MAO-Free Polymerization of Propylene by rac-Me$_2$Si(1-C$_5$H$_2$-2-Me-4-tBu)$_2$Zr(NMe$_2$)$_2$ Compound

IL KIM, JIA-MIN ZHOU

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

Received 23 March 1998; accepted 25 July 1998

ABSTRACT: Ansa-zirconocene diamide complex rac-Me$_2$Si(CMB)$_2$Zr(NMe$_2$)$_2$ (rac-1, CMB = 1-C$_5$H$_2$-2-Me-4-tBu) reacts with AlR$_3$ (R = Me, Et, i-Bu) and then with [CPh$_3$]$_2$[B(C$_6$F$_5$)$_4$]$_2$ (2) in toluene in order to in situ generate cationic alkylzirconium species. In the sequential NMR-scale reactions of rac-1 with various amount of AlMe$_3$ and 2, rac-1 transforms first to rac-Me$_2$Si(CMB)$_2$Zr(Me)(NMe$_2$) (rac-3) and rac-Me$_2$Si(CMB)$_2$ZrMe$_2$ (rac-4) by the reaction with AlMe$_3$, and then to [rac-Me$_2$Si(CMB)$_2$ZrMe]$_1$ (5) cation by the reaction of the resulting mixtures with 2. The activities of propylene polymerizations by rac-1/Al(i-Bu)$_3$/2 system are dependent on the type and concentration of AlR$_3$, resulting in the order of activity: rac-1/Al(i-Bu)$_3$/2 > rac-1/AlEt$_3$/2 > rac-1/MAO > rac-1/AlMe$_3$/2 system. The bulkier isobutyl substituents make inactive catalytic species sterically unfavorable and give rise to more separated ion pairs so that the monomers can easily access to the active sites. The dependence of the maximum rate ($R_{p,max}$) on polymerization temperature ($T_p$) obtained by rac-1/Al(i-Bu)$_3$/2 system follows Arrhenius relation, and the overall activation energy corresponds to 0.34 kcal/mol. The molecular weight (MW) of the resulting isotactic polypropylene (iPP) is not sensitive to Al(i-Bu)$_3$ concentration. The analysis of regiochemical errors of iPP shows that the chain transfer to Al(i-Bu)$_3$ is a minor chain termination. The 1:3-addition of propylene monomer is the main source of regiochemical sequence and the [mr] sequence is negligible, as a result the meso pentad ([mmmm]) values of iPPs are very high ([mmmm] > 94%). These results can explain the fact that rac-1/Al(i-Bu)$_3$/2 system keeps high activity over a wide range of [Al(i-Bu)$_3$]/[Zr] ratio between 32 and 3,260. © 1999 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 37: 1071–1082, 1999

Keywords: methylaluminoxane (MAO) free; propylene polymerization; ansa-metallocene diamide; alkylzirconium cations; characterization of polymer

INTRODUCTION

The most promising ansa-metallocene catalyst for the isospecific polymerization of $\alpha$-olefins contain R$_2$Si-bridged bis(cyclopentadienyl) or bis(indenyl) ligands. Brintzinger and Rieger have reported that the C$_2$-symmetric metalloence rac-Me$_2$Si-(CMB)$_2$ZrCl$_2$ yields a highly isoselective propylene polymerization catalyst in the presence of MAO. Brintzinger prepared rac-Me$_2$Si(CMB)$_2$ZrCl$_2$ by the reaction of Me$_2$Si(CMB)$_2$K$_2$ and ZrCl$_4$(THF). Pure rac-Me$_2$Si(CMB)$_2$ZrCl$_2$ was obtained only after repeated recrystallization in 9% yield.

Jordan et al. have recently developed an efficient synthesis method of ansa-metallocene $^{ch}$C$_2$Zr-(NR$_2$)$_2$ ($^{ch}$C$_2$Zr = chiral ansa-zirconocene framework) via an amine elimination route. As a result, the reaction of Me$_2$Si(CMB)$_2$ with Zr(NMe$_2$)$_4$ affords Me$_2$Si(CMB)$_2$Zr(NMe$_2$)$_2$ in 90% NMR yield (rac/meso = 2.5/1) and pure rac-1 in 52% isolated yield. The rac-1 catalyst has been demonstrated to be directly used for the propylene polymerization in
the presence of MAO. There are two more standard procedures to activate metallocenes for the olefin polymerizations other than the procedure using MAO as a coactivator. They include 1) reaction of $^{1}$Cp$_2$ZrR$_2$, complexes with ammonium salts (e.g., [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$]), oxidizing agents (e.g., Ag$^+$, Cp$_2$Fe$^+$), or alkyl abstraction reagents (e.g., CPh$_3$, B(C$_6$F$_5$)$_3$) or 2) in situ alkylation of $^{1}$Cp$_2$ZrX$_2$ complexes with AlR$_3$ or other reagents followed by ionization as in 1). The second procedure has advantage over the first procedure and the procedure using MAO, because the alkylation step of $^{1}$Cp$_2$ZrX$_2$ complexes and the use of excess amount of MAO can be avoided.

