of Ti^{2+}, Ti^{3+}, and Ti^{4+}. Redox titration was used by Goto and Takeyama [75] to determine $[Ti^{2+}]$, $[Ti^{3+}]$ and $[Ti^{4+}]$. Kashiwa *et al.* [76] used H_2 evolution for $[Ti^{2+}]$ determination and polarography for determination of $[Ti^{3+}]$ and $[Ti^{4+}]$. Baulin *et al.* [72] used potentiometric titrations for $[Ti^{n+}]$ determination. Chien *et al.* [59] used two redox titrations for $([Ti^{3+}] + [Ti^{2+}])$ and $([Ti^{3+}] + 2[Ti^{2+}])$ determination and atomic adsorption for $[Ti^{n+}]$, whereas $[Ti^{4+}]$ was obtained by working out the difference.

While it is generally accepted that in the $TiCl_3$/DEAC system Ti^{3+} species are almost exclusively present [77], a more extensive reduction of Ti from the initial tetravalent oxidation state is likely to occur in supported catalysts. Keii *et al.* [78] reported that premixing of catalyst and cocatalyst reduced the activity of $MgCl_2$-supported type catalyst, which means that the cocatalyst has some role in catalyst deactivation. On the other hand, they suggested that the rapid decay of the polymerization rate may be attributed to the deactivation of the surface active sites by a strongly adsorbed cocatalyst species, which may lead to the reduction of Ti^{3+} to Ti^{2+}. Tait *et al.* [79] suggested that an increase in cocatalyst concentration causes an overreduction of the oxidation states of titanium ions. Kashiwa *et al.* [76] showed that the Ti^{2+} species polymerizes ethylene only, whereas the Ti^{3+} species polymerizes α-olefin. They reported that pretreatments of catalyst with TEA result in a catalyst that is active only for ethylene polymerization. However, reoxidation of the catalyst with Cl_2 results in reactivating the catalyst for propylene polymerization. In the same way, Soga *et al.* [80-86] established that Ti^{3+} species are active for the polymerization of both ethylene and propylene during copolymerization. However, further reduction of Ti^{3+} to Ti^{2+} results in polymerization of ethylene only.

From the above results, despite the different catalysts and conditions investigated, it seems reasonable to conclude that under polymerization conditions a considerable reduction of Ti takes place; Ti^{3+} is believed to be the active site for propylene polymerization while Ti^{2+} is supposed to be active for ethylene polymerization only.

2.8 Lewis Base Effects

In the case of propylene polymerization, not only the enhancement of catalyst activity but also control of the catalyst stereospecificity are of great importance. In order to increase stereospecificity, various types of Lewis bases were employed as additives in the solid catalyst (called "internal donor") and also in the polymerization system (called "external donor"). The addition of these compounds often increased catalyst stereospecificity but was accompanied by a significant decrease in catalyst activity. Surprisingly, some aromatic esters like ethyl benzoate were found to increase not only catalyst stereospecificity but catalyst activity as well [87]. Much effort has been expended so far in finding better combinations of internal and external donors, and the combination of dialkyl phthalate and alkoxysilane as internal and external donor, respectively, was found to be most efficient [88-91]. More recently, some hindered diethers were claimed to function as excellent internal donors that do not require any external donor [92,93].



Phthalate Diether Succinate Silane

Figure 2.9 General formulas of internal and external donors.

Once stated that two donors are required, it is clear that a proper matching of their chemical nature is necessary as well [94-96]. This is already evident from Tables 2.1 and 2.3, which clearly show that both the activity and the stereospecificity are remarkably higher in the fourth generation catalysts, based on the couple phthalate/silane, than in the third generation containing aromatic monoesters as both ID and ED. On the other hand, an even higher activity can be seen in the fifth generation catalysts containing only one donor, but of completely different chemical structure. Additional differences can be found if the polymer molecular properties are considered. As a matter of fact, while no significant differences are usually observed in microtacticity, the molecular weight (MW) is known to decrease, at the same H_2

concentration, on passing from the third to the fourth and then to the fifth generation. As far as the MWD is concerned, unequivocal GPC values can hardly be found in the literature; nonetheless, it can be said that a progressive narrowing takes place in the same order.

Table 2.3 Performance of $MgCl_2$ catalysts with different Lewis bases [34]

Catalyst	Cocatalyst	Maximum isotactic index (wt%)	Remarks
$MgCl_2/TiCl_4$	$AlEt_3$	50	–
	$AlEt_3$/MPT	90	$ED/Al \geq 0.3$
$MgCl_2/TiCl_4$/EB	$AlEt_3$	60	Normal Al/Ti
		90	Very low Al/Ti
	$AlEt_3$/MPT	95	$ED/Al \geq 0.3$
$MgCl_2/TiCl_4$/DIBP	$AlEt_3$	70 to 80	All Al/Ti's
	$AlEt_3$/DPMS	94 to 99	$ED/Al \geq 0.02$
$MgCl_2/TiCl_4$/DE	$AlEt_3$	95 to 99	Depending on DE/Ti

EB = Ethylbenzoate; MPT = methyl-*p*-toluate; DIBP = diisobutylphthalate;
DPMS = diphenyldimethoxysilane: DE = 1,3-diether.

Within each donor's pair, the ED/AlR_3 (or ED/Ti) ratio is without doubt the most critical parameter determining the catalyst performance and particularly the productivity and the stereospecificity. The specific effect of this parameter, however, varies according to the particular ID/ED combination used and will be discussed in detail with reference to the most widely used systems (i.e., EB/MPT or other similar aromatic monoesters) and phathlate/alkoxysilane).

The superiority of the phthalate/silane system over the EB/MPT one appears due to its higher efficiency in both increasing the productivity of the isotactic polymer and decreasing the productivity of the atactic one as a function of the ED/Al molar ratio. As a consequence, the former system shows a much better isotacticity/productivity balance and entails a much lower ED consumption than the latter.

In all systems the polymer molecular properties also appear to depend to some extent on the amount of the external donor. For instance, the average MW of the polymer and especially that of the isotactic fraction reportedly increases with the ED/Al ratio in both the EB/MPT and the phthalate/silane systems, the increase being particularly evident in the absence of H_2. The effect is less clear for the MWD, for which either no effect or at most a slight broadening of the isotactic fraction has been reported.

