

Propylene Polymerization over MgCl₂-Supported TiCl₄ Catalysts Bearing Different Amounts of a Diether Internal Electron Donor: Extrapolation to the Role of Internal Electron Donor on Active Site

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ABSTRACT: In this work, the composition of MgCl₂-supported Ziegler-Natta (ZN) catalysts bearing different amounts of 9,9-bis(methoxymethyl)fluorine (BMMF) and the propylene polymerization over these catalysts are investigated. Based on the experimental results, the models of active sites suitable for ZN catalysts with/without internal donor BMMF are established, and they can be described as follows: atactic site (I)—isolated TiCl₄ monomeric species on the (110) lateral cut (around which there is no complexes), weakly isospecific site (II)—semi-isolated and surrounded TiCl₄ monomeric species on the (110) lateral cut (in the vicinity of which BMMF or other TiCl₄ is adsorbed), and highly isospecific site (III)—dimeric TiCl₄ species (Ti₂Cl₈) on the (104) lateral cut. Meanwhile, the

mechanism underlying the role of BMMF on active sites is revealed (i) convert atactic sites (I) to weakly isospecific site (II) by occupying either or both of L₁ or/and L₂ vacancies around site; (ii) improve the isotacticity of weakly isospecific site (II) in donor-free ZN catalyst by adsorbing at L₂ vacancy or/and replacing the Cl for TiCl₄ at L₁; and (iii) replace highly isospecific site (III). In addition, these roles of BMMF are successively achieved according to the amount of BMMF added. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 1265–1270, 2012

Key words: polyolefins; internal donor; active site model; Ziegler-Natta polymerization; gel permeation chromatography (GPC)

INTRODUCTION

Isotactic polypropylene (*i*-PP) finds widespread applications in modern human life due to its high cost performance, and by far the major fraction of global polymer is obtained with MgCl₂-supported Ziegler-Natta (ZN) catalysts.¹ The performances of MgCl₂/TiCl₄/donor systems are mainly improved by application of different electron donor compounds (Lewis bases), and nowadays, the catalytic systems have reached amazing performances, allowing for the morphological control of the polymer particles and the design of economical industrial processes. Lewis bases can be added in catalyst preparation (the so-called internal donors) or during polymerization (the so-called external donors).^{2–4} In general, the specific pair of internal and external donors, such as phthalate/alkoxysilane,⁵ is necessary to obtain *i*-PP with high isotacticity. However, the discovery of 1,3-diethers has made it possible to

obtain highly isospecific catalysts by using only an internal donor.⁶

The presence of Lewis bases is essential to affect the performance of the catalyst, since they can strongly modify the catalyst activity,^{4,7} stereoselectivity,^{8–10} regioselectivity,^{7,11,12} molecular masses distribution,^{13,14} and the response to molecular hydrogen.^{7,11–12} In fact, all these modifications can be attributed to the effect of internal donor on active sites of catalyst. Therefore, many experimental and theoretical efforts have been devoted to establish active sites models and to reveal the mechanism underlying the role of internal donor.^{15–25}

For MgCl₂/TiCl₄ catalyst, distribution of Lewis acidic sites on MgCl₂ surfaces and nuclearity difference of TiCl₄ precursor are considered to be the main sources for the multiple active sites nature.¹⁵ It is well accepted that active surfaces of MgCl₂ are mainly (110) and (104) lateral cuts with fourfold and fivefold coordinated Mg ions, respectively, displaying different Lewis acidity.¹⁶ The (104) face is proposed to be prevalingly occupied by polynuclear species of TiCl₄, such as Ti₂Cl₈ dimers.^{8,17,18} Moreover, through the molecular mechanics and density functional theory studies on TiCl₄-based catalytic

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system, these polynuclear sites are suggested to be highly isospecific, because they are similar to the C_2 symmetric sites which are proposed to be isospecific.^{8,17,19,20} On the other hand, monomeric $TiCl_4$ species complexed along the (110) lateral cut in an octahedral coordination are considered as aspecific active sites.^{17,21,22} Accordingly, models have been used to explain the effect of electron donors on the stereospecificity of propylene polymerization. One model has suggested that preferential coordination of donor onto the (110) surface of $MgCl_2$ suppresses the formation of aspecific active site, resulting in the improvement of isotacticity.²³ Other models have attributed the improvement of isotacticity to the direct sterical modification of donors locating in the vicinity of active sites.^{24,25}

