

## Isospecific Propylene Polymerization Behavior of Lewis Base Functionalized Unbridged Zirconocenes under Bulk Conditions

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Isospecific propylene polymerization behavior of *meta*- and *para*-Lewis base (**E**) functionalized unbridged zirconocenes ( $[1-(\mathbf{E}_n\text{-Ph})\text{-}3,4\text{-Me}_2\text{C}_5\text{H}_2]_2\text{ZrCl}_2$ , **E** = NMe<sub>2</sub>, OMe; *n* = 1 or 2) was investigated under bulk conditions. Catalytic activity of the zirconocenes, and molecular weight and isotacticity of polypropylenes are found to be dependent on the position and number of the Lewis base functional groups in the zirconocenes. All the crude polypropylenes possess a broad molecular weight distribution and multi-melting transitions, indicating an involvement of multi-catalytic active species in the polymerization. The highest  $[mmmm]$  value of an isotactic portion of the polypropylenes reached 89%, which is higher than that (85%) from the well-known *C*<sub>2</sub>-symmetric EBIZr (*rac*-Et(Ind)<sub>2</sub>ZrCl<sub>2</sub>) catalyst. These results support that the *in situ* generated, rigid *rac*-like cation-anion pair through the Lewis acid-base interactions between the functional groups of zirconocenes and methylaluminoxane anion is effective in the formation of isotactic polypropylene under bulk propylene polymerization conditions.

**Key Words** : Metallocenes, Isotactic polypropylene, Lewis base, Bulk polymerization

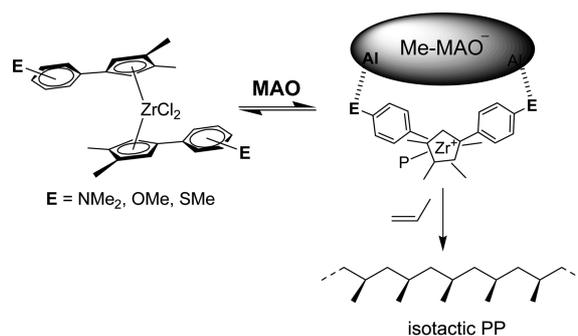
### Introduction

Since the development of the *C*<sub>2</sub>-symmetric ansa-metallocene catalysts such as *rac*-Et(H<sub>4</sub>Ind)<sub>2</sub>ZrCl<sub>2</sub> for isospecific polymerization of propylene by Ewen<sup>1</sup> and Brintzinger,<sup>2</sup> a large number of metallocenes have been reported and some of them are now being used in commercial production of isotactic polypropylene (iPP). The commercial production of iPP has mainly focused on the increase in molecular weight (*M*<sub>w</sub>) and isotacticity of polypropylene, as well as the increase in catalytic activity by the change of catalyst structure.<sup>3-6</sup> Although many elaborated catalyst structures suitable for commercial iPP have been reported,<sup>7-14</sup> the synthetic procedures towards such *C*<sub>2</sub>-symmetric catalysts usually require many difficult steps giving rise to the increase in catalyst costs during the course of commercialization of iPP products. The high cost has been one of the principal reasons why the portion of metallocene-iPP products is below 1% of the total iPP market.<sup>15,16</sup> Although attempts to synthesize the metallocene catalysts via simple and cost effective methods have been achieved, the isotacticity of the resulting polypropylene was usually moderate to low.<sup>17-20</sup>

In this regard, our group disclosed new isospecific but unbridged metallocenes ( $[1-(\mathbf{E}_n\text{-Ph})\text{-}3,4\text{-Me}_2\text{C}_5\text{H}_2]_2\text{ZrCl}_2$ , **E** = NMe<sub>2</sub>, OMe, SME; *n* = 1 or 2) which have a much simpler structure than the well-known *C*<sub>2</sub>-symmetric metallocenes.<sup>21-23</sup> When activated by methylaluminoxane (MAO), these unbridged metallocenes produced iPP through the *in situ* formation of *C*<sub>2</sub>-symmetric-like structure by forming Lewis acid-base pair between the functional groups in the metallocenes and MAO anions ([Me-MAO]<sup>-</sup>) (Chart 1).<sup>21-23</sup> Although

the polymerization behavior of such unbridged metallocenes has been extensively investigated by changing the position, number, and kind of Lewis base groups (**E**), the polymerizations were all carried out under atmospheric pressure of propylene, which, however, is far from the commercial bulk propylene polymerization conditions. Because isotacticity of polypropylene and catalyst activity (propagation rate) are largely affected by propylene concentration in the polymerization medium, it is important to investigate the polymerization behavior of the unbridged metallocenes under bulk polymerization conditions which are usually adopted in the commercial plants.

