## Propylene Polymerization with *rac*-(EBI)Zr(NC<sub>4</sub>H<sub>8</sub>)<sub>2</sub> Cocatalyzed by MAO or AlR<sub>3</sub> and Anionic Compounds

IL KIM\*

University of Ulsan, Department of Chemical Engineering, P.O. Box 18, Ulsan 680-749, Korea

Received 15 September 1997; accepted 18 April 1998

**ABSTRACT:** Propylene polymerization was carried out using an *ansa*-zirconocene pyrrolidide based catalytic system of racemic ethylene-1,2-bis(1-indenyl)zirconium dipyrrolidide [rac-(EBI)Zr(NC<sub>4</sub>H<sub>8</sub>)<sub>2</sub> or (rac-1)] and methylaluminoxane (MAO) or a noncoordinating anion. In situ generation of cationic alkylzirconium species was also investigated by NMR-scale reactions of rac-1 and MAO, and rac-1, AlMe<sub>3</sub>, and [Ph<sub>3</sub>C]  $[B(C_6F_5)_4]$ . In the NMR-scale reaction using  $CD_2Cl_2$  as a solvent, a small amount of MAO ([Al]/[Zr] = 30) was enough to completely activate *rac-1* to give cationic methylzirconium cations that can polymerize propylene. The resulting isotactic polypropylene (iPP) isolated in this reaction showed a meso pentad value of 91.3%. In a similar NMR-scale reaction rac-1 was stoichiometrically methylated by AlMe<sub>3</sub> to give rac-(EBI)ZrMe\_2, and the introduction of  $[Ph_3C]~[B(C_6F_5)_4]$  into the reaction mixture containing rac-(EBI)ZrMe<sub>2</sub> led to in situ generation of cationic [rac-(EBI)Zr( $\mu$ -Me)<sub>2</sub>AlMe<sub>2</sub>]<sup>+</sup> species that can polymerize propylene to give iPP showing a meso pentad value of 94.7%. The catalyst system *rac*-1/MAO exhibited an increase of activity as the [Al]/[Zr] ratio increased within an experimental range ([Al]/[Zr] = 930-6511). The meso pentad values of the resulting iPPs were in the range of 83.2-87.5%. The catalytic activity showed a maximum ( $\overline{R_p} = 6.66 \times 10^6$  g PP/mol Zr h atm) when [Zr] was 84.9 imes 10<sup>-6</sup> mol/L in the propylene polymerization according to the concentration of catalyst. MAO-free polymerization of propylene was performed by a rac-1/AlR<sub>3</sub>/noncoordinating anion catalytic system. The efficiency of AlR<sub>3</sub> was decreased in the order of  $AlMe_{3} (\overline{R_{p}} = 13.0 \times 10^{6} \text{ g PP/mol Zr h atm}) > Al(i-Bu)_{3} (8.9 \times 10^{6}) > AlPr_{3} (8.8 \times 10^{6}) > AlPr$  $\times$  10<sup>6</sup>) > Al(*i*-Bu)<sub>2</sub>H (8.4 × 10<sup>6</sup>) > AlEt<sub>3</sub> (8.4 × 10<sup>6</sup>). The performance of the noncoordinating anion as a cocatalyst was on the order of [HNMePh<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] ( $\overline{R_p}$  = 13.0  $\times \ 10^{6} \ {\rm g} \ {\rm PP/mol} \ {\rm Zr} \ {\rm h} \ {\rm atm}) > [{\rm HNMe_2Ph}] [{\rm B}({\rm C_6F_5})_4] \ (10.8 \times 10^{6}) > [{\rm Ph_3C}] [{\rm B}({\rm C_6F_5})_4]$  $(8.4 \times 10^6) > [\text{HNEt}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$  (7.8 × 10<sup>6</sup>). The properties of iPP were characterized by <sup>13</sup>C-NMR, FTIR, DSC, GPC, and viscometry. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 875-885, 1999

**Key words:** metallocene amide; propylene polymerization; cationic species; NMR-scale reaction

#### INTRODUCTION

Chiral group 4 *ansa*-metallocenes are the basis of a new class of stereoselective olefin polymeriza-

tion catalysts.<sup>1</sup> However, practical application of *ansa*-metallocene catalysts has been hindered by the fact that the racemic (rac) isomers required for the stereospecific polymerization of  $\alpha$ -olefin are difficult to prepare. Current synthetic routes of *ansa*-metallocenes based on salt elimination reactions of MCl<sub>x</sub> salts and bis-cyclopentadienyl dianion reagents are inefficient and require te-

<sup>\*</sup> E-mail: ilkim@uou.ulsan.ac.kr.

Contract grant sponsor: Korea Research Foundation (1997). Journal of Applied Polymer Science, Vol. 71, 875–885 (1999)

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dious separation and purification steps. Collins et al. prepared the prototypical chiral *ansa*-metallocene *rac*-(EBI)ZrCl<sub>2</sub> [EBI, ethylene-1,2-bis(1-indenyl)] by reaction of ZrCl<sub>4</sub>(THF)<sub>2</sub> and (EBI)Li<sub>2</sub> and reported a low variable yield (30-50%).<sup>2</sup> Grossman et al. employed (EBI)K<sub>2</sub> and obtained (EBI)ZrCl<sub>2</sub> in a 70% yield with a rac/meso ratio of 2/1.<sup>3</sup> In general the current syntheses of chiral *ansa*-metallocenes produce the desired rac isomer in 10–30% yield, and separation is not always possible.

Recently Jordan and colleagues reported an efficient synthesis method of ansa-metallocene <sup>ch</sup>Cp<sub>2</sub>Zr(NR<sub>2</sub>)<sub>2</sub> (<sup>ch</sup>Cp<sub>2</sub>Zr is the chiral ansa-metallocene framework) via an amine elimination route.<sup>4</sup> They prepared rac-(EBI)Zr(NMe<sub>2</sub>)<sub>2</sub> by the reaction of (EBI)H $_2$  and Zr(NMe $_2$ ) $_4$  with a 90% yield with a rac/meso ratio of 13/1.4b The ansametallocene amide complexes were demonstrated to be effective for the isospecific polymerization of propylene by employing conventional coactivator formulation.<sup>4c</sup> Diamond et al. extended the amine elimination route to ansa-metallocene pyrrolidide complex.  $^{\rm 4d}$  By the reaction of (EBI)H $_2$  with the pyrrolidide complex  $Zr(NC_4H_8)_4$  they produced rac-(EBI) $Zr(NC_4H_8)_2$  with a 95% yield (rac/meso of 6/1). This article describes a study of the possibility that the amide derivative *rac*-1 can be used directly in catalyst formulations for propylene polymerization.

