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ISOSPECIFIC POLYMERIZATION OF PROPYLENE BY *ansa*-ZIRCONOCENE DIAMIDE COMPOUND COCATALYZED BY MAO

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Key Words: Polymerization, Propylene, Kinetics, *ansa*-Metallocene diamide, methylaluminoxane

ABSTRACT

The kinetics of propylene polymerization initiated by racemic ethylene-1,2-bis(1-indenyl)zirconium bis(dimethylamide) [*rac*-(EBI)Zr$(NMe_2)_2$ (*rac*-**1**)] cocatalyzed by methylaluminoxane (MAO) were studied. The polymerization behaviors of *rac*-**1**/MAO catalyst investigated by changing various experimental parameters are quite different from those of *rac*-(EBI)$ZrCl_2$ (*rac*-**2**)/MAO catalyst, due to the differences in the generation procedure of cationic actives species of each metallocene by the reaction with MAO. The activity of *rac*-**1**/MAO catalyst showed maximum when [Al]/[Zr] is around 2000, when [Zr] is 137.1 μM, and when polymerization temperature is 30°C. The negligible activity of *rac*-**1**/MAO catalyst at a very low MAO concentration seems to be caused by the instability of the cationic active species. The *meso* pentad values of polymers produced by *rac*-**1**/MAO catalyst at 30°C are in the range of 82.8% to 89.7%. The *rac*-**1**/MAO catalyst lost stereorigid character at the polymerization temperature above 60°C. The molecular weight of polymer decreased as [Al]/[Zr] ratio, polymerization temperature, and [Zr] increased. The molecular weight distributions of all polymers are in the range of 1.8–2.3, demonstrating uniform active species present in the polymerization system.

INTRODUCTION

Chiral group 4 *ansa*-metallocenes are the basis of a new class of stereoselective olefin polymerization catalysts [1]. However, practical application of *ansa*-metallocene catalysts has been hindered by the fact that the racemic (*rac*) isomers required for the stereospecific polymerization of α-olefin are difficult to prepare. Current synthetic routes of *ansa*-metallocenes based on salt elimination reactions of MCl_x salts and bis-cyclopentadienyl dianion reagents are inefficient and require tedious separation and purification steps. Brintzinger and Collins prepared the prototypical chiral *ansa*-metallocene *rac*-(EBI)$ZrCl_2$ (EBI = ethylene-1,2-bis(1-indenyl), *rac*-**2**) by reaction of $ZrCl_4(THF)_2$ and (EBI)Li_2, and reported low, variable yield (30-50%) [2]. Buchwald employed (EBI)K_2 and obtained (EBI)$ZrCl_2$ in 70% yield with a *rac/meso* ratio of 2/1 [3]. In general, current syntheses of chiral *ansa*-metallocenes produce the desired rac isomer in 10-30% yield, and separation is not always possible.

Recently, Jordan reported an efficient synthesis method of *ansa*-metallocene $^{ch}Cp_2Zr(NR_2)_2$ ($^{ch}Cp_2Zr$ = chiral *ansa*-metallocene framework) via an amine elimination route [4]. They prepared *rac*-**1** by the reaction of (EBI)H_2 and $Zr(NMe_2)_4$ with 90% yield in *rac/meso* ratio of 13/1 [4b]. The efficiency of amine elimination route would be more fully exploited if the amide derivatives could be used directly in catalyst formulation without converting them to the corresponding dihalide or dialkyl complexes.

Based on the detailed spectroscopic studies, Kim showed that the *ansa*-metallocene amide complexes have been demonstrated to be effective for the isospecific polymerization of propylene by employing conventional coactivator formulation [5]. There were some differences in the procedure of generating cationic $[^{ch}Cp_2ZrMe]^+$ species between $^{ch}Cp_2Zr(NR_2)_2$ and $^{ch}Cp_2ZrCl_2$ by the reaction with MAO. The $^{ch}Cp_2Zr(NR_2)_2$/MAO catalyst generates the methylzirconium cations via a complete alkylation of $^{ch}Cp_2Zr(NR_2)_2$ to $^{ch}Cp_2ZrMe_2$ mainly by the free $AlMe_3$ contained in MAO, while the $^{ch}Cp_2ZrCl_2$/MAO catalyst to generate the cations is much less efficient at the similar reaction conditions [5d,e,f].

It was reported earlier that the chiral metallocene amide complex $Cp_2Zr(NEt_2)_2$ is activated for ethylene polymerization by excess MAO [6];

however there have been few detailed results on the propylene polymerizations by ${}^{ch}Cp_2Zr(NR_2)_2$/MAO catalysts [5], even if there have been enormous amounts of reported result on the propylene polymerizations by ${}^{ch}CpZrCl_2$/MAO catalyst [1]. This paper describes a study of propylene polymerizations by *rac*-(EBI)$Zr(NMe_2)_2$ (*rac*-**1**) in the presence of MAO, compares the polymerization behavior with that obtained by *rac*-(EBI)$ZrCl_2$ (*rac*-**2**)/MAO catalyst, and characterizes the resulting polymers.

EXPERIMENTAL

Materials

All reactions were performed under a purified argon atmosphere using standard glove box and Schlenk techniques. Polymerization grade of propylene (Yukong Co., Korea) was purified by passing it through columns of Fisher RIDOX catalyst and molecular sieve 5A/13X. MAO was obtained from Albemarle as a 10% solution in toluene, which contained 1.85 wt% $AlMe_3$ and 8.15 wt% MAO (4.49 wt% total Al) and *rac*-**2** was purchased from Aldrich. The *ansa*-metallocene diamide *rac*-**1** was prepared by amine elimination [4a, b] and $[Ph_3C][B(C_6F_5)_4]$ was prepared by literature procedures [7]. Solvents were distilled from Na/benzophenone and stored over molecular sieves (4 A).

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 desired temperature. When the reactor temperature had equilibrated to the bath temperature, propylene was introduced into the reactor after removing argon gas under vacuum. When no more absorption of propylene into toluene was observed, polymerization was started by injecting a prescribed amount of metallocene catalyst dissolved in toluene into the reactor. Polymerization rate was determined at every 0.01 s from the rate of consumption, measured by a hot-wire flowmeter (model 5850 D from Brooks Instrument Div.) connected to a personal computer through an A/D converter. The reaction was stopped by introducing 150 mL ethanol containing HCl (5 vol-%) into the reactor.

Characterization of Polymer

Thermal analysis of polymers was carried out by using Dupont differential scanning calorimeter (DSC, Model-900) at 10°C/min heating rate under nitrogen atmosphere. The crystallinity is calculated from the heat of fusion, $(\Delta H_f/\Delta H_f^0)$ (100, where ΔH_f is the heat of fusion of the sample as determined from the DSC curve, and $(H_f^0$ is the fusion of folded-chain of isotactic polypropylene with the value of 208.3 J/g [8].

