

MgCl₂-Supported Catalyst Containing Mixed Internal Donors for Propylene Polymerization

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ABSTRACT: A MgCl₂-supported catalyst containing diisobutyl phthalate (DIBP) and 2,4-pentadiol dibenzoate (PDDB) as internal donors was prepared. Propylene polymerizations were carried out using the catalyst in the absence or presence of an external donor. The resulting polymers were characterized by ¹³C-NMR, crystallization analysis fraction (CRYSTAF) and gel permeation chromatography (GPC). The performance of the catalyst was compared with that of other catalysts containing donor-free, DIBP and PDDB as internal donors respectively. The results demonstrated that the catalyst containing mixed internal donors not only had high activity and stereospec-

ificity but also produced the polymer with relatively broad molecular weight distribution and the highest [mmmm] value. ¹³C-NMR analysis results indicated that strongly coordinating donors gave more stereoregular polymers, which was further confirmed by CRYSTAF data. The effects of mixed internal donors on the catalyst properties were discussed systematically. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 36–42, 2011

Key words: mixed internal donors; catalysts; MgCl₂-supported; poly (propylene) (PP); Ziegler-Natta polymerization

INTRODUCTION

After the discovery of MgCl₂-supported Ziegler-Natta catalysts,¹ it was soon realized that some electron donors were indispensable for achieving much more active and stereoselective catalysts.^{2,3} A number of electron donors, differing in basic strength, steric hindrance and functionality, were investigated as internal or external donors.⁴ Until now, many efforts have been devoted to find the most suitable donors.^{5–8} Nowadays, the most widely used electron donors are phthalate and alkoxysilane compounds as internal and external donors, respectively.⁹

Since there still exist certain defects in some properties of the catalysts containing the single internal donor, much more attention has recently been paid to developing the catalysts containing mixed internal donors. It was reported that this type of catalyst had much better properties in some respects. For example, Garoff et al.¹⁰ selected a less soluble internal donor and a more soluble internal donor as mixed internal donors in the catalysts. Their findings showed that this catalyst system had high stereospecificity while retaining the activity and hydrogen sensitivity. Morini et al.¹¹ reported that the ethers

containing two or more ether groups and the esters of mono- or polycarboxylic acids were selected as mixed internal donors in the catalysts. The resulting polymers gave a wide range of isotacticity with very high xylene insoluble fractions. Furthermore, more study about the catalysts containing mixed internal donors for propylene polymerization has been reported.^{12,13} Nevertheless there are very little in-depth research on propylene polymerization using catalysts containing mixed internal donors. Therefore, further study is necessary in this field.

In this article, the effects of the catalyst containing mixed internal donors [diisobutyl phthalate (DIBP) and 2,4-pentadiol dibenzoate (PDDB)] on catalyst activity, polymer isotacticity, microstructure and molecular weight distribution were investigated. The polymers prepared with the catalyst were analyzed by GPC, ¹³C-NMR and CRSTAF. The properties of this catalyst were compared with those of other catalyst systems with donor-free, DIBP or PDDB as internal donors, respectively. The obtained results showed that the catalyst with mixed internal donors gave higher activity, polymer isotacticity, stereoregularity and broader molecular weight distribution.

EXPERIMENTAL

Materials

Propylene of industrial grade (from Yanshan Petrochemical Co.), MgCl₂·nEtOH (Beijing Research

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Institute of Chemical Industry, SINOPEC), TiCl₄ (from Beijing Aoda Catalyst Branch, SINOPEC), triethylaluminum (TEA, from Aldrich, 95% purity) and cyclohexanemethyldimethoxyilane (CHMDMS) were used without further purification. Nitrogen of an extra pure grade (99.999%) was dried through a molecular sieves 4 Å column. Diisobutyl phthalate (DIBP, from Aldrich), 2,4-pentadiol dibenzoate (PDDB was synthesized according to the methods described in the Ref. 14), hexane and heptane (from Tianjin Chemical reagent Co.) were used after dehydration with molecular sieves (4 Å).