In this work we have studied propylene polymerization by rac-1 by using activation procedure 2). Through the sequential NMR-scale reactions of rac-1 with AlMe$_3$ and then with 2, the formation procedure of cationic active species is also investigated.

**EXPERIMENTAL**

**Materials**

All materials were handled with Schlenk or glovebox techniques under argon atmosphere. Toluene was distilled from sodium prior to use. Propylene of polymerization grade (SK Co., Korea) was purified by passing it through columns of Fisher RIDOX catalyst and molecular sieves 5A/13X. Alkyl aluminums, Al(i-Bu)$_3$, AlEt$_3$, and AlMe$_3$, were donated by Korea Petrochem. Co. and used without purification. The catalyst rac-1$^{1c}$ and the anionic compound 2$^a$ were synthesized according to literature procedures.

**Sequential NMR-Scale Reaction**

The procedure for in situ generating solutions of zirconium cationic species by the sequential reaction of rac-1, AlMe$_3$, and 2 is as below. Rac-1 (12.65 mg, 25.0 $\mu$mol) was dissolved in CD$_2$Cl$_2$ (0.5 mL) at room temperature to give a yellow solution. In the dry box, prescribed amount of AlMe$_3$ was sequentially added to the solution mixture for the methylation of rac-1. Addition of 10 equiv. of AlMe$_3$ resulted in a colorless solution representing complete methylation. After analyzing the solution mixture, compound 2 (23.1 mg, 25.0 $\mu$mol) was introduced into the NMR tube at room temperature to generate cationic methylzirconium complex. After NMR analysis, approximately 0.5 mL of liquid propylene was added to the mixture at $-78^\circ$C, followed by a slow increase of the temperature to room temperature. Solid iPP formed from the solution mixture was isolated and dried for the analysis.

**Polymerization**

The polymerization was carried out in a 250-mL glass reactor. A Teflon magnetic stirring bar was used for the agitation. First, 80 mL of toluene, prescribed amount of AlR$_3$, and 38.4 $\mu$M of rac-1 were introduced into the reactor sequentially in a dry box. After attaching the reactor to the polymerization setup, argon was pumped off, and the reactor was then filled with propylene. After the temperature was stabilized at a desired point, 38.4 $\mu$M of 2 was injected into the reactor by a hypodermic syringe, and then the polymerization started. Polymerization was stopped by introducing 150 mL of ethanol containing HCl (5 wt %) into the reactor. The detailed polymerization setup was described elsewhere.

**Characterization of Polymer**

Polymers were fractionated by the following solvents sequentially: ethyl ether (E), n-pentane (C$_5$), n-hexane (C$_6$), and n-heptane (C$_7$), by using a Soxhlet apparatus for 6 h. Thermal analysis of polymer was carried out by using Dupont differential scanning calorimeter (DSC, Model-900) at 10°C/min heating rate under nitrogen atmosphere. The intrinsic viscosity was measured in tetrahydronaphthalene at 135 ± 0.1°C by using an modified Ubbelohde viscometer and converted into viscosity-average molecular weight using a following relationship:

$$[\eta] = 1.0 \times 10^{-4} M_v^{0.8}$$

Also tested were molecular weight and its distribution ($M_w/M_n$) by gel permeation chromatography (GPC) on a Water 150-C equipped with TSK columns (Model GM-HXL-HT) and a data processor at 135°C with 1,2-dichlorobenzene as solvent. Solution $^{13}$C NMR spectra were run at 75.4 MHz on a Varian UNITY-300 NMR spectrometer. Samples were run as 10% solution in benzene-$d_6$/1,2,4-trichlorobenzene-$d_3$ (1/5 v/v) at 120°C. Chemical shifts are referenced to tetramethylsilane using as a secondary reference the methyl peak of polypropylene at 21.8 ppm. A total of
6,000 transients were accumulated for each spectrum with a 12-s delay between pulses. Decoupling was always on during acquisition so the nuclear Overhauser enhancement was present.

RESULTS AND DISCUSSION

NMR-Scale Reaction of rac-1 with AlR₃ and Anionic Compound

From the sequential NMR-scale reaction of rac-1 with MAO, we have shown that rac-1 is completely transformed into the methylzirconium cations, [rac-Me₂Si(CMB)₂ZrMe]⁺, by reacting 40 equiv. of MAO. Free AlMe₃ contained in MAO plays an important role to alkylate rac-1 in this system because rac-1 is mainly alkylated by free AlMe₃ to afford dimethyl complex rac-4. By applying the fact that rac-1 is easily alkylated by AlMe₃, we have investigated the procedures to generate cationic species by using rac-1/AlMe₃/2 system. Rac-1 was first reacted with various amounts of AlMe₃ in an NMR tube containing CD₂Cl₂ as a solvent, and then 2 was added to the resulting solution mixture containing alkylated compound of rac-1 in order to in situ generate cationic active species. We used CD₂Cl₂ solvent in place of toluene-d₆, which is generally used as a solvent for the metallocene polymerization, for the NMR-scale reactions due to the following reasons. Firstly, CD₂Cl₂ solvent is characterized by much better solubility for rac-1 than toluene-d₆. The high solubility is required for dissolving 12.6 mg of rac-1 and 23.1 mg of 2 at the same time in the NMR tube. Second, after in situ generating cationic species, a small amount of liquid propylene is introduced into the NMR tube containing the resulting cationic complex at −78°C in order to perform NMR-scale polymerization. If toluene-d₆ is used, the reaction mixture solidifies at this temperature before adding propylene monomer, resulting in phase separation. However, CD₂Cl₂ remains liquid at this temperature, resulting in no phase separation. Third, chlorinated CD₂Cl₂ is generally known to be inert to metallocene compounds like toluene-d₆ or benzene-d₆.