In this report, we carried out propylene polymerization of the unbridged catalysts under bulk conditions and investigated the polymerization behavior in detail to evaluate the potential commercial utilization of the catalysts. As a result, we find that the highest  $[mmmm]$  methyl pentad value of an



**Chart 1.** Isospecific propylene polymerization by Lewis base functionalized unbridged zirconocene with MAO cocatalyst.

isotactic portion of polypropylenes reaches 89%, which is higher than that (85%) of the well-known *rac*-Et(Ind)<sub>2</sub>ZrCl<sub>2</sub>, and at the same time, the crude polypropylenes have broad molecular weight distributions (MWD = 6-24), which could be beneficial for the production of reactor-blended polypropylene products for easy processing.

## Experimental

**Materials and Instrumentation.** All polymerizations were performed under dry nitrogen or argon using standard Schlenk and glovebox techniques. Unbridged zirconocene catalysts were prepared according to the previous reports.<sup>21-23</sup> Toluene (Samchun Chemicals) was purified by passing it through an activated alumina column and then was stored over activated molecular sieves (5 Å, Yakuri Pure Chemicals Co.). Methylaluminoxane (MAO, HS-MAO 10% in toluene) was purchased from Albemarle and used as a solid form after drying toluene. Propylene was supplied from LOTTE CHEMICAL and used without any further purification. Diethyl ether and *n*-heptane (Samchun Chemicals) were used in the solvent extraction of polypropylene. Molecular weight (*M<sub>w</sub>*) and molecular weight distribution (MWD) of polypropylenes were measured by the gel permeation chromatography (GPC, PL-GPC220, Polymer Laboratories) and the melting transition was measured by differential scanning calorimetry (MDSC2910, TA Instruments). <sup>13</sup>C NMR spectra of polypropylenes were recorded on a Bruker Avance 400 spectrometer at 100 °C and all chemical shifts (δ) are reported in ppm with reference to tetramethylsilane (TMS, δ = 0.0 ppm).

### Bulk Polymerization of Propylene – in 50 mL Propylene.

A toluene solution containing pre-weighed zirconocene and s-MAO (solid MAO; [Al]/[Zr] = 2,000) was transferred into a well-degassed 100 mL stainless-steel reactor charged with nitrogen. The reactor temperature was adjusted by an automatic temperature controlling system. Polymerization was started by the addition of 50 mL of liquid propylene. After 1 h, all the reactions were finished by exhausting the remaining propylene monomer. The resulting polypropylene was dried in a vacuum oven at 80 °C to constant weight.

### Bulk Polymerization of Propylene – in 1 L Propylene.

A toluene solution containing pre-weighed zirconocene and s-MAO (solid MAO; [Al]/[Zr] = 2,000) in toluene was transferred into a well-degassed 2 L stainless-steel reactor charged with nitrogen. And then, 1 L of propylene was added to the reactor and the temperature was raised to 70 °C. Polymerization was performed at this temperature for 1 h and finished by exhausting the remaining propylene monomer. The resulting polypropylene was dried in a vacuum oven at 80 °C to constant weight.

**Solvent Extraction of Polypropylene.** Solvent extraction of polypropylene was carried out using a Soxhlet extractor. Pre-weighed samples (*ca.* 1.5 g) of polypropylenes from 1 L-scale polymerizations were extracted first with boiling diethyl ether (100 mL) for 12 h. The residue was then extracted with boiling *n*-heptane (100 mL) for another 12 h.

Evaporation of each solution afforded diethyl ether soluble and diethyl ether insoluble/*n*-heptane soluble portions of the polypropylene sample, respectively. The two separated portions and the remaining residue (diethyl ether insoluble/*n*-heptane insoluble portion) were finally dried under vacuum at 80 °C to constant weight.

## Results and Discussion

**Propylene Polymerization in 50 mL Propylene.** *Meta*- and *para*-Lewis base (E) functionalized unbridged zirconocenes prepared from our previous studies<sup>21-23</sup> were employed to investigate the detailed propylene polymerization behavior under bulk conditions (Figure 1).