The external donor structure, too, appears to have a significant effect on the catalyst performance, as well as on the polymer structure. As previously mentioned, within the monoester systems the most frequently used external donors are methyl- or ethyl benzoates bearing in *para* position an electron-releasing group (CH_3, OCH_3, OEt, *t*-Bu, etc.) to decrease their reactivity toward the Al-alkyl. Guyot *et al.* [97] recently reported some polymerization results obtained with a $TiCl_4/EB/MgCl_2$ catalyst combined with TEA and EB, EA, EPT (ethyl-p-toluate) as external donors, at a ED/Al ratio of 0.2. From his data, it appears that EB, EA and EPT give the same I.I. (~93%), whereas the productivity is somewhat higher for EPT. On the contrary, higher steric hindrance that limits its ability to form a complex with TEA, which according to the author, is the true stereoregulating component.

A superior performance of MPT over EB as ED has been claimed by Kashiwa *et al.* [98], especially as far as productivity is concerned (about three times higher). He also showed that best overall results are obtained when MPT is used as both ID and ED.

More results are available for the effect of the silane structure in phthalate/silane systems. According to Proto *et al.* [95], Sacchi *et al.* [99], Seppälä *et al.* [100], Härkönen *et al.* [101,102], the performance of silanes is affected by the number and size of the alkoxy group as well as by the bulkiness of the moiety attached to Si (most often a hydrocarbyl radical). Two, or at most three, small OR groups (methoxy or ethoxy) are required for high performance. As regards the non-alkoxy moiety, the I.I. appears to increase with its bulkiness in the following order: Me < n-Bu < i-Bu ≈ C_6H_5 < i-Pr.

The MWD, at the same time, is said to become narrower, though an opposite trend (i.e., a broadening with increasing the bulkiness of Si substituents) is perhaps more likely. On the other hand, no correlation between MWD and the silane structure has been observed by Seppälä *et al.* [100]. MW is generally reported to increase with the steric hindrance of silanes.

In the same way, the microtacticity of the heptane insoluble fraction was shown to increase on passing from $MeSi(OMe)_3$ to the bulkier *i*-$BuSi(OMe)_3$. Härkönen *et al.* [101] concluded that optimum silanes are those bearing two small alkoxy groups and branched hydrocarbyl substituents on the Si atom. On the other hand, according to the patent literature [103,104], cycloalkyl- and amino-substituents afford high performance, as well. Within dimethoxysilanes, Okano *et al.* [105], by means of Modified Neglect of Diatomic Overlap (MNDO) calculations, concluded that the isotactic productivity increases with the overall molecular volume, whereas the atactic productivity decreases as the electron density on the oxygen atoms decreases. He thus speculated that both electronic and steric factors are important in determining the performance of the external donor. Similar conclusions were drawn by Härkönen *et al.* [101].

If as was suggested by the above results, the structure and the concentration of the external Lewis base are critical for the catalyst performance, the role of the internal one, though less clear, cannot in any way be neglected. As a matter of fact, as already shown in Table 2.3, I.I.'s higher than 90% can hardly be obtained in the absence of ID, irrespective of the type and amount of the ED used, whereas I.I.'s as high as 98% can be obtained even without ED if a proper internal donor (1,3-diether is used). The internal donor seems, thus, to be at least as important as the external one. In addition, as mentioned earlier, the structure of the internal donor also appears to be the factor which determines the need for the external base and the type to be used, the selection rule being roughly as follows:

ID type	Best ED type
• Monofunctional (aromatic monoester)	• Monofunctional (aromatic monoester)
• Bifunctional (aromatic diester)	• Polyfunctional (silylethers) or monofunctional (TMP)
• Bifunctional (1,3-diester)	• None or bifunctional (silane, diether)

Thus, a monofunctional ED appears to be required for monofunctional ED, whereas with a bifunctional ID, a bifunctional ED seems more appropriate, though a monofunctional one like TMP also works fairly well.

This behavior can be explained by assuming that to afford a high stereospecificity a certain amount of Lewis base, possessing the proper requisites, must be present in the catalyst in the course of polymerization, and this can be obtained either by using as ID a Lewis base that shows a strong preference for coordination to $MgCl_2$ or through the exchange equilibrium between the internal and the external donor discussed earlier. In more detail, the situation appears to be as follows:

1. If ID is highly reactive toward AlR_3, it usually tends to be displaced from the catalyst. If, in addition, it is highly stereoregulating, as are aromatic esters, stereospecificity becomes lower as the donor extraction proceeds. Two possibilities are then opened to preserve the stereospecificity

- The ID extraction is prevented, as for instance by lowering the AlR_3 concentration or by using hindered Al-alkyls
- An equally effective external base is used to replace the internal one in the catalyst thus preserving its stereospecificity (this actually appears to be the case for aromatic monoester donors such as EB and MPT).

On the other hand, if ID is not so highly stereoregulating, as for instance phthalates, the use of a highly efficient external donor able to quickly replace it on the catalyst is absolutely required. This is what appears to happen with silanes.

2. If, on the contrary, ID possesses high stereoregulating ability and no or little reactivity toward AlR_3, it cannot be removed from the catalyst, and thus no external donor is required. This appears to be the case with 1,3-diethers. Clearly, Lewis bases not reactive toward AlR_3 but not having a sufficient stereoregulating power cannot provide a high stereospecificity.

Besides these direct effects, the ID also appears to improve the catalyst performance indirectly (e.g. by favoring the support activation during milling and by helping the elimination of undesired by-products, such as Cl_3TiOR, which are formed during the catalyst synthesis from $Mg(OR)_2$ or $MgCl_2 \cdot n ROH$ precursors)

Not much has been reported about the effect of the ID structure. On the whole, EB is the preferred donor for the third generation catalysts, though MPT has been recently claimed to give better overall performance. As far as phthalates are concerned, the following ranking was established by Soga *et al.* [106]: Bu > Et > Me. From both the patent and the open literature, however, similar performance are obtained with phthalates containing from ethyl to isodecyl OR groups.