Table I summarizes the chemical shifts and relative compositions of identified compounds existed in solution mixtures. As the amount of AlMe₃ increases from [AlMe₃]/[rac-1] = 2 to 10, zirconocene dimethyl compound rac-4 is formed via an intermediate compound rac-3. The methylation of rac-1 is completely accomplished with 10 equiv. of AlMe₃ (5 equiv. of Al₂Me₆). Two methylaluminum compounds, Al₂Me₅(NMe₂) and Al₂Me₆, are observed in the mixture. Addition of 1 equiv. of 2 to the solution mixture of AlMe₃/rac-1 (10/1) results in immediate conversion to 5⁺ cation. This reaction is proceeded as a stoichiometric yield. It is interesting to note that the addition of 2 to the solution mixture of AlMe₃/rac-1 (8/1), which contains both rac-3 and rac-4, results in complete conversion to the same cationic species, 5⁺. These results demonstrate that the methylzirconium cations can be formed according to the procedures shown in Scheme 1.

It has been shown that ansa-metallocene amides such as rac-(SBI)Zr(MeNMe₂)₂9 (SBI = Me₂Si(Ind)₂) and rac-(EBI)Zr(MeNMe₂)₁₀ (EBI = 1,2-ethylenebis(indenyl)) are completely transformed to the corresponding dimethyl zirconocenes by reacting them with 4 equiv. of AlMe₃ and then to [rac-(SBI)Zr(μ-Me₂Me₂AlMe₃)]⁺ and [rac-(EBI)Zr(μ-Me₂Me₂AlMe₃)]⁺, adducts of the base-free cation and AlMe₃, analogue of which was previously identified by Bochmann¹¹ as the principal component in the mixture of these species. Comparing with the previous results obtained by above two metallocenes, rac-1/AlMe₃/2 system is characterized by the fact that 1) the alkylation of rac-1 by AlMe₃ is not proceeded stoichiometrically and 2) in situ alkylated rac-4 affords 5⁺ cations instead of dinuclear cationic species 6⁺.

In order to confirm the formation of cationic active species, NMR-scale polymerization of propylene was carried out by introducing 0.5 mL of liquid propylene into the NMR tube containing rac-1/10 AlMe₃/2 system at −78°C. Immediately after introducing propylene monomer, solid iPP showing very high stereoregularity ([mmm] = 99.6%) was precipitated.

Effect of Trialkyl Aluminum on Polymerization

For methylzirconocene cations paired with anion compound, for example [B(C₆F₅)₄]⁻, isospecific polymerizations are, more frequent than not, either runaway reactions or resulting in the low yields of polymer.¹² The runaway phenomenon is usually caused by high exotherms that present a potential danger as they generate very high pressure. The reports on the polymerizations by metallocene dichloride coactivated by anionic compound are much rarer than those coactivated by MAO. The runaway exotherms were not found in our system. Figure 1 is the rate profiles of pro-
polyethylene polymerization catalyzed by rac-1/Al(i-Bu)₃/2 system. All polymerizations show very high activities in a wide range of [Al]/[Zr] ratio between 32 and 3,260, even if the average rate of polymerization (Rp) decreases somewhat at high [Al]/[Zr] ratios (say 1,950 and 3,260). All the rates increase rapidly to maximum activity within 3 min and then decrease sharply to stable rates (about one third of maximum rate). These results demonstrate that cationic zirconocene ions are satisfactorily generated by rac-1/Al(i-Bu)₃/2 system as in the case of rac-1/AlMe₃/2 system:

\[
\text{rac-Me₂Si(CMB)₂Zr(NMe₂)₆ + b Al(i-Bu)₃} \rightarrow \text{rac-Me₂Si(CMB)₂Zr(i-Bu)₃} + x \text{AlMe₆} \]

\[
+ (a-x) \text{rac-Me₂Si(CMB)₂Zr(i-Bu)₃} \rightarrow \text{rac-Me₂Si(CMB)₂Zr(i-Bu)₃} \text{[2]}
\]

\[
+ [\text{CPh₃}[\text{B(C₆F₅)₄}]] \rightarrow [\text{rac-Me₂Si(CMB)₂Zr(i-Bu)₃}]^+ + [\text{B(C₆F₅)₄}^-] + \text{Ph₃C(i-Bu)} \text{[3]}
\]