Preparation of PDDB

Preparation of 2,4-pentadiol

Two point five grams of sodium borohydride, 0.1 g of sodium hydroxide and 25 mL of deionized water were mixed together in a 250 mL three-neck flask equipped with an agitator, condenser tube, charge funnel, thermometer and tube for the introduction of nitrogen. The mixture was stirred at the temperature from 0 to 10°C for a few minutes and then another mixture of 10 g of 2,4-pentanedione and 30 mL of methanol was added dropwise in a given time. The used solvents were distilled off at reduced pressure, and the remainder was extracted continuously with 40 mL of ethyl acetate for 15 h. After the solvent was distilled off at reduced pressure, the remainder was purified by column chromatography, to yield 9.4 g of a colorless 2,4-pentadiol with a purity of 90%. The product, which was characterized by FTIR spectrum, showed there was a strong absorption peak at 3400 cm⁻¹ and no absorption peak at 1700 cm⁻¹. The analytical results proved that reduction reaction carried out completely.

Preparation of PDDB

Into the same apparatus as described above in (1) was introduced, under nitrogen, 3.1 g (0.03 mol) of 2,4-pentadiol, 30 mL of tetrahydrofuran and 7.1 g (0.09 mol) of pyridine 10.5 g (0.075 mol) of benzoyl chloride was added dropwise. The mixture was stirred and refluxed for 4 h, cooled and diluted with 20 mL saturated salt solution. Then, the mixture was extracted with ethyl acetate and dried with anhydrous sodium sulfate. The solvent was distilled off and purified by column chromatography, to yield 8.9 g of a colorless PDDB with a purity of 95%.

¹H-NMR (TMS, CDCl₃, ppm): δ = 1.3–1.4 (m, 8H, CH₃), 2.0–2.1(m, 2H, CH₂), 5.2–5.3(m, 2H, CH of ester group), 7.3–8.0 (m, 10H, benzene ring).

Catalyst preparation

All operations were carried out under dry nitrogen using standard Schlenk techniques. Catalyst prepara-

tion was carried out via the reaction of MgCl₂·nEtOH adduct with TiCl₄ in the presence or absence of the internal donor according to Ref. 15 The titanium and internal donor contents of the catalysts were analyzed as follows:

MgCl₂/TiCl₄ (Cat-A): 6.95 wt.-%Ti

MgCl₂/TiCl₄/DIBP (Cat-B):

3.06 wt.-%Ti, 16.69 wt.-%DIBP

MgCl₂/TiCl₄/PDDB (Cat-C):

2.94 wt.-%Ti, 12.59 wt.-%PDDB

MgCl₂/TiCl₄/DIBP/PDDB (Cat-D):

2.12 wt.-%Ti, 5.10 wt.-%DIBP,

7.12 wt.-%PDDB

Polymerization

In a 250 mL reactor purged with nitrogen and propylene, 150 mL of anhydrous *n*-heptane was added and the system was charged with propylene. Then, 40–60 mg of catalyst, prescribed amount of AlEt₃(Al/Ti = 100 molar ratio) and cyclohexanemethyl dimethoxyilane(CHMDMS) (Al/Si = 25 molar ratio) were added under the polymerization temperature (70°C). Polymerization was carried out under the pressure of 0.11–0.13 MPa for 1 h. The polymer was recovered through filtration and dried for certain time. The polymerization rate was determined by measuring the rate of monomer consumption from a mass flow meter. At least two experiments were performed with the same polymerization conditions. The isotacticity index and productivity were based on the average.

Treatment and analysis of solid catalyst

About 1 g of solid catalyst was placed in a glass reactor equipped with a stirrer and immersed in a thermostatic bath. The temperature was raised to 70°C. Then 450 mL of heptane and the solution of AlEt₃ or the AlEt₃/silane mixture (50 mL) were added in the given order. All the operations were carried out under nitrogen. After stirring for 1 h at 70°C, the solid was rapidly filtered, washed several times with hexane, and dried under vacuum. The amount of electron donors in a catalyst dissolved in a proper solvent was determined by Waters 600E high-performance liquid chromatographic (HPLC).