Because of low activity in the preliminary polymerization test, the *ortho*-functionalized zirconocenes were not used in this study. The 6-parallel reactor system (amtec SPR6) in which an individual reactor size of 100 mL was used to run the polymerization. The polymerization temperature was varied from 50 to 110 °C, which is the most significant temperature range in the commercial production of polypropylene products. The polymerization test of each zirconocene was performed at different temperatures in the four reactors simultaneously (Table 1).

As shown in Table 1 and Figure 2, the *para*-functionalized zirconocenes show much higher catalytic activity than *meta*-zirconocenes and the activity of mono-substituted zirconocenes is higher than that of di-substituted ones in both NMe<sub>2</sub> (ZrN) and OMe (ZrO) functionalized zirconocenes. Thus the activity is in the order of *p*ZrN1 > *m*ZrN1 > *m*ZrN2 and *p*ZrO1 > *m*ZrO1 > *m*ZrO2 at all temperatures (Figure 2). This result is consistent with the results obtained at atmospheric pressure of propylene,<sup>22,23</sup> indicating that propylene insertion is affected by steric hindrance of substituent.<sup>24,25</sup> Namely, since the *meta*-functional group is closer to the zirconium active site than the *para*-functional group, it may give rise to more steric hindrance on the incoming monomer and the growing polymer chain, retarding monomer insertion. Moreover, such hindrance should be greater in the di-substituted zirconocenes than in the mono-substituted ones.

The overall activity of OMe-functionalized zirconocenes is higher than that of the corresponding NMe<sub>2</sub>-functionalized analogs at the same temperature. In particular, the activity difference is more apparent in the *meta*-functionalized zirconocenes. This finding could also be related to the different steric effect between NMe<sub>2</sub> and OMe groups. However, the activity of OMe-functionalized zirconocenes

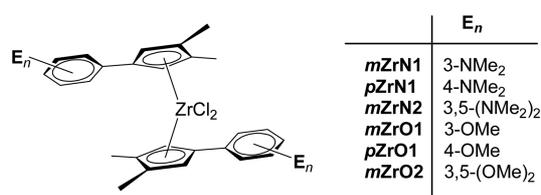
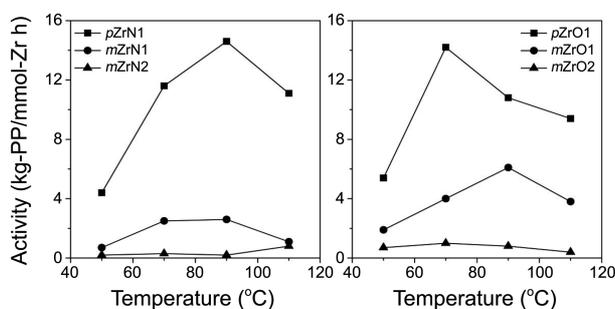


Figure 1. Lewis base functionalized unbridged zirconocenes.

**Table 1.** Propylene polymerization results in 50 mL of propylene<sup>a</sup>

Entry	Cat.	$T_p$ (°C)	Yield (g)	Act. <sup>b</sup>	$T_m$ (°C)	$M_w$ ( $\times 10^{-3}$ )	MWD	$[mmmm]^c$ (%)
1	<i>pZrN1</i>	50	1.11	4.4	157.1	134	7.0	73
2		70	2.89	11.6	146.6/154.8	99	7.3	70
3		90	3.66	14.6	151.5	43	15.9	57
4		110	2.77	11.1	150.1	39	20.9	56
5	<i>mZrN1</i>	50	0.18	0.7	156.7	198	14.9	69
6		70	0.63	2.5	149.2/156.7	111	22.4	67
7		90	0.64	2.6	155.1	61	20.6	64
8		110	0.28	1.1	153.8	52	22.6	60
9	<i>mZrN2</i>	50	0.04	0.2	156.2	503	12.2	n.d. <sup>d</sup>
10		70	0.69	0.3	155.1	284	8.7	85
11		90	0.06	0.2	152.8	147	12.2	n.d.
12		110	0.20	0.8	142.5/150.9	32	24.7	n.d.
13	<i>pZrO1</i>	50	1.35	5.4	156.9	191	6.1	74
14		70	3.55	14.2	146.4/155.2	93	11.2	69
15		90	2.71	10.8	151.7	68	19.8	62
16		110	2.36	9.4	151.1	45	22.5	56
17	<i>mZrO1</i>	50	0.47	1.9	151.5/157.7	182	7.4	74
18		70	1.01	4.0	149.7/157.4	89	8.9	70
19		90	1.52	6.1	146.2/154.5	29	11.0	58
20		110	0.95	3.8	144.2/153.1	26	14.3	55
21	<i>mZrO2</i>	50	0.18	0.7	154.4	235	6.5	85
22		70	0.25	1.0	153.1/157.5	172	15.3	78
23		90	0.20	0.8	152.1/157.7	106	16.4	n.d.
24		110	0.10	0.4	151.8	99	13.9	n.d.