#### **EXPERIMENTAL**

#### Measurements

<sup>1</sup>H- and <sup>13</sup>C-NMR spectra of compounds and polymers were recorded on a Bruker WM-300 spectrometer using tetramethylsilane as an internal standard. Samples for <sup>13</sup>C-NMR spectra were prepared by dissolving 50 mg of polymer in 0.5 mL of  $C_6D_6/1,2,4$ -trichlorobenzene (1/5) and measuring at 120°C. IR spectra were obtained with an ATI Mattson Genesis Series FTIR. Samples were prepared for IR examination by mixing polymer powder with KBr, and the meso pentad value of polypropylene (PP) was calculated by comparing the absorption ratio  $A_{998}/A_{973}$  according to the equation shown below<sup>5</sup>:

$$A_{998}/A_{973} = (0.864 + 0.004) [mmmm] + 0.10$$
 (1)

The molecular weight and its distribution  $(M_w/M_n)$  were determined by GPC on a Waters 150-C

at 135°C in 1,2-dichlorobenzene with a data processor equipped with polystyrene gel columns. Melting and crystallization curves were recorded with a DuPont differential scanning calorimeter (model 910) at a 10°C/min rate. The results of the second scan are reported to eliminate differences in sample history. The intrinsic viscosity of the polymers was determined in decalin at 135°C using an Ubbelohde viscometer, and values of  $M_v$  were calculated by the equation

$$[\eta] = 10^{-4} [\overline{M_v}]^{0.8}$$
 (2)

developed for monodisperse PP fractions.<sup>6</sup>

#### **General Procedures**

All reactions were performed under a purified argon atmosphere using standard glove box and Schlenk techniques. Polymerization grade propylene (Yukong Co., Korea) was purified by passing it through columns of Fisher RIDOX catalyst and a 5-Å molecular sieve 13 times. Alkyl aluminums (AlMe<sub>3</sub>, AlEt<sub>3</sub>, AlPr<sub>3</sub>, Al(*i*-Bu)<sub>3</sub>, and Al(*i*-Bu)2H) were obtained from Aldrich and used without purification. ZrCl<sub>4</sub>, LiNMe<sub>2</sub>, (EBI)H<sub>2</sub>, and pyrrolidine were purchased from Aldrich. Methylaluminoxane (MAO) was obtained from Albemarle as a 10% solution in toluene, which contained 1.85 wt % AlMe<sub>3</sub> and 8.15 wt % MAO (4.49 wt % total Al). Solvents were distilled from Na and benzophenone and stored over molecular sieves (4 Å).  $Zr(NMe_2)_4$  and  $Zr(NC_4H_8)_4$  were prepared according to the literature procedures.<sup>4</sup> Various anionic complexes  $\{[HNMe_2Ph][B(C_6F_5)_4],$  $[HNMePh_2][B(C_6F_5)_4], [Ph_3C] [B(C_6F_5)_4], and$  $[HNEt_2Ph][B(C_6F_5)_4]]$  were also prepared by literature procedures.<sup>4,7,8</sup>

#### Synthesis of rac-(EBI)Zr(NC<sub>4</sub>H<sub>8</sub>)<sub>2</sub>(rac-1)

The rac-1 was synthesized by the reaction of (EBI)H<sub>2</sub> with the pyrrolidide complex  $\text{Zr}(\text{NC}_4\text{H}_8)_4$ in *m*-xylene at 140°C (7 h) and recrystallized from Et<sub>2</sub>O.<sup>4c</sup> <sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.70 (*d*, *J* = 9 Hz, 2 H, indenyl), 7.39 (*d*, *J* = 8 Hz, 2 H, indenyl), 7.02 (pseudo *t*, 2 H, indenyl), 6.83 (pseudo *t*, 2 H, indenyl), 6.33 (*d*, *J* = 3 Hz, 2 H, C<sub>5</sub> indenyl), 6.10 (*d*, *J* = 3 Hz, 2 H, C<sub>5</sub> indenyl), 3.68 (*m*, 2 H, CH<sub>2</sub>), 3.45 (*m*, 2 H, CH<sub>2</sub>), 3.08 (*m*, 4 H, NCH<sub>2</sub>), 2.74 (*m*, 4 H, NCH<sub>2</sub>), 1.34 (*m*, 4 H, NCH<sub>2</sub>CH<sub>2</sub>), 1.15 (*m*, 4 H, NCH<sub>2</sub>CH<sub>2</sub>).

#### NMR-Scale Reaction of rac-1 and MAO

An NMR tube was charged with MAO (74 mg, which is composed of 8.15 wt % MAO and 1.85 wt

% AlMe<sub>3</sub>, 1.34 mmol total Al) dissolved in toluene as a 10 wt % solution, and then rac-1 (20 mg, 0.041 mmol) was introduced into the NMR tube. The [Al]/[Zr] ratio of this reaction mixture was expected to be about 30. The color of the homogeneous solution changed immediately from red to orange. Toluene was removed under a vacuum  $(10^{-6} \text{ mmHg})$  for 24 h, and then 0.5 mL of CD<sub>2</sub>Cl<sub>2</sub> was added for the NMR analysis. The tube was maintained at 23°C and monitored periodically by <sup>1</sup>H-NMR. The <sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>) of the chemical species in the reaction mixture is as follows: rac-(EBI)ZrMe<sup>+</sup>:  $\delta$  8.01 (*d*, *J* = 9 Hz, 2 H, indenyl), 7.64 (d, J = 8 Hz, 2 H, indenyl), 7.58 (pseudo t)2 H, indenyl), 7.40 (pseudo t, 2 H, indenyl), 6.54  $(d, J = 3 \text{ Hz}, 2 \text{ H}, C_5 \text{ indenyl}), 6.51 (d, J = 3$ Hz, 2 H,  $C_5$  indenyl), 3.90 (m, 4 H,  $CH_2$ ), -0.64 (s, 3 H, Zr—CH<sub>3</sub>); Al<sub>2</sub>Me<sub>5</sub>(NC<sub>4</sub>H<sub>8</sub>):  $\delta$  2.90 (*m*, 4 H,  $NCH_2$ ), 1.71 (*m*, 4 H,  $NCH_2CH_2$ ), -0.56 (br *s*, 15) H). MAO could not be interpreted, and all free  $Al_2Me_6$  ( $\delta - 0.29, s$ ) contained in the MAO was transformed to  $Al_2Me_5(NC_4H_8)$ .