Characterization

The isotacticity index (II) of polymer was obtained by refluxed heptane extraction for 6 h. The molecular weight and its distribution (MWD) of each sample were determined with Waters GPCV2000 gel

TABLE I
Results of Propylene Polymerization with Different MgCl₂-Supported Catalysts^a

Run	Catalyst	External donor	Activity (kg PP/gTi·h)	II ^b	$M_w \times 10^{-4}$	M_w/M_n
1	Cat-A	No	1.35	45.2	15.8	12.1
2		CHMDMS	0.85	83.7	19.2	9.2
3	Cat-B	No	3.60	80.9	22.8	8.5
4		CHMDMS	2.90s	97.6	34.9	7.2
5	Cat-C	No	4.79	94.5	25.8	7.2
6		CHMDMS	4.08	96.9	31.0	6.6
7	Cat-D	No	8.10	95.7	28.3	9.1
8		CHMDMS	7.50	98.8	38.4	8.7

^a Polymerization conditions: catalyst = 40–60 mg, heptane = 150 mL, time = 1 h, propylene pressure = 0.11–0.13 Mpa, Al/Ti = 100 mr, Al/Si = 25 mr.

^b Isotacticity index, weight percent of heptane-insoluble fraction.

permeation chromatography with three Polymer Laboratory MIXED-B columns and 1,2,4-trichlorobenzene as solvent at 150°C. The weight-average and number-average molecular weight (M_w and M_n , respectively) values were reported using polystyrene standard. ¹³C-NMR spectra of isotactic PPs were run with a Bruker DMX 400 spectrometer operating at 100.6 MHz, using 10–20 mg/mL solutions in deuterated dichlorobenzene at 110°C (Conditions: 5mm probe; pulse repetition 4s; number of scans, 20,000). A crystallization analysis fractionation (CRYSTAF) was performed by a CRYSTAF apparatus, model 200, from Polymer Char S.A. (Valencia, Spain). About 30 mg sample was dissolved in 30 mL distilled 1,2,4-trichlorobenzene at 160°C for 2 h. The temperature was decreased at a rate of 0.2°C/min between 160°C and 30°C. Fractions were collected automatically and the polymer concentration in solution was determined by an infrared detector using 3.5 μm as the measuring wavelength.

RESULTS AND DISCUSSION

The results of the propylene slurry polymerization with four catalyst systems using AlEt₃ as cocatalyst are given in Table I. Cat-A, Cat-B, Cat-C, and Cat-D represented the catalysts with donor-free, DIBP, PDDB and mixed donors as internal donors, respectively, and the first three catalysts were used as reference. As shown in Table I, different internal donors in catalysts had an important influence on catalyst activity, polymer isospecificity, molecular weight (M_w) and molecular weight distributions (MWD).

Catalyst activity

Compared with Cat-A, Cat-B and Cat-C, the Cat-D gave much higher activity under the identical poly-

merization conditions. More specifically, the activity of Cat-D was about 2 times higher that of the Cat-B and Cat-C.

To get further in depth on this catalyst behavior, it can be interpreted from the standpoint of the kinetic behaviors of propylene polymerization in Figure 1. As it can be seen, the Cat-D had the highest propylene consumption rate while the decay trends were similar to Cat-B and Cat-C. Regardless of the presence or absence of the external donor, propylene consumption rate of different catalysts always increased in the order Cat-B < Cat-C < Cat-D (see Fig. 1). This observation was in good agreement with the activity performance given in Table I. In addition, it demonstrated in Table I that the introduction of external donor slightly decreases the

