

## Additive Effects of Lewis Bases on Propene Polymerization over MgCl<sub>2</sub>-Supported TiCl<sub>4</sub> Catalysts Combined with Cp<sub>2</sub>TiMe<sub>2</sub>

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**ABSTRACT:** Propene polymerization was conducted with TiCl<sub>4</sub>/(Lewis base)/MgCl<sub>2</sub>-Cp<sub>2</sub>TiMe<sub>2</sub> catalysts in the presence of ethyl benzoate (EB) and/or 2,2-diisobutyl-1,3-dimethoxypropane (DBDMP). The addition of small amounts of these Lewis bases to MgCl<sub>2</sub> before supporting TiCl<sub>4</sub> decreased the amount of Ti in the catalyst and improved catalyst isospecificity. The results suggested that the Lewis base is selectively coordinated on the MgCl<sub>2</sub> surface where specific sites had been formed. The addition of the Lewis bases during the polymerization increased polymerization rate followed by rapid deactivation. Deactivation was second order on the polymerization rate and the deactivation rate constant depended on both structure and amount of the Lewis base. GPC analysis of the produced polymers indicated that the addition of the Lewis bases increased the molecular weight of isotactic polypropene (IPP). Polydispersity depended on the Lewis base: it became narrower by EB and broader by DBDMP. The <sup>13</sup>C NMR spectra of IPPs revealed that EB improved the microtacticity of IPP more effectively than DBDMP. ESR spectra of the catalysts indicated that the amount of isolated Ti<sup>3+</sup> species increased in the presence of EB.

**KEY WORDS** Polypropene / Lewis Base / Isotacticity / Polydispersity / MgCl<sub>2</sub>-Supported TiCl<sub>4</sub> Catalysts / Cp<sub>2</sub>TiMe<sub>2</sub>

In propene polymerization, it is of great importance to control stereoregularity, molecular weight and molecular weight distribution (MWD) of the produced polymer. The stereospecificity of MgCl<sub>2</sub> supported Ti catalysts can be improved by suitable Lewis bases. Two Lewis bases are generally needed to obtain a catalyst with high stereospecificity. One is used in catalyst preparation (internal donor) and the other is used in polymerization process (external donor). Usually donor compounds improve the amount and microtacticity of isotactic polypropene (IPP). Many articles discuss the functions of the donor compounds.<sup>1–7</sup> However, the reactivity of the donors toward alkylaluminum and MgCl<sub>2</sub> has prevented us from clarifying the precise mechanism of improvement. Recently, Albizzati *et al.* reviewed their work concerning the additive effects of the donors.<sup>8</sup> According to them, the main effect of an internal donor is to prevent the formation of non-stereospecific site on the (110) cut of MgCl<sub>2</sub>, whereas, an external donor prevents the extraction of an internal donor by alkylaluminums or replaces with the internal donor. They also showed that a suitable internal donor like hindered diethers was very effective without any external donor because of its low reactivity toward alkylaluminum.

Therefore, if cocatalyst is changed from alkylaluminum to other alkylmetals, the effects of donors might be different. Hercules Inc. reported that the TiCl<sub>3</sub>/(RCp)<sub>2</sub>TiMe<sub>2</sub> catalyst caused isospecific polymerization of propene in living manner although the activity was low.<sup>9</sup> We previously found that TiCl<sub>4</sub>/MgCl<sub>2</sub>-Cp<sub>2</sub>TiMe<sub>2</sub> catalyst achieved isospecific polymerization with high activity even in the absence of internal and external donors.<sup>10</sup> Since Cp<sub>2</sub>TiMe<sub>2</sub> is coordinately saturated and less reactive to Lewis bases than alkylaluminums, it is

expected that effects of donor compound on the active Ti species should be observed more clearly in this catalyst system.

In this study, propene polymerization was conducted with the TiCl<sub>4</sub>/MgCl<sub>2</sub>-Cp<sub>2</sub>TiMe<sub>2</sub> catalyst in the presence of ethyl benzoate (EB) and/or 2,2-diisobutyl-1,3-dimethoxypropane (DBDMP) as typical donor compound.

### EXPERIMENTAL

#### Materials

Propene (from Mitsubishi Petrochemical Co.), MgCl<sub>2</sub> (80 m<sup>2</sup>/g, from Toho Titanium Co.), and TiCl<sub>4</sub> (from Kanto Chemicals Co.) were used without further purification. Research grade heptane and ethyl benzoate (EB) commercially obtained were purified according to the usual procedures. 2,2-Diisobutyl-1,3-dimethoxypropane (DBDMP) was synthesized according to the literature.<sup>11</sup>

#### Catalysts Preparation

MgCl<sub>2</sub> (9.5 g) was brought in contact with EB or DBDMP (0, 0.1, or 0.2 mmol) in toluene (50 ml) under vigorous stirring at room temperature for 3 h. TiCl<sub>4</sub> (0.8 mmol) was added to the slurry and the mixture was stirred for 10 h. After the supernatant was decanted, the solid residue was washed with toluene until the solution became colorless.