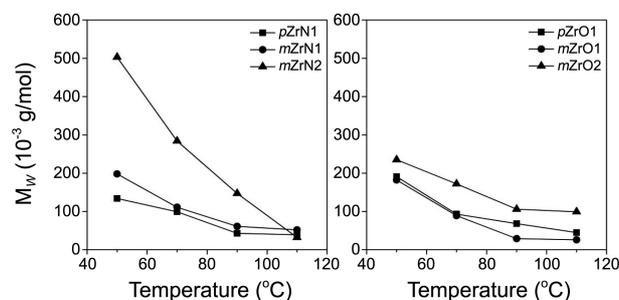
<sup>a</sup>Conditions: [Zr] = 0.25  $\mu$ mol; [Al]/[Zr] = 2,000; propylene = 50 mL. <sup>b</sup>Activity in kg-PP/(mmol-Zr)·h. <sup>c</sup>Determined by <sup>13</sup>C NMR spectroscopy. <sup>d</sup>not determined due to low yield.



**Figure 2.** Catalytic activity of NMe<sub>2</sub>-functionalized zirconocenes (left) and OMe-functionalized zirconocenes (right) with polymerization temperature.

decreases more rapidly than that of the NMe<sub>2</sub>-functionalized ones as the polymerization temperature increases (> 90 °C). This might indicate that the steric effect of functional group becomes less significant at high polymerization temperature.

Molecular weight ( $M_w$ ) of polypropylenes from the zirconocenes is shown to be dependent on both the polymerization temperature and the position and number of Lewis base functional groups in the phenyl ring (Table 1 and Figure 3). The  $M_w$  of polypropylenes decreases with increasing polymerization temperature for all zirconocenes probably due to the increased rate of chain transfer reaction at high temperature.<sup>26,27</sup> At the same temperature, the  $M_w$  of polypropyl-



**Figure 3.** Molecular weight of polypropylene from NMe<sub>2</sub>-functionalized zirconocenes (left) and OMe-functionalized zirconocenes (right) with polymerization temperature.

enes from *meta*-di-functionalized zirconocenes was higher than that from both *meta*- and *para*-mono-functionalized ones ( $mZrN2 > mZrN1 > pZrN1$  and  $mZrO2 > pZrO1 > mZrO1$ ). This result could also be explained by steric effect of functional groups. As the number of *meta*-functional group increases, the increased steric hindrance may not allow the growing polymer chain to be positioned for efficient  $\beta$ -H elimination leading to the increase in  $M_w$ .<sup>28</sup> Note that the *meta*-di-substituted *mZrN2* shows the highest molecular weight at the given temperature, but the activity is very low probably due to steric effect.

On the other hand, molecular weight distribution (MWD)