Although those studies have provided us important knowledge on the role of donor on active site, there is still no complete agreement on the models of active sites and the role of internal donor because of the complexity of the catalytic system. Previous studies in the field were mostly implemented on the basis of catalysts comprising different internal donors,^{3,9,13,26–28} however, in this manuscript, we have paid more attention to ZN catalysts with a certain internal donor but different donor contents, which are realized by changing the internal-donor/ Mg molar ratios added. This route has been provided by Cui et al.²⁹ and proven to be a good method to investigate the effect of internal donor on $MgCl_2$ -supported ZN catalyst for propylene polymerization. Herein, we study the effect of internal donor on active sites through further analysis of PP obtained and are committed to establishing active site models suitable for $MgCl_2$ -supported ZN catalyst with/without internal donor by considering the chemical reactions in catalyst preparation.

In this study, the typical 1,3-diether 9,9-bis(methoxymethyl)fluorine (BMMF) is selected as internal donor due to its advantages. During propylene polymerization, 1,3-diethers in diether-based catalysts cannot be extracted by alkylaluminum and no external donor is added, so the active sites formed in diether-based catalyst are the ones catalyzing propylene polymerization and hence they can be characterized through the polymers obtained.^{6,9,10} Moreover, there are fewer interactions between 1,3-diether and $MgCl_2$, which make it simple to study the influence of 1,3-diether on active sites.³⁰ Meanwhile, BMMF, as a typical 1,3-diether, is proved to be able to prepare ZN catalyst with higher isotacticity.^{29,31} Therefore, we chose BMMF as internal donor, and prepare a series of ZN catalysts containing different BMMF amount. Then the properties of ZN catalysts and PP obtained are studied with the aim to reveal the role of BMMF on active sites. The molecular weight and molecular weight distribution

of PP are paid more attention because of their close relationship with the number and nature of active sites.

EXPERIMENTAL

Materials

All O_2 and moisture-sensitive manipulations were carried out inside an argon-filled Vacuum Atmosphere dry-box equipped with a dry train. Chemical pure grade solvents (hexane and heptane) were refluxed over Na/benzophenone and freshly distilled prior to use. $TiCl_4$ was purchased from Beijing Yili Fine Chemical and used without further purification. Internal donor BMMF and support—solid, spherical adducts of magnesium chloride, and ethanol, $MgCl_2 \cdot 2.8EtOH$, were kindly donated by Xiangyang Chemical, China. Triethylaluminum (TEA, from Albemarle, US) was diluted by heptane (1.8 mol/L). Polymerization grade propylene gas was supplied by Yanshan Petrochemical, China.

Catalyst preparation

In a typical ZN catalyst preparation, a Schlenk type reactor was used to prepare the catalysts using procedures similar to those reported previously.²⁹ A large excess of $TiCl_4$ was introduced into the reactor and kept at $-20^\circ C$. An amount of solid, spherical adducts of magnesium chloride and ethanol, $MgCl_2 \cdot 2.8EtOH$, was added slowly, with agitation and maintained at this temperature for 1 h. The suitable amount of internal electron donor BMMF was/was not added after the temperature was raised to $60^\circ C$. The reactor mixture was allowed to react at $110^\circ C$ for 2 h. The resulting solid was filtered and washed with hexane five times at $60^\circ C$ and two times at room temperature. Finally, the catalysts $MgCl_2/TiCl_4$ (Cat-0) and $MgCl_2/TiCl_4/BMMF$ (ZNB catalysts, Cat-1 to Cat-6) were obtained after being dried under vacuum.

Propylene polymerization

In a typical experiment, a 500-mL stainless steel autoclave equipped with a mechanical stirrer was removed O_2 , then 100 mL of hexane, desired TEA (1.8 mol/L in heptane) and catalyst ($Al/Ti = 100$) were injected into it under 1 atm of propylene, respectively. After that, the polymerization started with 4 atm of propylene at $60^\circ C$. Propylene pressure and temperature were kept constant during the reaction. After 30 min, the reaction was terminated with acidic ethanol and filtered, the product was washed with ethanol and water several times, and then dried overnight under vacuum at $60^\circ C$.