# NMR-Scale Reaction of *rac*-1, $Al_2Me_6$ , and $[Ph_3C][B(C_6F_5)_4]$

The rac-1 (20 mg, 0.041 mmol) was dissolved in CD<sub>2</sub>Cl<sub>2</sub> (0.5 mL) at room temperature to give a red solution. Two equivalents of  $Al_2Me_6$  (12 mg, 0.083 mmol) was then added to the NMR tube. The color of the solution mixture immediately turned to orange and conversion to rac-(EBI)-ZrMe<sub>2</sub> was complete with no sign of isomerization. The <sup>1</sup>H-NMR  $(CD_2Cl_2)$  of the chemical species in the reaction mixture follows: rac-(EBI)- $\operatorname{ZrMe}_2$ : 7.48 (d, J = 9 Hz, 2 H, indenyl), 7.42 (d, J = 8 Hz, 2 H, indenyl), 7.19 (pseudo t, 2 H, indenyl), 7.06 (pseudo t, 2 H, indenyl), 6.54 (d, J = 3 Hz, 2 H,  $C_5$  indenyl), 6.00 (d, J = 3 Hz, 2 H, C<sub>5</sub> indenyl), 3.35 (m, 2 H, CH<sub>2</sub>), 3.19 (m, 2 H,  $CH_2$ ), -1.43 (s, 6 H, Zr— $CH_3$ );  $Al_2Me_5(NC_4H_8)$ :  $\delta$  $2.90 (m, 4 H, NCH_2), 1.71 (m, 4 H, NCH_2CH_2),$ -0.56 (br s, 15 H). The [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (38 mg, 0.041 mmol) was introduced to this reaction mixture  $(rac-1/Al_2Me_6 = 1/2)$  at room temperature. The color of the resulting solution mixture immediately changed from orange to light yellow. In this reaction  $[rac-(EBI)Zr(\mu-Me)_2AIMe_2]^+$  the adduct of the base-free rac-(EBI)ZrMe<sup>+</sup> cation and AlMe<sub>3</sub> was generated as a stochiometric yield.<sup>9</sup> The <sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>) of [rac-(EBI)Zr(µ-Me)<sub>2</sub>AlMe<sub>2</sub>]<sup>+</sup>is  $\delta$  7.89 (*d*, *J* = 9 Hz, 2 H, indenyl), 7.59 (d, J = 8 Hz, 2 H, indenyl), 7.33 (pseudo t, 2 H, indenyl), 6.45 (d, J = 3 Hz, 2 H,

C<sub>5</sub> indenyl), 6.20 (d, J = 3 Hz, 2 H, C<sub>5</sub> indenyl), 4.06 (s, 4 H, CH<sub>2</sub>), -0.62 (s, 6 H,  $\mu$ -CH<sub>3</sub>), -0.58 (s, 6 H, Al—CH<sub>3</sub>); the 7.00 to 7.38 ppm region was partially obscured by Ph<sub>3</sub>CMe.

#### NMR-Scale Polymerization of Propylene

To the resulting reaction mixtures obtained above, rac-1/30 MAO containing *in situ* generated cationic [rac-(EBI)ZrMe]<sup>+</sup>[MAO]<sup>-</sup> species and rac-1/2 Al<sub>2</sub>Me<sub>6</sub>/[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] containing cationic [rac-(EBI)Zr( $\mu$ -Me)<sub>2</sub>AlMe<sub>2</sub>]<sup>+</sup>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup> species, 0.5 mL of liquid propylene was added at  $-78^{\circ}$ C. The temperature of the NMR tube was slowly increased to room temperature. The solid isotactic PP (iPP) precipitated in this procedure was washed with ethanol and dried under a vacuum for the analysis.

#### **Polymerization of Propylene**

Propylene polymerizations were performed in a 250-mL round-bottom flask equipped with a magnetic stirrer and a thermometer. In a dry box the reactor was charged with toluene (80 mL) and a prescribed amount of MAO. The reactor was immersed in a constant temperature bath previously set to the desired temperature. When the reactor temperature had equilibrated to the bath temperature, propylene was introduced into the reactor after removing the argon gas under a vacuum. When no more absorption of propylene into toluene was observed, a prescribed amount of metallocene catalyst dissolved in toluene was injected into the reactor and then the polymerization was started. The polymerization rate was determined at every 0.01 s from the rate of consumption and was measured by a hot-wire flowmeter (model 5850 D, Brooks Instrument Div.) connected to a personal computer through an analog to digital converter. When anionic compound was used as a cocatalyst instead of MAO, a prescribed amount of alkyl aluminum reagent and metallocene catalyst was added to the toluene. Injecting the anionic compound into the reactor started the polymerization.

#### **RESULTS AND DISCUSSION**

#### NMR-Scale Reaction and Polymerization of rac-1

Catalysts derived from *ansa*-metallocene have been studied extensively for the stereoselective polymerization of propylene and other olefins.<sup>1</sup>

The active species in these catalysts are  $^{ch}Cp_2Zr(R)^+$  cations, which are generated by alkylation and ionization of neutral metallocene precursors.<sup>1,7,8,9</sup> Standard activation procedures include (i) treatment of  ${}^{ch}Cp_2ZrX_2$  (X = Cl, R, OR) with excess MAO; (ii) reaction of the <sup>ch</sup>Cp<sub>2</sub>ZrR<sub>2</sub> complex with ammonium salts {e.g., [HNMe<sub>2</sub>Ph]  $[B(C_6F_5)_4], [HNMePh_2][B(C_6F_5)_4], [HNEt_2Ph]$  $[B(C_6F_5)_4]$ , alkyl abstract reagents {e.g.,  $[Ph_3C]$  $[B(C_6F_5)_4]$ ,  $[B(C_6F_5)_3]$ , or oxidizing agents (e.g.,  $Ag^+$ ,  $Cp_2Fe^+$ ); or (iii) *in situ* alkylation of  $^{\rm ch}{\rm Cp}_2{\rm Zr}{\rm X}_2$  complexes with  ${\rm AlR}_3$  or other reagents followed by ionization as in (ii). In NMR-scale reactions the ansa-metallocene bis-dimethylamide compounds rac-(EBI)Zr(NMe<sub>2</sub>)<sub>2</sub> and rac- $(SBI)Zr(NMe_2)_2$  [SBI,  $Me_2Si(1-indenyl)_2$ ] were shown to be completely activated by 40 equiv of MAO or by 1 equiv of noncoordinating anions such as  $[HNMe_2Ph][B(C_6F_5)_4]$ ,  $[HNMePh_2][B(C_6F_5)_4]$ ,  $[Ph_{3}C][B(C_{6}F_{5})_{4}], \text{ and } [HNEt_{2}Ph][B(C_{6}F_{5})_{4}].$ Similar NMR-scale reactions were carried out with a *rac*-1 compound that has much bulkier pyrrolidide ligands. By reacting 1 equiv of rac-1 with 30 equiv of MAO, which is composed of 81.5 wt % MAO and 18.5 wt %  $AlMe_3$  in  $CD_2Cl_2$  solvent, the ansa-metallocene pyrrolidide complex was completely activated to give cationic rac-(EBI)ZrMe<sup>+</sup> species. MAO must activate the metallocene by forming the metallocene alkyl complex if the metallocene is not introduced into the reaction system as the alkyl complex. MAO purportedly methylates  $Cp_2MCl_2$  by a transmetallation mechanism involving bridging halides.<sup>12</sup> However, the functions of MAO are complicated by the presence of variable amounts of free AlMe<sub>3</sub>, which cannot be removed during preparation, as well as the uncertainty about the structure and the composition of MAO. In the present system free AlMe<sub>3</sub> seemed to be a principal reagent to remove pyrrolidide ligand and replace it with a methyl group. In the NMR-scale reaction it can be observed that all the AlMe<sub>3</sub> contained in the MAO is transformed to form the bridging pyrrolidide compound  $Al_2Me_5(NC_4H_8)$  as shown in reaction (3), and there is no signal indicating the presence of free  $Al_2Me_6$ .

