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The Use of Donors to Increase the Isotacticity of Polypropylene

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Abstract Since the discovery of electron donors for $MgCl_2$-supported Ziegler–Natta catalysts, donors have become key components for improving the stereospecificity and activity of these catalysts. Starting from benzoate for third-generation catalysts, the discovery of new donor structures has always updated the performance of Ziegler–Natta catalysts. Numerous efforts have been devoted since the early 1970s, in both industry and academy, not only for discovering new donors but also for understanding their roles in Zielger–Natta olefin polymerization. This chapter reviews the history of these efforts, especially after the twenty-first century. The first half of the chapter describes the history of catalyst developments, with special focus on industrialized donors, and then introduces recent trends in the development of new donors. The second half reviews historical progress in the mechanistic understanding of how donors improve the performance of Ziegler–Natta catalysts.

Keywords Donor · Heterogeneous Ziegler–Natta catalyst · Propylene polymerization

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1 History

Polypropylene (PP) is one of the most widely used plastics and features a wide range of advantages such as low cost, light weight, high melting temperature, good processability, balanced mechanical properties in terms of stiffness and impact resistance, etc. Moreover, PP is regarded as a clean material with respect to urgent environmental requirements, not only due to the halogen- and benzene-free structure but also due to the ease of reuse and recycle. The world production of PP in 2012 reached approximately 60 million tons per year, and is forecasted to stably grow in the future (Fig. 1). The diverse properties of PP enable its application in a variety of fields from commodity to specialty.

The immense growth of the polypropylene industry has been greatly driven by the continuous developments in catalyst technology (Table 1) [1, 2 and references therein]. The history of propylene polymerization started with the landmark discovery of a solid $TiCl_3$ pro-catalyst combined with diethylaluminum chloride (DEAC) by Natta in 1954 [3, 4]. This so-called first generation catalyst enabled the first catalytic isoselective propylene polymerization, but its poor activity and isospecificity necessitated additional processes to extract poorly isotactic products and violet catalyst residues from the obtained polymer. Significant efforts were then devoted to improving the activity and isospecificity of the catalyst. For the catalyst activity, there were two main directions of study in order to enhance the utilization efficiency of the Ti species: preparation of $TiCl_3$ with larger surface area and the search for an efficient support material for Ti halide species. The Solvay corporation invented the so-called Solvay-type $TiCl_3$ in the early 1970s, which was prepared by the reduction of $TiCl_4$ with DEAC followed by the removal of Al residues with the aid of ether [5]. The resultant catalyst, regarded as a second generation catalyst, achieved improved activity and isospecificity over the first generation of catalysts, but the level of the improvements was still insufficient to eliminate the above-mentioned purification processes for the obtained polymer. Regarding a support material, metal oxide (SiO_2, Al_2O_3) or hydroxide materials [$Mg(OH)_2$] were initially considered due to the ease of the immobilization of Ti species through covalent bonds. However, successful improvement in activity was not achieved until Montedison and Mitsui discovered $MgCl_2$ support, almost at the same time in 1968 [6, 7]. The catalysts, consisting of $TiCl_4$ active site precursor, $MgCl_2$ support, and triethylaluminum (TEA) activator, exhibited much higher activities than the former generation of catalysts, but their use was limited to ethylene polymerization due to poor isospecificity. That is the story before the appearance of "donors," i.e., the main topic of this chapter.

The first donors in Ziegler–Natta catalysis appeared as a result of collaborative efforts between Montedison and Mitsui to improve the isospecificity of the above-mentioned $MgCl_2$-supported catalyst [8, 9]. The developed catalyst, termed third generation, achieved not only high activity but also high isospecificity by adding benzoate to the $TiCl_4/MgCl_2$ catalyst. The term "donor" originates from the fact that additives to improve the catalyst isospecificity are Lewis bases with

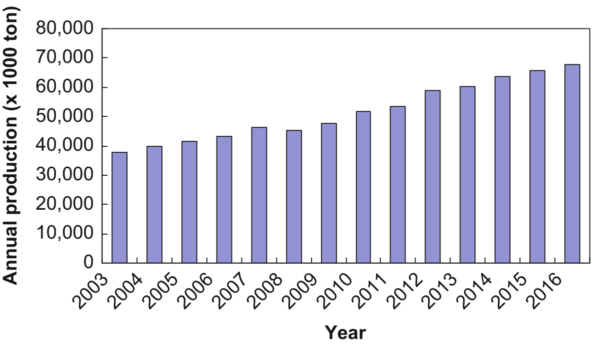


Fig. 1 Annual production of polypropylene (from Ministry of Economy, Trade and Industry, Japan, 2012)

Table 1 Propylene polymerization performance of Ziegler–Natta catalysts of different generations[a]

Generation	Pro-catalyst	External donor	Activity (g-PP/mmol-Ti h atm)	I.I.[b] (%)
First	$TiCl_3$	–	ca. 4	90
Second	Solvay-type $TiCl_3$	–	ca. 30	95
Third	$TiCl_4/MgCl_2$/benzoate	Benzoate	ca. 1,000	92–94
Fourth	$TiCl_4/MgCl_2$/phthalate	Alkoxysilane	ca. 1,000–3,000	>98
Fifth	$TiCl_4/MgCl_2$/1,3-diether	Alkoxysilane	ca. 3,000–5,000	>98