TABLE I
Propylene Polymerization^a Results Using the MgCl₂/TiCl₄/BMMF Catalysts Prepared with Various BMMF/Mg Molar Ratios in Feed

Catalyst	BMMF/mg in feed (mol/mol)	Activity (10 ⁻⁶ g/mol Ti.h ⁻¹)	II%	T _m (°C)	ΔH (J/g)	M _n (10 ⁻⁵ g.mol ⁻¹)	MWD
Cat-0	0	1.18	50.1	145.8/155.9	30.6	1.92	11.7
Cat-1	0.05	0.80	58.6	150.6/158.7	41.3	1.84	13.1
Cat-2	0.10	1.42	87.1	156.2/162.3	56.8	3.15	8.58
Cat-3	0.15	3.48	97.6	158.9/162.4	57.7	7.84	6.16
Cat-4	0.21	3.04	98.4	159.1/162.2	67.0	9.79	5.53
Cat-5	0.33	2.27	98.2	160.3/162.3	68.4	9.56	5.45
Cat-6	0.50	1.91	98.9	160.8/162.4	71.3	7.20	5.70

^a Polymerization conditions: Catalyst, 25 ± 1 mg; hexane, 100 ml; propylene pressure, 4 atm; cocatalyst, TEA, Al/Ti = 100 mol/mol; reaction temperature, 60°C; polymerization time, 30 min.

Characterization

Titanium content was determined by spectrophotometer at 410 nm in the solution of catalyst, which was treated with sulfuric acid (7.2N). BMMF content was measured by gas chromatogram on heptane extract of the catalyst solutions. Magnesium content was determined from the titanium and BMMF contents.

The melting temperatures (*T_m*) and heat of fusions (Δ*H*) of the polymers were measured by differential scanning calorimetry (DSC) using a PerkinElmer DSC-7 instrument controller. The DSC curves were recorded during the second heating cycle from 50 to 180°C with a heating rate of 10°C/min. The isotacticity index (II) of polymer was defined as the fraction insoluble in boiling heptane extraction for 24 h. The molecular weight and molecular weight distribution of the polymers were determined by gel permeation chromatography (GPC) using a Waters Alliance GPC 2000 instrument equipped with a refractive index (RI) detector and a set of u-Styrigel HT columns of 10⁶, 10⁵, 10⁴, and 10³ pore size in series.

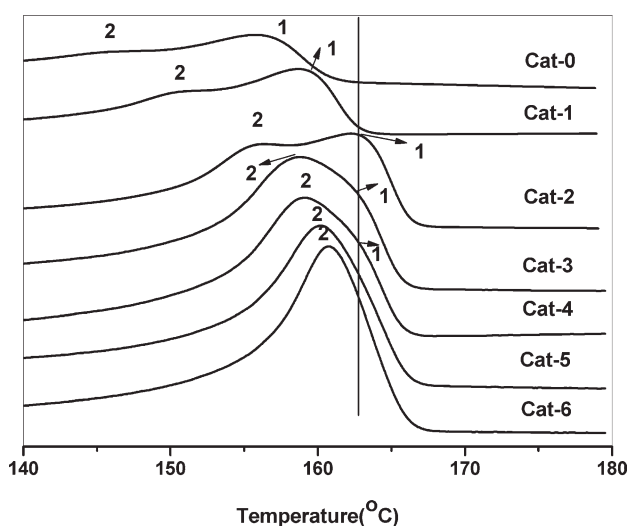


Figure 1 DSC curves (second fusion) of polypropylenes produced by ZN catalysts bearing different amounts of BMMF.

The measurement was performed at 150°C with 1, 2, 4-trichlorobenzene as the eluent with a flow rate of 1.0 mL/min. Narrow molecular weight PS samples were used as standards for calibration.