$$rac-(EBI)Zr(NC_{4}H_{8})_{2} + 2 Al_{2}Me_{6} \rightarrow$$
$$rac-(EBI)ZrMe_{2} + 2 Al_{2}Me_{5}(NC_{4}H_{8}) \quad (3)$$

MAO is proposed to remove one of the methyl ligands from rac-(EBI)ZrMe<sub>2</sub> to provide a coordinatively unsaturated complex and stabilize the

resulting cationic complex by functioning as a noncoordinating anion.

Reaction (3) can be directly demonstrated by the reaction of *rac*-1 and 2 equiv of  $Al_2Me_6$  in  $CD_2Cl_2$  solvent. In this reaction *rac*-1 is immediately converted to rac-(EBI)ZrMe<sub>2</sub> as a stoichiometic NMR yield. Addition of 1 equiv of noncoordinating anion,  $[Ph_3C][B(C_6F_5)_4]$ , to the resulting reaction mixture  $(rac-1/2 \operatorname{Al}_2 \operatorname{Me}_6)$  containing rac-(EBI)ZrMe<sub>2</sub> leads to *in situ* generation of cationic  $[rac-(EBI)Zr(\mu-Me)_2AIMe_2]^+$  species, the adduct of the base-free rac-(EBI)ZrMe<sup>+</sup> cation, and AlMe<sub>3</sub> which was previously identified by Bochmann and Lancaster as the principal component in the mixture of these species.<sup>9</sup> This reaction also proceeded as a stoichiometric yield. In similar sequential reactions using  $[HNMePh_2][B(C_6F_5)_4]$ as an anionic compound, the same cationic species,  $[rac-(EBI)Zr(\mu-Me)_2AIMe_2]^+$ , can be generated as a stoichiometric yield. In this case the resonances of the cationic species are broadened. To be active for the polymerization of propylene the  $[rac-(EBI)Zr(\mu-Me)_2AIMe_2]^+$  cation presumably undergoes loss or displacement of AlMe<sub>3</sub>, ultimately leading to [rac-(EBI)ZrMe]<sup>+</sup> or [rac-(EBI)Zr(Me)(propene)]<sup>+</sup> species.

From the NMR-scale polymerization carried out at  $-78^{\circ}$ C by introducing 0.5 mL of liquid propylene into the NMR tube containing the *rac*-1/30 MAO mixture or *rac*-1/2 Al<sub>2</sub>Me<sub>6</sub>/[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] mixture, we could isolate solid iPPs showing a meso pentad value of 91.3 or 94.7%, respectively.

#### **Effect of MAO Concentration**

The catalytic activity of the metallocene compound is strongly dependent upon the amount of MAO used for activation. Figure 1 shows the rate profiles of propylene polymerizations obtained by the rac-1/MAO catalyst system. For all polymerizations, there is only a simple rapid rise to a maximum rate  $(R_{p,\max})$ , followed by a moderate decay. This simple kinetic behavior is similar to those found for other metallocene dichloride/MAO catalyzed ethylene polymerizations<sup>13,14</sup> and for propylene polymerization.<sup>15</sup> In the propylene polymerization initiated by the rac-(EBI)ZrCl<sub>2</sub>/ MAO system the activity increases sigmoidally with MAO concentration in a wide range of [Al]/ [Zr] ratios ([Al]/[Zr] = 350-100,000).<sup>15</sup> The metallocene pyrrolidide/MAO system shows activity similar to that of the rac-(EBI)ZrCl<sub>2</sub>/MAO system. At a low [Al]/[Zr] ratio ([Al]/[Zr] < 1000) the catalytic activity was very low, but the activity



**Figure 1**  $R_p$  versus time of propylene polymerizations catalyzed by the *rac*-1/MAO system with [Zr] = 42.5  $\mu$ M, 80 mL of toluene, P = 1.3 atm, 30°C temperature, and [Al]/[Zr] of (a) 930, (b) 1860, (c) 2790, (d) 4651, and (e) 6511.

increased monotonically with a higher [Al]/[Zr] ratio within an experimental range (Fig. 2). There was a short induction period at a low [Al]/[Zr] ratio, but the induction period was shortened at high [Al]/[Zr] ratios. These results demonstrate that it takes some time to form active sites with a low concentration of MAO.

An NMR-scale polymerization showed that a very small amount of MAO ([Al]/[Zr] = 30) is needed to activate rac-1 in a  $CD_2Cl_2$  solvent. However, the rac-1/MAO system did not show any activity at a low [Al]/[Zr] ratio (e.g., [Al]/[Zr] = 300). The reason is uncertain why an excess amount of MAO is required for the activation of *rac*-1 in the lab-scale polymerization of propylene using toluene as a solvent. A considerable amount of MAO can act as a scavenger for the removal of impurities such as moisture. When a toluene solution of  $Cp_2ZrCl_2$  is treated with MAO, a fast ligand exchange takes place, producing primarily Cp<sub>2</sub>Zr(Me)(Cl); and the use of excess MAO produces Cp<sub>2</sub>ZrMe<sub>2</sub>.<sup>16</sup> However, these systems only become catalytically active when [Al]/[Zr] ratios of higher than 200 are used. The way in which excess MAO induces this activity has been studied in detail, mainly by spectroscopic means.<sup>16,17</sup> It is now recognized that either methyl or chloride abstraction by Al centers in the MAO takes place.

