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THE ROLE OF PHENYLTRIETHOXYSILANE AS AN INTERNAL DONOR FOR THE PROPYLENE POLYMERIZATION OVER BuMgCl-BASED TITANIUM CATALYST

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Abstract—The effect of phenyltriethoxysilane (PTES) as an internal donor, on propylene polymerization with butylmagnesium chloride (BuMgCl)-based titanium catalyst has been investigated in terms of activity and stereospecificity. The X-ray diffraction (XRD) pattern of the catalytic system including PTES as internal donor showed that $TiCl_4$ did not seem to diffuse into the interlayer of the $MgCl_2$-support matrix. In comparison with the ethylbenzoate (EB)-containing or donor-free catalyst, the catalyst (MPT) with PTES as an internal donor alone showed a significant increase in isotacticity but a decrease in the catalytic activity. FTIR analysis suggested that the interaction of PTES with the catalytic titanium species seemed to be stronger than that of EB. The polypropylene prepared from the MPT catalyst showed a lower molecular weight, and the molecular weight distribution is broader (somewhat bimodal). Microstructure analysis of the boiling heptane–soluble polymer also indicated that PTES as an internal donor alone could selectively deactivate non-stereospecific active sites even without external donors. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

In propylene polymerization, the electron donor plays a major role in controlling the stereospecificity in highly active Mg-supported Ziegler–Natta catalysts [1, 2]. The role of electron donor, internal donor as a modifier in the catalyst precursor and/or external donor as a cocatalyst with aluminum alkyl, was somewhat unclear and even controversial due to the multiplicity nature of the catalytic active site. Until recently the effect of electron donors, especially external donors, on catalytic active sites has been discussed in various ways [3–13] : (1) the selective poisoning of non-stereospecific sites, (2) the transformation of non-stereospecific sites into stereospecific sites, (3) enhancement of the active site concentration and the propagation rate constant of the isospecific sites, and/or (4) the decrease in the alkylaluminum reducing power. It is generally believed that the external donors can interact with the active sites.

The role of internal donors, however, is ambiguous. Terano *et al.* [14] and Yano *et al.* [15] proposed that $TiCl_4$ and ethylbenzoate (EB) are supported independently at separate sites of $MgCl_2$, while Rytter *et al.* [16] and Soga *et al.* [5] insisted that EB can interact with both $MgCl_2$ and $TiCl_4$. Also, in the model of Busico *et al.* [3, 4], internal donors have no effect on isospecific active sites and inhibit the formation of aspecific sites through titanium fixation on $MgCl_2$. On the other hand, Sacchi *et al.* [17] suggested that internal donors can change the steric feature of the isospecific active sites and enhance the stereoregularity of the obtained polypropylene.

In general, both internal and external donors are needed to improve the catalytic activity and stereospecificity of propylene polymerization. The particular combination of internal and external donors has a significant effect on the catalytic performance, and there exist some donor exchanges during the polymerization [17–20]. In addition, a complex between aluminum alkyl and external donor may take part in the formation of isospecific active sites [5, 8, 21, 22], while the external donor itself was believed to be an actual stereoregulating agent [23, 24].

In the present work, highly active titanium catalysts for propylene polymerization were prepared with an $MgCl_2$ support which was obtained by the chlorination of *n*-butylmagnesium chloride (BunMgCl). In order to gain more insight into the effect of electron donors on the catalytic active sites, the performance of PTES-containing catalyst is compared with that of EB-containing catalyst

Table 1. Notation of supports and catalysts

Support	Internal donor	Catalyst
BM	–	BMT
M	–	MT
ME	Ethylbenzoate (EB)	MET
MP	Phenyltriethoxysilane (PTES)	MPT

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Table 2. Chemical composition and surface area of supports and catalysts prepared with different internal donors