<table>
<thead>
<tr>
<th>Compounds or Mixtures</th>
<th>Identified Compound</th>
<th>Chemical Shifts (δ), Identified (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>rac-Me₂Si(CMB)₂Zr(NMe₂)₆</td>
<td>rac-1</td>
<td>6.260 (d, 2H, Cp), 5.519 (d, 2H, Cp), 2.623 (s, 12H, NMe₂), 2.132 (s, 6H, Cp–Me), 1.234 (s, 18H, t-Bu), 0.645 (s, 6H, Si-Me)</td>
</tr>
<tr>
<td>AlMe₃</td>
<td>Al₂Me₆</td>
<td>-0.29 (s)</td>
</tr>
<tr>
<td>[CPh₃][B(C₆F₅)₄]⁻</td>
<td>2</td>
<td>8.27 (t, 3H), 7.87 (t, 6H), 7.66 (d, 6H)</td>
</tr>
<tr>
<td>rac-1/2 AlMe₃</td>
<td>rac-1</td>
<td>Chemical shifts are the same as above.</td>
</tr>
<tr>
<td>Al₂Me₆</td>
<td>-0.29 (s) No reaction between rac-1 and Al₂Me₆.</td>
<td></td>
</tr>
<tr>
<td>rac-1/4 AlMe₃</td>
<td>rac-1</td>
<td>Chemical shifts are the same as above.</td>
</tr>
<tr>
<td>rac-1/6 AlMe₃</td>
<td>rac-1, rac-3, rac-4</td>
<td>Chemical shifts are the same as above and the ratio of rac-1/rac-3/rac-4 in this mixture is 3/2/1.</td>
</tr>
<tr>
<td>Al₂Me₆, Al₂Me₆(NMe₂)</td>
<td>2.417 (s, 6H, NMe₂), -0.554 (br s, 15H, Al-Me). Al₂Me₆/Al₂Me₆(NMe₂) ratio is about 1/1.</td>
<td></td>
</tr>
<tr>
<td>rac-1/8 AlMe₃</td>
<td>rac-3, rac-4</td>
<td>No rac-1 is observed and the ratio of rac-3/rac-4 in this mixture is 1/2.</td>
</tr>
<tr>
<td>Al₂Me₆, Al₂Me₆(NMe₂)</td>
<td>Chemical shifts are the same as above and the ratio of Al₂Me₆/Al₂Me₆(NMe₂) ratio is 5/2.</td>
<td></td>
</tr>
<tr>
<td>rac-1/10 AlMe₃</td>
<td>rac-4</td>
<td>rac-3 is completely transformed to rac-4.</td>
</tr>
<tr>
<td>Al₂Me₆, Al₂Me₆(NMe₂)</td>
<td>Al₂Me₆/Al₂Me₆(NMe₂) ratio is 3/1.</td>
<td></td>
</tr>
<tr>
<td>rac-1/8 AlMe₃/2 or rac-1/10 AlMe₃/2</td>
<td>[rac-Me₂Si(CMB)₂Zr(μ-Me₂)AlMe₆]⁺ (5⁺)</td>
<td>6.620 (br d, 2H, Cp), 5.706 (br d, 2H, Cp), 2.110 (br s, 6H, Cp–Me), 1.286 (s, 18H, t-Bu), 0.786 (br s, 6H, Si-Me), -0.780 (s, 3H, Zr-Me).</td>
</tr>
<tr>
<td>Al₂Me₆, Al₂Me₆(NMe₂)</td>
<td>Chemical shifts are the same as above.</td>
<td></td>
</tr>
</tbody>
</table>
rac-Me2Si(CMB)2Zr(i-Bu)(NMe2)

In this method Al(i-Bu)3 functions also to scavenge impurities contained in the polymerization medium. Since the cationic species rac-Me2Si-(CMB)2Zr(i-Bu)3 are in situ generated via alkylzirconocene intermediates, the order of addition of reactants is expected to be an important factor. In order to check this effect, we have carried out polymerization by changing the order of reactants [see Fig. 1(a)]. The polymerization carried out by using 38.4 μM of rac-1 coactivated by 38.4 μM of 2 prior to alkylation shows no activity. After 15 min of polymerization with this condition, 6.2 mM of Al(i-Bu)3 is injected into the reactor. No conspicuous activity is observed as shown in Figure 1(a). These results show clearly that the order of addition of reactants influences on the polymerization behavior very much in the present catalyst system. The polymerization recovers the activity by injecting 95.6 mM of MAO after 25 min of polymerization.