RESULTS AND DISCUSSION

Table I summarizes the results of propylene polymerization using the MgCl₂/TiCl₄/BMMF catalysts bearing various BMMF contents, prepared with different BMMF/Mg molar ratios in feed. The DSC and GPC curves of the PPs obtained are demonstrated in Figures 1 and 2, respectively. It is generally felt that isospecific active center products polymer with high isotacticity and molecular weight, while atactic center produces polymer with low isotacticity and molecular weight.^{4,32} Therefore, the analysis of DSC and GPC data provides us an opportunity to study active site. With respect to DSC, GPC is less affected by test conditions and can give more accurate information about polymer, so the following analysis is mainly based on GPC data.

Figure 1 shows the fusion curves of PP obtained and it is obvious that all curves are bi-modal. As far

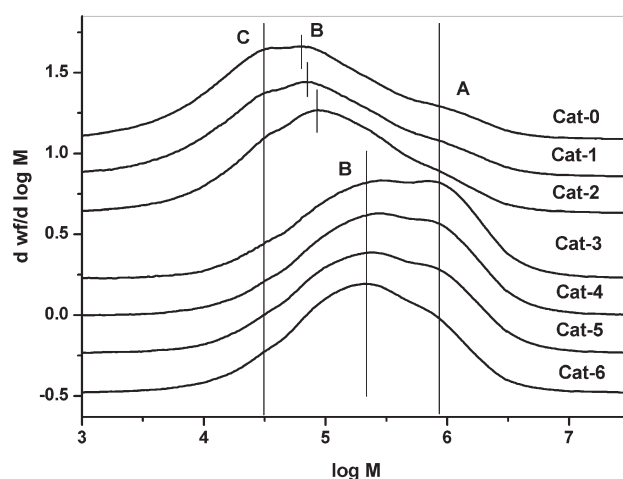


Figure 2 GPC curves of polypropylenes produced by ZN catalysts bearing different amounts of BMMF.

TABLE II
The Composition of MgCl₂/TiCl₄/BMMF Catalysts

Catalyst	Ti (mmol/ 100 g Cat.)	BMMF (mmol/ 100 g Cat.)	Mg (mmol/ 100 g Cat.)	BMMF/Ti (mol/mol)	(Ti+BMMF)/ Mg (mol/mol)
Cat-0	173	0	707	0	0.245
Cat-1	159	9.69	710	0.06	0.238
Cat-2	123	42.1	694	0.34	0.238
Cat-3	78.1	58.3	740	0.75	0.184
Cat-4	75.2	63.8	732	0.85	0.190
Cat-5	55.1	74.0	745	1.34	0.173
Cat-6	52.0	81.1	732	1.56	0.182

The introduction of BMMF has an important impact on the number of active sites, therefore we are committed to study the effect of BMMF content on the number of active sites to reveal the mechanism underlying the role of BMMF on active sites. Table II shows the influence of the BMMF/Mg molar ratios added in catalyst preparation on the catalyst composition. As shown in Table II, Cat-0 without any electron donor owns the highest Ti content, and as the increase BMMF/Mg molar ratio added, Ti content decreases with the increase of BMMF content. Meanwhile, the total content of both Ti and BMMF changes in a small range, especially for Cat-3 to 7. This result clearly indicates that BMMF occupies some vacancies on MgCl₂ support, preventing TiCl₄ from coordinating on MgCl₂ crystal faces.

Considering that the relative peak area in GPC curve is highly related to PP fractions of different isotacticity and the last ones are generated from the specific active site, respectively, we can find out the influence of BMMF content on the relative number of three types of active sites, which is more useful to speculate the role of BMMF on active site in MgCl₂-supported ZN catalyst. As shown in Figure 2, for Cat-0 to 2, the main active sites are atactic site (I) and weakly isospecific site (II), whereas for Cat-3 to 7, the main active sites are weakly isospecific site (II) and highly isospecific site (III). When BMMF content is lower than that in Cat-3, the increase of BMMF content mainly results in the decrease of atactic site (I) content (Peak C) and the increase of weakly isospecific site (II) content (Peak B). In addition, the isotacticity of site (II) is improved. These results indicate that some atactic sites (I) are converted to weakly isospecific sites (II) by BMMF adsorption at the vacancies around sites (I). As the stronger steric hindrance of BMMF than Cl for TiCl₄, the new weakly isospecific sites (II) are more isotactic than those in donor-free catalyst. Meanwhile, weakly isospecific sites (II) in donor-free catalyst can also be transferred to those with BMMF in the nearby due to the preference of BMMF versus TiCl₄ coordination on the (110) lateral cut.²³ When BMMF content reaches high enough (herein, it is that in Cat-3),