#### Polymerization

Propene polymerization was conducted in a 0.2 dm<sup>3</sup> glass reactor equipped with a magnetic stirrer. After measured amounts of the catalyst and heptane were added to the reactor, the solvent was saturated with atmospheric pressure of propene at 40°C. Polymerization was started by introducing Cp<sub>2</sub>TiMe<sub>2</sub> as cocatalyst into the reactor. EB or DBDMP was added after 0.1 dm<sup>3</sup>

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(STP) of monomer was consumed if necessary. Polymerization was terminated by adding dilute hydrochloric acid in methanol.

#### Analytical Procedure

The content of titanium in the catalyst was determined by inductively coupled plasma spectrometry (Seiko SPS-1500VR). The content of EB or DBDMP was determined by gas chromatography (GL Sciences GC 353). Electron spin resonance (ESR) spectra were recorded at  $-100^{\circ}\text{C}$  on a JEOL JES-RE3X spectrometer. ESR samples were prepared by adding 0.01 mmol of  $\text{Cp}_2\text{TiMe}_2$  to toluene slurry of solid catalyst (*ca.* 5 mg) in a 5 mm-diameter quartz tube, which contained  $0.1 \times 10^{-3} \text{ M}$  of 1-octene in place of propene. After the mixture was aged for 2 min at room temperature, EB or DBDMP was added and the tube was cooled by liquid nitrogen. Spin concentrations were derived from comparisons of numerical double integrations of spectra for the samples with those for freshly prepared 1,1-diphenyl-2-picrylhydrazyl standards.

The polymer was fractionated by extraction with boiling heptane for 10 h to determine isotactic index (I.I.). The  $^{13}\text{C}$  NMR spectra of polymers were recorded at  $120^{\circ}\text{C}$  on a JEOL GX-500 spectrometer in pulse Fourier-Transform (FT) mode. Sample solutions were made in *o*-dichlorobenzene/benzene- $d_6$  (9/1 in vol) up to 12% by weight. Differential scanning calorimetry (DSC) measurements were made on a Seiko DSC-220. Polymer samples (*ca.* 4 mg) were encapsulated in aluminum pans, preheated at  $200^{\circ}\text{C}$  for 5 min, and scanned at  $10^{\circ}\text{C}/\text{min}$ . Molecular mass distribution curves were recorded on a Waters 150C at  $135^{\circ}\text{C}$  using *o*-dichlorobenzene as solvent.

## RESULTS

#### Compositions of the Catalysts

$\text{MgCl}_2$ -supported catalysts were prepared by successive adsorption of an internal donor and  $\text{TiCl}_4$  on  $\text{MgCl}_2$  in toluene at room temperature. Ethyl benzoate (EB) or 2,2-diisobutyl-1,3-dimethoxypropane (DBDMP) was used as an internal donor. Table I shows the contents of donors and Ti in the prepared catalysts (A–E). Small amounts of internal donors were almost quantitatively adsorbed. Ti contents decreased monotonously with increasing internal donor.

#### Propene Polymerization

Propene polymerization was conducted at  $40^{\circ}\text{C}$  under atmospheric pressure with catalysts A–E. The results are summarized in Table II. Polypropene obtained with the  $\text{TiCl}_4/\text{MgCl}_2\text{-Cp}_2\text{TiMe}_2$  catalyst contained more than 90% of boiling heptane-insoluble fraction without any donor. We previously investigated the additive effect of ethyl benzoate (EB) on this system.<sup>10</sup> When 5 g of  $\text{MgCl}_2$  were pretreated with 8 mmol of EB in toluene, the prepared  $\text{MgCl}_2$ -supported  $\text{TiCl}_4$  showed no activity for propene polymerization. Addition of external EB equivalent to supported Ti also decreased activity very effectively. In this study, EB was added shortly after the polymerization had started. Activity for isotactic PP increased with decrease in that for atactic PP in this case.

**Table I.** Compositions of the catalysts

Catalyst	ID <sup>a</sup>	[ID]/[MgCl <sub>2</sub> ] ( $\times 10^{-3}$ mol/mol)		[Ti]/[MgCl <sub>2</sub> ] ( $\times 10^{-3}$ mol/mol)	
		Added	Supported	Added	Supported
A		0	0	8.00	4.53
B	EB	1.00	0.97	8.00	3.92
C	EB	2.00	1.82	8.00	3.26
D	DBDMP	1.00	0.70	8.00	4.14
E	DBDMP	2.00	1.73	8.00	3.02

<sup>a</sup> ID, internal donor; EB, ethyl benzoate; DBDMP, 2,2-diisobutyl-1,3-dimethoxypropane.