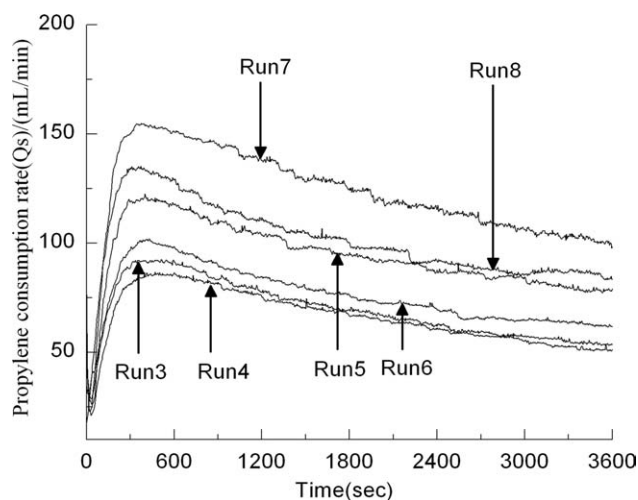


Figure 1 Rate-time profiles of propylene slurry polymerization with different catalysts Polymerization conditions: 70°C, propylene pressure = 0.11–0.13 MPa, heptane = 150 mL, catalyst = 40–60 mg, Al/Ti = 100 mr, Al/Si = 25 mr, time = 1 h.

TABLE II
Donor Content of Catalysts Treated with AlEt₃/External Donor Mixture^a

Catalyst	Treatment	Donor content, mmol/100g		
		Internal ^b		External ^c
		DIBP	PDDB	
Cat-B ([Ti] = 3.06%)	None	60	0	–
	AlEt ₃	11	0	–
	AlEt ₃ /CHMDMS	1	0	100
Cat-C ([Ti] = 2.94%)	None	0	40	–
	AlEt ₃	0	26	–
	AlEt ₃ /CHMDMS	0	19	93
Cat-D ([Ti] = 2.12%)	None	18	34	–
	AlEt ₃	8	27	–
	AlEt ₃ /CHMDMS	3	15	111

^a DIBP, diisobutyl phthalate; PDDB, 2,4-pentadiol dibenzoate; CHMDMS, cyclohexanemethyl dimethoxy silane. Contact conditions: Temperature, 70°C; time, 1h; catalyst concentration, 2 g/L, Al/Ti = 20 mr, Al/Si = 10 mr, solvent, heptane.

^b By high-performance liquid chromatographic (HPLC).

^c By wavelength disperse X-ray fluorescence analysis (WDXRF).

catalyst activity which can be ascribed to the deactivation of some active sites due to the addition of external donor.^{16–18}

In addition, Barino and Scordamaglia¹⁹ proposed that the best donors were strongly coordinated to MgCl₂. The strong coordination between the donors and MgCl₂ can be expected to stabilize energetically the surface of the supported catalyst to prevent active species from migrating from the surface. Therefore the catalyst activity was improved. According to the assumption, the catalyst activity showed a good consistence with the stability of the donor coordinated in the vicinity of the active species, which was elaborated in Table II. In other words, the catalyst activity is strongly dependent on the coordination strength between the donors and MgCl₂.

PPs isotacticity

As shown in Table I, isotacticity index (II) increased significantly with the addition of internal donor and/or external donor. The II of PP obtained by Cat-D in the presence of CHMDMS (Run 8) was the highest. It also said in Table I that the polymer prepared by the Cat-D without external donor still had high isotacticity. It is well established that the catalyst with diether as internal donor exhibits high isospecificity even in the absence of external donor, which is due to the fact that the diether is not displaced from the catalyst by the cocatalysts.^{20–22} In terms of the Cat-D, it can be assumed that mixed internal donors functions similarly as diether does,

which makes it difficult to be removed from the catalyst system in contact with alkylaluminium.

To ascertain the real relationship between the PP isotacticity and the amount of donor contained in the catalyst, we designed the experiments via exchange reaction between the solid catalyst and the AlEt₃ solution or AlEt₃/external donor mixture. It is known that part of internal donors will be replaced by AlEt₃ or external donor when the solid catalyst is contacted with AlEt₃ or AlEt₃/external donor mixture.^{3,23} The donor content of Cat-B, Cat-C and Cat-D after treatment with AlEt₃ or AlEt₃/external donor mixtures is given in Table II. The contact conditions were similar to polymerization conditions (see the Experimental Section). As shown in Tables I and II, for Cat-B, most of DIBP was extracted from the catalyst surface by TEA, indicating the weaker interaction between DIBP and MgCl₂ as compared to TEA, which results in the relatively low isotacticity (80.9%, Run 3 in Table I). In contrast to Cat-B, more than half of PDDB still remained in Cat-C, which suggests the presence of greater affinity of PDDB towards MgCl₂ than TEA. As a result, highly isotactic polypropylene can also be obtained even in the absence of external donor (94.5%, Run 5 in Table I). Nevertheless, in contrast to the DIBP- and PDDB-based catalyst systems, the amount of the remaining mixed internal donors was much higher. As a consequence, the isotacticity index (II) of polymer produced by Cat-D without external donor still reached the highest value of 95.7% (Table I, Run 7), which can be ascribed to the synergistic effect between PDDB and DIBP. Based on the results so far, it could be concluded that the coordination strength of internal donors to MgCl₂ is in the order DIBP < PDDB < mixed internal donors (see Tables II), which is consistent with the isotacticity of PPs increasing in the order of DIBP < PDDB < mixed internal donors in Table I.