[a] Reproduced from [1]

[b] Insoluble fraction in boiling heptane

electron-donating ability. Usually, donors are classified into two types according to their roles: internal donors contained in the solid component ($TiCl_4/MgCl_2$) and external donors, which are added together with alkylaluminum in order to prevent the deterioration of the catalyst isospecificity during the course of polymerization. It should be noted that the idea to add Lewis bases already existed for $TiCl_3$-based catalysts, where the addition of some Lewis bases during polymerization improved the isotactic index (I.I.) by, at maximum, up to 10%. However, donors for $MgCl_2$-supported catalysts are totally different in terms of the dramatic improvements in the isospecificity; it is not exaggerating to say that donors “endow” isospecificity to $MgCl_2$-supported catalysts. The third generation catalyst typically combines ethylbenzoate (EB) as an internal donor with EB or *para*-substituted benzoate as an external donor (Fig. 2). The third generation catalysts achieved propylene polymerization activity of 100 times higher than the second generation (Table 1), and high isospecificity (I.I. of 92–94%). However, the remaining 6–8% of poorly isotactic fraction triggered further research, mainly focused on improvements in catalyst preparation procedures as well as on finding a more efficient combination of internal and external donors. The extraction process for poorly isotactic fraction was finally eliminated in 1977 by use of a catalyst employing a new donor combination. i.e., phthalic diester as an internal donor and alkoxysilane as an external donor (Fig. 2) [10, 11]. This catalyst, termed a fourth generation catalyst,

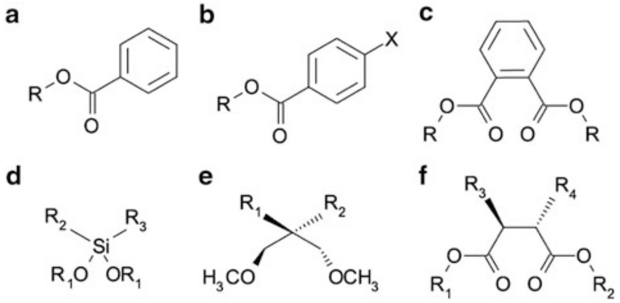


Fig. 2 Industrially developed internal and external donors: (**a**) benzoate, (**b**) *para*-substituted benzoate, (**c**) phthalate, (**d**) dialkoxysilane, (**e**) 1,3-substituted diether, and (**f**) 2,3-substituted succinate. Note that (**a**), (**c**), (**e**), and (**f**) are employed as internal donors, whereas (**a**), (**b**), and (**d**) are used as external donors

comprises $TiCl_4/MgCl_2$/phthalate and $AlEt_3$/alkoxysilane, and has been widely employed for the industrial production of polypropylene (PP) since its discovery.

From the late 1980s to 1990s, a series of 1,3-diether compounds were proposed as a new type of internal donor (Fig. 2) [12]. Catalysts containing 1,3-diether as an internal donor exhibit quite high activity and isospecificity without the addition of an external donor, whereas ester-type internal donors for the former generations require the addition of external donors to suppress or compensate for decreases in the activity and isospecificity during the course of polymerization. Furthermore, the new catalysts are generally characterized by a superior hydrogen response as well as narrower molecular weight distribution (M_w/M_n around 4) as compared with the former generation of catalysts. Owing to these distinct characteristics, the catalysts are recognized as fifth generation and are especially employed to produce PP grades suitable for unwoven fabric applications.

In the late 1990s, a research group from Ube Industries (later Grand Polymer) patented a series of unique nitrogen-containing alkoxysilane external donors [13–19]. In contrast to the original patent [10, 11] for the fourth generation catalyst, which specified external donors containing at least one Si-OR, Si-OCOR, or $SiNR_2$ group, the research group systematically explored external donors containing both Si-OR and $SiNR_2$ groups. They found that the addition of dialkoxysilane with N-containing polycyclic groups (examples are shown in Fig. 3) enables the production of highly isotactic PP featuring a molecular weight distribution as broad as that given by the $TiCl_3$-based catalysts [14]. The significance of their findings was twofold: they allowed broadening of the molecular weight distribution by means of external donors without sacrificing the activity and isospecificity of the fourth generation catalyst, and they opened up development of heteroatom-containing donors. Based on this trend, several N-containing external donors with much higher hydrogen response (i.e., better melt flowability of PP) were presented (examples are listed in Fig. 3) [19]. At present, the industrial application of N-containing donors is limited for several reasons, e.g., the absence of the highest molecular weight tail in

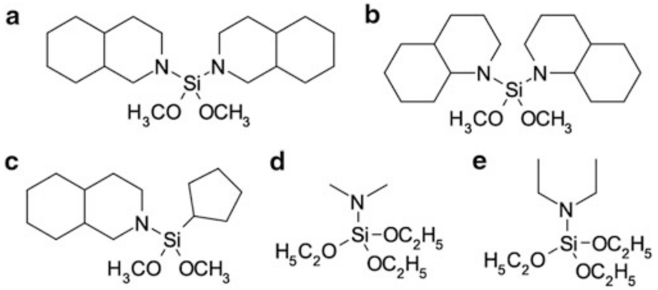


Fig. 3 Examples of nitrogen-containing external donors: (**a**) bis(perhydroisoquinolino) dimethoxysilane, (**b**) bis(perhydroquinolino)dimethoxysilane, and (**c**) cyclopentylisoquinolinodimethoxysilane for broad molecular weight distribution; (**d**) dimethylaminotriethoxysilane and (**e**) triethylaminotriethoxysilane for high hydrogen response