The intrinsic viscosity was measured in decalin solution at 135 ± 0.1°C by using an Ubbelohde viscometer and viscosity-average molecular weight ($\overline{M}_v$) was calculated by the following relationship [9]:

$$[\eta] = 1.0\ (\ 10^{-4}\ (\overline{M}_v)^{0.8} \qquad (1)$$

developed for monodisperse PP fractions. Also tested were molecular weight (MW) and its distribution (MWD) by gel permeation chromatography (GPC) on a Waters 150°C at 135°C in 1,2-dichlorobenzene with a data processor, equipped with polystyrene gel columns.

^{13}C NMR spectra of polymers were recorded and measured at 120°C on a Varian Unity Plus 300 spectrometer operating at 75.5 MHz. Samples for ^{13}C NMR spectra were prepared by dissolving 50 mg of polymer in 0.5 mL of benzene-d_6/1,2,4-trichlorobenzene-d_3 (1/5 v/v). IR spectra were obtained with a ATI Mattson Genesis Series FTIR. Samples were prepared for IR examination by mixing polymer powder with KBr, and the *meso* pentad value of polypropylene was calculated by comparing absorption ratio A_{998}/A_{973} according to the equation shown below [10].

$$A_{998}/A_{973} = (0.864 + 0.004)[mmmm] + 0.10 \qquad (2)$$

RESULTS AND DISCUSSION

Effect of MAO Concentration

The catalytic activity of metallocene compound is strongly dependent upon the amount of MAO used for activation. Figure 1 shows the rate profiles of propylene polymerizations obtained by *rac*-1/MAO catalyst. For all polymerizations, there is only a simple rapid rise to a maximum rate ($R_{p,max}$) followed by a moderate decay. At low [Al]/[Zr] ratio, the rate of formation of active sites is slow, so that there is an induction period. This simple kinetic profiles are similar to those found for the propylene polymerization initiated by *rac*-(EBI)$ZrCl_2$/MAO

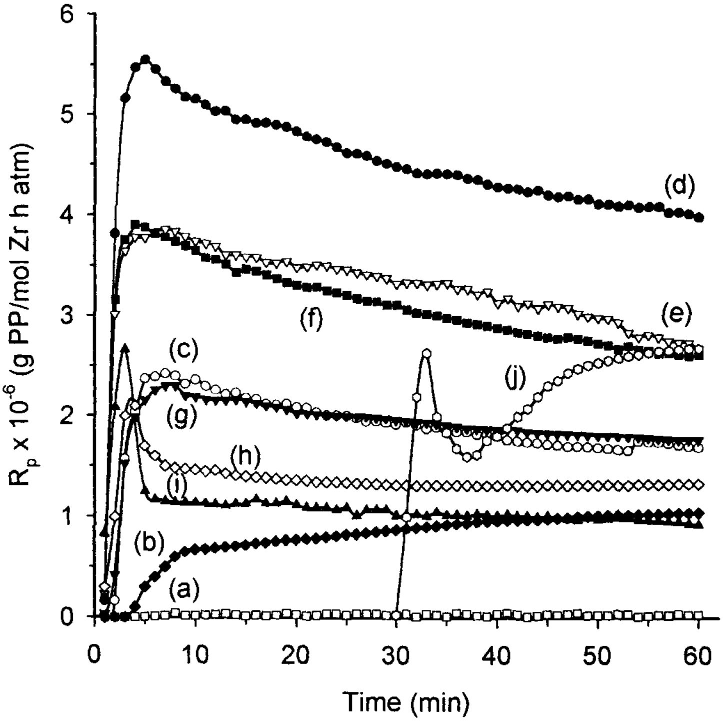


Figure 1. R_p versus time of propylene polymerizations catalyzed by *rac*-1/MAO system with [Zr] = 68.5 μM, toluene = 80 mL, P = 1.3 atm, and temperature = 30°C. The [Al]/[Zr] ratio is (a) 347, (b) 833, (c) 1151, (d) 1728, (e) 2100, (f) 2450, (g) 3500, (h) 4000, and (i) 5206. The rate curve (j) was obtained by adding 68.5 μM of $[Ph_3C][B(C_6F_5)_4]$ after performing polymerization for 30 minutes by the conditions of (a).

catalyst [11]. The plot of activity versus [Al]/[Zr] ratio did not show maximum and sigmoidally increased in an wide range of [Al]/[Zr] ratio ([Al]/[Zr] = 350 to 100,000) [11]. It is very interesting to note that *rac*-1/MAO catalyst shows maximum activity when [Al]/[Zr] ration is around 1800 as shown in Figure 2. This difference of activity dependence according to the concentration of MAO seems to be greatly related with the differences in the formation procedure of cationic active species during polymerization.

When a toluene solution of Cp_2ZrCl_2 is treated with MAO, a fast ligand exchange reaction takes place to produce primarily $Cp_2Zr(Me)Cl$ [12].

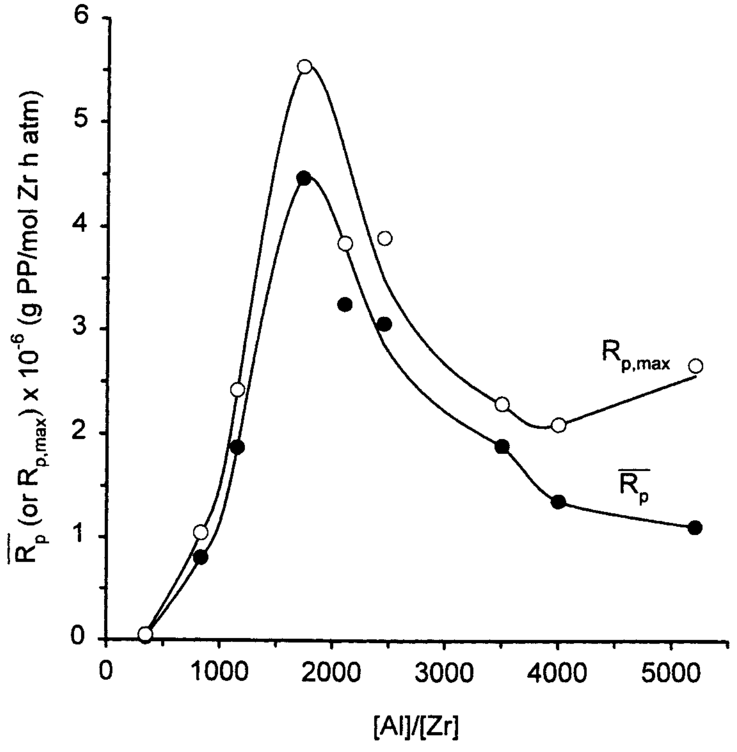
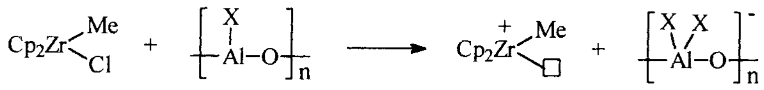


Figure 2. R_p and $R_{p,max}$ versus time plots of the data in Figure 1.