	Sample	Surface area (m^2/g)	Ti (wt %)	THF (wt %)	ID[a]/Mg (mol/mol)
Support	BM[b]	8	–	–	–
	M	31	–	10.2	–
	ME	45	–	2.2	0.22 (EB)
	MP	39	–	4.3	0.20 (PTES)
Catalyst	BMT	25	3.0	–	–
	MT	240	4.5	n.d.[c]	–
	MET	262	3.5	n.d.	0.13 (EB)
	MPT	198	6.0	n.d.	0.11 (PTES)

[a] ID, internal donor.
[b] ball-milled $MgCl_2$.
[c] not detected

and also with that of donor-free catalyst. Characterizations were made by elemental analysis, X-ray diffraction (XRD), FTIR, and ^{13}C-NMR. Discussions have been made on the role of PTES in terms of molecular weight (distribution) and the stereoregularity of polymer.

EXPERIMENTAL

Catalyst preparation

All the operations for the catalyst preparation were conducted in a dry, deoxygenated nitrogen atmosphere. 75 ml of BuMgCl (2 M in THF) was added dropwise to 500 ml Schlenk reactor containing 200 ml of $SiCl_4$ at 0°C over 30 min. After the addition was completed, the temperature was kept at 0°C for 1 hr and gradually raised to room temperature. Subsequently, the temperature was raised to 50°C and the mixture was stirred at that temperature for 2 hr. After filtering the formed white precipitate (M), the support was washed five times with hexane and dried under vacuum at 30°C for 2 hr. The support (5 g) was suspended in hexane (50 ml) followed by addition of the fixed amount of electron donor (donor/Mg = 0.33, mole ratio) and reacted for 2 hr at 50°C. The support containing electron donor was separated by filtration and washed five times with hexane. The solid treated with electron donor was activated with 50 ml of $TiCl_4$ for 2 hr at 90°C. The resulting solid catalyst was obtained by hot filtration, washing five times with hexane (50 ml), and vacuum drying. The support and catalyst are denoted in Table 1 depending on the internal donor.

A ball-milled catalyst denoted by BMT was prepared for comparison; 4.76 g of anhydrous-$MgCl_2$ were ground in a Fritsch Pulverisette ball mill at room temperature for 2 hr, and activation with $TiCl_4$ was carried out.

The detailed procedures of polymerization and characterization of polymers have been described elsewhere [13].

Characterization of catalysts and polymers

The content of Ti and Mg was measured by an inductively coupled plasma spectrophotometer, and the content of electron donor and THF in the solid sample was measured by gas chromatography (GC). The specific surface area of supports and catalysts was measured by nitrogen adsorption technique at 78 K with Area Meter II. Powder XRD using CuKα radiation was obtained at 30 KeV and 25°C. Powdered samples were loaded into a sample holder with a poly(ethylene terephthalate) film window under nitrogen atmosphere. Diffraction patterns of samples were taken in the range $5° < 2\theta < 60°$. The β-form of the $MgCl_2$ sample was prepared by dehydrating $MgCl_2 \cdot 6H_2O$ with $SOCl_2$ at 78°C for comparison [25]. FTIR spectra were recorded under a nitrogen atmosphere on a Bomem MB-102 spectrometer with a sample wafer mixed with KBr powder.

The ^{1}H-decoupled ^{13}C-NMR spectra of the polymer was recorded at 120°C using a Bruker AMX-500 spectrometer operating at 125.6 MHz. Sample solutions of polypropylene were made in *o*-dichlorobenzene/benzene-d_6 up to 15 wt.%. Tetramethylsilane was used as an internal standard. The molecular weight and molecular weight distribution were measured by gel permeation chromatography (Waters 150 CV) at 135°C with 1,3,5-trichlorobenzene as solvent.