These results can be summarized by Scheme 2. When 2 is firstly introduced to the reactor, the rac-1 changes to the cationic species (a) that are not active for the polymerization possibly due to the coordination of amine byproduct, Ph3C(NMe2), to the vacant sites. The similar cationic species have been identified through the NMR-scale reaction of rac-(EBI)Zr(NMe2)2 with 2.10 When Al(i-Bu)3 is injected into the reactor after 15 min, the species (a) is alkylated to form cationic species (b); however, these species are still inactive, because Ph3C(NMe2) remains coordinated to the cationic species. When additional MAO is injected into the reactor, the amine byproduct can react with MAO and is removed away from the cationic species. As a result, active species (c) and/or (d), which can polymerize propylene, seem to be formed. The detailed NMR-scale reactions of rac-(EBI)Zr(NMe2)2, 2, and AlMe3 in this order have been reported in the previous literature.10

Either diffusion limitation or acceleration of chain terminations or both generally causes the rapid decay of polymerization rates after reaching maximum rate. The diffusion limitation is caused by dramatic change of media viscosity and poly-

Figure 1. $R_p$ versus time of propylene polymerizations initiated by rac-1/Al(i-Bu)3/2 catalyst with [Zr] = 38.4 μM, [rac-1] = 1, toluene = 80 mL, $T_p$ = 30°C, and $P_{C3H6}$ = 1.3 atm under different [Al]/[Zr] ratios of (b) 32, (c) 330, (d) 650, (e) 980, (f) 1950, and (g) 3260. (a) Polymerization is started by rac-1 and 2 ([rac-1]/[2] = 1) and 6.2 mM of Al(i-Bu)3 and 95.6 mM of MAO are injected into the reactor at 15 and 25 min, respectively.
mer precipitation during polymerization. The chain terminations are mainly caused by deactivation of bimolecular process between two catalytic sites, which follow the second-order decay kinetic model. In our system the highly stereo-regular polymers were precipitated early in the polymerization due to a very rapid initial rate that then settles to a slower and more or less constant rate. The insoluble polymer must coat the catalytic active sites erecting a diffusion barrier to incoming monomer. As a result, both chemical and physical effects seem to cause the rapid decay of the polymerization rate for the present catalytic system.

Propylene polymerizations were also carried out by using AlEt₃, which exists as a dimer in solution, as an alkylating reagent. As shown in Figure 2, polymerizations reach maximum rates within 3 min and then decrease sharply within 10 min to stable rates (about half of maximum rate) when [Al]/[Zr] ratio is 980 and 1,300. At low [Al]/[Zr] ratios, i.e., 300 and 650, the polymerizations decay very rapidly to zero rates after reaching maximum rates. At very high [Al]/[Zr] ratio, i.e., 1,950, the maximum rate is fairly suppressed. These results demonstrate that: 1) some of free AlEt₃ that exists in polymerization medium is not the cocatalyst in the rac-1/AlEt₃/2 system and 2) the concentration of AlEt₃ influences the formation of active and inactive species. Therefore, there is an amount of AlEt₃ that is crucial for obtaining high activity. What remains unclear is how active species change rapidly to inactive species at low [Al]/[Zr] ratios and why such a high concentration of AlEt₃ (approximately 1,000 of [Al]/[Zr] ratio) is needed in rac-1/AlEt₃/2 system.

The similar polymerizations have been performed by using rac-1/AlMe₃/2 system in the wide range of [Al]/[Zr] ratio between 60 and 3,000, resulting in negligible activities. Considering the previous results obtained in the NMR-scale reactions by using rac-1/AlMe₃/2 and rac-1/MAO systems, this is an interesting result. The rac-1/MAO system, in which MAO contains about 18.5 wt % of free AlMe₃, showed fairly high activity in the wide range of [Al]/[Zr] ratio as shown in Figure 3. The negligible activity of rac-1/AlMe₃/2 system may be due to the fact that in the presence of AlMe₃, the 5⁺ cation goes preferentially to a heterodinuclear complex [rac-Me₅Si(CMB)₂Zr(μ-Me₂AlMe₂)]⁺ (6⁺) in toluene solvent. There exists equilibrium between 5⁺ and 6⁺ during reaction. The AlMe₃ adduct 6⁺ is coordinatively saturated and lacks a vacant orbital suitable for binding the propylene monomer. The initiation of chain growth requires, therefore, the dissociation of the AlMe₃ to 5⁺, but in the presence of AlMe₃, the...
equilibrium favors the heterodinuclear complexes. This may be the same case for rac-1/AlEt₃/2 system of high [Al]/[Zr] (Fig. 2) in which an increase in the concentration of AlEt₃ from 1,300 equiv. to 1,950 causes a decrease of the activity by a factor of 5. The high activity of rac-1/MAO system in the wide range of [Al]/[Zr] ratio, even if the system contains considerable amount of AlMe₃, is possibly because MAO makes the equilibrium go to species 5⁺ and reactivate the inactive species. Bochmann did the propylene polymerization with the system rac-(SBI)ZrMe₂/AlR₃/2 in the presence of 1 to 500 equivalents of AlEt₃ or AlMe₃. The highest activity was found for an [AlEt₃]/[Zr] ratio of 10 : 1 and [AlMe₃]/[Zr] ratio of only 1 : 1. Based on this result and detailed spectroscopic results, Bochmann concluded that in the presence of AlEt₃ or AlMe₃, the heterodinuclear complexes [rac-(SBI)Zr(μ-R)₂AlR₃]⁺ (R = Me, Et) are major cationic species.