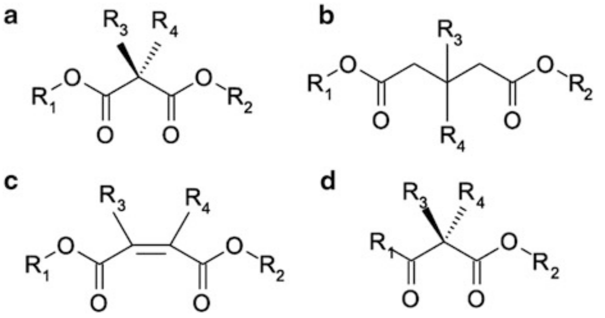


Fig. 4 Internal donors developed for catalysts equipping both high activity and high isospecificity: (**a**) malonate, (**b**) β,β-substituted glutarate, (**c**) 2,3-substituted maleate, and (**d**) β-ketoester

the molecular weight distribution of PP, an odor problem, and so on. However, heteroatom-containing donors are doubtless promising in order to facilitate unique properties.

Though the fifth generation catalysts achieved almost two times higher activity than the fourth generation catalysts, their application is limited to some special grades. This is mainly because of the lower isospecificity as well as the narrower molecular weight range, which is disadvantageous in terms of balanced solid stiffness and melt flowability of the resultant PP. Consequently, the decade after the late 1990s was devoted to the finding of new donor systems that facilitated not only high activity but also high isospecificity. For instance, malonate (1998) [20], β-substituted gultarate (2000) [21], maleate (2003) [22], and β-ketoester (2005) [23] are such internal donors (Fig. 4). Of these donors, 2,3-substituted succinate (2000) [24] not only achieved high isospecificity, but also offered broader molecular weight distribution of PP than that given by the fourth generation catalysts (Fig. 2). Because succinate enabled the first production of PP with broad molecular weight distribution without the above-mentioned problems of $TiCl_3$-based catalysts

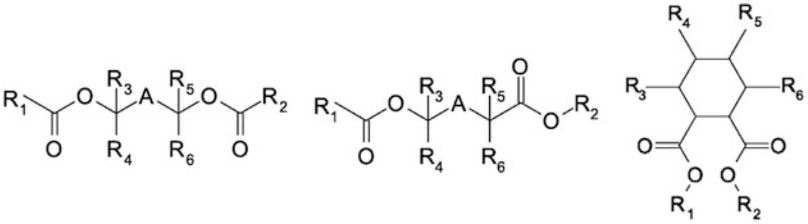


Fig. 5 Internal donors developed for broad molecular weight distribution of PP

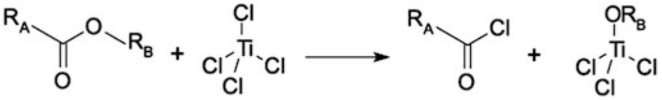
and of N-containing external donors, the catalyst employing succinate as an internal donor is nominated as a sixth generation catalyst. The specific features of succinate are commonly attributed to the presence of chiral centers in the framework, which plausibly enables the coexistence of donors having different stereostructures. Figure 5 shows donors that have been developed on the basis of a similar idea [25–27].

Thus, it is not too much to say that the history of heterogeneous Ziegler–Natta catalysts is almost identical to the history of finding new donors since the third generation. This is because donors modify not only the catalyst activity but also physical properties of PP through isotacticity, molecular weight distribution, and comonomer incorporation. However, great modifications in the preparation of solid catalyst components must not be overlooked in terms of the historical improvements in the activity and isospecificity. This is reasonable when one considers that catalyst structures are affected not only by donors but also by preparative routes. In this sense, a seventh generation catalyst may appear as the result of synergistic combination between new donors and new preparative techniques.

2 Mechanistic Aspects

It is known that the addition of donors causes a variety of consequences in the performance of Ziegler–Natta catalysts such as activity enhancement, drastic improvement in the isospecificity, the elongation of molecular weight, and so on. Considering that olefin polymerization catalysis results from a catalytic function of active Ti species, these consequences must result from interactions of donors with active Ti species. Interactions can not only be direct but also indirect, whereby donors interact with other catalytic components that interact with Ti species, thus indirectly affecting its performance. This section briefly summarizes the mechanistic aspects of how donors interact with other catalytic components to modify the performance of Ziegler–Natta catalysts, especially focusing on progress since 2000. A reader who is interested in more details, especially before 2000, is referred to [2, 28, 29] together with references therein.