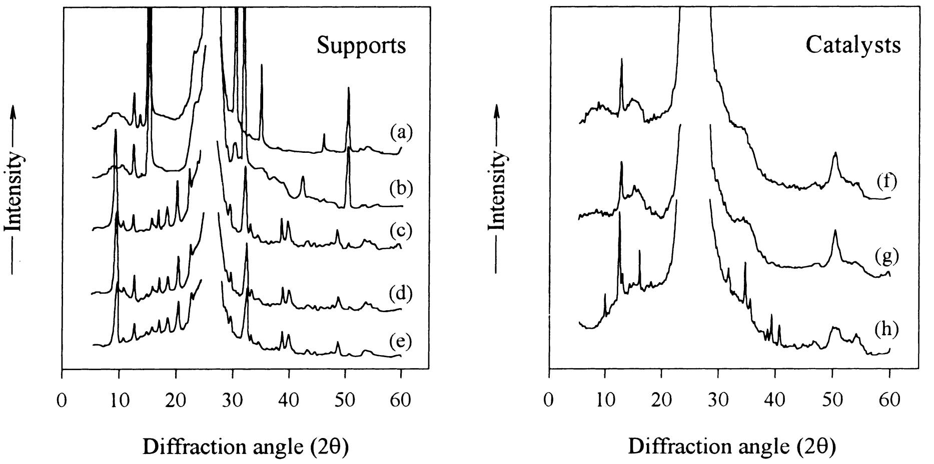

Fig. 1. Powder X-ray diffraction patterns of the supports and catalysts: (a) α-$MgCl_2$, (b) β-$MgCl_2$, (c) M, (d) ME, (e) MP, (f) MT, (g) MET, (h) MPT.

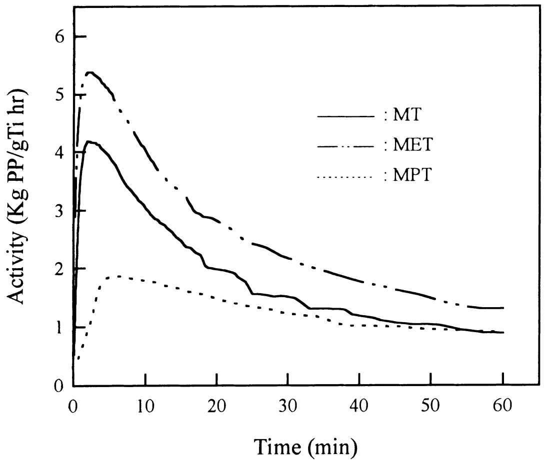

Fig. 2. The kinetic curves of propylene polymerization for each catalyst ([Ti] = 0.2 mM, T = 50°C, propylene = 0.3 atm, hexane = 100 ml, [Al]/[Ti] = 50 (mole ratio), no external dono).

RESULTS AND DISCUSSION

Effect of electron donor on the chemical composition and surface area

The chemical composition and specific surface area of supports and catalysts are given in Table 2. It is well known that BuMgCl is chemically converted into anhydrous $MgCl_2$ by the chlorinating agent $SiCl_4$. Each of the supports (M, ME and MP) prepared by chemical conversion of BuMgCl showed a higher surface area than the mechanically activated $MgCl_2$ (BM). The surface area increased drastically through the addition of internal donor, as shown in Table 2. The internal donor seems to prevent the microcrystallites in the $MgCl_2$ support from being agglomerated. Treatment of the resulting solid support with $TiCl_4$ gave a drastic increase in the specific surface area possibly due to the lubricating effect of $TiCl_4$ [26]. In particular, the catalyst MPT showed a lower surface area and higher titanium content than the catalysts MT and MET. Because the BuMgCl reagent is stored in THF solvent, a lot of THF remained in the $MgCl_2$ supports. However, after the treatment of supports with excess $TiCl_4$, THF was almost completely removed, while a significant portion of electron donors (EB, PTES) remained in the catalysts.