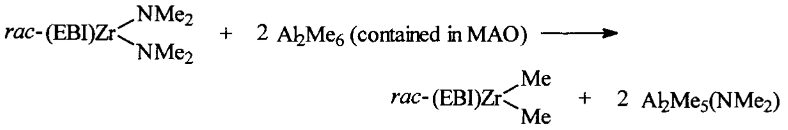

(3)

However, Cp_2ZrCl_2/MAO catalyst only becomes catalytically active when [Al]/[Zr] ratio of greater than 200/1, or even higher, is used. The way in which excess MAO induces this activity has been studied in detail, mainly by spectroscopic means [12, 13]. It is now recognized that either methyl or chloride abstraction by Al centers in the MAO takes place to produce the metallocene cation, $[Cp_2ZrMe]^+$.


(4)

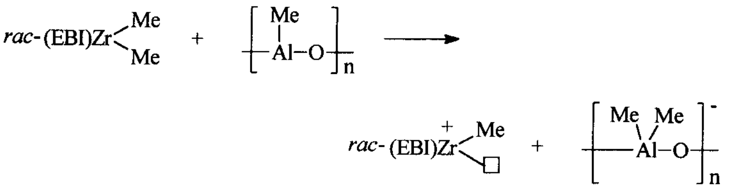
If reactions (3) and (4) are true, MAO plays many roles in the metallocene polymerizations: (i) it acts as an alkylating agent for the generation of a transition metal-alkyl molecule, (ii) it acts as a Lewis acid for anion abstraction from the metal-alkyl molecule, generating an electrophillic $[Cp_2ZrMe]^+$ species, and (iii) it acts as a scavenger for the removal of impurities such as water. The same mechanism can be applied to *rac*-**2**/MAO system [1, 5, 12, 13].

On the contrary, diamide complex *rac*-**1** is completely alkylated mainly by free Al_2Me_6 contained in MAO to afford *rac*-(EBI)ZrMe$_2$ [5e].



$$rac\text{-}(EBI)Zr(NMe_2)_2 + 2\ Al_2Me_6\ \text{(contained in MAO)} \longrightarrow rac\text{-}(EBI)ZrMe_2 + 2\ Al_2Me_5(NMe_2) \qquad (5)$$

Then, Al centers in MAO abstract methyl from *rac*-(EBI)ZrMe$_2$ to give the methylzirconium cations.



$$rac\text{-}(EBI)ZrMe_2 + \left[\!-\overset{Me}{\overset{|}{Al}}-O-\!\right]_n \longrightarrow rac\text{-}(EBI)\overset{+}{Zr}(Me)\square + \left[\!-\overset{Me\ Me}{\overset{\backslash\,/}{Al}}-O-\!\right]^-_n \qquad (6)$$

This mechanistic difference in generating cationic species between *rac*-**2**/MAO and *rac*-**1**/MAO system is most probably caused by the difference of alkylation capability of each metallocene by alkylaluminum, which was demonstrated by detailed spectroscopic studies [5]. In the NMR-scale reactions carried out in CD_2Cl_2 solvent the *rac*-**1**/MAO system generates the cationic species at low MAO concentration ([Al]/[Zr] = 40) via *rac*-(EBI)ZrMe$_2$ intermediate; however, the same cationic species cannot be generated by using much higher amount of MAO (say [Al]/[Zr] > 200) in *rac*-**2**/MAO system, because *rac*-**2** is not easily alkylated by MAO and/or free Al_2Me_6 contained in it. The electron deficient Cl or Me bridges with MAO or $AlMe_3$ may cause low efficiency in the generation of cations as compared to the electron rich NMe_2.

The fact that the activity of *rac*-**1**/MAO catalyst is decreased at high MAO concentration ([Al]/[Zr] > 1800), while the activity of *rac*-**2**/MAO system is increased in a wide range of [Al]/[Zr] ratio ([Al]/[Zr] = 350 to 100,000), may be interpreted by considering the previous reported results [5d, 5e, 14]. It can be assumed that *rac*-**1** transforms into *rac*-(EBI)ZrMe$_2$ intermediate prior to the formation of the cationic species by the reaction with MAO at high [Al]/[Zr] ratios, while *rac*-**2** transforms into *rac*-(EBI)Zr(Me)Cl intermediate. In this condition there also exists a considerable amount of free $AlMe_3$, since 10% of MAO solution in toluene is consisted of 1.85 wt% $AlMe_3$ and 8.15 wt% MAO (4.49 wt% total Al). It has been shown that *ansa*-metallocene dimethyl compounds such as *rac*-$Me_2Si(Ind)_2ZrMe_2$ [5d] and *rac*-$(EBI)ZrMe_2$ [5e] are transformed into the corresponding methylzirconium cations, [*rac*-$Me_2Si(Ind)_2ZrMe]^+$ and [*rac*-$(EBI)ZrMe]^+$ by the reaction with MAO [Equation 6)]; however, in the presence of free $AlMe_3$, these cationic species are in equilibrium with the dinuclear cationic species, [*rac*-$Me_2Si(Ind)_2Zr(\mu\text{-}Me)_2AlMe_2]^+$ and [*rac*-$(EBI)Zr(\mu\text{-}Me)_2AlMe_2]^+$, adducts of the base-free cation and $AlMe_3$, analogue of which was previously identified by Bochmann [14] as the principal component in the mixture of these species.

In the presence of excess $AlMe_3$, [*rac*-$(EBI)ZrMe]^+$ cations converts to the inactive cationic [*rac*-$(EBI)Zr(\mu\text{-}Me)_2AlMe_2]^+$ species. Whereas, Al_2Me_6 is fluxional, with rapidly exchanging terminal and bridging methyl ligands, no such exchange processes were found in the dinuclear cations [14]. This rigidity no doubt contributes to the stability of the compounds. Similar $AlMe_3$ adducts are well known from the chemistry of lanthanide complexes. Holton, *et al.* prepared a series of complexes, $Cp_2M(\mu\text{-}Me)_2AlMe_2$ (M = Sc, Y, Gd, Dy, Ho, Er, Tm, Yb), that were stable enough to be purified by sublimation [15]. Such lanthanide complexes are of course isoelectronic to [*rac*-$(EBI)Zr(\mu\text{-}Me)_2AlMe_2]^+$ cation. These cationic species cannot be catalytically active because they lack vacant orbitals suitable for olefin coordination before the alkyl migration (chain growth) step. However, dissociation can take place to release a finite concentration of the active species, [*rac*-$(EBI)ZrMe]^+$. Thus, it might be proposed that the formation methyl bridged [*rac*-$(EBI)Zr(\mu\text{-}Me)_2AlMe_2]^+$ compounds should suppress the activity in the same way as the coordination of electron donor ligands such as ethers and amines.