**Table 2.** Propylene polymerization results in 1 L of propylene at 70 °C<sup>a</sup>

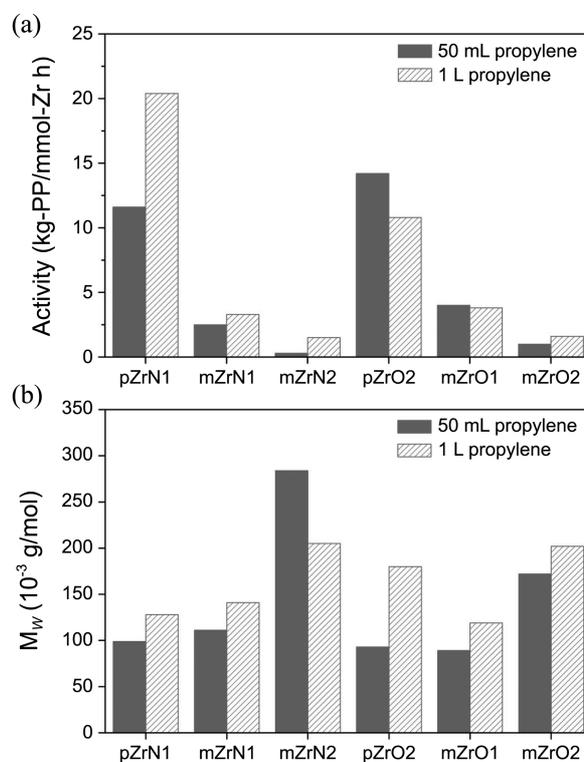
Entry	Cat.	Yield (g)	Act. <sup>b</sup>	$T_m$ (°C)	$M_w$ ( $\times 10^{-3}$ )	MWD	[ <i>mmmm</i> ] <sup>c</sup> (%)
25	<i>p</i> ZrN1	102.0	20.4	149.9/157.1	128	12.2	74
26	<i>m</i> ZrN1	16.5	3.3	156.7	141	8.9	67
27	<i>m</i> ZrN2	7.6	1.5	154.7	205	7.1	82
28	<i>p</i> ZrO1	54.0	10.8	149.7/156.4	180	9.4	73
29	<i>m</i> ZrO1	18.8	3.8	155.8	119	7.0	67
30	<i>m</i> ZrO2	8.0	1.6	152.4/158.0	202	7.8	78
31	<i>p</i> ZrN1Me <sub>2</sub> <sup>d</sup>	14.0	2.5	n.o. <sup>e</sup>	54	12.5	10
32	EBIZr <sup>f</sup>	80.0	26.7	130.6	30	2.6	78
33	BIZr <sup>g</sup>	40.0	13.3	n.o. <sup>e</sup>	5	2.6	7

<sup>a</sup>Conditions: [Zr] = 5.0  $\mu$ mol; [Al]/[Zr] = 2,000; propylene = 1 L;  $T_p$  = 70 °C;  $t_p$  = 1 h. <sup>b</sup>Unit of activity: kg-PP/(mmol-Zr)·h. <sup>c</sup>Determined by <sup>13</sup>C NMR spectroscopy. <sup>d</sup>*p*ZrN1Me<sub>2</sub> = {1-(*p*-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>)-3,4-Me<sub>2</sub>C<sub>3</sub>H<sub>2</sub>}-ZrMe<sub>2</sub>; [Zr] = 5.6  $\mu$ mol; [Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]/[Zr] = 1.5; [Al]/[Zr] = 360 (TIBA = 2 mmol). <sup>e</sup>n.o.: not observed. <sup>f</sup>EBIZr: *rac*-Et(Ind)<sub>2</sub>ZrCl<sub>2</sub>; [Zr] = 3.0  $\mu$ mol; [Al]/[Zr] = 2,000. <sup>g</sup>BIZr: Ind<sub>2</sub>ZrCl<sub>2</sub>; [Zr] = 3.0  $\mu$ mol; [Al]/[Zr] = 2,000.

of polypropylenes from the zirconocenes was all above 6.0 and the broad melting transition or sometimes two distinct melting peaks were observed. As similarly shown in the polymerization under the atmospheric pressure of propylene,<sup>21-23</sup> this result clearly indicates the involvement of multi-catalytic active species in the bulk polymerization of propylene through the interactions between Lewis base functional groups in the zirconocenes and methylaluminoxane anion ([Me-MAO]<sup>-</sup>).

The isotacticity of the crude polypropylene was determined from <sup>13</sup>C NMR spectroscopy. The [*mmmm*] methyl pentad values of polypropylenes are in the range of 55-85% and the value gradually decreases as the polymerization temperature increases. Comparison of the [*mmmm*] values at 70 °C indicates that the *meta*-di-functionalized zirconocenes produce polypropylene of the highest [*mmmm*] value (max. 85% for both *m*ZrN2 and *m*ZrO2), as similar to the results from the atmospheric pressure of propylene.<sup>22,23</sup> This result can be explained by the increased chance of the formation of C<sub>2</sub>-symmetric-like structure by forming Lewis acid-base pair between the functional groups in the metallocenes and [Me-MAO]. The difference in the [*mmmm*] values is not apparent for the mono-functionalized zirconocenes in terms of the position and kind of Lewis base functional groups.