Although MAO undoubtedly acts to methylate metallocene, to scavenge impurities, and to act as a Lewis acid for anion abstraction from the metalalkyl molecule, which generates an electrophilic species, these cannot explain the need for an excess amount of MAO for the activation.

To investigate the function of MAO a noncoordinating anion  $[Ph_3C][B(C_6F_5)_4]$  was used for the activation of rac-1 together with MAO. [Ph<sub>3</sub>C]  $[B(C_6F_5)_4]$  was also introduced into the polymerization medium consisting of rac-1 and MAO ([Al]/[Zr] = 300), which showed no activity for the propylene polymerization. Figure 3 shows that the rate of polymerization sharply increased by injecting 1 equiv  $[Ph_3C][B(C_6F_5)_4]$  into the catalytic system after 15 and 30 min of polymerization by rac-1/MAO ([Al]/[Zr] = 300). In fact, 300 equiv of Al should be an excess amount of cocatalyst if we consider the results of previous NMR-scale reactions of rac-1 and MAO in which 30 equiv of Al were enough to completely activate *rac*-1. If we assume that the cationic metallocene methyls are generated by a low concentration of MAO (e.g., [Al]/[Zr] = 300) and the cationic sites are not stabilized, the anion can attack the metallocene cation nucleophillically, which is the most common termination process in classical cationic polymerization. The sharp increase of activity right after the introduction of  $[Ph_3C][B(C_6F_5)_4]$ demonstrates that the anionic species  $[B(C_6F_5)_4]^$ can easily attack and stabilize the cationic active



**Figure 2**  $\overline{R_p}$  versus time plot and  $R_{p,\max}$  versus time plot of the data in Figure 1.



**Figure 3**  $R_p$  versus time of propylene polymerizations catalyzed by the *rac*-1/MAO system with [Zr] = 42.5  $\mu$ M, 80 mL of toluene, P = 1.3 atm, 30°C temperature, and [Al]/[Zr] of (a) 300. An amount of 42.5  $\mu$ M of [HNMePh<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] was injected after (b) 15 min and (c) 30 min of polymerization.

sites instead of MAO. As a result, it may be said that *rac*-(EBI)ZrMe<sup>+</sup> species can be generated by the reaction of *rac*-1 and a small amount of MAO, but the catalytic species are not stable enough to protect the attack by the anion and to prevent catalyst deactivation by the bimolecular process between two metallocenes. In a propylene polymerization by the rac-1/MAO system, MAO not only produces the cation but also stabilizes the anion. An excess amount of MAO is needed for the stabilization of the anion, even if the exact mechanism of stabilization remains uncertain. The lower maximum activity reached by injecting  $[Ph_3C][B(C_6F_5)_4]$  after 30 min of polymerization than that obtained by injecting  $[Ph_3C][B(C_6F_5)_4]$ after 15 min shows that unstable active species generated by using a small amount of MAO are gradually converted to inactive species by the deactivation, such as the bimolecular process between two metallocene molecules.

#### **Effect of Metallocene Concentration**

In a conventional Ziegler–Natta catalyst the activity of olefin polymerization is linearly proportional to the catalyst concentration:  $R_p = k_p [C^*][M]$ , where  $R_p$  is the rate of polymer-

ization,  $k_p$  is the rate constant of propagation,  $[C^*]$  is the concentration of active sites, and [M]is the concentration of olefin monomer. The propylene polymerization was examined in toluene at 30°C under a variation of the metallocene concentration ranging from 21.3 to 148.8  $\mu M$ . The [Al]/[Zr] ratio was kept constant at 1860. Figure 4 shows the polymerization rate dependent on the metallocene concentration at a constant [Al]/[Zr] ratio, and Figure 5 summarizes the average polymerization rate  $(\overline{R_p})$  versus [Zr] and the maximum polymerization rate  $(R_{p,\max})$ versus [Zr] relationships. Even if short induction periods appeared at low [Zr], all polymerizations showed similar rate curves (i.e., the kinetic profile is a simple increase to a maximum rate within 6 min, followed by rate decay). As shown in Figure 5,  $\overline{R_p}$  and  $R_{p,\max}$  both increase exponentially at the low concentration of metallocene ranging from [Zr] = 21.3 to 85.2 $\mu M$  but decrease linearly above [Zr] = 85.2  $\mu M$ . The decrease of activity at high [Zr] was probably due to the acceleration of deactivation by that bimolecular processes between two metallocene molecules through either reductive elimination of PP chains<sup>18</sup> or oxidative coupling that generates a hydrocarbon bridge between two zirconium atoms.<sup>15</sup>



**Figure 4**  $R_p$  versus time of propylene polymerizations catalyzed by the *rac*-1/MAO system with [Al]/[Zr] = 1860, 80 mL of toluene, P = 1.3 atm, 30°C temperature, and at a [Zr] of (a) 21.3  $\mu$ M, (b) 42.5  $\mu$ M, (c) 63.6  $\mu$ M, (d) 84.9  $\mu$ M, (e) 106.1  $\mu$ M, (f) 127.3  $\mu$ M, and (g) 148.5  $\mu$ M.



**Figure 5**  $\overline{R_p}$  versus time plot and  $R_{p,\max}$  versus time plot of the data in Figure 4.

The decrease of catalytic activity with the increase of metallocene concentration was demonstrated by many reports. Chien and Wang<sup>13</sup> reported that polymerization activity is proportional to  $[Zr]^{-0.77}$  for the polymerization of ethylene with the Cp<sub>2</sub>ZrCl<sub>2</sub>/MAO system. Fischer and Mulhaupt<sup>19</sup> found a similar situation for propylene polymerization with the same catalytic system. On the other hand, the activity increased monotonically with [Zr] in the case of ethylene polymerization with bis- $h^5$ -(neomentyl cyclopentadienyl)ZrCl<sub>2</sub>/MAO.<sup>20</sup> Therefore, the relationship between activity and catalyst concentration should be determined for each catalyst system.