**Table II.** Results of propene polymerizations with  $\text{TiCl}_4/\text{MgCl}_2\text{-Cp}_2\text{TiMe}_2$  catalysts<sup>a</sup>

Run	Catalyst	ED <sup>b</sup>	[ED]/[Ti]	Activity (kg-PP/g-Ti·h) <sup>c</sup>		I.I. <sup>c</sup> %
			(mol/mol)	Isotactic	Atactic	
1	A	—	0	3.05	0.25	92.5
2	A	EB	0.2	4.36	0.21	95.4
3	A	EB	1.0	3.36	0.11	96.7
4	A	DBDMP	0.2	2.91	0.22	93.1
5	A	DBDMP	1.0	2.52	0.15	94.5
6	B	—	0	4.14	0.15	96.5
7	B	EB	0.2	4.70	0.14	97.1
8	C	—	0	3.18	0.11	96.8
9	C	EB	0.2	3.49	0.10	97.1
10	C	EB	1.0	3.40	0.08	97.8
11	C	DBDMP	0.2	3.76	0.10	97.3
12	C	DBDMP	1.0	4.07	0.10	97.6
13	D	—	0	4.39	0.24	94.9
14	D	EB	0.2	5.02	0.23	95.7
15	D	EB	1.0	4.74	0.14	97.1
16	D	DBDMP	0.2	4.89	0.24	95.4
17	D	DBDMP	1.0	4.11	0.19	95.6
18	E	—	0	1.98	0.10	95.0
19	E	EB	0.2	2.41	0.10	95.9
20	E	EB	1.0	1.93	0.07	96.7
21	E	DBDMP	0.2	2.24	0.12	94.8
22	E	DBDMP	1.0	1.66	0.08	95.2
23 <sup>d</sup>	A	—	0	1.34	5.18	20.5

<sup>a</sup> Polymerization conditions: propene = 1 atm, heptane vol = 0.1 dm<sup>3</sup>;  $[\text{Cp}_2\text{TiMe}_2] = 5.20 \text{ mM}$ ;  $[\text{Ti}] = 0.26 \text{ mM}$ ,  $40^{\circ}\text{C}$ , 0.5 h. <sup>b</sup> EB, ethyl benzoate; DBDMP, 2,2-diisobutyl-1,3-dimethoxypropane. <sup>c</sup> Isotactic index (weight fraction of boiling heptane-insoluble part). <sup>d</sup>  $\text{AlEt}_3$  was used instead of  $\text{Cp}_2\text{TiMe}_2$ .

As a consequence, isotactic index reached as high as 95% as shown in Table II. Catalysts B–E which contained a small amount of Lewis base as an internal donor showed high activity (2–4 kg-PP/g-Ti·h) and high isotactic indexes. Especially, isotactic index of the polymer obtained with the catalyst C reached more than 97%. The results can be interpreted as follows. When an excess internal donor is used, or when an external donor is present before the addition of  $\text{Cp}_2\text{TiMe}_2$ , the donor coordinates potentially active  $\text{Ti}^{4+}$  species to give coordinatively saturated Ti species. Considering the fact that the interaction between  $\text{Cp}_2\text{TiMe}_2$  and the donors is very weak,  $\text{Cp}_2\text{TiMe}_2$  probably cannot pull out the donor from such Ti species. Accordingly, the coordinatively saturated Ti species cannot be activated by  $\text{Cp}_2\text{TiMe}_2$ .

*Effects of Lewis Bases on the APP- and IPP-Activity*

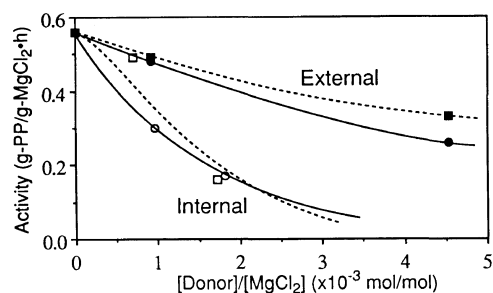
Figure 1 shows the effects of internal and external donors on the activity of APP. Regardless of EB or DBDMP, the internal donor decreased APP-activity more effectively than the external one. Figure 2 illustrates a plot of IPP-activity vs. an amount of Lewis base. Big difference was observed when EB and DBDMP were used as external donors: the IPP-activity increased by a very small amount of EB ( $[donor]/[Ti] = 0.2$ ) but almost unchanged or rather decreased by DBDMP.