In summary, the bulkier isobutyl substituents may render inactive heterodinuclear complexes sterically unfavorable, and this could result in a higher number of active sites. In addition, the bulkiness of isobutyl substituents gives rise to more separated ion pairs and this facilitates the access of the monomers to the active sites. However, as the bulkiness of the substituents decreases, as in the case of ethyl and methyl, the equilibrium of cationic species is inclined to direct to inactive heterodinuclear species.

**Figure 3.** $R_p$ versus [Al]/[Zr] ratio plots. Polymerization conditions: (a) same as in Figure 1, (b) same as in Figure 3, and (c) from Ref. 5 of rac-1/MAO.

**Figure 4.** $R_p$ versus time of propylene polymerizations initiated by rac-1/Al(i-Bu)s/2 catalyst with [Zr] = 38.4 μM, [Al]/[Zr] = 650, 2/rac-1 = 1, toluene = 80 mL, and P C₃H₆ = 1.3 atm under different polymerization temperatures of (a) 10, (b) 20, (c) 30, (d) 40, (e) 50°C.

**Figure 5.** Arrhenius plots of $\bar{R}_p$ and $R_p,max$. 
Effect of Polymerization Temperature ($T_p$): 
rac-1/Al(i-Bu)$_3$/2 System

Polymerizations initiated by rac-1/Al(i-Bu)$_3$/2 system ([Al]/[Zr] = 650) were performed at the $T_p$ range between 10 and 50°C (Fig. 4). All polymerizations rise to maximum rates very rapidly and then decrease sharply. The maximum rate increases as $T_p$ decreases. The polymerization rate decays to one tenth of maximum rate after only 20 min when $T_p = 10°C$ because high viscosity of the reaction medium during the early period of polymerization makes the stirring bar agitate inefficiently. The precipitation of polymer during the initial acceleration period may hinder the monomer from coordinating to the propagating sites. The higher maximum rate at lower $T_p$ is unprecedented in Ziegler-Natta catalysis. In previous catalysts, either heterogeneous or homogeneous, activity decreases sharply with a decrease of $T_p$. Chien et al.\textsuperscript{17,18} reported unexpectedly high propylene polymerization activity for the system rac-(EBI) ZrMe$_2$/2, particularly when $T_p < -20°C$, the polymerizations were agitation limited after only a few minutes.

Figure 5 shows an Arrhenius plot of polymerization rate ($R_p$ and $R_p$,$\text{max}$). The ln $R_p$ versus $T^{-1}$ plot deviates from the linearity, possibly because the physical phenomenon like the diffusion limitation of monomer deeply influences the overall rate of polymerization especially at lower $T_p$. The ln $R_p$,$\text{max}$ versus $1/T$ plot shows good linearity over the whole $T_p$ range. The physical influences on the polymerization rate are negligible during the initial acceleration period. The overall activation energy obtained from the slope of the plot is calculated to be 0.34 kcal/mol. This value is much lower than that obtained by rac-1/MAO system\textsuperscript{5} in which the overall activation energy was 12.2 kcal/mol ($T_p = 10$ to 70°C). The reason of the big difference of apparent activation energy between two catalytic systems remains uncertain. The complicated equilibria, which should be overcome for the chain growth, formed by using MAO as coactivator seem to be related with the difference of activation energy.

Characterization of iPP

A $C_2$-symmetric metallocene with a Si-atom bridging the two ligands, due to higher stereori-
gidity and favorable electronic characteristics, affords iPP with high molecular weight (MW) and isotacticity. The high MW is attributed mainly to the electron-donating effect of the alkyl substituents, which effectively lowers Lewis acidity of the central metal atom to alleviate β-H chain-transfer. High isotacticity benefits mainly from rigidity of the ligand framework, which can be strengthened further by alkyl substituent on the most favorable positions.

The characterization results of iPPs produced in this study are summarized in Table II. The crystallinity is calculated from the heat of fusion, \((\Delta H_f/\Delta H^0_f) \times 100\), in which \(\Delta H_f\) is the heat of fusion of the sample as determined from the DSC curve, and \(\Delta H^0_f\) is the fusion of folded-chain of isotactic polypropylene with the value of 208.3 J/g. The \(^{13}\)C NMR analysis of polymer shows that the polymers produced by rac-1/AlR\(_3\)/2 catalysts is characterized by very high stereoregularity. The high stereoselectivity comes from the small centroid-Zr-centroid angle for the Me\(_2\)Si bridge metallocene. Many Me\(_2\)Si-bridged metallocenes polymerize propylene with a high isotacticity more than 90% of [mmmm]. When \(T_p\) increases, the isotacticy of iPP decreases to some degree, resulting in 87% of [mmmm] at \(T_p = 50^\circ\)C. Generally ansa-metallocene complexes in solution are rather soft. The thermal disturbance at raised \(T_p\) causes a strong vibration of ligands and a deformation of their rigid conformation, which results in the loss of their stereoregulating ability.