#### MAO-Free Cocatalyst Systems: Effect of Alkyl Aluminum

The first well-defined zirconocene MAO-free catalyst systems capable of polymerizing propylene and higher  $\alpha$ -olefins at high rates were obtained by Hlatky and coworkers and Marks et al.<sup>21,22</sup> through the use of the poorly coordinating anion perfluorinated tetraphenylborate as the cocatalyst. In general metallocene alkyl compounds are utilized to generate cationic metallocene alkyls by the reaction with noncoordinative anions. Although cationic metallocene alkyl compounds can yield catalyst systems of very high activity, these systems can be deactivated easily. The addition of  $AlMe_3$  or  $AlEt_3$  has been shown to stabilize the metallocene catalyst system.<sup>23</sup>

Propylene was polymerized by in situ generated cationic zirconocene species by reacting rac-1 (42.5  $\mu$ mol/L), [HNMePh<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (42.5  $\mu$ M), and 4.5 mM of alkyl aluminum in 80 mL of toluene. The [Al]/[Zr] ratio of these systems was 106. For a successful generation of alkyl zirconocene cations rac-1 was first reacted with alkyl aluminum and then with  $[HNMePh_2][B(C_6F_5)_4]$ . Figure 6 shows the rate curves of propylene polymerization obtained by using different alkyl aluminums such as AlMe<sub>3</sub>, AlEt<sub>3</sub>, AlPr<sub>3</sub>, Al(*i*-Bu)<sub>3</sub>, and Al(*i*- $Bu)_2H$ . The rates of propylene polymerization were simply increased to maximum rates and then decayed slowly, except for  $Al(i-Bu)_2H$  that showed a constant-rate profile. The rate decay decreased in the order  $AlMe_3>AlEt_3>AlPr_3$  $> Al(i-Bu)_3$ ; the reverse order was true for the induction period. It is interesting to note that there was a 13-min induction period with Al(i- $Bu_{3}$ , but there was no induction period with Al(i- $Bu)_2H$ . By the reaction with  $Al(i-Bu)_2H$ , rac-1 seemed to be converted to metallocene dihydride, rac-(EBI)ZrH<sub>2</sub>. The metallocene dihydride reacts readily with propylene monomer to afford *rac*-(EBI) $Zr(CH_2CH_2CH_3)_2$ .<sup>24</sup>



**Figure 6**  $R_p$  versus time of propylene polymerizations catalyzed by the *rac*-1/AlR<sub>3</sub>/[HNMePh<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] system with [Al]/[Zr] = 106, 80 mL of toluene, P = 1.3 atm, 30°C temperature, [Zr] = 42.5  $\mu$ M, and (a) AlEt<sub>3</sub>, (b) Al(*i*-Bu)<sub>2</sub>H, (c) AlPr<sub>3</sub>, (d) Al(*i*-Bu)<sub>3</sub>, and (e) AlMe<sub>3</sub>.

### rac-(EBI)Zr(NC<sub>4</sub>H<sub>8</sub>)<sub>2</sub> ↓ AIR<sub>3</sub> rac-(EBI)ZrR<sub>2</sub> ↓ "NMePh<sub>2</sub>, RH [rac-(EBI)ZrR]<sup>+</sup>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>



$$rac-(EBI)Zr(NC_{4}H_{8})_{2} + 2 Al(i-Bu)_{2}H \rightarrow$$
$$rac-(EBI)ZrH_{2} + 2 Al(i-Bu)_{2}(NC_{4}H_{8}) \quad (4)$$

$$rac$$
-(EBI)ZrH<sub>2</sub> + 2 CH<sub>2</sub>=CHCH<sub>3</sub>  $\rightarrow$   
 $rac$ -(EBI)Zr(CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> (5)

The resulting rac-(EBI)Zr(CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> compound forms active species, [rac-(EBI)Zr-(CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)]<sup>+</sup>, upon addition of noncoordinating anionic species. The short induction period demonstrates that the above reactions proceed very quickly. The detailed NMR-scale reactions between *ansa*-metallocene amide compounds and Al(*i*-Bu)<sub>3</sub> or Al(*i*-Bu)<sub>2</sub>H will be published elsewhere.<sup>25</sup>

The average rate of polymerization carried out at 30°C for 1 h in the presence of the same amount of  $AlR_3$  ([Al]/[Zr] = 106) decreased in the order  $AlMe_3$  (13.0 × 10<sup>6</sup> g PP/mol Zr h atm) >  $Al(i-Bu)_3$  $(8.9 \times 10^6) > \text{AlPr}_3 (8.8 \times 10^6) > \text{Al}(i-\text{Bu})_2 \text{H} (8.4)$  $\times$  10^6) > AlEt\_3 (8.4  $\times$  10^6). The amount of AlR\_3 also had a great influence on the catalytic activity of the rac-1/AlR<sub>3</sub>/[HNMePh<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] system,<sup>26</sup> so this order activity can be changed according to the amount of AlR<sub>3</sub>. In summary, the above polymerization results demonstrate that the cationic zirconocene species are successfully generated in *situ* by reacting *rac*-1 with common alkyl aluminums followed by  $[HNMePh_2][B(C_6F_5)_4]$  as shown in Scheme 1. In this method the alkyl aluminum also functions to scavenge impurities contained in the polymerization systems.

#### MAO-Free Cocatalyst Systems: Effect of Anionic Compounds

Propylene was polymerized by *in situ* generated cationic zirconocene species by reacting *rac*-1 (42.5  $\mu$ M) with AlMe<sub>3</sub> (1 mM) and then with 42.5  $\mu$ M of a noncoordinating anion such as [HNMe<sub>2</sub>Ph][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], [HNMePh<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], or [HNEt<sub>2</sub>Ph][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]. The



**Figure 7**  $R_p$  versus time of propylene polymerizations catalyzed by the *rac*-1/AlMe<sub>3</sub>/anionic compound system with [Al]/[Zr] = 106, 80 mL of toluene, P = 1.3 atm, 30°C temperature, [Zr] = 42.5  $\mu$ M, and 42.5  $\mu$ M of (c) [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], (d) [HNEt<sub>2</sub>Ph][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], (e) [HNMe<sub>2</sub>Ph][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], and (f) [HNMePh<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]. Curve (a) is the same as Figure 1(b) and, curve (b) was obtained at the same conditions as curve (a) except that AlMe<sub>3</sub> ([Al]/[Zr] = 106) was added before activating *rac*-1 directly with MAO ([Al]/[Zr] = 1860).