For the same catalyst, after the introduction of a small quantity of external donor, a gradual decrease of the internal donor was observed in accompany with the fixation of increasing amounts of the external donor, which lead to the increase of isotactic index to a great extent (see Tables I and II). In addition, for several different catalyst systems, it was found that the catalysts with the highest stereospecificity were those in which the external donor was able to absorb on the solid catalysts to the largest extent. Therefore, the isotacticity of the polymer strongly depends on the degree of the exchange of internal/external donors in the presence of both internal and external donors during propylene polymerization. These findings are in accordance with the results reported by Soga et al. and Sacchi et al.^{24,25}

TABLE III
Pentad Sequence Distributions of Heptane Insoluble Fraction of Polymers (in %)

Polymer	Pentad sequence distribution of iso-PPs (%)								
	mmmm	mmmr	rmmr	mmrr	mmrm + rmrr	rmrm	rrrr	rrrm	mrrm
Run1	86.8	4.0	0.7	2.6	1.9	0.3	1.4	1.3	1.0
Run3	90.0	3.8	0.2	2.6	0.9	0.1	0.6	0.7	1.1
Run5	91.9	2.5	0.4	1.8	1.0	0.2	0.9	0.9	0.4
Run7	93.9	2.3	0.2	1.4	0.6	0.1	0.5	0.4	0.6
Run8	95.5	2.0	0.2	1.0	0.5	0.1	0.3	0.2	0.2

¹³C-NMR and CRYSTAF analysis of PPs

¹³C-NMR and crystallization analysis are widely used to study the microstructure of PPs. Part of the isotactic PPs (abbr. iso-PPs) in Table I were selected for ¹³C-NMR analysis. The pentad sequence distributions of these iso-PPs are listed in Table III.²⁶ The ¹³C-NMR data in Table III indicates that the internal donors affect the stereoregularity of iso-PPs. It was observed that the [mmmm] value obtained from the Run7 were much higher than that of others in the absence of external donor.

Busico et al.²⁷ proposed that active species in MgCl₂-supported catalyst can isomerizes very rapidly between three different propagating species, namely, a “three sites” model. PP produced with MgCl₂-supported catalysts consists of three different types of stereosequences: highly isotactic, moderately isotactic (isotactoid), and syndiotactic (See Fig. 2). It suggested that a stable donor coordination in the vicinity of active species gave higher stereoregularity than a labile donor coordination in the polymer chain.²⁸ According to the model, for Cat-A, Cat-B, Cat-C and Cat-D, donors coordinated to a Mg atom adjacent to Ti atom are chloride atoms, DIBP, PDDB and mixed internal donors, respectively. It was reported that the steric hindrance from chloride atoms was so small that the active sites are liable to fluctuate,²⁹ resulting in low [mmmm] value and a lot of sequence defects. As shown in Table II, most of DIBP was displaced from the catalyst surface as a result of the alkylation and/or complexation reac-

tions with AlEt₃. While PDDB wasn't so easy to be removed from the catalyst surface, as a result, the [mmmm] value was higher than that of DIBP. In contrast, the mmmm pentads of the isotactic fraction from Cat-D distributed the most regularly, possibly because the remaining mixed internal donors strongly coordinate to the surface of the catalyst. We propose that highly isotactic species of the Cat-D are difficult to convert into moderately isotactic species or weakly isotactic species. Consequently, it proves that the introduction of strongly coordinating groups (eg. bulky alkyl) instead of weakly coordinating groups (eg. chlorine atoms) into the neighborhood of active sites is vital for generating the active sites with the highest isospecificity.³⁰

In Table III, Run 7 and Run 8 support that more stereoregular polypropylene formed in the presence of external donor. The possible explanation is that the external donor has much stronger stereoregulating effect to stabilize the surface structure and alleviate species migration.