The decrease of catalytic activity at excess MAO concentration might thus be due to the increased concentration of [*rac*-$(EBI)Zr(\mu\text{-}Me)_2AlMe_2]^+$ cations, which are favorably formed in the presence of excess $AlMe_3$. In the case of *rac*-**2**/MAO, the formation of the inactive dinuclear species is seemed to be suppressed due to the delayed methylation of *rac*-**2** to *rac*-$(EBI)ZrMe_2$ by MAO and/or free $AlMe_3$ contained in it [5e], resulting in continuous increase of activity at much higher MAO concentration. The decline of catalytic activity at high [Al]/[Zr] ratios has been reported for the propylene polymerization with *rac*-$(EBTHI)ZrCl_2$/MAO (EBTHI = ethylene bis(4, 5, 6, 7-tetrahydro-1-indenyl)) system [11]. In this catalyst, the maximum activity was observed when [Al]/[Zr] ratio is around 3500. The relationship between activity and catalyst composition should therefore be determined for each catalyst system.

We have been shown that through the detailed NMR-scale reactions [5e] very small amount of MAO ([Al]/[Zr] = 40) is enough to completely activate *rac*-**1** to generate cationic active species in a CD_2Cl_2 solvent. However, in the present lab-scale polymerizations *rac*-**1** shows no conspicuous activity at low concentration of MAO, i.e. at [Al]/[Zr] < 300. The reason why excess amount of MAO is required for the activation of *rac*-**1** in the lab-scale polymerization of propylene using toluene as a solvent remains uncertain. Considerable amount of MAO can act as a scavenger for the removal of impurities such as moisture. Though MAO undoubtedly acts to methylate metallocene as shown in Equation 3), to scavenge impurities, and to act as a Lewis acid for anion abstraction from the metal-alkyl molecule [Equations 4 and 6], generating an electrophilic species, these cannot explain the need of excess amount of MAO for the activation. The complexation of monomer may contribute to the observation.

As a means of investigating the function MAO, noncoordinating anion $[Ph_3C][B(C_6F_5)_4]$ has been used for the activation of *rac*-**1** together with MAO. The anionic compound is additionally injected into the reactor after carrying out the polymerization by *rac*-**1**/MAO catalyst ([Al]/[Zr] = 347, Figure 1(a)) for 30 minutes. As shown in Figure 1(j), the activity is sharply increased by injecting 1 equivalent of $[Ph_3C][B(C_6F_5)_4]$. Based on this result we may assume that (i) *rac*-**1** is methylated by MAO and/or free $AlMe_3$ to afford *rac*-(EBI)$ZrMe_2$ or (ii) methylzirconium cations [*rac*-(EBI)ZrMe]$^+$ are generated by the reaction of *rac*-(EBI)$ZrMe_2$ and MAO, but the cationic sites are not stabilized. The assumption (i) seems to be correct, because 347 equiv. of Al contain 32 equiv. of Al originated from free $AlMe_3$, which is a sufficient concentration to methylate *rac*-**1** completely [5 d, e]. If the assumption (ii) is reasonable, the anions in the reaction medium 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 sites. As a result, it may be assumed that [*rac*-(EBI)ZrMe]$^+$ cations might be generated by the reaction of *rac*-**1** and low amount of MAO, but they are not stable enough to protect the attack by anions and to prevent catalyst deactivation by bimolecular process between two metallocenes. If not stabilized, the tendency of electron-deficient species such as [*rac*-(EBI)ZrMe]$^+$ cation to form methyl-bridged dimeric complexes [{*rac*-(EBI)ZrMe}$_2$(μ-Me)]$^+$ wherever possible as a means of stabilization is also evident in the activation of Cp_2MMe_2 with MAO or $[Ph_3C][B(C_6F_5)_4]$. Various dimeric complexes such as $[(Ind_2TiMe)_2(\mu\text{-}Me)]^+$, $[(Cp'_2ZrMe)_2(\mu\text{-}Me)]^+$, $[(Cp_2MMe)_2(\mu\text{-}Me)]^+$ (M = Zr, Hf), and [{*rac*-$Me_2Si(Ind)_2ZrMe\}_2(\mu\text{-}Me)]^+$ have been identified during activation by spectroscopic means at low temperature [14, 16].

Transformation of [*rac*-(EBI)ZrMe]$^+$ cation to the dimeric [{*rac*-(EBI)ZrMe}$_2$(μ-Me)]$^+$ cations might be assumed to be a main deactivation of the polymerization by *rac*-**1**/MAO catalyst at low concentration of MAO (say [Al]/[Zr] = 347). However, considerable amount of the inactive and dimeric cations dissociate to active [*rac*-(EBI)ZrMe]$^+$ cations by the reaction with additional $[Ph_3C]^+$, resulting in the sharp recovery of activity [Figure 1(j)]. As a result, it may be concluded that excess amount of MAO to attain a high activity is for the stabilization of the monomeric cations.

Effect of Polymerization Temperature (T_p)

Polymerization initiated by *rac*-**1** /MAO catalyst was performed from T_p range between 10°C and 60°C at [Al]/[Zr] = 1728. As shown in Figure 3, polymerization at 10°C has a induction period of 10 minutes and then increases slowly to the maximum rate. The induction period becomes negligible above the polymerization temperature of 30°C. For polymerizations above 30°C, there is only a simple rise to a maximum rate within 5 minutes, followed by a moderate decay to a stationary rate of polymerization. The longer induction time at low T_p (say 10 and 20°C) demonstrates that it take some time to generate cationic active species from by *rac*-**1** /MAO catalysis.

Looking into the rate profiles shown in Figure 3, it can be seen that the time to reach maximum rate ($R_{P,max}$) changes according to T_p. In order to investigate the effect of T_p on activity during initial acceleration period, short-time rate profiles are recorded (Figure 4). The induction periods change according to T_p, followed by a S-shape acceleration period. Early in the study of Ziegler-Natta catalysts the coordination-anionic mechanism for olefin polymerization with these catalysts was proposed [17-19] and it is widely accepted to be the mechanism of propagation in metallocene catalysis as well. According to this mechanism the addition of monomer to a polymer chain consists of two consecutive steps: (i) the coordination of an olefin monomer with the transition metal atom of an active site, i.e., the reversible formation of π-complex, and (ii) the insertion of the olefin monomer between the metal atom and the growing polymer chain.