The [mmmm] value shows maximum according to the concentration of AlR\(_3\), i.e., 99.2% at [Al(\(i\)-Bu)\(_3\)][Zr] = 1,950 and 99.3% at [AlEt\(_3\)][Zr] = 1,300. The decrease of [mmmm] value at excess AlR\(_3\) concentration indicates that the behavior of active species is somewhat changed by affecting both the mechanism of chain termination and propagation rates.

The isotacticy of polypropylene depends on two kinds of errors, regiochemical and stereochecmical errors. Regiochemical errors are based on the chain sequences as shown in Figure 6. This kind of error is from some special reactions:

\[
\begin{align*}
\text{CH}_3 & \\
\text{Zr--CH} & \text{CH}_2 \text{Pn} + \text{C}_3\text{H}_6 \rightarrow \\
\text{CH}_3 & \text{CH}_3 \\
\text{Zr--CH} & \text{CH}_2 \text{CH} = \text{CH} \text{Pn} \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 & \\
\text{Zr--CH} & \text{CH}_2 \text{Pn} + \text{C}_3\text{H}_6 \rightarrow \\
\text{CH}_3 & \text{CH}_3 \\
\text{Zr--CH} & \text{CH} = \text{CH} \text{Pn} \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 & \\
\text{Zr--CH} & \text{CH}_2 \text{Pn} + \text{C}_3\text{H}_6 \rightarrow \\
\text{CH}_3 & \text{CH}_3 \\
\text{Zr--CH} & \text{CH} = \text{CH} \text{Pn} \\
\end{align*}
\]

Figure 6. Regiochemical and stereochemical errors on the course of isospecific polymerization of propylene.
Grass et al. suggested that the 1,3 units of structure (A) in Figure 6 are formed via isomerization of 2,1 units, possibly according to Eq. (5). The tail-tail linking [Eq. (6)] and head-head linking [Eq. (7)] result in the regioirregular sequences of structure (B) and (C). Because of the chain termination, the endgroup of unsaturated structure (D) comes from $\beta$-H elimination [Eq. (8)] and/or chain transfer to monomer [Eq. (9)], structure (E) from chain transfer to Al(i-Bu)$_3$ [Eq. (10) and (11)], and structure (F) from 1,2-propylene insertion into a Zr-H bond [Eq. (12)]. Figure 7 is the $^{13}$C NMR spectrum of representative iPP sample [Fig. 4(e)]. All three kinds of endgroups of structure (D), (E), and (F) are found. According to the intensity of signal, it would be said structure (F) is the main endgroup and structure (E) is much weaker than (D) and (F). This result demonstrates that chain transfer to Al(i-Bu)$_3$ plays minor role in chain termination reaction. The spectrum shows some regioirregular sequences of structure (A) but no regioirregular sequences of structure (C), which gives the evidence that there are almost no [mr] stereochemical errors during polymerization.

The dependence of MW on $T_p$ is a popular phenomenon in the olefin polymerization. The MW declined by a factor of 10 when $T_p$ changes from 10 to 50°C (Table II). The $M_n/M_w$ value is quite sensitive to temperature and becomes very narrow when $T_p$ increases. Same result was found with rac-1/MAO system.

The $^{13}$C NMR above. These results give support that the high activity keeps in a broad range of [Al(i-Bu)$_3$/[Zr] ratio as shown in Figure 3. However, excess amount of AlEt$_3$ reduces the MW value slightly. The iPPs produced by rac-1/AlR$_3$/2 system are characterized by high $T_m$ (i.e., 160.9°C at $T_p = 10°C$). Even if the $T_m$ value decreases with the increase of $T_p$, polymers produced at high $T_p$ sustain quite high $T_m$ values due to the uniform polymer chain causing perfect crystal with a high crystallinity. The change of AlR$_3$ concentration does not influence the melting point and crystallinity.

Three kinds of iPP samples were fractionated by refluxing with ethyl ether (E), n-pentane (C$_5$), n-hexane (C$_6$), and n-heptane (C$_7$) sequentially, and the results are summarized in Table III. The samples are polymerized by using rac-1/Al(i-Bu)$_3$/2 ([mmm] = 96.2%), rac-1/AlEt$_3$/2 ([mmm] = 99.3%), and rac-1/MAO ([mmm] = 96.9%)$^5$ systems at $T_p = 30°C$. Almost no refluxing E, C$_5$, and C$_6$ soluble products are isolated. The amount of C$_7$ fraction (C$_7$ soluble, C$_6$ insoluble) and remaining fraction (C$_7$ insoluble) are more than 98%, demonstrating that the samples are characterized by compositional homogeneity. The polymer obtained by rac-1/AlEt$_3$/2 system has the highest amount of remained fraction (67.5%) and the sample of the remained fraction has the highest $T_m$ (157.4°C).