**Propylene Polymerization in 1 L Propylene.** Based on the small scale bulk polymerization results above, we further investigated the bulk propylene polymerization in a 1 L-scale at 70 °C, which is one of the typical polymerization temperature in commercial plants, to study reproducibility and commercial applicability (Table 2). The order of catalytic activity of the zirconocenes was found to be *p*ZrN1 > *m*ZrN1 > *m*ZrN2 for NMe<sub>2</sub>-functionalized zirconocenes and *p*ZrO1 > *m*ZrO1 > *m*ZrO2 for OMe-functionalized zirconocenes, respectively, which is the same order with that found in 50 mL bulk polymerization. The  $M_w$  of the polypropylenes also shows the same trend with that found in 50 mL polymerization, *i.e.* *m*ZrN2 > *m*ZrN1 > *p*ZrN1 and *m*ZrO2 > *p*ZrO1 > *m*ZrO1 (Figure 4). It can also be seen that the involvement of multi-catalytic active species in the polymerization is still maintained in 1 L polymerization



**Figure 4.** Comparison of (a) catalytic activity and (b) molecular weight of polypropylene under 50 mL and 1 L propylene bulk polymerization conditions.

when judging from the melting transition ( $T_m$ ) and molecular weight distribution (MWD) of polypropylenes. Namely, all the polypropylenes show broad melting transition or two distinct melting peaks and broad MWD of the polypropylenes. Moreover, the [*mmmm*] methyl pentad values of polypropylenes from 1 L polymerization are almost same with that from 50 mL polymerization. Therefore, it can be said that the polymerization behavior of the zirconocenes in 50 mL propylene is reproduced well in 1 L scale.

**Comparative Propylene Polymerization in 1 L Propylene.** To compare the bulk polymerization behavior of the functionalized zirconocenes with that of other zirconocenes,

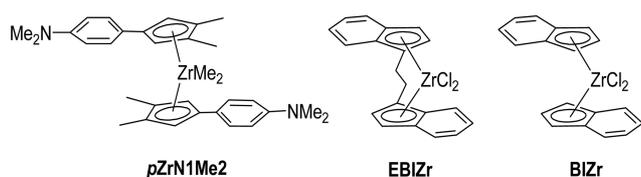


Figure 5. Zirconocenes for comparative bulk polymerization.

{1-(*p*-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>)-3,4-Me<sub>2</sub>C<sub>5</sub>H<sub>2</sub>)}<sub>2</sub>ZrMe<sub>2</sub> (**pZrN1Me<sub>2</sub>**), *rac*-Et(Ind)<sub>2</sub>ZrCl<sub>2</sub> (**EBIZr**), and Ind<sub>2</sub>ZrCl<sub>2</sub> (**BIZr**) were used for comparative bulk polymerization at 70 °C (Figure 5).

**pZrN1Me<sub>2</sub>** was selected to investigate the role of MAO in isospecific propylene polymerization. When this zirconocene was used instead of **pZrN1**, the activated catalyst solution was prepared by treating **pZrN1Me<sub>2</sub>** with 1.5 molar equivalent [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in the presence of a measured amount of triisobutylaluminum (TIBA, 1.0 M of Al purchased from Aldrich, [Al]/[Zr] = 360). The polypropylene from the borate-activated **pZrN1Me<sub>2</sub>** was shown to be completely amorphous and showed low molecular weight (Table 2). This indicates that the interaction between the Lewis base functional groups in the functionalized zirconocenes and [Me-MAO]<sup>+</sup> is essential for achieving isospecificity in bulk propylene polymerization, as consistent with the previous results of our group.<sup>21-23</sup> Next, the well-known C<sub>2</sub>-symmetric metallocene, **EBIZr** showed isospecific behavior (*[mmmm]* = 78%) with the involvement of single active catalytic species (MWD = 2.6) in the polymerization, but **BIZr** produced amorphous low molecular weight polypropylene similar to

other achiral unbridged metallocenes (Table 2).<sup>29-31</sup> Therefore, it can be concluded that the isospecific polymerization behavior of the Lewis base functionalized zirconocenes comes from the interaction between the Lewis base functional groups in the zirconocenes and [Me-MAO]<sup>+</sup>.