*Kinetic Curve on Propene Polymerization*

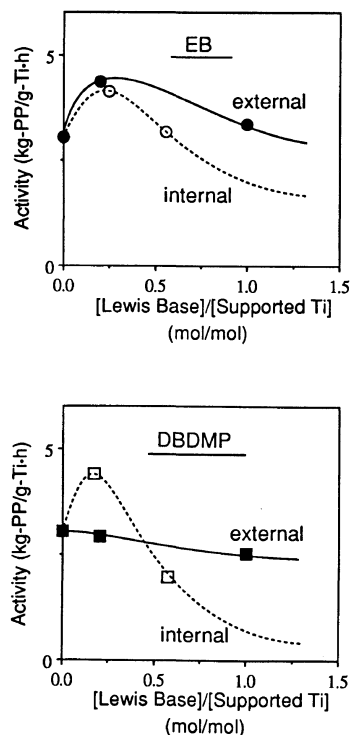
The polymerization rate curves are displayed in Figure 3 (Run 1, 2, 3, 4, and 5). Activity was increased immediately after the addition of EB or DBDMP. Figure 3 shows that deactivation rates were dependent on the kind and amount of donor. Second-order deactivation plots according to eq 2 are illustrated in Figure 4.

$$-dR/dt = k_{2d}R^2 \quad (1)$$

$$1/R = k_{2d}t + A \quad (2)$$



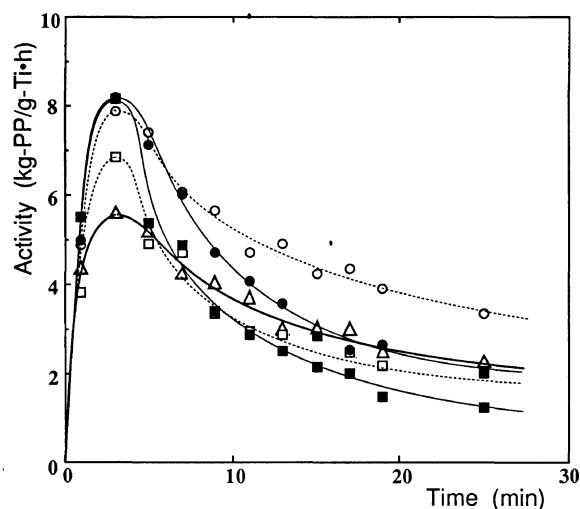
**Figure 1.** Additive effects of Lewis bases on the APP-activity: ●, external EB; ■, external DBDMP; ○, internal EB; □, internal DBDMP.



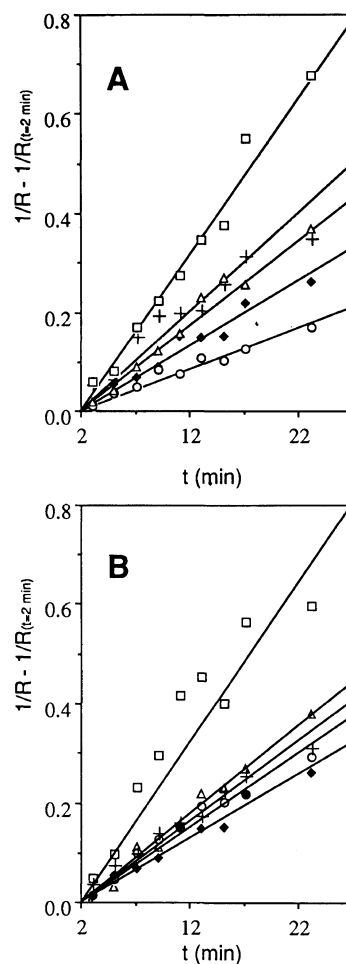
**Figure 2.** Additive effects of Lewis bases on the IPP-activity: ●, external EB; ■, external DBDMP; ○, internal EB; □, internal DBDMP.

$R$ , Polymerization rate at time =  $t$   
 $k_{2d}$ , Rate constant of second-order deactivation

The rate constant of second-order deactivation de-



**Figure 3.** Rate curves on the propene polymerizations with the  $TiCl_4/MgCl_2-Cp_2TiMe_2$  catalyst:  $\Delta$ , donor free;  $\circ$ ,  $[EB]/[Ti] = 0.2$ ;  $\bullet$ ,  $[EB]/[Ti] = 1.0$ ;  $\square$ ,  $[DBDMP]/[Ti] = 0.2$ ;  $\blacksquare$ ,  $[DBDMP]/[Ti] = 1.0$ .



**Figure 4.** Second-order deactivation plots for polymerization rate. **A.** Lewis base was added as an external donor:  $\blacklozenge$ , donor free;  $\circ$ ,  $[EB]/[Ti] = 0.20$ ;  $\Delta$ ,  $[EB]/[Ti] = 1.00$ ;  $+$ ,  $[DBDMP]/[Ti] = 0.20$ ;  $\square$ ,  $[DBDMP]/[Ti] = 1.00$ . **B.** Lewis base was added as an internal donor:  $\blacklozenge$ , donor free;  $\circ$ ,  $[EB]/[Ti] = 0.25$ ;  $\Delta$ ,  $[EB]/[Ti] = 0.56$ ;  $+$ ,  $[DBDMP]/[Ti] = 0.17$ ;  $\square$ ,  $[DBDMP]/[Ti] = 0.57$ .