Crystallization analysis fractionation (CRYSTAF), which in principal is similar to TREF, is widely used for analysis of semicrystalline materials on the basis of the principle of crystallizability.³¹ In recent years, this analytical technique has found increasing application for the characterization of polymers prepared using MgCl₂-supported catalysts.^{32,33}

To order to understand more about the polymers, CRYSTAF analysis corresponding to ¹³C-NMR samples are given in Table IV and plotted in Figure 3.

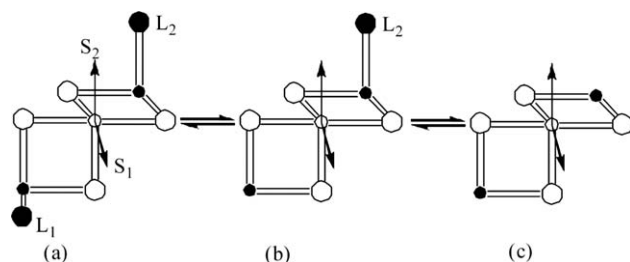


Figure 2 Possible models of active species for highly isotactic (a), isotactoid (b) and syndiotactic propagation (c).²⁷ ○ = Ti; ● = Ti or Mg; ○ = Cl; ● = Cl or donor, S₁ and S₂ are vacant positions.

TABLE IV
Results Obtained from CRYSTAF^a

Polymer	T_w (°C)	R	Crystallization fraction (%)		Ratio (Hi:Mi)
			Mi < 65°C	Hi ≥ 65°C	
Run1	72.1	0.8	3.0	97.0	32.3
Run3	73.4	0.6	1.9	98.1	51.6
Run5	73.9	0.7	1.7	98.3	57.8
Run7	73.1	0.4	1.4	98.6	70.2
Run8	75.1	0.3	1.3	98.7	76.9

^a Weight-average temperature: $T_w = \sum c_i T_i / \sum c_i$; number-average temperature: $T_n = \sum c_i / \sum (c_i / T_i)$; dispersion parameters: $R = 100 \times (T_w / T_n - 1)$.