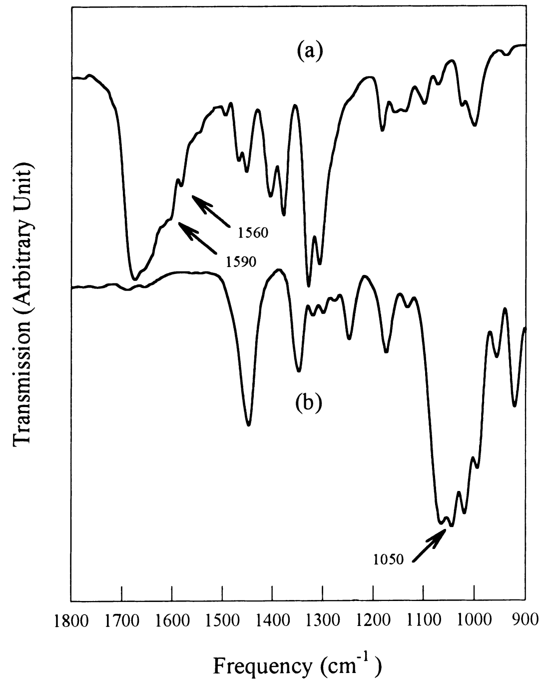

Fig. 3. FTIR spectra of catalysts: (a) MET and (b) MPT.

X-ray diffraction analyses

Figure 1 shows the XRD peak pattern of supports and catalysts prepared by chemical conversion. The broad peaks at 21–28° are due to the polymer (PET) film window. The structure of each support remained almost unchanged with different internal donors and most of the strong peaks are located in a lower angular region than 15°. In the case of supports, the (103) reflection at 15° in the α, β-$MgCl_2$ disappeared and a new strong reflection at 10° appeared. It indicates that the donors are coordinated along the $MgCl_2$ to give a comparable steric hindrance [27].

The α-form of $MgCl_2$ most appearing in the mechanically pulverized or recrystallized $MgCl_2$ supports has the cubic close packed (ccp) structure and was characterized by the intense reflection at (104) directions at 35° [1], whereas a strong reflection at the (101) direction located at 32° is characterized by the β-form of $MgCl_2$ with a hexagonal close packed (hcp) structure [25]. All the chemically converted $MgCl_2$ supports have a strong reflection

Table 3. Catalytic activity and isotacticity for propylene polymerization with BuMgCl-based Ti catalysts[a]

Catalyst	Al/Ti (mole ratio)	Activity (g-PP/g-Ti h)	I. I[b] (wt. %)	mmmm (%)[c]
MT	10	3375	64	–
MT	50	2823	69	51.6
MT	100	1774	61	–
MET	10	5351	75	–
MET	50	3663	71	52.0
MET	100	2496	57	–
MPT	10	1474	73	–
MPT	50	1342	77	71.4
MPT	100	1035	78	–

[a] Polymerization conditions: [Ti] = 0.2 mM, propylene = 0.3 atm, hexane = 100 ml, T = 50°C, t = 1 hr.
[b] Isotactic index: boiling heptane-insoluble fraction.
[c] Unfractionated polypropylene

Table 4. Effect of electron donors on the molecular weight[a]

	Overall		Isotactic[b]		Atactic	
Catalyst	$M_w \times 10^{-4}$	M_w/M_n	$M_w \times 10^{-4}$	M_w/M_n	$M_w \times 10^{-4}$	M_w/M_n
MT	15.5	5.2	24.3	3.1	6.3	3.5
MET	14.8	5.9	26.1	3.6	7.1	3.7
MPT	10.8	9.2	25.8	3.8	3.3	4.0

[a] Polymerization conditions: [Ti] = 0.2 mM, propylene = 0.3 atm, hexane = 100 ml, T = 50°C, [Al]/[Ti] = 50, t = 1 hr.
[b] The whole polymer was separated into isotactic and atactic parts by extracting it with boiling heptane

at $2\theta = 32°$ suggesting that the hcp structures are abundant in the supports. There were no differences in the XRD patterns with respect to each internal donor. Upon treatment with $TiCl_4$, the (110) reflection at 49° was recovered significantly and the (101) reflection was broadened in the case of catalysts MT and MET, which indicates the structural disorder of the $MgCl_2$ support due to activation with $TiCl_4$ or an increase in the surface area [26, 28]. However, most of the characteristic peaks for the MP support were retained in the catalyst MPT which showed a lower surface area as shown in Table 2. It seems that $TiCl_4$ cannot diffuse into the interlayer of the $MgCl_2$ matrix containing PTES and cannot facilitate the formation of crystal cleavage in $MgCl_2$.