**Table III.** Rate constants of second-order deactivation on the propene polymerizations with  $\text{TiCl}_4/\text{MgCl}_2\text{-Cp}_2\text{TiMe}_2$  catalysts

Run	ID <sup>a</sup>	ED <sup>a</sup>	[Lewis base]/[Ti]	$k_{2d}$ (g-Ti/kg-PP) <sup>b</sup>
1	—	—	0	0.82
2	—	EB	0.20	0.52
3	—	EB	1.00	1.13
4	—	DBDMP	0.20	1.17
5	—	DBDMP	1.00	2.08
6	EB	—	0.25	0.96
8	EB	—	0.56	1.12
13	DBDMP	—	0.17	1.04
18	DBDMP	—	0.57	2.12

<sup>a</sup> ID, internal donor; ED, external donor. <sup>b</sup> Rate constants of second order deactivation.

**Table IV.** Isotacticity of the IPP obtained with the  $\text{TiCl}_4/\text{MgCl}_2\text{-Cp}_2\text{TiMe}_2$  catalysts

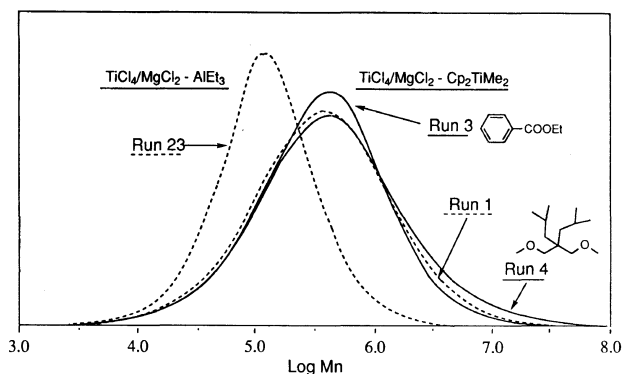
Run	ID <sup>a</sup>	ED <sup>a</sup>	<i>mmmm</i> / % <sup>b</sup>	$T_m$ /°C <sup>c</sup>
1	—	—	93.3	160.3
3	—	EB	94.7	161.6
5	—	DBDMP	93.8	160.8
6	EB	—	95.0	161.1
8	EB	—	96.4	161.3
10	EB	EB	96.5	161.4
12	EB	DBDMP	95.1	161.9
13	DBDMP	—	92.9	160.9
15	DBDMP	EB	94.8	161.6
17	DBDMP	DBDMP	93.6	160.8
18	DBDMP	—	93.5	160.3
20	DBDMP	EB	95.7	161.1
22	DBDMP	DBDMP	92.8	160.1

<sup>a</sup> ID, internal donor; ED, external donor; EB, ethyl benzoate; DBDMP, 2,2-diisobutyl-1,3-dimethoxypropane. <sup>b</sup> Determined by 125 MHz <sup>13</sup>C NMR. <sup>c</sup> Determined by DSC.

pended on kind and amount of external donor (Table III).  $k_{2d}$  increased with EB or DBDMP as an external donor, but DBDMP tended to enhance deactivation more than EB. Addition of the Lewis base increase activity probably due to more active centers by changing the dispersion state of Ti species. Such newly formed active centers may easily recombine to be deactivated by bimolecular reactions. It seems that the dispersion state and/or mobility of Ti species on  $\text{MgCl}_2$  surfaces should be affected by both kind and amount of base added. Table III also shows the results obtained in the presence of internal donors. The effects of the internal donors on  $k_{2d}$  were very similar to those of the external donors.

#### Properties of IPP

The microtacticity of IPP obtained with the  $\text{TiCl}_4/\text{MgCl}_2\text{-Cp}_2\text{TiMe}_2$  catalyst was investigated by <sup>13</sup>C NMR. The isotactic pentad (*mmmm*) are summarized in Table IV. *mmmm* increased by the addition of EB regardless of the internal or external donor. The addition of DBDMP hardly affected *mmmm* under all conditions. The melting points ( $T_m$ ) of IPPs were investigated by DSC, and are summarized in Table IV. The data are in good agreement with the results of <sup>13</sup>C NMR.  $T_m$  was improved by the addition of EB, but not

**Figure 5.** Molecular weight distribution curves of IPPs obtained with  $\text{TiCl}_4/\text{MgCl}_2\text{-Cp}_2\text{TiMe}_2$  and the  $\text{TiCl}_4/\text{MgCl}_2\text{-AlEt}_3$  catalysts.**Table V.** Number-average molecular weight and molecular weight distribution of the IPP obtained with the  $\text{TiCl}_4/\text{MgCl}_2\text{-Cp}_2\text{TiMe}_2$  catalysts