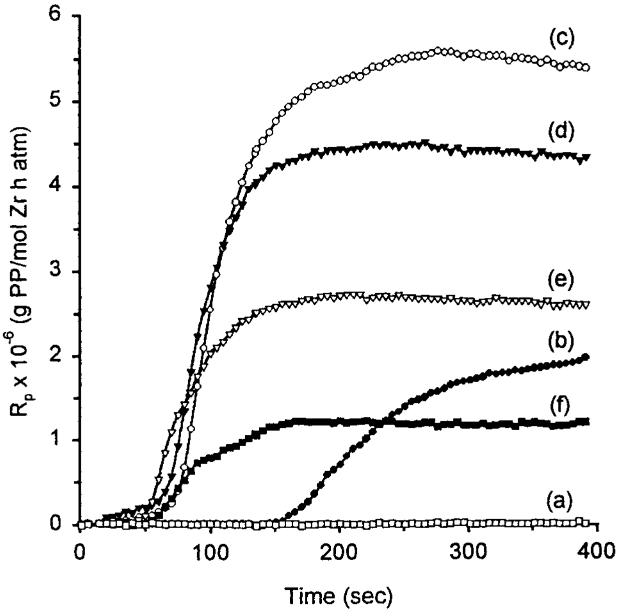


Figure 3. R_p versus time of propylene polymerizations catalyzed by *rac*-1/MAO system with [Zr] = 68.5 μM, [Al]/[Zr] = 1728, toluene = 80 mL, and P = 1.3 atm. Polymerization temperature is (a) 10°C, (b) 20°C, (c) 30°C, (d) 40°C, (e) 50°C, and (f) 60°C.

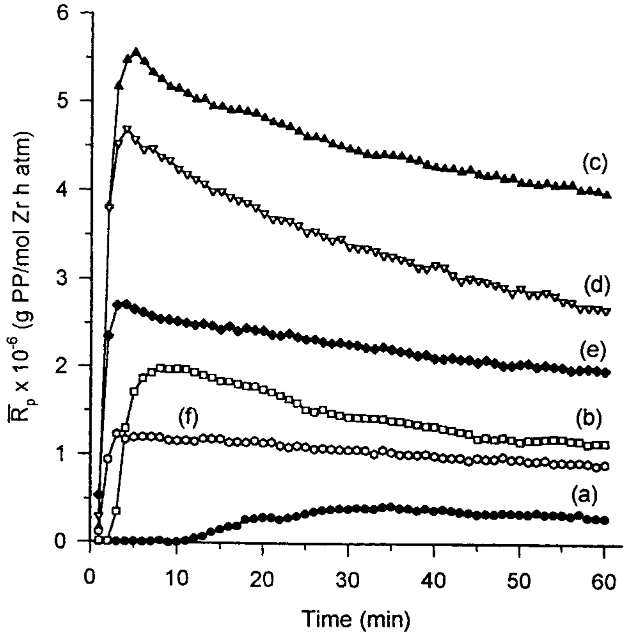
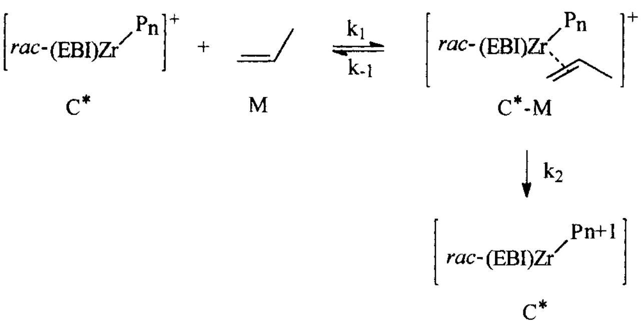


Figure 4. Short-time rate profiles of propylene polymerization catalyzed by *rac*-1/MAO system with [Zr] = 68.5 μM, [Al]/[Zr] = 1728, toluene = 80 mL, and P = 1.3 atm. Polymerization temperature is (a) 10°C, (b) 20°C, (c) 30°C, (d) 40°C, (e) 50°C, and (f) 60°C.



(7)

In this equation, k_1, k_{-1}, and k_2 are the rate constants, C* is a cationic active site of catalyst, M is a propylene monomer, and C*-M is a cationic alkyl propylene intermediate. The pseudo-steady-state expression for the polymerization rate can be expressed by Equation 7, by assuming that Zr^+-P_n and Zr^+-P_{n+1} are kinetically indistinguishable, $d[C^*\text{-}M]/dt = 0$, and $[C^*]_0 = [C^*] + [C^*\text{-}M]$.

$$R_p = [C^*]_0\,(k_1k_2[M])/(k_1[M] + k_{-1} + k_2) \tag{8}$$

This is the same as the standard equation to express the initial reaction velocity for the simplest enzyme reaction. If the monomer coordinates to the propagating sites strongly, $k_1[M] >> k_{-1} + k_2$.

$$R_p = k_2[C^*]_0 \tag{9}$$

In this case, i.e., the rate of polymerization is independent of [M], which contradicts experimental findings [1a]. In addition the cationic alkyl propylene p-complex is expected to be unstable at the T_p range of this study. If the strength of monomer coordination is very weak, $k_{-1} >> k_1[M]$. In this case Equation 8 is simplified as follows.

$$R_p = [C^*]_0\,(k_1k_2[M])/(k_{-1} + k_2) \tag{10}$$

As shown in Figure 4, R_p is almost linearly proportional to time at the early period of polymerization before R_p reaches maximum rate ($R_{p,max}$). Thus, if we assume that the change of R_p in this period with time is represented by an equation of the form

$$dR_p/dt = k'(R_{p,max} - R_p) \tag{11}$$

where k' is a rate constant. Equation 12 is obtained on integration by assumung $d[M]/dt = 0$,