2.9 Mechanisms of Olefin Polymerization

Usually, Ziegler-Natta catalyst consists of two components (i.e., a transition metal salt such as a $TiCl_3$ or $TiCl_4$ (catalyst) and main-group metal compounds involving alkyl-Al (cocatalyst). It is generally accepted that the formation of active sites on Ziegler-Nata catalysts for olefin polymerization is accomplished through reduction and alkylation of surface Ti species by interaction of the catalyst with Al-alkyl cocatalyst [107].

The mechanisms of chain propagation can be divided into two groups (i.e., monometallic and bimetallic mechanism) according to the role of the cocatalyst. In monometallic mechanism proposed by Cossee and Arlman [108,109], the cocatalyst generates the active species from the transition metal but is not involved in the chain growth reaction itself (see Figure 2.9). The Ti atom is in an octahedral coordination environment with one vacant site and an adjacent coordination site bonded to an alkyl group of polymer chain. For $MgCl_2$-supported catalysts this structure is created when bound $TiCl_4$ reacts with alkyl-Al. The two-step mechanism for propagation involves π-coordination of an incoming monomer by the Ti atom at its vacant coordination site, followed by insertion, via a four-center transition state, into the Ti-polymer bond. An insertion reaction takes place, shifting the vacant octahedral position. Then migration of the polymer chain occurs to reestablish the vacant site on the original position. The weakness of this mechanism is that active Ti^{3+} has only one outer shell electron available for the formation of π back-bonding, which is a requirement for metal-olefin π-bond formation [110,111].

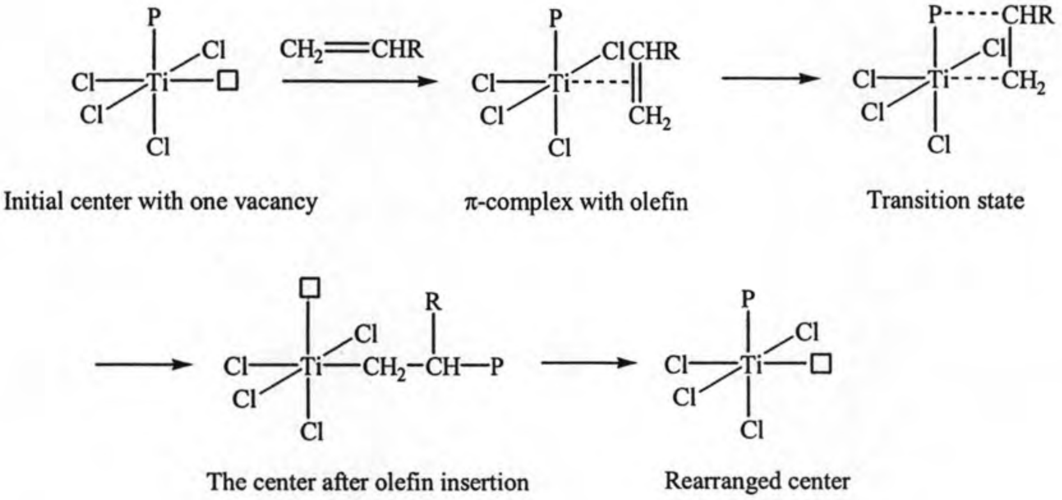


Figure 2.10 Monometallic polymerization mechanism [108].

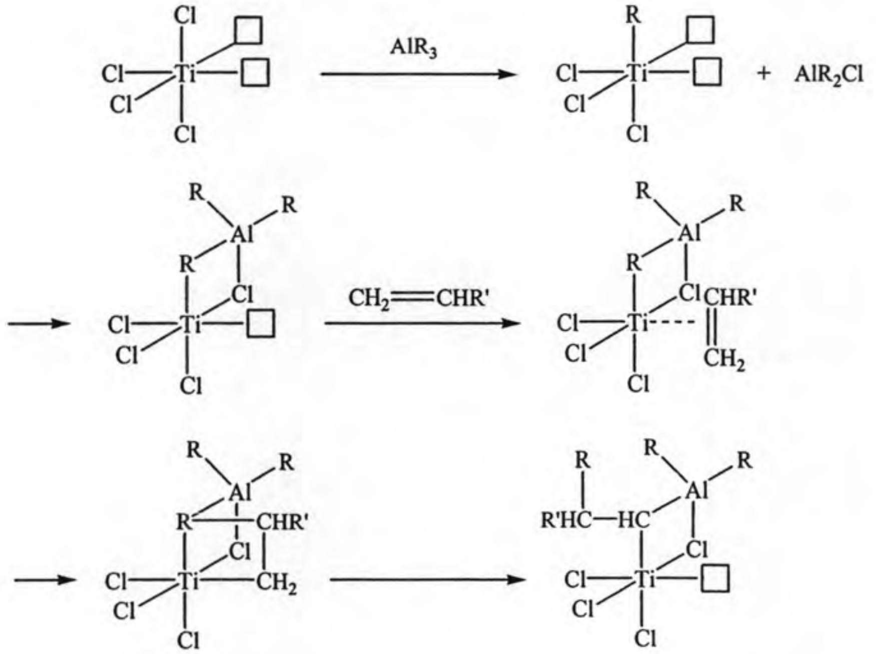


Figure 2.11 Bimetallic polymerization mechanism [112].

Bimetallic mechanism proposed by Rodrigues and van Looy [112] involves initial π complexation of monomer to Ti atom that is bridged through alkyl groups to an Al atom (Figure 2.10). This is followed by ionization of the transition metal-alkyl bond, formation of a six-membered cyclic transition state, then insertion. In both mechanisms, the polymer chain grows from the catalyst surface by successive insertion reactions of complexed monomer, and the alkyl group originally present in the cocatalyst ends up as one of the terminal group of the polymer chain.

2.10 Stereospecific Active Sites

2.10.1 Nature of Active Sites

The PPs obtained with Ziegler-Natta catalysts have various molecular weight and tacticity. This result means existence of various active sites having different propagation rate and stereospecificity. The presence in Ziegler-Natta catalysts of at least two types of active sites associated with the isotactic and atactic PP fractions is well known. The active sites having higher isospesificity are known to have faster propagation rate compared to that having lower stereospecificity [113]. However, this simple picture is inadequate to explain the experimental data that showed the broad distribution of tacticity and molecular weight even for the polymer fraction insoluble in xylene.