Run	ID <sup>a</sup>	ED <sup>a</sup>	$M_n(\times 10^4)$ <sup>b</sup>	$M_w/M_n$ <sup>b</sup>
1	—	—	12.7	8.3
23 <sup>c</sup>	—	—	7.4	2.9
2	—	EB	15.1	7.2
3	—	EB	14.5	6.1
4	—	DBDMP	15.0	14.1
5	—	DBDMP	15.6	11.4
6	EB	—	13.3	5.8
8	EB	—	11.8	7.0
10	EB	EB	14.7	5.9
12	EB	DBDMP	12.2	6.8
13	DBDMP	—	13.7	12.4
15	DBDMP	EB	13.3	10.4
17	DBDMP	DBDMP	13.2	14.2
18	DBDMP	—	14.9	12.3
20	DBDMP	EB	16.0	7.2
22	DBDMP	DBDMP	15.9	8.3

<sup>a</sup> ID, internal donor; ED, external donor; EB, ethyl benzoate; DBDMP, 2,2-diisobutyl-1,3-dimethoxypropane. <sup>b</sup> Determined by GPC. <sup>c</sup>  $\text{AlEt}_3$  was used instead of  $\text{Cp}_2\text{TiMe}_2$ .

#### DBDMP.

Molecular weight distribution (MWD) was measured by GPC. Figure 5 shows the MWD curves of IPPs (Run 1, 3, and 4). For comparison, the MWD curve of IPP obtained with the  $\text{TiCl}_4/\text{MgCl}_2\text{-AlEt}_3$  catalyst (Run 23) is also shown. The  $\text{TiCl}_4/\text{MgCl}_2\text{-Cp}_2\text{TiMe}_2$  catalyst system gave a broader MWD curve compared with the  $\text{TiCl}_4/\text{MgCl}_2\text{-AlEt}_3$  catalyst (Run 1 vs. Run 23). This suggests that several isospecific sites should exist in the  $\text{TiCl}_4/\text{MgCl}_2\text{-Cp}_2\text{TiMe}_2$  catalyst. When EB was added as external donor (Run 3), the MWD curve became narrower. On the other hand, the addition of DBDMP broadened it in high molecular weight region. Number-average molecular weight ( $M_n$ ) and polydispersity of IPPs are summarized in Table V.  $M_n$  increased to some extent by the addition of EB or DBDMP. However, polydispersity was dependent on the kind of Lewis base: the addition of EB, regardless of internal or external donor, tended to give narrower MWD, and the addition of DBDMP, broader MWD.

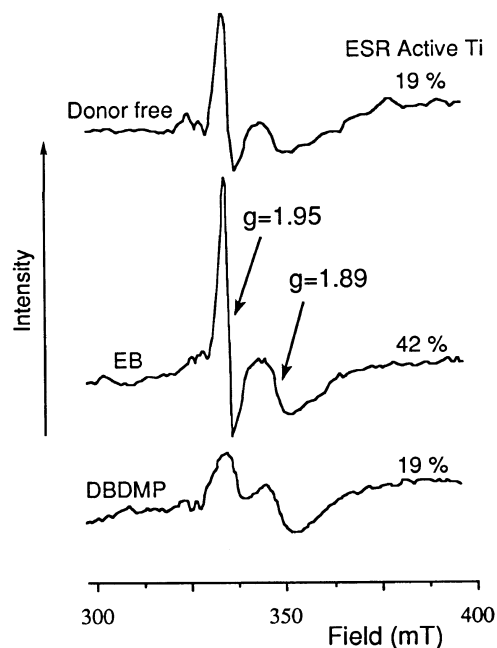


Figure 6. ESR spectra of  $\text{TiCl}_4/\text{MgCl}_2\text{-Cp}_2\text{TiMe}_2$  catalysts.

#### The Dispersion State of Ti Species

Ti species on the  $\text{MgCl}_2$  supported catalysts were investigated by ESR. The spectra were obtained at  $-100^\circ\text{C}$  in the absence and presence of EB or DBDMP. The samples were prepared according to the method described in EXPERIMENTAL part. Figure 6 shows the ESR spectra obtained. Two main signals with  $g$  of 1.95 and 1.89 were observed in all the spectra. Without a donor compound, 19% of Ti on the  $\text{MgCl}_2$  was ESR active. In the presence of EB, the intensity of the 1.95 signal increased and 42% of Ti became ESR-active. The addition of DBDMP decreased the intensity of the 1.95 signal and increased that of the 1.895 signal although the total concentration of  $\text{Ti}^{3+}$  was constant (19%).