Kinetic behavior of polymerization

Figure 2 shows the typical kinetic curves of propylene polymerization with $Al(C_2H_5)_3$ (TEA) as cocatalyst. The polymerization rate of the catalyst MET was higher than that of the catalyst MT and lower than that of the catalyst MPT. The rate–time profiles are quite different. The catalysts MT and MET showed a rather fast deactivation, while the catalyst MPT showed a slower deactivation as well as slower activation. The rate of decay of propylene polymerization has been attributed to the deactivation of active sites by TEA, resulting in the reduction of Ti species [3, 29]. The active sites modified by PTES as internal donor seem to be hardly affected by TEA.

The effects of the Al/Ti mole ratio (or the TEA concentration) on the activity and the isotacticity were shown in Table 3. Regardless of TEA concentration, the catalytic activity was found to decrease according in the following order: MET > MT > MPT. Also, these catalysts showed a decrease in activity with an increase in the concentration of TEA. Among the catalysts investigated, the catalyst MPT showed the highest isotacticity, which was confirmed by ^{13}C-NMR analyses of the obtained polymer to show the highest fraction of the *mmmm* isotactic pentad. It should be noted that with an increase in concentration of TEA, the isotacticity (I.I) increased for the catalyst MPT while it decreased for the catalyst MET.

The kinetic feature of catalyst MET could be explained by the weak interaction between EB and the active sites resulting in higher deactivation rate and lower isotacticity with TEA concentration, as proposed by Soga *et al.* [5]. In this regard, the internal donor PTES in the catalyst MPT seems to make strong interaction with the active sites, resulting in the TEA–PTES complex.

In order to better understand the different kinetic behavior between MET and MPT catalysts, the interaction between the electron donor and the Ti species was investigated by IR spectroscopy. Figure 3 depicts the IR spectra of (a) MET and (b) MPT catalysts, respectively. Two peaks at 1560 cm^{-1} and 1590 cm^{-1} in Fig. 3(a) has been characterized as the C=O bond stretching mode of the $(TiCl_4\text{–}EB)_2$ complex [13–15]. In the case of the catalyst MET,

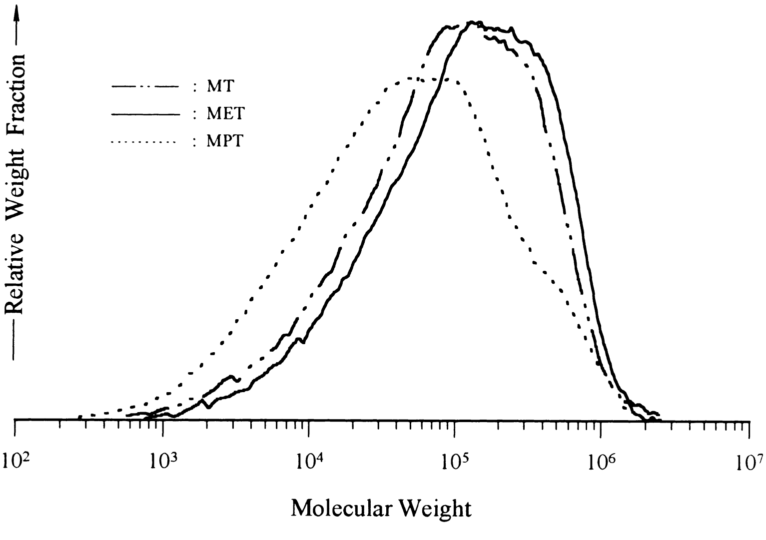

Fig. 4. Molecular weight distribution of polypropylene obtained with BuMgCl-based Ti catalyst in the absence of external donor (T = 50°C, propylene = 0.3 atm, [Al]/[Ti] = 50 (mole ratio), t = 1 hr).