The presence of at least two types of isospecific sites, differing in stereospecificity, in $TiCl_3$ and $MgCl_2$-supported catalysts was suggested by Kakugo *et al.* [114], to explain the isotacticity distribution in PP fractions eluted by temperature rising elution fractionation (TREF) above 100°C. The relative proportion of the two active centers varies with the nature of the catalyst; the fraction of the highly isospecific centers increases with the isotactic index of the polymer [115]. The above model also accounts for the decreasing stereospecificity of AA-$TiCl_3$/DEAC catalyst with polymerization time, assuming that higher isospecific active centers would decay more quickly [19]. Kashiwa *et al.* [116], to explain the change of the shape of the GPC curve of the iso-PP fraction obtained with $MgCl_2$-supported catalyst from monomodal to bimodal upon addition of the electron donor, suggested the formation of a new type of active site modified by the donor and characterized by a higher reactivity. Besides the pronounced effect from the catalyst substrate (including neighboring Ti species and/or $MgCl_2$ support) has been observed to affect the stereospecific nature of active sites by some researchers [16,58,106,117,118]. As for donor-free $MgCl_2$-supported catalysts, Soga *et al.* [106,117] and Busico *et al.* [58] speculated that isospecific active sites might be generated from multinuclear Ti species, which was also called titanium island by others [119,120].

At the same time, the induction-potential of the surface Ti species in the formation reaction of active sites may greatly depend on the type of catalyst as well as the surface heterogeneity of the catalyst [121-123]. This means that Ti species of potential active sites on different types of catalysts or on different surface location of the same type catalyst may exhibit different tendency in the formation of active sites. It would be most interesting if the formation tendency of active sites could also be correlated with the stereospecificity of these active sites.

For supported Ziegler-Natta catalysts, electron donor is often employed as a necessary third component to improve the stereospecificity of the catalysts. Concerning the stereospecificity of the active sites, several possible models [60,124-126] and specific features of their functioning which determine their stereospecific polymerization mechanism have been discussed. These models differ mainly in the description of the particular intrinsic asymmetry they assumed and in the influence of an alkyl group (a polymer chain) on the stereospecificity of the active site.

Busico *et al.* [124] showed that reduced $TiCl_4$ on the (100) $MgCl_2$ crystal face has two vacant sites and the (110) face has only one site. Vacant sites, of course, are necessary for polymerization, but sites with more than one vacancy are aspecific, as shown convincingly by Sun and Soga [125]. Site poisoning, or rather vacancy coordination by external electron donor, would then be envisioned as in Figure 2.11. Dimerized $TiCl_3$ on the (100) face are believed to be stereospecific sites by Busico *et al.* [124] since they are in a chiral environment. Chirality of the metal ion is thought to be responsible for the inherent stereospecificity of the catalyst. This conclusion was based on observations that steric errors in polymer chains were not perpetuated after they occurred [127,128].

In propylene polymerization the stereospecificity has always been found to increase upon addition of the electron donor, often accompanied by a loss of productivity. On the basis of these results, many authors have explained the increase in polymer isotacticity by the ability of the Lewis bases to poison selectively the aspecific polymerization centers. However other authors have observed that, in some cases, the production of isotactic PP increases as long as the donor/aluminum molar ratio is kept small enough. Therefore the way by which electron donors affect the initiator system stereospecificity is more complex than a simple poisoning, as at least one further effect has to be considered, i.e. the activation of the isotactic sites.

Although many understandings have been achieved on the effects of electron donors, the specific mechanism still remained unclassified [57,129-131]. For example, how the existence of internal electron donor in the neighborhood of the surface titanium species of potential active sites would affect the formation, deactivation and transformation of stereospecific active sites after interaction with Al-alkyl cocatalysts is waiting for elucidation.

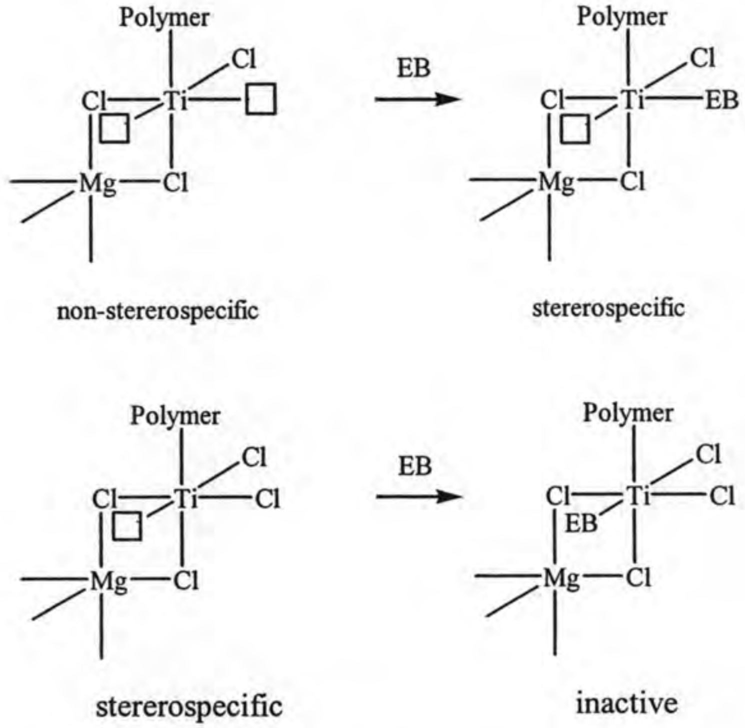


Figure 2.12 Proposed EB poisoning mechanism [125].

2.10.2 Traditional Active Sites Models

A great number of models for active sites have been proposed to interpret the stereospecific polymerization of olefins with Ziegler-Natta catalyst. The model proposed in early stages was arguing about monometallic or bimetallic active center.