almost all sites (II) become those with two BMMF molecules adopting at L₁ and L₂, and a few atactic sites (I) are left, which may be these coordinated on the uncoordinated edge and corner sites. With further increase in BMMF content, the nature and number of atactic sites (I) and weakly isospecific site (II) almost keep constant, indicating that they are no longer affected by BMMF. On the other hand, the number of site (III) has a close relationship with BMMF content when BMMF content is higher than that in Cat-3. In Cat-3, the number of site (III) reaches highest, and then it gradually decreases with the further increase of BMMF content. Combining with decrease of Ti content and increase of BMMF content, this result indicates that dimeric TiCl₄ species (Ti₂Cl₈) on the (104) MgCl₂ lateral cut [site (III)] can be replaced by BMMF. Based on above analysis, the roles of internal electron donor BMMF on active site can be divided into three groups and include: (i) convert atactic sites (I) to weakly isospecific site (II) by occupying either or both of L₁ or/and L₂; (ii) improve the isotacticity of weakly isospecific site (II) in donor-free ZN catalyst by adsorbing at L₂ vacancy or/and replacing the Cl for TiCl₄ at L₁; and (iii) replace highly isospecific site (III). In addition, these roles of BMMF are successively achieved according to the amount of BMMF added.

From above results, it is concluded that BMMF can replace all the TiCl₄ molecules coordinated on MgCl₂, meanwhile, the TiCl₄ molecules coordinated on (110) lateral cut be replaced more easily than that on (104) lateral cut. However, why so many sites (II) on (110) lateral cut still exist when BMMF content is so high that it begins to replace sites (III) on (104) lateral cut? It can be well explained that the remaining TiCl₄ on (110) lateral cut is that mainly occupies the adsorption sites that are inaccessible for Di because of steric reasons. This is in good agreement with that coadsorption of internal donor and TiCl₄ is virtually noncompetitive and TiCl₄ occupies the adsorption sites that are inaccessible to internal donor for steric reasons.²²

Additionally, it is noteworthy that there is a positive correlation between the activity of ZN catalysts and the content of highly isospecific site (III),

indicating the faster polymerization kinetics of propylene at the highly isospecific site (III) than other sites. This is in good agreement with the studies before²⁹ and gives guidance for the design of better internal donor, which is more effective for higher activity and stereoselectivity through increasing the content of highly isospecific sites (III) in ZN catalyst.

CONCLUSIONS

In this article, a series of BMMF-based ZN catalysts bearing different BMMF contents were prepared, and the composition and propylene polymerization of these catalysts were investigated. Through DSC and GPC analysis of PP obtained, it is found that there are three kinds of active sites in MgCl₂-supported ZN catalysts: atactic site (I), weakly isospecific site (II), and highly isospecific site (III). The nature of site (I) and site (III) has nothing to do with BMMF content, however, the isotacticity of site (II) is improved with the increase of BMMF content and then keep constant when BMMF content is high enough. Based on the result, a modified three-site model is speculated as: atactic site (I)—isolated Ti species on the (110) lateral cut, weakly isospecific site (II)—semi-isolated and surrounding Ti species on the (110) lateral cut, highly isospecific site (III)—dimeric Ti species on the (104) lateral cut.

Based on the effect of BMMF content on the number of active sites, the mechanism underlying the roles of internal electron donor BMMF on active site are revealed (i) convert atactic sites (I) to weakly isospecific site (II) by occupying either or both of L₁ or/and L₂; (ii) improve the isotacticity of weakly isospecific site (II) in donor-free ZN catalyst by adsorbing at L₂ vacancy or/and replacing the Cl for TiCl₄ at L₁; and (iii) replace highly isospecific site (III). In addition, these roles of BMMF are successively achieved according to the amount of BMMF added.

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