Table 5. ^{13}C-NMR pentad sequence distributions (in %) of the fractions of boiling heptane extraction[a]

Catalyst	*mmmm*	*mmmr*	*rmmr*	*mmrr*	*mmrm* + *rmrr*	*rmrm*	*rrrr*	*mrrr*	*mrrm*
				Heptane-insoluble polypropylene					
MT	83.9	4.9	2.1	3.6	1.5	0.9	0.8	1.1	1.1
MET	81.9	5.8	1.3	3.7	1.9	0.8	1.3	0.8	2.4
MPT	82.5	6.1	1.8	3.9	1.6	0.4	1.1	0.6	2.0
				Heptane-soluble polypropylene					
MT	39.0	11.1	3.0	11.0	10.3	3.1	9.2	7.2	6.1
MET	44.3	10.5	3.1	10.3	8.4	3.5	8.5	6.4	5.0
MPT	52.7	8.6	2.2	7.9	5.8	1.9	10.7	5.6	4.6

[a]Polymerization conditions as mentioned in Table 4

these peaks appeared very weak, while the peak at 1690 cm^{-1} indicating formation of the EB-MgCl$_2$ complex appeared very strong. Therefore, EB on the catalyst MET might hardly interact with Ti species, as suggested by Terano *et al.* [15] and Yano *et al.* [16]. On the other hand, a strong and broad band at 1050 cm^{-1} appeared in the catalyst MPT, which is a typical stretching frequency of a C—O single bond of titanium alkoxide [30, 31]. The decrease of activity and the lower decay rate of propylene polymerization obtained by the catalyst MPT could be explained by the formation of a Ti—O—C moiety, i.e. strong interaction between PTES and TiCl$_4$. The IR investigation of catalyst may not be sufficient for explaining the enhancement of isotacticity when the PTES was used as in-