In monometallic active sites proposed by Cossee and Arlman [110,112,132], the cocatalyst generates the active species from the transition metal but is not involved in the chain growth reaction itself (see Figure 2.13 (a)). The Ti atom is in an octahedral coordination environment with one vacant site and an adjacent coordination site bonded to an alkyl group of polymer chain. For $MgCl_2$-supported catalysts this structure is created when bound $TiCl_4$ reacts with Al-alkyls. In this model, the two-step mechanism for propagation involves π-coordination of an incoming monomer by the Ti atom at its vacant coordination site, followed by insertion, via a four-center transition state, into the Ti-polymer bond. Stereoselectivity is assumed only if, before a further insertion, the chain skips back to the position occupied before the insertion.

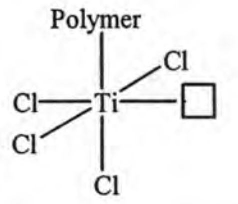


Figure 2.13 (a) Monometallic active sites proposed by Cossee [132].

The surface model proposed by Allegra [133] obviates the necessity of the back skip step to assure the stereoselectivity because a C_2 symmetry axis locally relates the atoms relevant to the non-bonded interactions with the monomer and the growing chain (see Figure 2.13 (b)). Therefore, the two situations resulting by exchanging, in the coordination step, the relative positions of the growing chain and of the incoming monomer are identical.

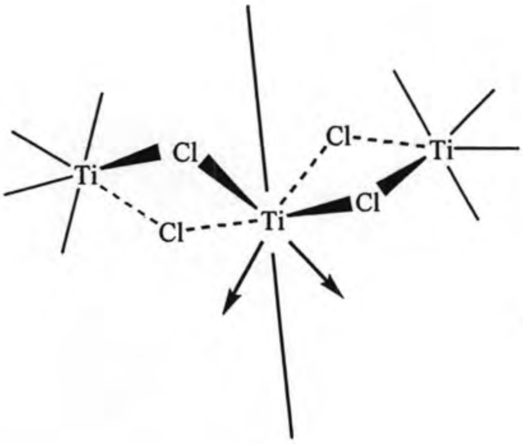


Figure 2.13 (b) Monometallic active sites proposed by Allegra [133].

Corradini *et al.* [134], on the basis of some evaluations of the non-bonded interactions for the Cossee and Allegra models, suggest that the chiral environment of the metal atom imposes a chiral orientation of the first C–C bond of the chain, and this orientation has been identified as a crucial factor in determining the stereospecificity (see Figure 2.13 (c)). As a matter of fact, the non-bonded interactions between the methyl group of the propylene molecule and the C–atom of the growing chain in β-position to the metal induce a preferential coordination of the enantioface of the monomer which allows the methyl group and the β-carbon atom to be located on opposite sites with respect to the plane defined by the Ti–C and the double bond.

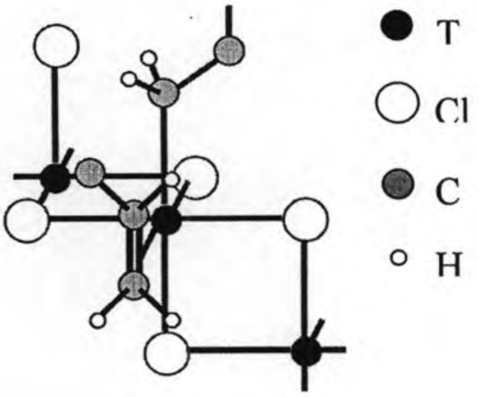


Figure 2.13 (c) Monometallic active sites proposed by Corradini [134].

This model is in good agreement with the experimental finding about the stereochemical structure of the end groups of PP obtained with □-$TiCl_3$ and ^{13}C-enriched different Al-alkyls [135,136]. Insertion of propylene into a Ti–CH_3 bond is not stereospecific, while insertion on Ti-$^{13}CH_2$-CH_3 is partially stereospecific; when the alkyl group is isobutyl, the first insertion is stereospecific as are the successive insertions. This model justifies also the retention of configuration, in the growing chain, after the insertion of an ethylene unit because the model maintains its behavior also when a secondary carbon atom is in β-position relative to the metal. According to the mechanism proposed by Brookhart and Green [137], the monomer insertion is assisted by strong α-agostic interactions between titanium and the C-H bond of the growing chain. Bimetallic catalytic centers have been proposed by Patat and Sinn [138], Natta [139], and Rodrigues and van Looy [112]. In these models, a ligand (Cl or alkyl group) and the last carbon atom of the growing chain link Ti and Al through a double bridge. Polymerization mechanism proposed by Rodrigues and van Looy involves initial π complexation of monomer to Ti atom that is bridged through alkyl groups to an Al atom (Figure 2.14). This is followed by ionization of the transition metal-alkyl bond, formation of a six-membered cyclic transition state, then insertion.

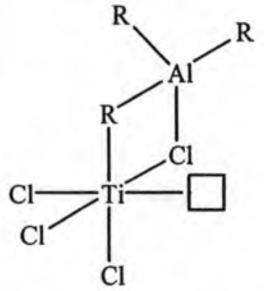


Figure 2.14 Bimetallic active sties proposed by Rodrigues and van Looy; □: vacant site, R: alkyl group [112].

In these traditional models, center metal of active sites is being fixed to one (Ti) or two (Ti and Al), however, there is no explanation of transformation of these active sites occurring during the polymerization.

2.10.3 Recent Active Sites Models

During the last several decades, various stereospecific active sites models regarding the interconversion of active sites on heterogeneous Ziegler-Natta catalysts have been reported. Based on the microstructural and stereochemical analyses of atactic PPs produced from various types of heterogeneous Ti-based catalysts, Doi [140] proposed a reversible interconversion between isospecific sites and syndiospecific sites to explain the coexistence of isotactic and syndiotactic stereoblocks (Figure 2.15). The stereoblock characteristic was also found in PP prepared from donor-free $TiCl_4/MgCl_2$-TEA catalyst system by Xu *et al.* [130]. To account for this, they suggested the existence of equilibrium between monometallic sites and bimetallic sites in terms of reversible complexation with TEA.