In principle, donors (Lewis basic compounds) can bind to catalytic components with Lewis acidic sites such as Ti of $TiCl_4$, undercoordinated Mg on $MgCl_2$ surfaces, and Al of alkylaluminum. The coordination of donors occurs through



Scheme 1 Reaction of an ester-type donor with $TiCl_4$

the donation of an unshared electron pair. In the case of ester-based donors, the coordination accompanies a red-shift of the C=O vibrational frequency, whose degree depends on the chemical nature of the Lewis acidic sites. This fact has been frequently utilized to examine the state and location of ester-type donors in solid catalysts by means of IR spectroscopy. Terano et al. clarified with IR spectroscopy and thermal analysis that EB dominantly resides on $MgCl_2$ surfaces without forming a $TiCl_4$·EB complex [30]. This is in agreement with quantum chemical calculations, which concluded that the dissociative adsorption of $TiCl_4$·EB on $MgCl_2$ surfaces is energetically more advantageous than non-dissociative adsorption [31]. Similar IR results were obtained for dibutylphthalate (DBP), for example, by Arzoumanidis and Karayannis [32] They studied catalysts that were activated at different temperatures and found that DBP dominantly coordinated to surface Mg sites at any activation temperature. However, a residual amount of $TiCl_4$·DBP complex was detected only when a catalyst was activated at a too-low temperature (called under-activation), whereas activation at a too-high temperature led to the formation of carbonyl halides according to Scheme 1 [32, 33] (called over-activation [32]), both of which resulted in a clear reduction in propylene polymerization activity.

Thus, it is well accepted that donors are supported on $MgCl_2$ surfaces separately from $TiCl_4$ in solid catalysts. As a consequence, most research since the 1990s has been directed towards understanding how internal donors affect the formation of solid catalysts during preparation, which $MgCl_2$ surfaces the donors prefer to be located on, and how donors interact with $TiCl_4$ or active Ti species.

The preparation of highly active $MgCl_2$-supported Ziegler–Natta catalysts generally requires activation of the $MgCl_2$ support, which is typically performed by co-grinding $MgCl_2$ with an internal donor and/or $TiCl_4$, treating a $MgCl_2$·donor adduct with $TiCl_4$, or by chlorinating MgX_2 (X = R, OR, OCOR, etc.) into $MgCl_2$ followed by treatment with an internal donor. In contrast to α- and β-$MgCl_2$ with well-dissolved X-ray diffraction (XRD) patterns, activated $MgCl_2$ usually exhibits an XRD pattern typical for δ-$MgCl_2$, featuring very broad peaks centered at around 15°, 32°, and 50° [corresponding to (0 0 3), (1 0 l), and (1 1 0) reflections, respectively] (Fig. 6) [34]. These broad peaks are usually ascribed to a rotational disorder in the Cl–Mg–Cl tri-layer stacking along the (0 0 1) direction and reduced crystalline dimensions [35, 36]. Since donors strongly bind to undercoordinated Mg sites and stabilize the corresponding sites, internal donors might affect the structure of the activated $MgCl_2$ support. However, full understanding of its structure has been prevented by the structural irregularity of δ-$MgCl_2$, and great progress has only recently been made, especially regarding the surface structures of δ-$MgCl_2$.

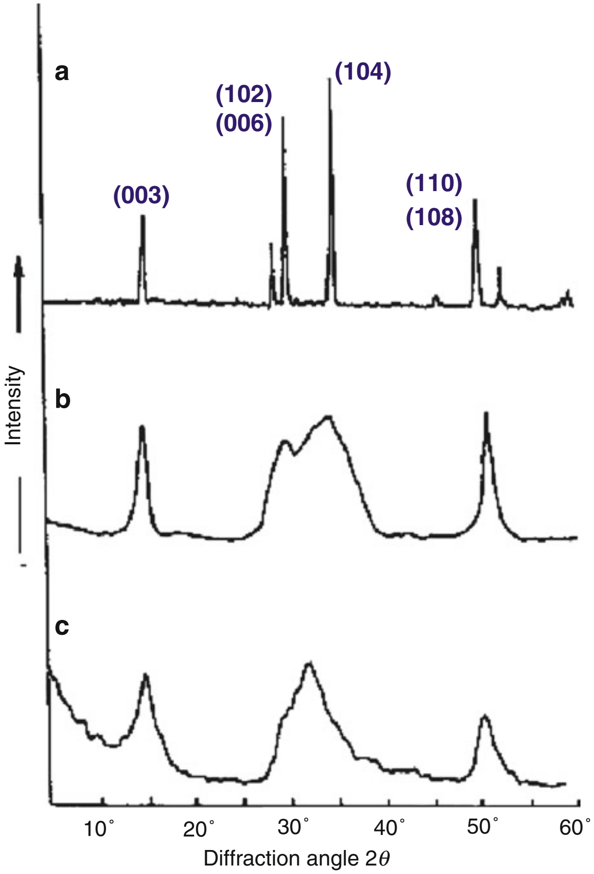


Fig. 6 X-ray diffraction patterns of (**a**) α-$MgCl_2$, (**b**) mechanically activated $MgCl_2$, and (**c**) chemically activated $MgCl_2$ (reproduced from [34]). The latter two show diffraction patterns characteristic for δ-$MgCl_2$