kinetic profiles of propylene polymerization by these catalytic systems are shown in Figure 7. The rate profiles obtained by the rac-1/MAO system [Fig. 7(a)] and rac-1/AlMe<sub>3</sub>/MAO system [Fig. 7(b)] are also included for comparison. There are only 1 to 2 min of induction periods in all rate profiles and the rates reach a maximum within a short period of polymerization. The performance of the noncoordinating anions as cocatalysts is in the order [HNMePh<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] ( $R_{p,1 \text{ h}} = 13.0$  $\times 10^6$  g PP/mol Zr h atm) > [HNMe<sub>2</sub>Ph][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]  $(10.8 \times 10^6) > [Ph_3C][B(C_6F_5)_4] (8.4 \times 10^6)$ > [HNEt<sub>2</sub>Ph][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (7.8 × 10<sup>6</sup>). The catalytic systems using the anionic compound as a cocatalyst show much higher activity than that using MAO ( $\overline{R_{p,1\ h}} = 2.8 \times 10^6$  g PP/mol Zr h atm). By adding AlMe<sub>3</sub> before activating *rac*-1 directly by MAO, the activity increased twofold. In the propylene polymerizations by the rac-(EBI)ZrCl<sub>2</sub>/ MAO system and the *rac*-ethylene-bis(4,5,6,7-tetrahydro-1-indenyl)ZrCl<sub>2</sub>/MAO system, the catalytic activities were lowered with the addition of  $AlMe_3$ .<sup>15</sup>

			$\overline{R_p}~ imes~10^{-6}$	[mmmn	ı] (%)					
Run No.	$\begin{array}{c} [\mathrm{Zr}] \times 10^6 \\ (\mathrm{mol/L}) \end{array}$	[Al]/[Zr]	(g PP/mol Zr h atm)	By NMR	By IR	$\overline{M_v}~ imes~10^{-4}$	$\overline{M_w}~ imes~10^{-4}$	$\overline{M_w}/\overline{M_n}$	$\begin{array}{c} T_m \\ (^{\circ}\mathrm{C}) \end{array}$	$\Delta H_f$ (J/g)
Figure 1(a)	42.5	930	0.08	83.2	83.8	2.07	_	_	135.3	51.3
Figure 1(b)	42.5	1860	1.27	86.6	84.8	2.02	2.38	1.9	134.9	54.6
Figure 1(c)	42.5	2790	2.84		85.1	1.85	_	_	135.6	58.0
Figure 1(d)	42.5	4651	4.23	86.7	85.2	1.74	_		137.8	51.3
Figure 1(e)	42.5	6511	6.98	87.5	85.5	1.69	1.84	1.8	134.0	51.1
Figure 4(a)	21.3	1860	0.36	86.2	87.3	2.27	_	_	134.7	70.7
Figure 4(c)	63.6	1860	3.43	_	83.8	1.82	_		136.8	54.6
Figure 4(d)	84.9	1860	6.66	_	85.3	1.80	2.09	1.9	134.8	59.6
Figure 4(e)	106.1	1860	4.80	85.6	84.6	1.69	_	_	133.4	64.3
Figure 4(f)	127.3	1860	3.65	_	87.7	1.64	_		133.6	69.6
Figure 4(g)	148.5	1860	1.51	87.0	86.4	1.49	—	_	133.5	57.2

Table I Properties of iPP Obtained with rac-(EBI)Zr(NC4H8)2/MAO Catalyst Systems

Polymerization conditions are given in the corresponding figures shown in the run no.

#### **Characterization of iPP**

Table I summarizes the properties of iPP obtained with the rac-1/MAO catalyst system. The intrinsic viscosities of the polymers decrease monotonically as the [Al]/[Zr] ratio increase, because chain transfer by the alkylation of MAO is activated at a high concentration of MAO. In solution polymerization the molecular weight of the polymer produced is inversely dependent on the metallocene concentration. This is the case for the present catalytic system. The intrinsic viscosities of the polymers decrease as the concentration of metallocene increases. This may be due to the bimolecular reversible deactivation of the cationic metallocene sites observed by Fischer and Mulhaupt.<sup>19</sup> Supporting evidence for the effect of metallocene concentration on the molecular weight is presented in the review article by Kaminsky et al.<sup>27</sup> who reported that increasing the metallocene concentration in the polymerization of ethylene<sup>28</sup> is one method to lower the molecular weight of the resulting polyethylene. In addition, an article<sup>23</sup> on the polymerization of propylene reported that there was an inverse dependence of molecular weight on the metallocene concentration when rac-(EBI)HfCl<sub>2</sub>/MAO was used as the catalyst for the polymerization. The iPPs obtained by the rac-1/MAO system are characterized by a narrow molecular weight distribution. As shown in Table I the  $\overline{M_w}/\overline{M_n}$  values of all polymers investigated in this study were in the range of 1.8 to 1.9. This range of  $\overline{M_w}/\overline{M_n}$  value of iPP was also obtained with various ansa-metallocene dichloride systems.<sup>27</sup> The narrow molecular weight distribution is indicative of uniform active

species present in the polymerization system. Table I shows that the melting temperature  $(T_m)$  is almost independent of the [Al]/[Zr] ratio and [Zr], and the  $\Delta H_f$  value varies from 51 to 70 kJ/mol. The melting points and the crystallinities of iPPs are similar to those obtained with the rac-(EBI)ZrCl<sub>2</sub>/MAO system<sup>20</sup> and are well below those of conventional Ziegler–Natta iPPs.

As the [Al]/[Zr] ratio increases, the [mmmm] value increases slightly. The MAO surrounding the cationic metallocene sites can affect the stereoselectivity of the catalyst. Chen and Razavi reported that lowering [MAO] resulted in an iPP containing lowered populations of the homosteric sequences [mm] and [mmmm] with the rac-(EBI)ZrCl<sub>2</sub>/MAO system.<sup>20</sup> The [mmmm] value of iPP prepared by changing [Zr] is independent of the concentration of metallocene as shown in Table I.

Table II summarizes the properties of iPP obtained with MAO-free catalytic systems. The [mmmm] values and the melting points of iPPs prepared with MAO-free catalytic systems show levels similar to those of iPPs prepared with the rac-1/MAO system, even if the former systems show much higher activity than the latter system. When a bulky AlR<sub>3</sub> such as Al(*i*-Bu)<sub>2</sub>H or Al(*i*- $Bu_{3}$  is used as an alkylating reagent for *rac-1*, the resulting iPPs show lower [mmmm] values of 74.3 and 82.0%, respectively. When  $AlM_3$  is used as an alkylating reagent the [mmmm] value of iPP obtained by changing the noncoordinating anions is in the range of 85.8 to 87.6%. These results demonstrate that the type of R in rac- $(EBI)ZrR_2$  that is generated in situ by reacting