Chien and Wu reported an ESR study of  $\text{MgCl}_2$  supported catalysts.<sup>12</sup> They described that the two ESR signals with  $g$  of 1.945 and 1.913 were assigned to single  $\text{Ti}^{3+}$  species probably with  $D_{3h}$  symmetry. Zakharov *et al.* investigated the ESR spectra of  $\text{MgCl}_2$  supported catalysts.<sup>13</sup> They observed three ESR signals with  $g$  value of 1.97, 1.940, and 1.915–1.925. They assigned the 1.97 signal to  $\text{Ti}^{3+}$  tetrahedrally coordinated on the  $\text{MgCl}_2$ , 1.940 signal to six-coordinated  $\text{Ti}^{3+}$  sites dissolved in  $\text{MgCl}_2$ , and 1.915–1.925 signal probably to  $[\text{Ti}^{3+}]_n$  clusters that were ordinarily ESR-silent, respectively. Brant and Speca reported that the ESR signal with  $g$  of 1.895 was observed by the interaction between  $[\text{Ti}^{3+}]_n$  clusters and  $\text{TiCl}_4$ .<sup>14</sup> According to the reports described above, we assigned the 1.95 signal to a single  $\text{Ti}^{3+}$  species and 1.89 signal to  $[\text{Ti}^{3+}]_n$  clusters, respectively.

## DISCUSSION

#### Effects of Internal Donors

Two aspecific sites are proposed in  $\text{MgCl}_2$  supported Ti catalysts (Figure 7). One is on the (100) cut of  $\text{MgCl}_2$  (site-I), and the other is on the (110) cut (site-III). Busico *et al.* described that the magnesium atom on (110) cut was more acidic than that on (100) cut, and only the

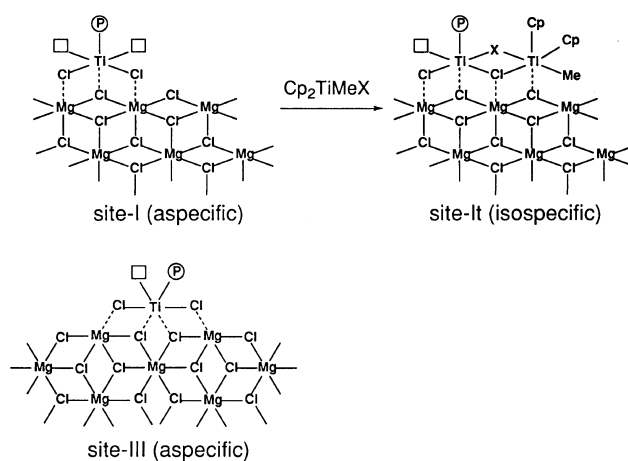


Figure 7. Plausible aspecific sites in  $\text{TiCl}_4/\text{MgCl}_2\text{-Cp}_2\text{TiMe}_2$  catalyst.

donor on (100) cut can be replaced with  $\text{TiCl}_4$  during catalyst preparation.<sup>15</sup> Furthermore, according to their electrostatic calculation, Ti species existing on the (110) cuts would be hardly coordinated by donor compounds. Therefore, it was necessary to use an internal donor to prevent the formation of site-III. Our results are in good agreement with this mechanism: the addition of the internal donors decreased Ti contents monotonously accompanied by the effective decrease in APP. In the  $\text{TiCl}_4/\text{MgCl}_2\text{-Cp}_2\text{TiMe}_2$  system, there is no difference between EB and DBDMP as an internal donor because of the low reactivity of  $\text{Cp}_2\text{TiMe}_2$  toward these Lewis bases.<sup>16</sup>

Galimberti *et al.* reported that the internal EB effectively improves the I.I. to 93% in the  $\text{TiCl}_4/\text{MgCl}_2\text{-zirconium tetrabenzyl (ZrBz}_4)$  catalyst, although  $\text{ZrBz}_4$  reacted with EB much faster than  $\text{Ali-Bu}_3$  in solution. Therefore, they proposed that the reaction products between  $\text{ZrBz}_4$  and EB remain on (110) surface of  $\text{MgCl}_2$  to prevent the formation of site-III.<sup>17</sup>

#### Interactions between Active Ti Species and Donors

Concerning the high isospecificity of the  $\text{TiCl}_4/\text{MgCl}_2\text{-Cp}_2\text{TiMe}_2$  catalyst without any donor compound, we previously proposed that the site-I is transformed to isospecific site (site It) by coordination of  $\text{Cp}_2\text{TiMeX}$  ( $X = \text{Me}$  or  $\text{Cl}$ ) (Figure 7).<sup>10</sup> When an external donor is added in this catalyst system, the donor can interact with coordinatively unsaturated active Ti species (site-It and/or site-II; binuclear isospecific species). Such reactions may strongly depend on the structure and Lewis basicity of the donor.