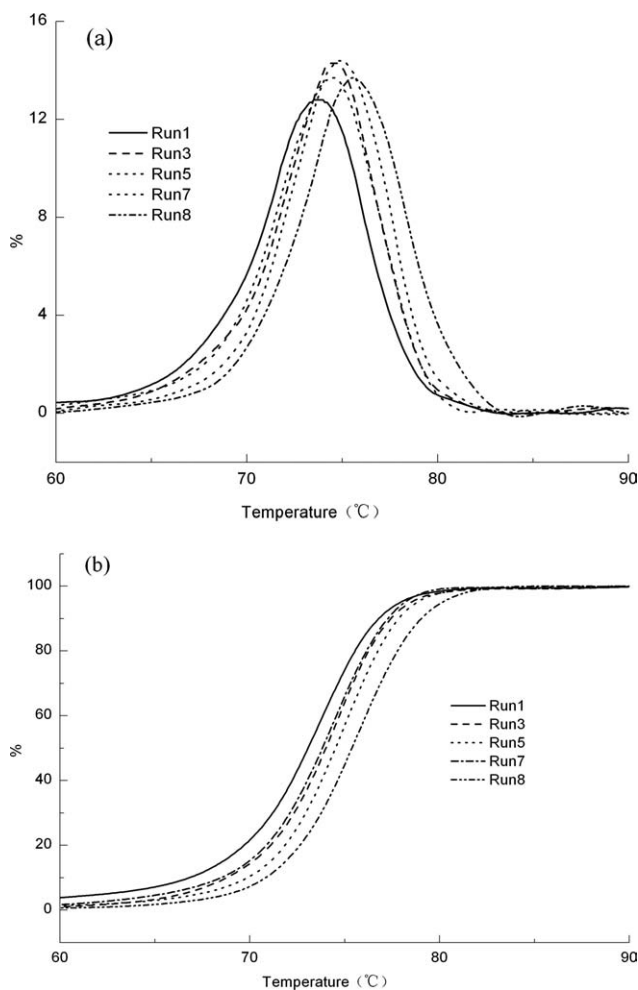


Figure 3 (a) CRYSTAF crystallization temperature profiles. (b) Cumulative fraction as a function of temperature obtained from CRYSTAF of samples in Table III.

The fractions of crystallization temperature above 65°C are considered as a highly isotactic fraction and the fraction of crystallization temperature below 65°C as an isotactoid fraction. From the CRYSTAF results in Table IV and Figure 3, internal donors affected iso-PPs crystallization behavior. Additionally, after the addition of external electron donor, weight average crystallization temperature (T_w) increased along with the significant increase of Hi:Mi and the decrease of dispersion parameters (R). It is apparent that the Hi:Mi values of the polymers decreases in the same order Run8 > Run7 > Run5 > Run3 > Run1. These results are in line with the measured $[mmmm]$ values. It reflects that the crystallizability of PPs is closely related to the microtacticity of PPs, as was reported by other authors.³⁴

GPC characterization of PPs

The effect of different catalysts on the M_w and MWD are shown in Table I. The molecular weight of the

polymer without an external donor decreased in the order Run7 > Run5 > Run3 > Run1 and corresponding polymer MWD decreased in the series Run1 > Run7 > Run3 > Run5. This can be explained that the catalyst system without internal and external donors gave a significant fraction of defect-rich polymer (Table III, Run1). It may be the result of active sites interconverting rapidly due to the weak coordination of chloride atom to MgCl₂. Meanwhile, the rapid interconversion results in relatively low M_w and broad MWD, on account of an increase in the probability of chain transfer associated with a lowering in site selectivity. Compared with Cat-A, DIBP is more stable than chloride atom in vicinity of the active species so that relative slow transformations of active species lead to the increase of M_w and the decrease of MWD. Table II point out that PDDB used as internal donor has greater affinity towards MgCl₂ than DIBP. So PPDB coordination near the active species is more stable than DIBP so that highly isotactic active sites are difficult to convert into moderately and syndiotactic active sites. This caused not only the increase of M_w but also the decrease of MWD. In addition, Table II point out that coordination stability of the mixed internal donors is much higher than that of others. According to the explanation mentioned above, in the Cat-D, the M_w of the polymer should be the highest with the narrowest MWD. Table I shows the M_w is in line with the law, however, the MWD is not. Indeed, the Cat-D gives a significant proportion of highly isotactic active sites, leading to high molecular weight and stereoregular polymer but doesn't obtain the narrowest MWD. We assume that this system also contains a certain proportion of species for which high selectivity is not dependent on the presence of an electron donor in immediate vicinity of the active sites.^{28,35}

When a small amount of external donor was added, the M_w of the resulting polymer was higher and MWD becomes narrower, probably due to the silane stabilizing "fluctuating" isospecific sites.²⁸

CONCLUSIONS

The catalyst containing mixed internal donors had high activity, stereospecificity and relatively broad molecular weight distribution of the resulting polymer, which might be ascribed to the synergistic effect between PDDB and DIBP.

The amount of remaining mixed internal donors was higher than that of DIBP or PDDB after the catalysts treated by AlEt₃/external donor. The coordination strength of internal donors to MgCl₂ surface was in the following order DIBP < PDDB < mixed internal donors.

From ^{13}C -NMR results, the stronger the coordinating ability of donors is, the better stereoregularity of the polymers chain will be.

Polymer yield, isotacticity, molecular weight and molecular weight distribution were mainly dependent on the liability of donor coordination in the vicinity of the active actives.

A more detailed study is now in progress and the results will be published in another article.

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