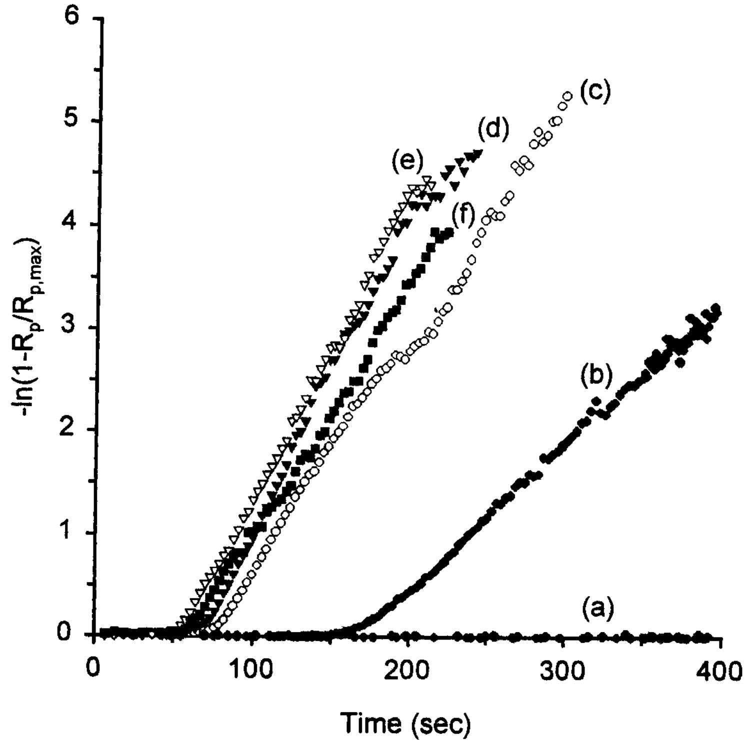


Figure 5. - $ln(1\text{-}R_p/R_{p,max})$ versus time plots of the data in Figure 4.

$$R_p = R_{p,max}\{1 - EXP(k_{eff}[M]t)\} \tag{12}$$

where $k_{eff} = k'k_1k_2[C^*]_0/(k_{-1} + k_2)$. Figure 5 plots $\ln(1\text{-}R_p/R_{p,max})$ versus time curve, and k_{eff} values from the slope of the curves are calculated as 0.03, 0.05, 0.09, 0.15, 0.22, and 0.27 (l/mol sec) when T_p = 10, 20, 30, 40, 50, and 60°C, respectively. The Arrhenius plot of k_{eff} versus 1/T shows linear relationship (Figure 6) and thus the apparent activation energy at the initial period of polymerization is calculated as 3.75 kcal/mol from the slope of the line.

Figure 6 also shows an Arrhenius plot of polymerization rate $\overline{R}_p$ and $R_{p,max}$). Activity is increased slowly from 10°C to 30°C and then decreased sharply from 40 °C to 60 °C. Here activity is given in g PP per mol of Zr per hour per mol of propylene for the normalization of different solubility of monomer in toluene. Previously the activities of propylene polymerizations by *rac*-(EBI)ZrCl$_2$/MAO and *rac*-(EBTHI)ZrCl$_2$/MAO were obtained in an wide range of temperature, -55 to 80°C [11]. The Arrhenius plot of activity is linear over the

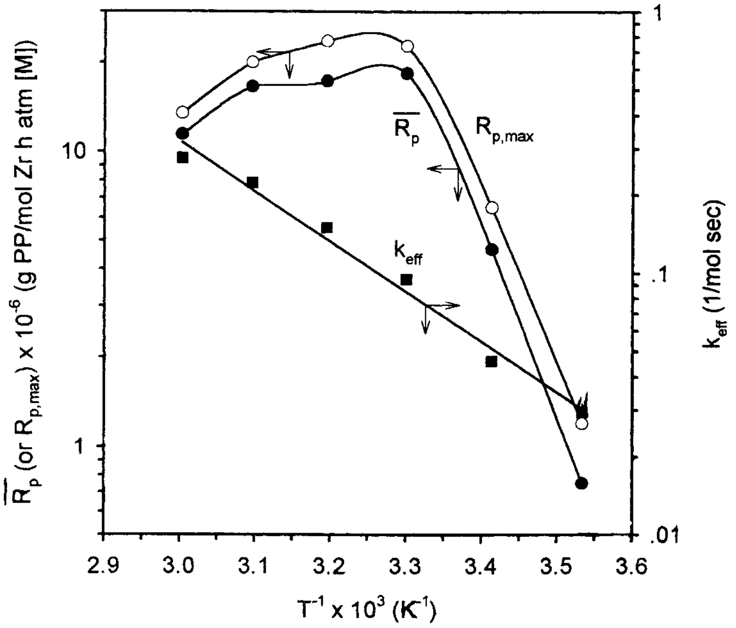


Figure 6. Arrhenius plots of R_p, $R_{p,max}$ (data in Figure 3), and k_{eff} (data in Figure 5).

entire temperature range for these catalytic systems. These results demonstrate that the activity becomes more sensitive to T_p by modifying the metallocene by changing Cl ligand to NMe_2 rather than by changing organic ligand moiety. This difference of T_p dependence on activity between *rac*-(EBI)Zr(NMe_2)$_2$/MAO catalyst and *rac*-(EBI)ZrCl_2/MAO catalyst seems to be deeply related with the discrepancy of the generation procedures of cationic active species (*vide ante*).

Effect of Metallocene Concentration

In a conventional Ziegler-Natta catalyst the activity of olefin polymerization is linearly proportional to catalyst concentration: $R_p = k_p[C^*][M]$. The propylene polymerization has been examined in toluene at 30°C under variation of the metallocene concentration ranging from 68.5 μM to 342.6 μM. The [Al]/[Zr] ratio has kept constant as 1150. Figure 7 shows the polymerization rate profiles in dependence on the metallocene concentration and Figure 8 summarizes and $R_{p,max}$ vs. [Zr] relationships. All polymerizations show similar rate curves, i.e. the kinetic profile is a simple increase to maximum rate within 5

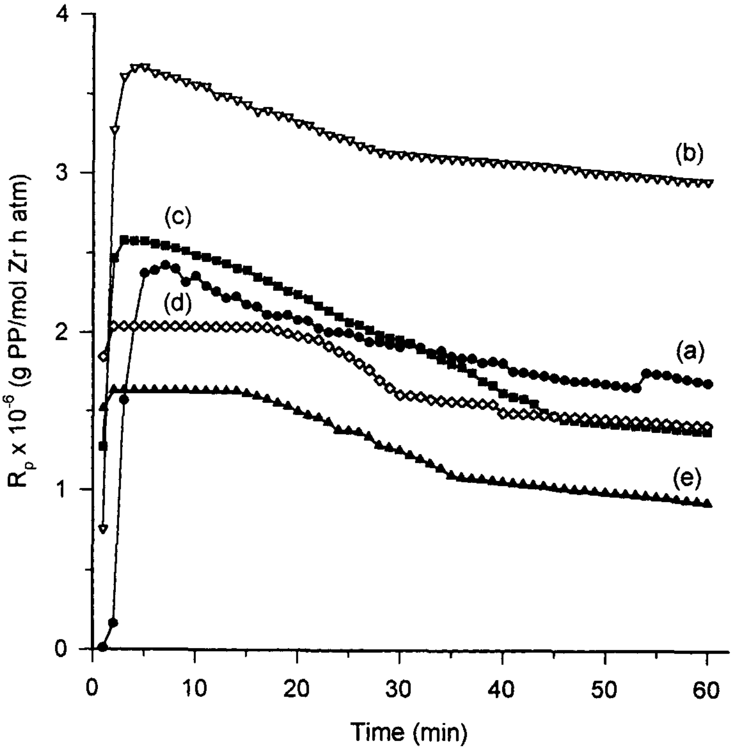


Figure 7. R_p versus time of propylene polymerizations catalyzed by *rac*-1/MAO system with [Al]/[Zr] = 1151, toluene = 80 mL, P = 1.3 atm, and temperature = 30°C. The metallocene concentration ([Zr]) is (a) 68.5 μM, (b) 137.1 μM, (c) 205.6 μM, (d) 274.1 μM, and (e) 342.6 μM.