The most stable surface of $MgCl_2$ is the (0 0 1) basal plane, which is obtained by cleaving the $MgCl_2$ tri-layer stacking. The (0 0 1) plane is coordinatively saturated [37] and therefore inactive to the adsorption of $TiCl_4$ and donors [38, 39], i.e., it is catalytically irrelevant. Catalytically relevant surfaces are low-index planes that expose unsaturated Mg^{2+} ions. The (1 1 0) and (1 0 4) lateral planes have been long believed to be representative [35, 36], consistent with the diffraction peaks for these planes. Note that the (1 0 4) plane is sometimes expressed as the (1 0 0) plane [37, 40]. The (1 1 0) and (1 0 4) surfaces, respectively, expose four- and fivefold coordinated Mg^{2+} ions in comparison with sixfold coordination in the bulk and on the (0 0 1) basal plane (Fig. 7 [41]). Busico et al. recently used dispersion-corrected density functional theory (DFT-D) calculations to show that $MgCl_2$ mainly exposes the (0 0 1) and (1 0 4) surfaces at an equilibrium crystallographic morphology (Fig. 8) [37]. However, activated $MgCl_2$ can also expose the (1 1 0) lateral plane, as a result of the morphology formation under kinetically non-equilibrated conditions and/or a shifted equilibrium in the presence of adsorbates such as $TiCl_4$ and donors [37, 40]. For example, Mori, Terano et al. observed with

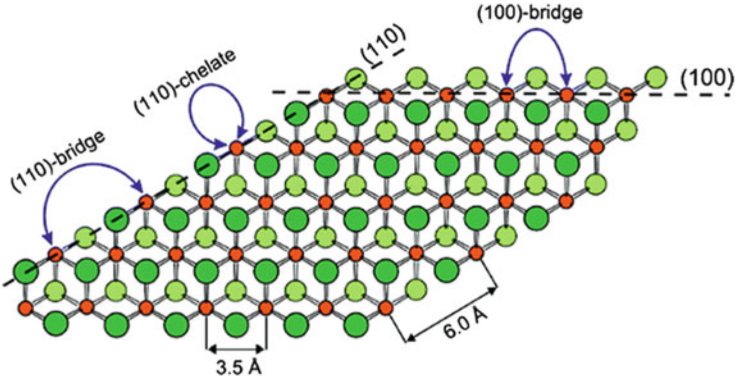


Fig. 7 Schematic view of a $MgCl_2$ monolayer with (1 1 0) and (1 0 0) terminations (reproduced from [41]). *Orange balls* represent Mg^{2+} ions, and *light* and *dark green balls* represent Cl^{-} ions. The top surface corresponds to the (0 0 1) basal plane without coordinative unsaturation

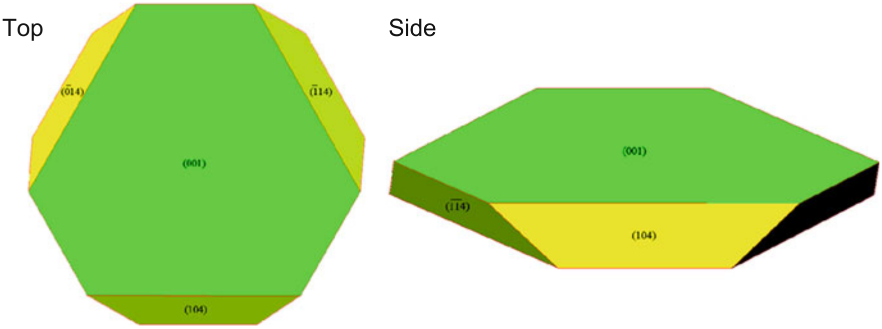


Fig. 8 Equilibrium crystallographic morphology of $MgCl_2$ estimated from surface energies of DFT-D calculations (reproduced from [37])

high-resolution transmission electron microscope (TEM) that lateral surfaces of mechanically activated $MgCl_2$ are dominantly composed of the (1 1 0) and (1 0 4) planes (Fig. 9) [42]. Andoni et al. reported preferential growth of $MgCl_2$ crystal along the (1 1 0) direction in the presence of 1,3-diether, while the growth occurred along both the (1 1 0) and (1 0 4) directions in the presence of DBP (Fig. 10) [43]. Recent DFT calculations by Credendino, Cavallo et al. pointed out that the equilibrium crystallographic morphology of $MgCl_2$ became completely different in the presence of a donor, where the (1 1 0) termination prevailed over the (1 0 4) termination in the presence of ether adsorbates [44].

Since donors bind to and stabilize undercoordinated Mg^{2+} ions during the formation of solid catalysts, their adsorption behaviors on $MgCl_2$ surfaces have been extensively studied, mainly based on IR spectroscopy and quantum chemical calculations. The adsorption structures of representative donors are summarized in Fig. 11 [40, 41]. In general, monoester-type donors for the third generation adsorb

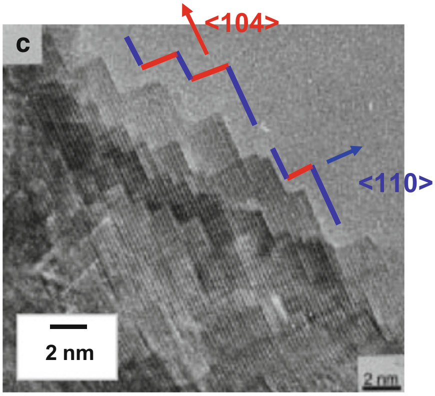


Fig. 9 High-resolution TEM image of milled $MgCl_2$, where the lateral cuts are mainly composed of the (1 1 0) and (1 0 4) surfaces (reproduced from [42])