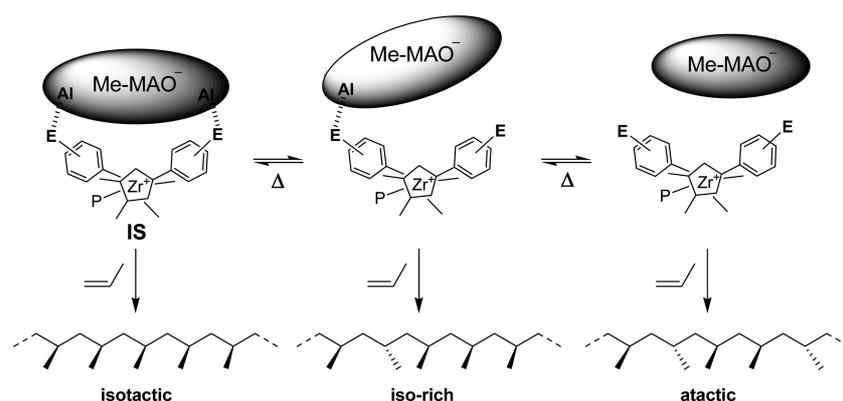
**Analysis of the Solvent Extracted Portions of Polypropylenes.** A stepwise solvent extraction method was used to obtain more information on the properties of polypropylenes from the Lewis base functionalized zirconocenes. The crude polypropylenes from 1 L polymerization were fractionated into three portions: diethyl ether soluble (E-sol), diethyl ether insoluble and *n*-heptane soluble (E-insol/H-sol), and diethyl ether insoluble and *n*-heptane-insoluble (H-insol) portions (Table 3). It is known that the foregoing portions correspond to the atactic-like, moderately isotactic, and highly isotactic polypropylene, respectively.<sup>21,32</sup> The H-insol portion is shown to comprise the major component of the crude polypropylenes (60-79 wt %). Note that the difunctionalized **mZrN2** (entry 27) and **mZrO2** (entry 30) similarly afforded the highest amount of H-insol portion (79 wt %) probably due to the increased chance of the generation of *rac*-like cation-anion pairs.

It can be seen that the amount of each extracted portion of the crude polypropylenes from the zirconocenes is dependent on the position and number of Lewis base functional groups in the zirconocenes, but not on the kind of the functional groups. For example, the amounts of the extracted portions from **mZrN1** (entry 26) and those from **mZrO1** (entry 29) are almost same. The relative amounts of **pZrN1**

Table 3. Detailed analysis of solvent extracted portions of the polypropylenes

Entry*	No.	Extract Portion	Ratio (wt %)	T <sub>m</sub> (°C)	M <sub>w</sub> (× 10 <sup>-3</sup> )	MWD	[mmmm] <sup>a</sup> (%)
25	25-1	E-sol <sup>b</sup>	17	62.0	14	9.8	n.d. <sup>c</sup>
	25-2	E-insol/H-sol <sup>d</sup>	23	142.4/153.7	41	4.3	n.d.
	25-3	H-insol <sup>e</sup>	60	154.3	179	4.1	88
26	26-1	E-sol	23	58.0	11	6.7	n.d.
	26-2	E-insol/H-sol	17	140.5/150.8	23	3.6	n.d.
	26-3	H-insol	60	155.3	221	5.1	87
27	27-1	E-sol	13	61.8	12	5.8	n.d.
	27-2	E-insol/H-sol	8	136.4/147.8	22	3.7	n.d.
	27-3	H-insol	79	156.8	222	4.9	89
28	28-1	E-sol	17	n.o. <sup>f</sup>	21	5.0	n.d.
	28-2	E-insol/H-sol	25	140.2/152.5	42	3.7	n.d.
	28-3	H-insol	58	154.3	217	3.8	89
29	29-1	E-sol	23	17.6/64.7	16	4.7	n.d.
	29-2	E-insol/H-sol	17	144.4/152.4	29	3.0	n.d.
	29-3	H-insol	60	154.6	173	4.0	86
30	30-1	E-sol	11	62.5	17	6.4	n.d.
	30-2	E-insol/H-sol	10	141.0/151.7	36	3.6	n.d.
	30-3	H-insol	79	156.0	218	4.5	88
32	32-1	E-sol	6	78.1	9	4.6	n.d.
	32-2	E-insol/H-sol	84	129.8	18	2.9	n.d.
	32-3	H-insol	10	139.0	34	2.7	85

\*Entry numbers correspond to those in Table 2. <sup>a</sup>Determined by <sup>13</sup>C NMR spectroscopy. <sup>b</sup>E-sol: diethyl ether soluble. <sup>c</sup>n.d.: not determined. <sup>d</sup>E-insol/H-sol: diethyl ether insoluble and *n*-heptane soluble. <sup>e</sup>H-insol: diethyl ether insoluble and *n*-heptane-insoluble. <sup>f</sup>n.o.: not observed.