		$K_p \times 10^{\circ}$	mmmm	(0%) [1				E	
Run No. AlR <sub>3</sub> Us	ed Anion Used	(g PP/mol Zr h atm)	By NMR	By IR	$\overline{M_v}~ imes~10^{-~4}$	$\overline{M_w}~ imes~10^{-4}$	$\overline{M_w}/\overline{M_n}$	$^{m}_{(\circ C)}$	$\Delta H_f$ (J/g)
Figure $6(b)$ Al( <i>i</i> -Bu) <sub>5</sub>	H [HNMePh <sub>9</sub> ][B( $C_6F_5$ ) <sub>4</sub> ]	8.4	74.3	75.9	3.49	3.87	2.3	134.1	59.3
Figure 6(d) $Al(i-Bu)_{s}$	$[HNMePh_{\tilde{g}}][B(C_{\tilde{6}}F_{\tilde{5}})_{\tilde{4}}]$	8.9	82.0	84.1	3.38	3.62	2.1	135.8	57.2
Figure 6(e) AlMe <sub>3</sub>	$[HNMePh_{2}][B(C_{6}F_{5})_{4}]$	13.0	86.3	85.3	2.87	2.67	1.9	135.2	54.8
Figure 7(c) $AlMe_{3}$	$[Ph_{3}C][B(\bar{C}_{6}F_{5})_{4}]$	7.8	87.6	90.8	3.14	3.62	1.9	132.7	53.9
Figure 7(d) AlMe <sub>3</sub>	$[HNEt_2Ph][B(C_6F_5)_4]$	8.4	85.8	85.6	2.68	3.09	2.3	134.8	58.7
Figure 7(e) AlMe <sub>3</sub>	$[HNMe_2Ph][B(C_6F_5)_4]$	10.8	86.4	87.2	3.74	3.96	2.1	135.4	57.5

Table II Properties of iPP Obtained with rac-(EBI)Zr(NMe<sub>2</sub>)<sub>2</sub>/AlR<sub>3</sub> and Noncoordinating Anion Catalytic Systems

rac-1 with AlR<sub>3</sub> influences on catalytic activity and stereospecificity very much in the present catalytic system. It has been shown in an NMRscale polymerization of propylene that *in situ* generated active species by the reaction of *rac-*1, AlM<sub>3</sub>, and various types of noncoordinating anions have the same structure.<sup>4c</sup> The  $\overline{M_v}$  values of iPPs obtained by MAO-free catalytic systems are higher than those of iPPs by the *rac-*1/MAO system, but they are still characterized by low values. As shown in Table II, the  $\overline{M_w}/\overline{M_n}$  values of all polymers obtained by MAO-free systems are in the range of 1.9 to 2.3, indicating that the active species are also uniform in the polymerization system.

#### CONCLUSION

The ansa-zirconocene pyrrolidide compound rac-1 was activated for propylene polymerization with a small amount of MAO ([Al]/[Zr] = 30) in an NMR-scale reaction using CD<sub>2</sub>Cl<sub>2</sub> as the solvent. In a similar NMR-scale reaction the rac-1 was stoichiometrically methylated by AlMe<sub>3</sub> to give rac-(EBI)ZrMe<sub>2</sub>, and the introduction of [Ph<sub>3</sub>C] [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] into the reaction mixture containing rac-(EBI)ZrMe<sub>2</sub> led to in situ generation of cationic [rac-(EBI)Zr( $\mu$ -Me)<sub>2</sub>AlMe<sub>2</sub>]<sup>+</sup> species that can polymerize propylene to give an iPP with a meso pentad value of 94.7%.

In the lab-scale polymerization of propylene the rac-1/MAO catalyst system exhibited an increase of activity as [Al]/[Zr] ratio increased within an experimental range ([Al]/[Zr] = 930-6511). The rac-1/MAO system did not show any activity with a low concentration of MAO ([Al]/ [Zr] = 300; however, the addition of  $[Ph_3C]$  $[B(C_6F_5)_4]$  to the catalytic system during polymerization initiated polymerization. The meso pentad values of the iPPs obtained by the rac-1/MAO system were in the range of 83.2 to 87.5%. The catalytic activity was sensitive to the concentration of zirconocene. The activity was maximum  $(\overline{R_p} = 6.66 \times 10^6 \text{ g PP/mol Zr h atm})$  when the such as [mmmm],  $T_m$ , and  $\overline{M_w}/\overline{M_n}$  were not sensitive to the [Al]/[Zr] ratio and [Zr]. The molecular weight of iPP decreased as the [Al]/[Zr] ratio and [Zr] increased.

The catalytic activity of the MAO-free catalytic system *rac*-1/AlR<sub>3</sub>/noncoordinating anion was much higher than that of the *rac*-1/MAO system and was

sensitive to the type of AlR<sub>3</sub> and the type of noncoordinating anion. When the same amount of AlR<sub>3</sub> ([Al]/[Zr] = 106) was used as an alkylating reagent, the activity decreased in the order AlMe<sub>3</sub> ( $R_n$ )  $= 13.0 \times 10^{6} \text{ g PP/mol Zr h atm} > \text{Al}(i-\text{Bu})_{3} (8.9)$  $\times$  10<sup>6</sup>) > AlPr<sub>3</sub> (8.8 × 10<sup>6</sup>) > Al(*i*-Bu)<sub>2</sub>H (8.4 × 10<sup>6</sup>) > AlEt<sub>3</sub> (8.4  $\times$  10<sup>6</sup>) in the *rac*-1/AlR<sub>3</sub>/[HNMePh<sub>2</sub>]  $[B(C_6F_5)_4]$  system and decreased in the order [HNMePh<sub>2</sub>][B(C\_6F\_5)\_4] ( $\overline{R_p} = 13.0 \times 10^6$  g PP/mol Zr h atm > [HNMe<sub>2</sub>Ph][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (10.8 × 10<sup>6</sup>)  $> [Ph_3C][B(C_6F_5)_4] (8.4 \times 10^6) > [HNEt_2Ph]$  $[B(C_6F_5)_4]$  (7.8 × 10<sup>6</sup>) in the *rac*-1/AlMe<sub>3</sub>/noncoordinating anion system. The iPP properties such  $T_m$ , molecular weight, and  $\overline{M_w}/\overline{M_n}$  were not sensitive to the type of AlR<sub>3</sub> and the type of noncoordinating anion. When bulky alkylaluminums such as Al(i-Bu)<sub>2</sub>H or Al(*i*-Bu)<sub>3</sub> were used as an alkylating reagent for rac-1, the resulting iPPs showed lower [mmmm] values than when AlMe<sub>3</sub>, AlEt<sub>3</sub>, or AlPr<sub>3</sub> were used.

Thanks are due to Miss Ghil-Nam Hwang for performing some polymerization runs and collecting viscometric data and to Dr. Mi-Sook Won at the Korea Basic Science Institute (Pusan Branch) for analyzing (<sup>13</sup>C-NMR) so many polymer samples.

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