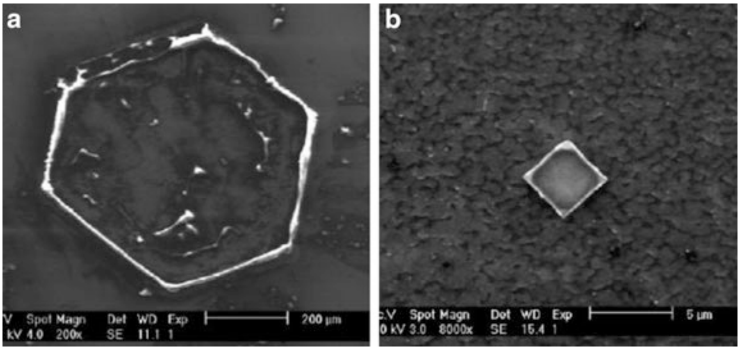


Fig. 10 Morphology of $MgCl_2$ grown from ethanol solution over silicon wafer in the presence of (**a**) 1,3-diether and (**b**) phthalate (reproduced from [43]). $MgCl_2$ formed in the presence of 1,3-diether exhibits only 120° corners, indicating the exposure of only one type of lateral cut, i.e., (1 1 0). On the other hand, 90° corners for phthalate indicate coexposure of the (1 1 0) and (1 0 4) lateral cuts

on $MgCl_2$ surfaces in a monodentate fashion through the carbonyl oxygen. Diester-type donors for the fourth and sixth generations can adsorb either in a bidentate fashion or in a bridging fashion. 1,3-Diethers (stereoregulating ones) and alkoxysilane preferentially adsorb in a bidentate fashion because the distance between two Lewis basic oxygens is not enough to bridge two neighboring Mg^{2+} ions on the $MgCl_2$ surfaces [45, 46]. In terms of the lateral planes, bidentate adsorption does not occur on the (1 0 4) surface with fivefold coordinated Mg^{2+} ions exposed. Namely, 1,3-diether poorly adsorbs on the (1 0 4) surface, i.e., hardly stabilizes the (1 0 4) surface as an internal donor. This is in contrast to ester-type donors, which can adsorb both on the (1 1 0) and (1 0 4) surfaces [40, 44]. This fact is consistent with the preferential growth of $MgCl_2$ crystal along the (1 1 0) direction in the presence of 1,3-diether [43] and with the narrow molecular weight

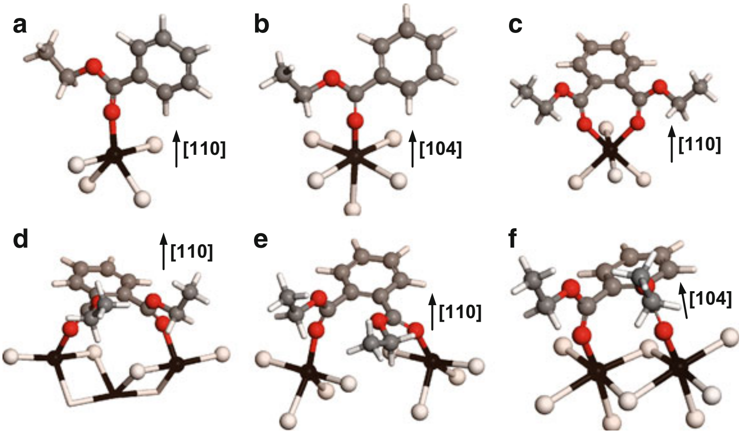


Fig. 11 Adsorption modes of donors on $MgCl_2$ surfaces (reproduced from [40]): (**a**, **b**) Benzoate adsorbed on the (1 1 0) and (1 0 4) surfaces in a monodentate fashion, (**c**–**e**) phthalate adsorbed on the (1 1 0) surface in bidentate, intra-bridging, and inter-bridging fashions, and (**f**) phthalate adsorbed on the (1 0 4) surface in an intra-bridging mode. *Black* Mg, *white* Cl (*balls*) and H (*sticks*), *gray* C, *red* O

distribution of PP produced by a 1,3-diether-containing catalyst. The number of adsorption modes for one donor may be important for the molecular weight distribution of PP [41]. Zakharov and coworkers conducted systematic IR studies to examine the adsorption states of benzoate and phthalate on $MgCl_2$ [47–50]. The carbonyl absorption bands of these donors were not only red-shifted but also broadened as compared with those of free (non-adsorbed) donors, which was explained by the adsorption of the donors at Mg^{2+} sites with different coordination vacancies. Brambilla et al. employed an advanced approach to identify the location of $TiCl_4$ or 1,3-diether in solid catalysts, where experimental Raman spectra were compared with simulated spectra by assuming molecular model structures [51, 52]. They found that the adsorption on the (1 1 0) surface led to better reproduction of the experimentally obtained spectra than that on the (1 0 4) surface.