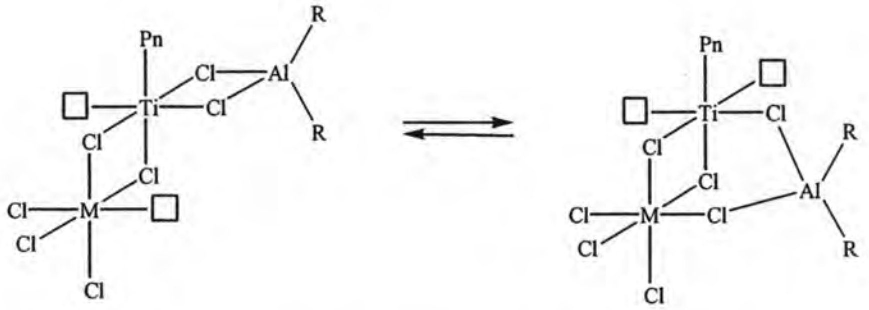


Figure 2.15 Bimetallic active sties proposed by Doi [140]; □: vacant site, R: alkyl group, Pn: growing polymer chain.

More recently, Corradini and Busico *et al.* [141-147] established a three-site model in terms of equilibrium interconversion between three kinds of stereospecific active sites namely highly isospecific, poorly isospecific and syndiospecific sites to explain the stereoblock characteristics of the synthesized PPs with $MgCl_2$-supported Ziegler-Natta catalysts within the last decade (Figure 2.16). the stereospecificity of the active sites providing reasonable explanation not only for Ziegler-Natta catalysts, but also for metallocene catalysts with well-defined steric structure [148]. Whereas, the influence of the difference in various groups (Cl atom, Alkyl group, and electron donor) which exists in the positions of L_1 and L_2 affects stereospecificity is not explained.

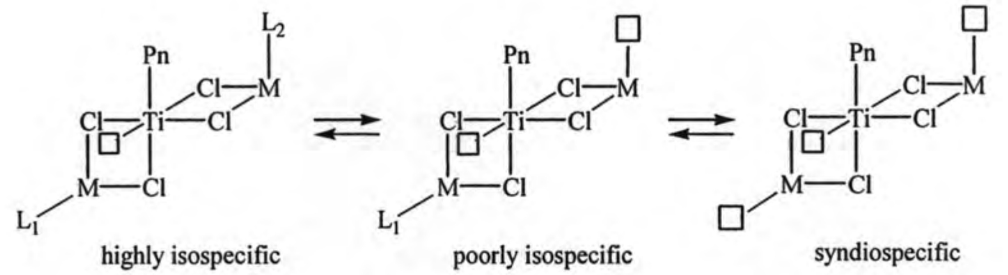


Figure 2.16 Three-sites model proposed by Busico *et al.* [149]; □: vacant site, Pn: growing polymer chain, L_1 and L_2: Cl atom, Al-alkyl or electron donor molecules.

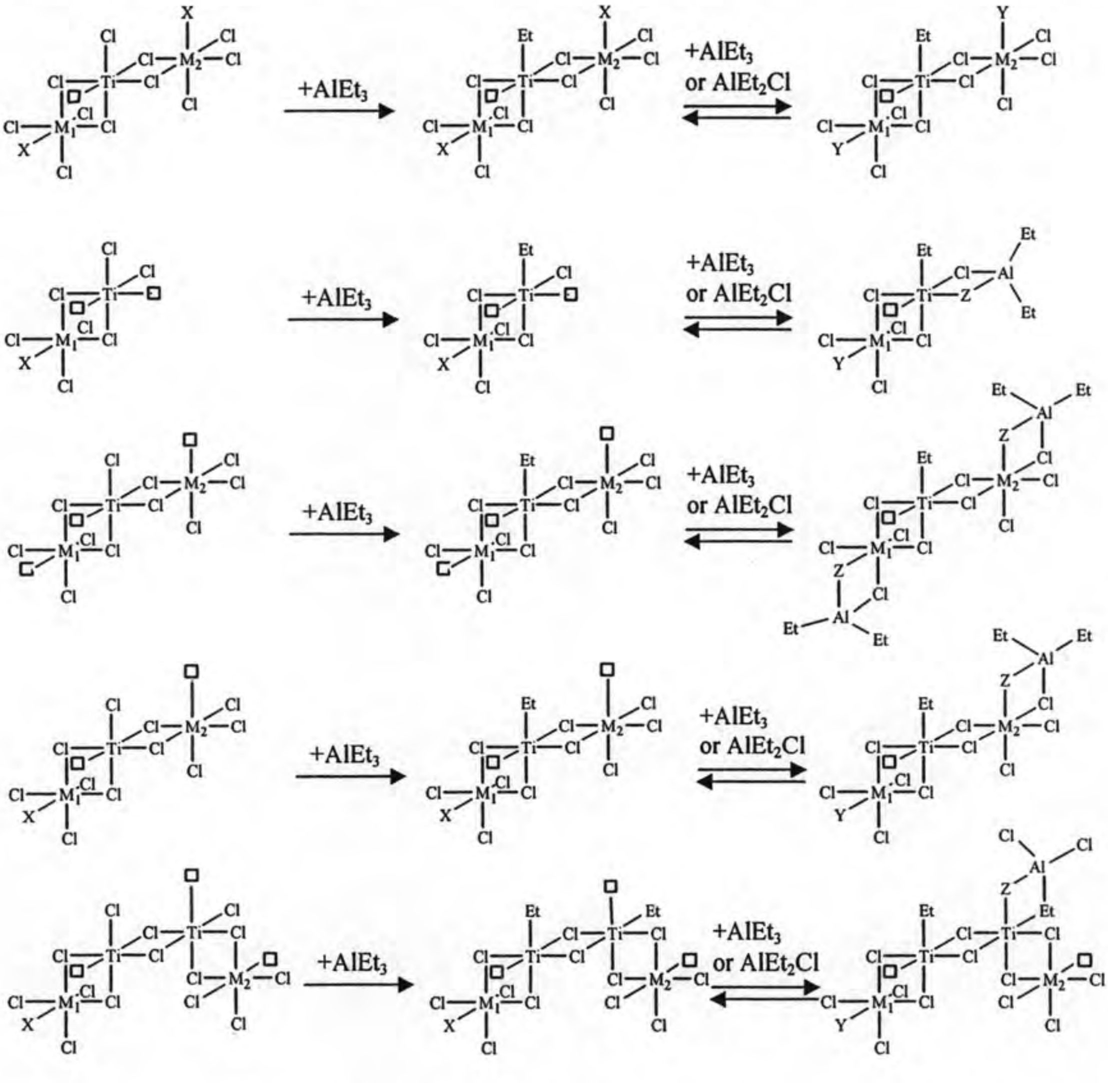


Figure 2.17 Modified three-sites model in terms of formation and transformation of stereospecific active sites on Ziegler-Natta catalyst, M_1 and M_2: Ti or Mg, and M_1 and M_2 are bound to the catalyst substrate through chlorine bridges; X: Cl, or ED; Y: Cl, Et or ED; Z: Cl or Et; □: coordination vacancy, for donor-free $TiCl_4/MgCl_2$ catalyst: X=Cl, Y=Cl or Et; for $TiCl_4/EB/MgCl_2$ and $TiCl_4/DBP/Mg(OEt)_2$ catalyst: X=Cl or ED, Y=Cl or ED or Et [150].