min. followed by rate decay. As shown in Figure 8, both and $R_{p,max}$ increase in the range of [Zr] = 68.5 μM to 137.1 mM, but decrease at [Zr] > 137.1 μM. The decrease of activity at high [Zr] is probably due to the acceleration of deactivation by bimolecular processes between two metallocene molecules through either reductive elimination of PP chains [20] or oxidative coupling generating methyl bridge between two zirconium atoms [11, 20].

The decrease of catalytic activity with increase of metallocene concentration was demonstrated by many reports [21-23]. Chien *et al.* [21] reported that polymerization activity is proportional to $[Zr]^{-0.77}$ for the polymerization of ethylene with Cp_2ZrCl_2/MAO system. Fischer and Mulhaupt [22] found a similar result for propylene polymerization with the same catalytic

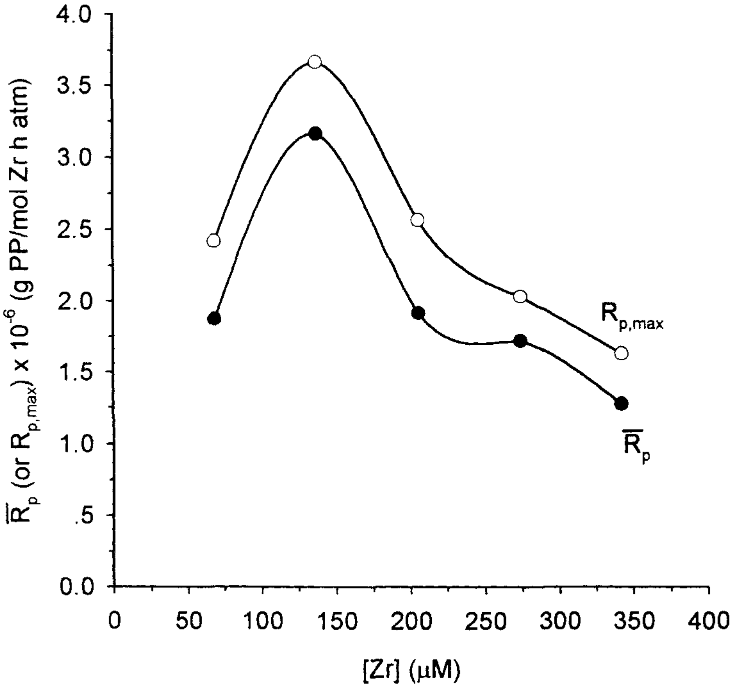


Figure 8. R_p and $R_{p,max}$ versus time plots of the data in Figure 7.

system. On the other hand, the activity increased monotonically with [Zr] in the case of ethylene polymerization with bis-η^5-(neomentylcyclopentadienyl)-$ZrCl_2$/MAO [23]. Therefore, the relationship between activity and catalyst concentration should be determined for each catalyst system.

Characterization of Polymers

In Table 1, the properties of polymers obtained with *rac*-**1**/MAO catalyst are summarized. The viscosity average molecular weight ($\overline{M}_v$) of the polymer decrease monotonically as T_p increases and as catalyst concentration increases. The $\overline{M}$ value slightly increases at very low MAO concentration and then decreases at high concentration. The MAO molecules may coordinate to the catalyst to slow the propagation rate by reversible inhibition, so that the molecular weight increases with increasing MAO concentration, to reach maximum and then declines with additional MAO due to the accelerated chain transfer reaction to MAO and free $AlMe_3$ contained in MAO. The decrease of $\overline{M}_v$ value of polymer according to T_p is a typical phenomenon found in the

Table 1. Properties of *i*PP obtained with *rac*-(EBI)Zr(NMe$_2$)$_2$/MAO catalyst systems.[a]

Run No.	[Zr] x 10^6 (M)	[Al]/[Zr]	Temp. (°C)	R_p x 10^{-6} (g PP/mol Zr h atm)	mmmm (%) by NMR	mmmm (%) by IR	M_v x 10^{-4}	M_w x 10^{-4}	M_w/M_n	T_m (°C)	ΔH_f (J/g)
Fig. 1(a)	68.5	347	30	0.02	-	82.8	3.48	-	-	134.3	51.3
Fig. 1(b)	68.5	833	30	0.80	88.0	87.5	3.69	4.15	2.2	136.2	54.6
Fig. 1(c)	68.5	1151	30	1.88	-	85.2	2.34	-		136.4	63.3
Fig. 1(d)	68.5	1728	30	4.48, 18.2[b]	89.0	85.7	1.94	2.29	1.9	134.9	63.7
Fig. 1(e)	68.5	2100	30	3.26	90.1	89.3	1.35	-	-	135.7	57.8
Fig. 1(f)	68.5	2450	30	3.07	-	85.8	1.30	2.12	1.9	134.9	64.8
Fig. 1(g)	68.5	3500	30	1.90	-	84.7	1.38	-	-	134.1	52.1
Fig. 1(h)	68.5	4000	30	1.36	91.3	89.7	1.24	1.57	2.1	133.6	52.8
Fig. 1(I)	68.5	5206	30	1.11	90.4	89.1	1.15	1.31	2.1	133.5	51.2
Fig. 3(a)	68.5	1728	10	0.54[b]	91.3	87.1	3.98	4.62	1.8	140.9	43.9
Fig. 3(b)	68.5	1728	20	3.38[b]	-	85.6	2.84	-	-	138.4	65.7
Fig. 3(d)	68.5	1728	40	12.9[b]	-	75.4	0.83	1.01	2.2	124.2	53.4
Fig. 3(e)	68.5	1728	50	11.8[b]	68.6	66.3	0.48	0.57	2.3	107.8	28.7
Fig. 3(f)	68.5	1728	60	9.1[b]	33.1	-	0.31	-	-	n.d.	n.d.
Fig. 5(b)	137.1	1151	30	3.17	-	86.1	1.65	-	-	132.2	61.7
Fig. 5(c)	205.6	1151	30	1.92	89.2	88.8	1.10	1.35	2.0	129.2	57.3
Fig. 5(d)	274.1	1151	30	1.72	-	81.2	1.08	-	-	129.0	56.1
Fig. 5(e)	342.6	1151	30	1.28	85.7	84.5	1.03	1.21	2.1	127.8	47.8

[a] Polymerization conditions are given in the corresponding figures shown in Run No.