The fact that donors adsorb on coordinatively unsaturated $MgCl_2$ surfaces is important in considering the state of $TiCl_4$ as active site precursor, since $TiCl_4$ competitively adsorbs on these surfaces. In fact, the treatment of donor/$MgCl_2$ by $TiCl_4$ or the treatment of $TiCl_4$/$MgCl_2$ by a donor at an elevated temperature generally reduces the content of the donor or $TiCl_4$, respectively. Consequently, mechanistic suggestions about how donors affect the catalytic performance, especially isospecificity, have been made on the basis of their competitive adsorption on $MgCl_2$ surfaces. The following paragraphs summarize the historical variation in academic consensuses on this subject from the late 1980s to the present.

The advantages of $MgCl_2$ as a catalytic support over the other halides are attributed to the facts that $MgCl_2$ has a similar crystallographic structure to violet $TiCl_3$ and that $TiCl_4$ can adsorb on unsaturated $MgCl_2$ surfaces in a epitactic manner due to resemblance between the atomic radii of Mg^{2+} and Ti^{4+} [28, 53]. When $TiCl_4$ adsorbs as mononuclear species on the (1 1 0) surface and

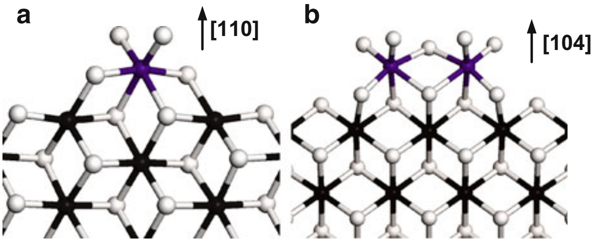


Fig. 12 $TiCl_4$ adsorbed on $MgCl_2$ surfaces: (**a**) mononuclear species on the (1 1 0) surface, and (**b**) dinuclear species on the (1 0 4) surface (reproduced from [40]). *Black* Mg, *white* Cl, *purple* Ti

as dinuclear species on the (1 0 4) surface , $TiCl_4$ can terminate these surfaces with Ti^{4+} ions located at positions that are supposed to be occupied by Mg^{2+} ions (Fig. 12) [53]. From structural analogy with active sites for $TiCl_3$-based catalysts, the mononuclear species on the (1 1 0) surface is regarded as precursor of an aspecific active site, while the dinuclear species on the (1 0 4) surface is regarded as precursor of an isospecific active site. The first persuading proposal on the mechanism for how donors improve the catalyst isospecificity was performed by Busico, Corradini, and coworkers: donors preferentially adsorb on the (1 1 0) surface with higher Lewis acidity, thus preventing the formation of the aspecific mononuclear species while increasing the ratio of the isospecific dinuclear species [53]. Corradini's model was widely accepted, but subsequent research progress posed several controversial points, two of which are:

- Not only the above-mentioned research by Brambilla et al. [51] but also most recent DFT calculations support the preferential adsorption of $TiCl_4$ on the (1 1 0) surface [31, 40, 54–58].
- Within Corradini's model, the isospecific active site always corresponds to the dinuclear species on the (1 0 4) surface, irrespective of the molecular structure of donors. However, microtacticity of isotactic PP produced in the presence of different donors was found to be sensitive to the molecular structure of donors (Fig. 13), clearly indicating that the active site structure and its nature are dependent on the structure of the donors [59–62].

Separately from their previous model [53], Busico et al. proposed a general active site model in Ziegler–Natta propylene polymerization, based on statistical analyses of polymer stereostructures acquired by high-resolution ^{13}C-NMR [63]. This so-called three-site model, after modification by Liu, Terano et al. [64], is at present widely accepted. As shown in Fig. 14, the stereospecificity of Ti species situated in an octahedral symmetry is described by the presence or absence of ligands $L_{1,2}$ at the neighboring metal centers, which are connected to the Ti center through chlorine bridges. $L_{1,2}$ sterically transfers underlying C_2 symmetry to the Ti center in a way that controls the configurational orientation of growing chain and propylene [40, 41, 63]. This model explicitly represents an active site that contain donors at the $L_{1,2}$ positions, where it is easy to imagine that the bulkiness of donors at $L_{1,2}$ affects the stereospecificity of the Ti center. Taniike and Terano conducted systematic DFT calculations on the coexistence of Ti species and donors on catalytic surfaces, and clarified that coadsorption of