Terano *et al.* [150-152] thereafter purposed a modified three-sites model with precise description of the stereospecific nature of various types of active sites stemmed from surface titanium species, Al-alkyl compounds, Mg-compounds and electron donors. They also suggested that isospecificity of active sites greatly depends upon the bulkiness of the ligands situated at the two most important ligand positions for construction of the asymmetry and chirality of the active sites with steric hindrance.

2.10.4 Island Model Theory

The model for the characteristic structure on the surface is the "surface monolayer multinuclear titanium species", namely an "island" of titanium species (see Figure 2.17). It was proposed by Terano. In the "island model", the isospecificity of the active sites might be created by the structure of the atoms adjacent to the active Ti species, which may be efficient enough to generate the highest isospecific active sites without a donor.

TREF results [153] clearly indicated the highest isospecific active sites can be created only by Ti, Mg and Cl atoms without any internal or external donors, even though their amount was rather small. TREF diagrams showed highest isospecific active sites corresponding to the highest isotactic fraction exist even in the donor-free catalyst system.

Boero *et al.* [120] suggested about dinuclear (Ti_2Cl_6) species models for $MgCl_2$-supported Ziegler-Natta catalyst. Large deformations and bond elongations are required for a Ti dinuclear adduct to stick on the (100) surface. He speculated the achievement of the Ti island to be efficient binding on (100) surface of the Mg of the substrate. This could have the advantage of gradually smoothing out the lattice mismatch from the bulk to the surface, allowing for a more stable dinuclear Ti center.

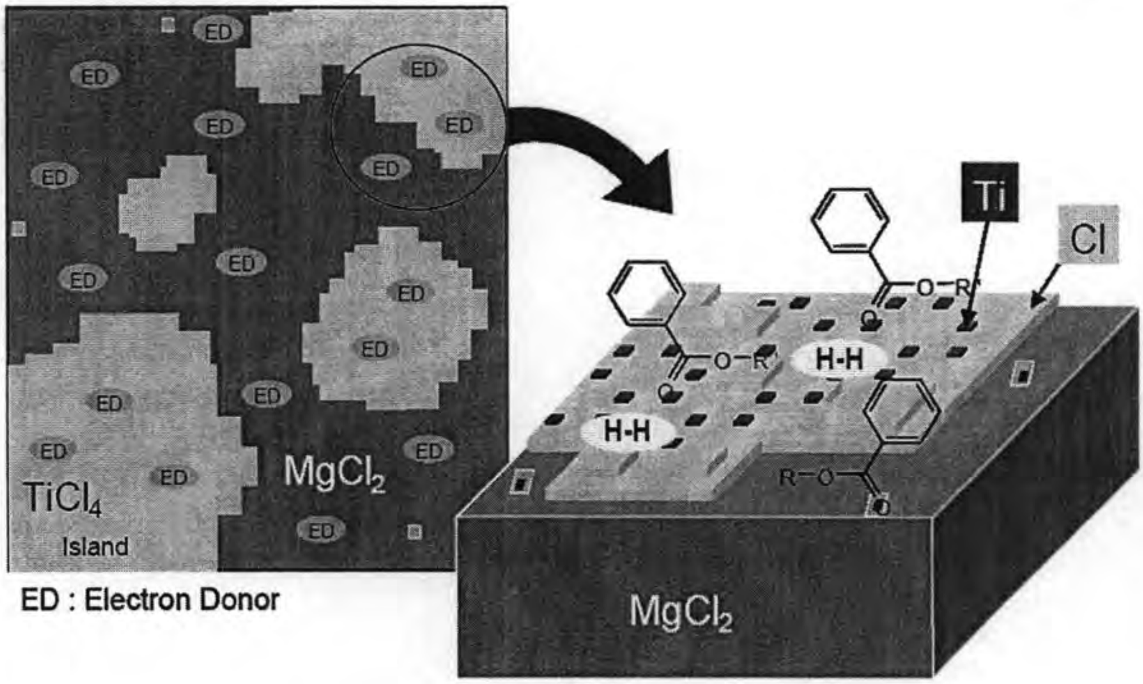


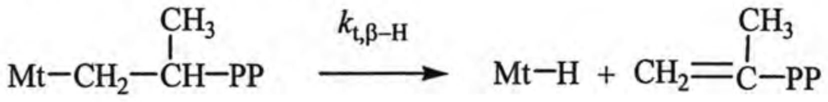
Figure 2.18 Island model on $MgCl_2$-support [154].

2.11 Chain Transfer Reactions

Polymer chain termination occurs mostly through the following reactions: where center metal (M) and PP denote the transition metal and polymer chain, respectively. Reactions 1 and 4 are followed by a rapid insertion of the olefin into the M-H bond. All the above reported reactions are well known in organometallic chemistry. The relative importance of the different chain transfer reactions depends on the catalyst system used and on the process conditions. Chain transfer by β-hydride elimination is not considered important in propylene polymerization with traditional and $MgCl_2$-supported heterogeneous catalysts at normal polymerization temperature [155-157]. This reaction becomes a significant chain transfer process in most metallocene-based catalyst system [158]. In the absence of hydrogen and under normal polymerization conditions, chain transfer to alkyl-Al is the most important chain termination process.