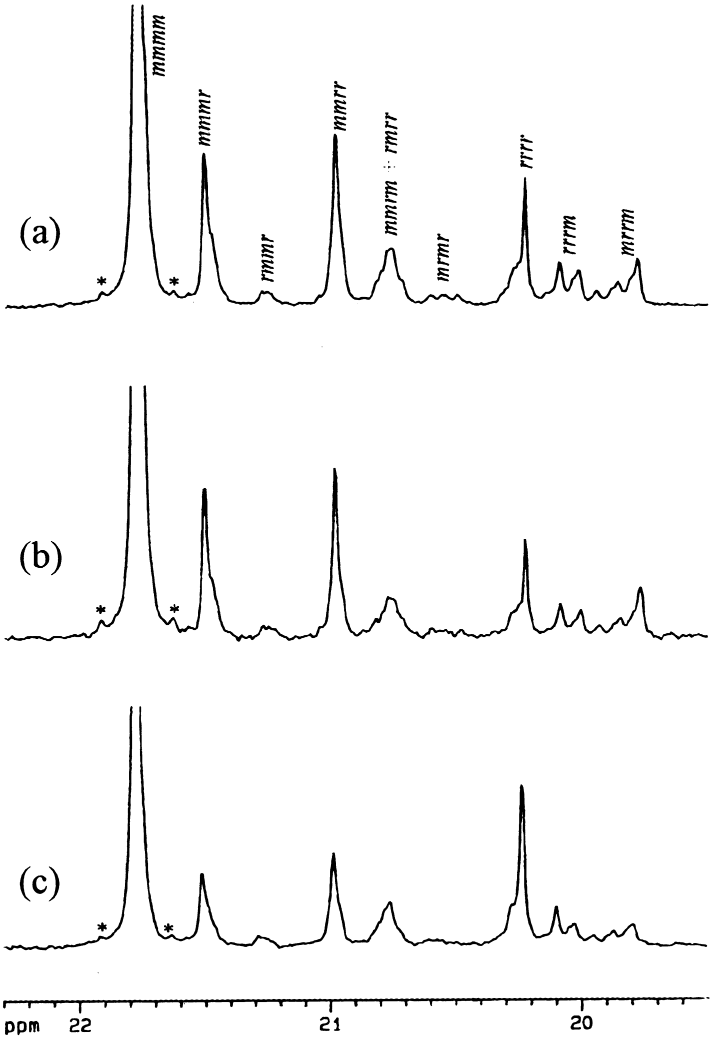

Fig. 5. Methyl region of the ^{13}C-NMR spectra of heptane-soluble fraction of the polypropylene obtained with catalyst (a) MT, (b) MET, (b) MPT, respectively. The asterisks indicate the ^{13}C satellite bands.

ternal donor, and the molecular weight distribution and microstructure of obtained polypropylene were investigated.

Molecular weight and microstructure of propylene polymer

Table 4 shows the molecular weight distribution (MWD) of the propylene polymer produced by the BuMgCl-based Ti catalysts as measured by gel permeation chromatogrphy. The molecular weight of the polymer produced by the catalyst MPT was smaller and its MWD (referred to as M_w/M_n) was broader. The MWD of the heptane-insoluble (isotactic) fraction and the heptane-soluble (atactic) fraction of obtained polypropylene does not seem to be affected by the addition of internal donor. The molecular weight of the isotactic fraction was almost the same regardless of the use of internal donor, whereas the molecular weight of the atactic portion produced by the catalyst MPT showed a significant decrease. Also, the MWD curve of the polymer obtained by the PTES-containing catalyst appeared to be of bimodal nature as shown in Fig. 4, which strongly suggested that there exist at least two kinds of active sites due to the modification of active sites by PTES.

In order to investigate the stereoregulating effects of the internal donor, microstructure analysis was carried out for insoluble and soluble polypropylenes of the boiling heptane, respectively, and the results are shown in Table 5. The boiling heptane-insoluble fractions of polymer obtained by each catalyst had almost the same pentad sequence distribution conforming well to the site-controlled stereochemistry ($\sigma \approx 0.97$, where σ is the probability of the enantiomorphic site model [32]). Therefore, it could be safely stated that PTES as internal donor does not take part in the formation of stereospecific sites. However, in the boiling heptane-soluble fractions of polymer, PTES as internal donor revealed a significant increase in the size of the syndiotactic *rrrr* pentad as well as the isotactic *mmmm* pentad (Fig. 5 and Table 5). On the other hand, Pino *et al.* [6] and Härkönen *et al.* [7] also observed that the syndiotactic *rrrr* pentad increased with the addition of external donor. The increase of stereoregularity, or syndiotactic *rrrr* pentad, was attributed to the selective deactivation of non-stereospecific sites by external donor. Thus, from the obtained results of the catalyst MPT, PTES as internal donor seems to be sufficient for the selective deactivation of non-stereospecific sites even without using external donors.

CONCLUSIONS

The role of PTES as an internal donor on propylene polymerization with $TiCl_4$ catalysts supported on the $MgCl_2$, which was prepared by BuMgCl as a starting material, has been investigated in terms of activity and stereospecificity. The hexagonal close packed structure was found to be abundant in chemically converted $MgCl_2$. The PTES-containing catalyst showed higher titanium content and smaller surface area, and $TiCl_4$ did not seem to diffuse into the layer of $MgCl_2$-support matrix. The polymer obtained by the PTES-containing catalyst showed a significant increase in isotacticity, a decrease in activity and a diminution in the decay rate. PTES as internal donor seems to form a complex with $TiCl_4$ and modify the active sites, resulting in the formation of more than one kind of active site. The molecular weight distribution and microstructure analyses seem to indicate that PTES as an internal donor selectively poisoned the non-stereospecific active sites even without the external donors.

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