[b] The unit is g PP(mol Zr)$^{-1}$h^{-1}M^{-1}

olefin polymerizations by metallocene/MAO catalyst. Ewen *et al.* [24] reported that the molecular weight of PP made with *rac*-(EBI)HfCl$_2$, *rac*-(EBTHI)HfCl$_2$ and the corresponding titano-cenes showed a decrease in $\overline{M}_v$ with increasing T$_p$. A subsequent paper reported that the $\overline{M}_v$ of *i*PP obtained with *rac*-**1**/MAO catalyst decreased from 5500 when the polymerization was carried out at –10°C to 2000 at 50°C [25]. The decrease of $\overline{M}_n$ of *i*PP was also reported for the propylene polymerization by *rac*-MeCH(Me$_4$Cp)(Ind)TiCl$_2$/ MAO catalyst [26].

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 $\overline{M}_v$ of *i*PP 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 [22]. Supporting evidence for this information on the effect of metallocene concentration on the molecular weight is the review paper by Kaminsky [27], which reported that increasing the metallocene concentration in the polymerization of ethylene is one method to lower the molecular weight of the resulting polyethylene. In addition, a paper [24] on the polymerization of propylene reported that there was an inverse dependence of molecular weight on the metallocene concentration when *rac*-(EBI)HfCl$_2$/MAO was used as the catalyst for the polymerization.

The *i*PPs obtained by *rac*-**1**/MAO system are characterized by narrow molecular weight distribution, which is the great promise of metallocene catalyst. As shown in Table 1, $\overline{M}_w/\overline{M}_n$ values of all polymers investigated in this study are in the range of 1.8 – 2.3 approaching the Poisson distribution. The $\overline{M}_w/\overline{M}_n$ values are not so sensitive to temperature, metallocene concentration and MAO concen-tration. The narrow molecular weight distribution is indicative of uniform active species present in the polymerization system. Table 1 also shows that both T$_m$ and ΔH$_f$ of *i*PP are independent of [Al]/[Zr] ratio and [Zr]. The T$_m$ of polymer decreases with the increase of T$_p$ and no T$_m$ is observed for the polymer obtained at T$_p$ = 60°C. The melting points and the crystallinities of *i*PPs are similar level with those obtained with *rac*-**1**/MAO system [23], and are well below those of conventional Ziegler-Natta *i*PPs.

The [*mmmm*] values of polymers obtained by using Equation 2 [10] are generally lower than those obtained by NMR. The [*mmmm*] of *i*PP obtained with very low [Al]/[Zr] ratio ([Al]/[Zr] = 347) shows low value (82.8% by IR), but it increases to 89.1% (IR) when [Al]/[Zr] is 5206. In the intermediate range of [Al]/[Zr] ratio, the [*mmmm*] value does not depend on the [Al]/[Zr] ratio. This result demonstrates that the MAO surrounding the cationic metallocene sites can affect the stereoselectivity of the catalyst. It was reported that lowering of [MAO] resulted in *i*PP containing lowered populations of homosteric sequences [*mm*] and [*mmmm*] with *rac*-**2**/MAO system [23]. The [*mmmm*] value of *i*PP decreases sharply with increasing T_p, and the polymer obtained at 60°C shows atactic features. Generally *ansa*-metallocene complexes in solution are rather soft, and thermal disturbance at raised T_p can cause the deformation of their rigid conformation, resulting in the loss of their stereoregulating ability. Even if the catalytic activity changes very much according to catalyst concentration, the isotacticity of *i*PP is independent of [Zr].

CONCLUSION

The *ansa*-zirconocene amide compound *rac*-**1** is activated for propylene polymerization with MAO. The propylene polymerizations carried out by *rac*-**1**/MAO catalyst showed maximum activity when [Al]/[Zr] is around 1800. This dependence of MAO concentration on the activity of *rac*-**1**/MAO catalyst is quite different from that of *rac*-**2**/MAO catalyst. The latter catalyst did not show maximum and sigmoidally increased in an wide range of [Al]/[Zr] ratio ([Al]/[Zr] = 350 to 100,000) [11]. This difference of activity dependence according to the MAO concentration seemed to be deeply related with the differences in the formation procedure of cationic active species during polymerization. The methylzirconium cations are generated by abstracting a methyl ligand from *rac*-(EBI)$ZrMe_2$ with MAO in the *rac*-**1**/MAO catalyst, but by abstracting a chlorine ligand from *rac*-(EBI)Zr(Cl)Me with MAO in the *rac*-**2**/MAO catalyst. The cationic species generated by *rac*-**1**/MAO catalyst in the presence of excess amount of MAO showed marked trend toward the formation of inactive heterodinuclear cationic species, [*rac*-(EBI)Zr(μ-Me)$_2$AlMe$_2$]$^+$, due to the free $AlMe_3$ contained MAO. The catalytic activity was negligible at low concentration of MAO ([Al]/[Zr] = 347), however it increased by injecting additional $[Ph_3C][B(C_6F_5)_4]$ to the reactor during polymerization initiated by very low MAO concentration. From this result, we could speculate that the cationic active species generated at low MAO concentration is unstable so that they can afford inactive but more stable dinuclear cationic [*rac*-(EBI)Zr(μ-Me)$_2$AlMe$_2$]$^+$ species. The *meso* pentad values of *i*PPs obtained by *rac*-**1**/MAO system were in the range of 82.8% to 89.7%. The molecular weight of *i*PP decreased as [Al]/[Zr] ratio increases.

The activity of *rac*-**1**/MAO catalyst reached maximum when T_p is 30 °C, which is also different from *rac*-**2**/MAO catalyst. From the simple kinetic analysis on the initiation reaction, the activation energy for the initiation reaction was calculated as 3.75 kcal/mol. The *rac*-1/MAO catalyst lost stereorigid character at $T_p > 60$°C. The activity of *rac*-1/MAO catalyst was also sensitive to the concentration of zirconocene. The activity shows maximum ($\overline{R}_p = 3.17 \times 10^6$ g PP/mol Zr h atm) when [Zr] is 137.1 μM. The properties of *i*PP such as [*mmmm*], T_m, and $\overline{M}_w / \overline{M}_n$ were almost independent on [Zr], but the molecular weight decreased with the increase of [Zr].

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