Therefore, there probably exist three isospecific sites in the  $\text{TiCl}_4/\text{MgCl}_2\text{-Cp}_2\text{TiMe}_2$  catalyst (Figure 8). Two of them are single  $\text{Ti}^{3+}$  species coordinated by  $\text{Cp}_2\text{TiMe}_2$  (site-It) and donor compound (site-Id). The other is  $[\text{Ti}^{3+}]_n$  clusters (site-II). However, site-II could be transformed to aspecific site (site-IIa) by Cl ligand migration, so that the produced polymer from site-II seems to have somewhat low isotacticity.<sup>4,18</sup>

The effects of the donors on the properties of produced IPPs and the ESR spectra is interpreted as follows (Figure 8). The addition of EB increases single  $\text{Ti}^{3+}$  species such as site-Id probably due to the splitting of  $[\text{Ti}^{3+}]_n$

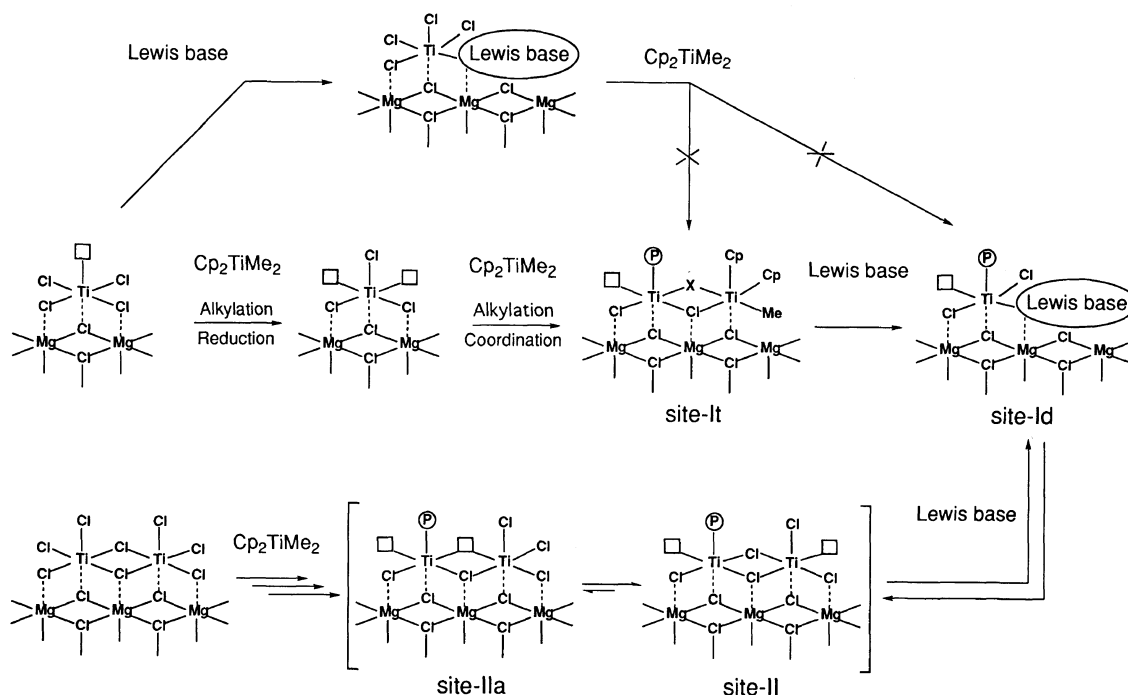


Figure 8. Plausible isospecific sites in  $\text{TiCl}_4/\text{MgCl}_2\text{-Cp}_2\text{TiMe}_2$  catalyst.

clusters (site-II) by adsorption of EB on the  $\text{MgCl}_2$  surface. It is also plausible that  $\text{Cp}_2\text{TiMe}_2$  in site-Ib is replaced by EB. Consequently, the single  $\text{Ti}^{3+}$  species related to EB occupies a large portion of active  $\text{Ti}^{3+}$  species, which causes improvement of isospecificity and narrower MWD curve. The reactions described above hardly occur by DBDMP probably due to bulkiness and/or Lewis basicity. As a consequence, the kinetic curves and MWD depend on the kind and amount of Lewis base added, although a precise mechanism is not clear at present.

In conclusion, the additive effects of Lewis bases in propene polymerization with the  $\text{TiCl}_4/\text{MgCl}_2\text{-Cp}_2\text{TiMe}_2$  catalyst system were investigated. The addition of a small amount of EB or DBDMP to the solid catalyst improved the catalyst isospecificity by preventing the formation of non-stereospecific sites. The properties of IPPs could also be changed by the Lewis bases. EB improved the microtacticity of IPP more effectively than DBDMP. The number-average molecular weight of IPP was increased by the addition of these Lewis bases. The polydispersity depended on the kind of Lewis base.

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