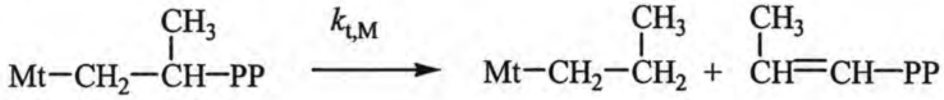
Chain transfer to hydrogen is, in all cases, the most efficient chain termination process. A half-order dependence of the chain transfer rate with respect to H_2 has been generally found for $TiCl_3$ [159,160] and $MgCl_2$-supported catalysts [161,162]. Hydrogen does not influence the molecular weight distribution of the polymer [162].

1. β-hydride elimination



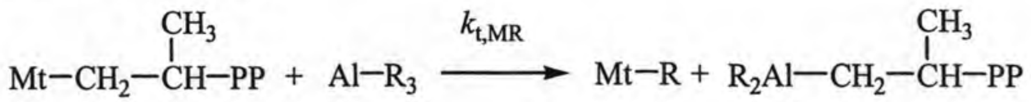
$$\mathrm{Mt{-}CH_2{-}\overset{\overset{CH_3}{|}}{C}H{-}PP} \xrightarrow{k_{t,\beta\text{-}H}} \mathrm{Mt{-}H + CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}PP}$$

2. transfer to monomer



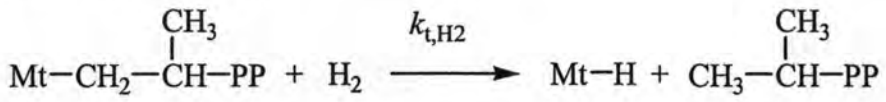
$$\mathrm{Mt{-}CH_2{-}\overset{\overset{CH_3}{|}}{C}H{-}PP} \xrightarrow{k_{t,M}} \mathrm{Mt{-}CH_2{-}\overset{\overset{CH_3}{|}}{C}H_2 + \overset{\overset{CH_3}{|}}{C}H{=}CH{-}PP}$$

3. transfer to cocatalyst



$$\mathrm{Mt{-}CH_2{-}\overset{\overset{CH_3}{|}}{C}H{-}PP + Al{-}R_3} \xrightarrow{k_{t,MR}} \mathrm{Mt{-}R + R_2Al{-}CH_2{-}\overset{\overset{CH_3}{|}}{C}H{-}PP}$$

4. transfer to hydrogen



$$\mathrm{Mt{-}CH_2{-}\overset{\overset{CH_3}{|}}{C}H{-}PP + H_2} \xrightarrow{k_{t,H2}} \mathrm{Mt{-}H + CH_3{-}\overset{\overset{CH_3}{|}}{C}H{-}PP}$$

2.12 Replication and Polymer Morphology

The reasons why a full control of the polymer morphology is highly desirable in PP manufacturing can be easily understood in terms of process economics and viability. A regular polymer morphology (i.e., particles with high density, regular shape, and narrow particle size distribution (PSD) means both a high reactor throughput, good flowability and packing, and even, as a limiting case, no need of further pelletization. In addition, a proper porosity, though lowering bulk density, helps the retention of the rubbery phase in heterophasic copolymers. Finally, the absence of fines prevents reactor fouling and explosion hazards during handling, and the absence of coarse eliminates undesirable fluidization effects.

In general, the $MgCl_2$-supported titanium catalysts consist of particles which average between 10 and 100 μm in diameter. The average particle size can be adjusted during the catalyst synthesis. The catalyst particle is composed of much smaller particles with a size in the nm range. These particles are called primary particles. By agglomeration of many primary particles, a catalyst particle with high porosity and high specific surface area is formed. The pore volume is in the range of 0.3 to more than 1 cm^3g^{-1}. The specific surface area reaches values between 50-300 m^2g^{-1} [163].

The catalyst particles are transformed into polymer particles during polymerization. When polymerization starts at the surface of the primary particles, the primary particle agglomerate is disrupted. The polymeric phase is formed around each catalyst fragment, growing larger and larger by polymer formation. In this way these catalyst fragments are distributed more homogeneously in the growing particle. The catalyst particle shape is replicated in the polymer particle shape. This means that particle shapes and particle size distributions are the same for the catalyst and the polymer [164]. The particle grows in diameter by a factor of 10 to 25 corresponding to a volume increase by a factor of 10^3 to 10^4.

A fast and extensive catalyst "fragmentation" and a uniform polymer growth rate across the particle seem, thus, to be the key features for a faithful replication [165]. However, several requirements concerning both the catalyst structure and the reaction conditions must be fulfilled for a uniform catalyst fragmentation and polymer growth rate to occur.

2.13 Stopped-flow Techniques

The stopped-flow method for olefin polymerization with Ziegler catalysts, was first developed by Keii and Terano in 1987 to evaluate specific kinetic parameters in the polymerization of propylene with a $MgCl_2$-supported Ziegler catalyst [78]. The information concerning the active sites and the polymerization procedures was obtained by direct analysis of the polymer produced at the initial polymerization stage. The most predominant feature of this technique is its quasi-living polymerization characteristic within a very short period of polymerization time (ca. 0.2 s). In this decade, the technique has been extensively applied to various kinds of investigations for olefin polymerization with Ziegler catalysts.

In a conventional process for propylene polymerization with a $MgCl_2$-supported Ziegler catalyst, the polymerization process is usually performed for 1–3 h during which the catalytic activity is varied with time accompanied by various chain-transfer reactions. In contrast, polymerization using the stopped-flow technique is conducted within an extremely short period (ca. 0.2 s) which is much less than the average lifetime of the growing polymer chains, and the states of the active sites are constant without time-dependent changes and occurrence of chain-transfer reactions, indicating that a quasi-living polymerization can be performed. One of the most attractive features of this method is the ability to observe the polymer produced in the initial polymerization stage, which reflects directly the nature of the active sites just after their formation. Accordingly, the method was found to be useful for the study of the nature of the active sites, as well as for the estimation of accurate kinetic parameters. Here, it must be noted that the excellent characteristics mentioned above, such as constant catalyst activity and negligible chain-transfer reactions within an extremely short period, cannot be found in any other polymerization system using Ziegler catalysts. However, an appropriate choice of suitable polymerization conditions and catalyst systems is required in order to obtain the desired results by taking advantage of the stopped-flow technique.