**CONCLUSION**

The ansa-zirconocene diamide, rac-1, could be directly used for the propylene polymerization in the absence of MAO without transforming it to the corresponding dialkyl or dihalide compounds.
In rac-1/AlMe$_3$/2 system, rac-1 is first converted to rac-3 and rac-4 by the reaction with AlMe$_3$, and then the resulting alkylated species are transformed to 5$^+$ cation by the reaction with 2.

The propylene polymerization by rac-1/AlR$_3$/2 (R = Me, Et, i-Bu) catalysts was sensitive to polymerization parameters such as $T_p$, and the type and concentration of AlR$_3$. The average polymerization rate decreased according to the order: rac-1/Al(i-Bu)$_3$/2 > rac-1/AlEt$_3$/2 > rac-1/MAO > rac-1/AlMe$_3$/2 system. The rac-1/AlMe$_3$/2 system showed no detectable activity. The bulky isobutyl substituents may render inactive heterodinuclear complexes sterically unfavorable and this could result in a higher number of active sites, but less bulky substituents such as methyl and ethyl have stronger tendency to form inactive heterodinuclear cationic species.

The rac-1/Al(i-Bu)$_3$/2 system showed maximum activity ($R_p = 5.90 \times 10^6$ g-PP/mol-Zr hr atm) when [Al]/[Zr] = 650 and $T_p = 30^\circ$C, and rac-1/AlEt$_3$/2 system showed maximum activity ($4.35 \times 10^6$ g-PP/mol-Zr hr atm) when [Al]/[Zr] = 1,300 and $T_p = 30^\circ$C. The polymerization rate by rac-1/Al(i-Bu)$_3$/2 catalyst kept a high value in a wide range of [Al]/[Zr] ratio between 32 and 3,260, but that by rac-1/AlEt$_3$/2 catalyst in a relatively narrow [Al]/[Zr] range between 650 and 1,950.

The results obtained by rac-1/Al(i-Bu)$_3$/2 system according $T_p$ (10 to 50$^\circ$C) showed that the polymerization rate decreases as $T_p$ increases and the rate profiles of polymerization carried out at low $T_p$ (i.e., 10$^\circ$C) is deeply influenced by the diffusion limitation of monomer. The dependence of the maximum polymerization rates on $T_p$ followed Arrhenius relation and the resulting overall activation energy is very small value, 0.34 kcal/mol.

The polymers showed very high stereoregularity and high $T_m$. With the increase of $T_p$ from 10 to 50$^\circ$C, [mmmm] pentad decreased from almost 99.4 to 87.1%, melting point from 161 to 141$^\circ$C, $M_v$ from $3.9 \times 10^4$ to 0.4 $\times 10^4$, and $M_w/M_v$ from 2.39 to 1.64. The detailed analysis of polymer indicates that 1,3-addition is the main source of regioirregular sequences in the present catalytic systems. Fractionation of iPP samples by using various solvents showed that the polymers produced in the present systems and that produced by rac-1/MAO catalyst are compositionally homogeneous.

Acknowledgment is made to the donors of Korea Research Foundation (Nondirected fund, 1997). We thank to Mr. Jinkee Sung (Korea Petrochemical Co.) for arranging GPC analysis and Dr. M.-S. Won (Korea Basic Science Institute) for thermal analysis.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Al and [Al]/[Zr]</th>
<th>Fraction</th>
<th>Polymer in Fraction (wt %)</th>
<th>$T_m$ (°C)</th>
<th>$\overline{M_v} \times 10^{-4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fig. 1(d)</td>
<td>Al(i-Bu)$_3$ 650</td>
<td>Total 100</td>
<td>156.6</td>
<td>1.31</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>E 1.0</td>
<td>138.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>C$_5$ 0</td>
<td>148.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>C$_6$ 0.7</td>
<td>151.6</td>
<td>0.78</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>C$_7$ 46.9</td>
<td>154.5</td>
<td>2.57</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Remained 51.4</td>
<td>154.5</td>
<td>2.57</td>
<td></td>
</tr>
<tr>
<td>Fig. 2(d)</td>
<td>Al(C$_2$H$_5$)$_3$ 1300</td>
<td>Total 100</td>
<td>156.6</td>
<td>1.18</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>E 0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>C$_5$ 0</td>
<td>134.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>C$_6$ 1.0</td>
<td>149.5</td>
<td>0.60</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>C$_7$ 31.5</td>
<td>157.4</td>
<td>1.78</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Remained 67.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ref. 5b</td>
<td>MAO 6250</td>
<td>Total 100</td>
<td>152.2</td>
<td>0.55</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>E 0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>C$_5$ 0</td>
<td>137.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>C$_6$ 1.8</td>
<td>149.7</td>
<td>0.60</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>C$_7$ 71.3</td>
<td>155.0</td>
<td>0.68</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Remained 26.9</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Polymerization conditions are given in correspondence with figure shown in run no.

*The iPP produced by rac-1/MAO at $T_p = 30^\circ$C.
Research Center, Pusan Branch) for arranging NMR analysis.

REFERENCES AND NOTES