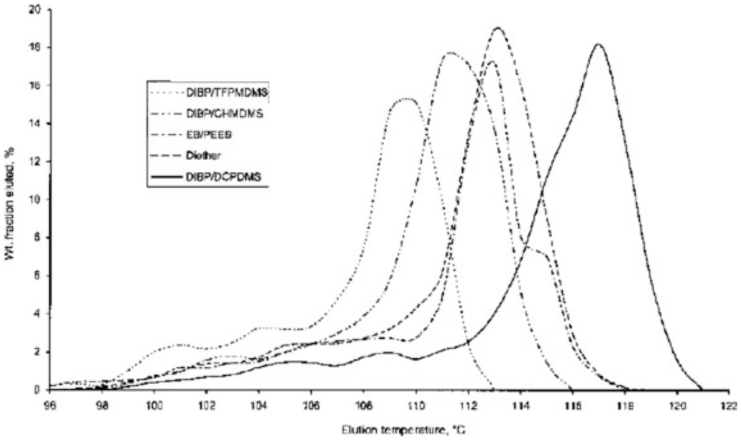


Fig. 13 Profiles of temperature rising elution fractionation of PP produced by catalysts with different internal and external donors (reproduced from [59]). *DIBP* disobutylphthalate, *TFPMDMS* 3,3,3-trifluoropropyl(methyl)dimethoxysilane, *CHMDMS* cyclohexyl(methyl)dimethoxysilane, *EB* ethylbenzoate, *PEEB* ethyl *p*-ethoxybenzoate, *DCPDMS* dicyclopentyldimethoxysilane. The deviation in the peak positions indicates that the isospecificity of the main active sites varies according to the combination of donors

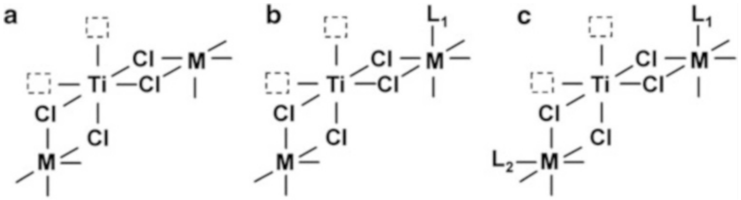
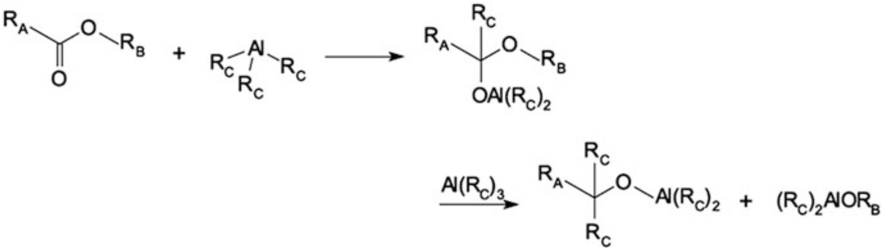


Fig. 14 Three-site model proposed by Busico et al. [63] (reproduced from [75]). Active site models relevant to the production of (**a**) syndiotactic (or atactic), (**b**) isotactoid (or isotactic), and (**c**) highly isotactic PP. A growing chain and propylene monomer occupy the chained squares. M = Ti, Mg, or Al; L = Cl, donor, or alkylaluminum moiety [64]

donors with $TiCl_4$ mononuclear species on the $MgCl_2$ (1 1 0) surface is the most plausible scenario from energetic, steric, and electronic points of views [40]. Thus, the proposed coadsorption model [40] succeeded in reproducing experimentally well-known results on the influences of donors on catalytic performance, such as improvements in isospecificity and regiospecificity, elongation of PP molecular weight, and so on [65–68].

Although the above paragraphs focused on the roles of donors in the formation of solid catalysts and the active sites thereon, the interaction between donors and alkylaluminum also plays a crucial role in catalysis. Lewis basic donors not only form a complex with alkylaluminum, but also react with highly reactive Al–R bonds: internal donors except 1,3-diether desorb from $MgCl_2$ surfaces through



Scheme 2 Reaction of an ester-type donor with alkylaluminum

complexation with alkylaluminum and lose their functionality through the reaction with Al–R. For instance, ester-type donors are known to react with alkylaluminum according to Scheme 2 [28, 29, 69, 70].

On the other hand, 1,3-diether is known to be difficult to extract by alkylaluminum from surfaces and therefore can retain high isospecificity even without external donors [71]. The extraction of internal donors not only decreases the catalyst isospecificity but also the activity. To prevent these deteriorations, external donors are usually added during polymerization. As stated above, benzoate is employed for the third generation catalysts and alkoxysilane for the later generations. It is known that benzoate as an external donor prevents the extraction of internal donors, whereas alkoxysilane accelerates it, but the mechanistic origin is not clear. The most widely employed dialkoxysilane forms a one-to-one complex with alkylaluminum and goes through a slow ligand exchange equilibrium between an alkoxy group of dialkoxysilane and an alkyl group of alkylaluminum [72]. Wrong combination between internal and external donors, such as an alkoxysilane external donor for a third generation catalyst and a benzoate external donor for the later generation catalysts, usually exhibit much poorer performance compared with the correct combination. This is known as a key-hole relation between internal and external donors [73, 74], whose origin is also still unclarified. In this way, chemistry of the interaction between (internal and external) donors and alkylaluminum has hardly progressed since 2000; nonetheless, it is certain that a good external donor must not only be tolerant against alkylaluminum but also compatible with the employed internal donor.

In summary, the present chapter has briefly reviewed the historical development and state-of-the-art academic understanding of donors in Ziegler–Natta propylene polymerization. The roles of donors have been gradually uncovered due to advances in characterization techniques and computational chemistry, while their development still relies on conventional trial-and-error methodology, mainly because of poor understanding of their structure–performance relationships. The authors strongly wish that further advances in the molecular-level elucidation will finally enable us to reach a priori design of a new class of donors, something that has not yet been fully achieved even for other heterogeneous catalysts.

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