**Scheme 1.** Proposed thermal equilibria and the propagation of polypropylene with the possible active species from Lewis base ( $E = \text{NMe}_2$ ,  $\text{OMe}$ ) functionalized unbridged zirconocenes upon MAO activation.

(entry 25) vs. **pZrO1** (entry 28) and **mZrN2** (entry 27) vs. **mZrO2** (entry 30) are also similar. These results are somewhat different from those observed at atmospheric pressure of propylene.<sup>22,23</sup> In that case, the amount of H-insol portion from **pZrN1** was larger than that from **pZrO1** due to the stronger Lewis acid-base interaction in the  $\text{NMe}_2$ -functionalized **pZrN1** system than that in the **pZrO1**.<sup>22,33</sup> In the case of *meta*-functionalized zirconocenes, the amount of H-insol portion from **mZrN1** was smaller than that from **mZrO1** due to higher steric hindrance of  $\text{NMe}_2$  group than that of  $\text{OMe}$ .<sup>23</sup> The different trend in the amounts of the H-insol portions between bulk and atmospheric propylene conditions could be explained by the different insertion rate of propylene. Namely, the insertion rate of propylene is so high in the bulk polymerization that the difference in the Lewis basicity or the steric effect between  $\text{NMe}_2$  and  $\text{OMe}$  groups might not be significant in controlling isospecificity.<sup>22,34</sup> The similar  $[mmmm]$  methyl pentad values of H-insol portions for the  $\text{NMe}_2$ -functionalized zirconocenes and the  $\text{OMe}$ -derivatives also support that once the  $C_2$ -symmetric-like cation-anion pairs form, the isospecific propagation rapidly proceeds.

The  $[mmmm]$  values of H-insol portions from all zirconocenes are similar regardless of the position or number of functional groups (86–89%) and are higher than that (85%) for the H-insol portion from EBIZr. This result indicates that *in situ* generated, rigid *rac*-like cation-anion pairs through the interaction between Lewis base functional groups in the zirconocenes and  $[\text{Me-MAO}]^-$  are fairly well maintained at high temperature (70 °C) under propylene bulk conditions. The  $T_m$  and  $M_w$  of the extracted portions increased in the order of E-sol < E-insol/H-sol < H-insol. The E-sol portions of the polypropylenes showed broad melting transition, while the E-insol/H-sol portions exhibited two  $T_m$ s in the high temperature region (Table 3). In particular, the  $T_m$  (154–156 °C) and  $M_w$  (173–222 kg/mol) of the H-insol portions are much higher than those from EBIZr (139 °C and 34 kg/mol). The high  $T_m$  also supports the formation of iPP from *rac*-like cation-anion pairs in bulk conditions (**IS** in Scheme 1).

Finally, in a commercial point of view, the Lewis base functionalized zirconocenes in this study could be useful in the production of iPP because the isospecific polymerization

behavior of the zirconocenes is well maintained under the typical commercial conditions, such as in bulk propylene and at 70 °C.<sup>35,36</sup> Furthermore, the generation of multi-catalytic active species through the interactions between Lewis base functional groups in the zirconocenes and  $[\text{Me-MAO}]^-$  could be commercially meaningful for the production of reactor-blended polypropylene products and the control of MWD of the polypropylenes for easy processing.<sup>37,38</sup>

## Conclusions

We have demonstrated that the Lewis base functionalized unbridged zirconocenes in combination with methylaluminum-oxane cocatalyst produce isotactic polypropylene under bulk propylene polymerization conditions. The  $[mmmm]$  methyl pentad values of the isotactic portions of polypropylenes reached 89%, which is higher than that (85%) of the well-known *rac*-Et(Ind)<sub>2</sub>ZrCl<sub>2</sub>, suggesting that the generation of rigid *rac*-like cation-anion pair through the interaction between Lewis base functional groups in the zirconocenes and methylaluminum-oxane anion is also well maintained under bulk conditions. The isospecific and multi-catalytic behavior of the functionalized zirconocenes in this study may be of commercial interest in the production of isotactic polypropylene products with the controlled molecular weight distribution.

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