

Syndiospecific Propylene Polymerization: Comparison of $\text{Me}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrMe}_2$ with $\text{Et}(\text{Cp})(\text{Flu})\text{ZrMe}_2$

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ABSTRACT: The kinetics and stereochemical control of propylene polymerization initiated by syndiospecific isopropylidene(1- η^5 -cyclopentadienyl)(1- η^5 -fluorenyl)-dimethylzirconium–methyl aluminoxane (**1**/MAO) and (1-fluorenyl-2-cyclopentadienylethane)-dimethylzirconium–MAO (**2**/MAO) were investigated. The influence of MAO concentration and polymerization temperature (T_p) on polymerization kinetics and polypropylene properties, such as molecular weight, molecular weight distribution (MWD), and stereoselectivity, have been studied in detail. The activity of both catalytic systems is very sensitive to the concentration of MAO. The **1**/MAO and **2**/MAO catalysts record maximum activity when [Al]/[Zr] ratio is around 1300 and 2500, respectively. The activity and the degree of stereochemical control are also sensitive to T_p . The **2**/MAO catalyst is much more thermally stable than **1**/MAO catalyst; the former shows maximum activity at 80°C, whereas the latter shows maximum activity at 20°C. The cationic active species generated by **2**/MAO is not so stereorigid as those by **1**/MAO so that **2**/MAO catalyst produces sPP of broad MWD (4.43–6.38) and low syndiospecificity at high T_p . When T_p is above 50°C, **2**/MAO catalyst produces completely atactic polypropylene. The results of fractionation of sPP samples produced by **1**/MAO and **2**/MAO demonstrate that **1**/MAO catalyst is characterized by uniform active sites, but **2**/MAO is characterized by multiple active sites. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 973–983, 1998

Key words: syndiospecific; metallocene catalysts; propylene; polymerization; methyl aluminoxane; homogeneous catalysts; syndiospecificity; molecular weight distribution

INTRODUCTION

Syndiotactic polypropylene (sPP) was firstly synthesized by vanadium-based homogeneous catalysts at low polymerization temperature.^{1–3} Doi et al.⁴ obtained sPP with tris(2-methyl-1,3-but-

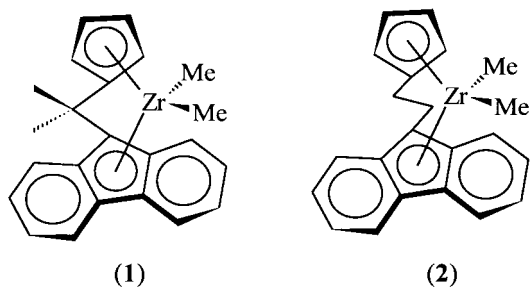
tanedionato)-vanadium–AlEt₂Cl catalyst system by living polymerization at –78°C. However, these vanadium-based catalytic systems are not commercially attractive because of the low polymerization temperature required and low productivity. Recently Ewen⁵ succeeded in producing highly syndiotactic PP by using an isopropylidene(1- η^5 -cyclopentadienyl)(1- η^5 -fluorenyl)-dichlorozirconium ($\text{Me}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ –MAO) catalytic system at a high polymerization temperature. Activity and stereoselectivity are strongly decreased by replacing the fluorenyl moiety with

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tetramethylcyclopentadienyl or 4,5-methylene-phenanthryl groups⁶ and by modifying the Me₂C bridging group with *t*-BuCH group.⁷ Significant improvement of Ewen's catalyst to increase molecular weight and syndiotacticity of polypropylene has been recently achieved by modifying the bridge Ph₂C rather than Me₂C.⁸ When Zr is replaced by Hf, the molecular weight of the polymer increases, but stereoregularity decreases.⁹ Activity reaches a maximum value at a polymerization temperature of about 30°C with the metallocene Me₂C(Cp)(Flu)ZrCl₂, while it increases at least up to 60°C by using the metallocene *t*-BuCH(Cp)(Flu)ZrCl₂.⁷

Recently Razavi et al.^{10–12} studied the effect of the structural flexibility of metallocene on the syndiospecific polymerization of propylene by changing the bridging group of Ewen's catalyst to C₂H₄. The polymers the ethano bridge metallocene, (Et)(Cp)(Flu)ZrCl₂, produces have higher molecular weights and broader polydispersities although it possesses somewhat lower stereoregularities.^{10–12} In this study, we have compared detailed kinetics of propylene polymerization by methylated metallocene analogs of the above 2 metallocene dichloride compounds, Me₂C(Cp)(Flu)ZrMe₂ (**1**) and Et(Cp)(Flu)ZrMe₂ (**2**) (Scheme 1):



EXPERIMENTAL

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 a Fisher RIDOX catalyst and molecular sieve 5A/13X. MAO was obtained from Akzo Chemical as a 8.4 wt % total Al solution in toluene. Solvents were distilled from Na–benzophenone and stored over molecular sieves (4 Å). Literature procedures were used to synthesize metallocene compounds **1**⁵ and **2**.^{10–13}

Polymerization

Propylene polymerization was 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 been 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, 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 consumption rate of the propylene monomer, which was measured by a hot-wire flowmeter (model 5850 D from Brooks Instrument Div.) connected to a personal computer through an A/D converter.

Polymerization was quenched by the addition of methanol, and then the unreacted monomer was vented. The sPP was washed with an excess amount of methanol and dried *in vacuo* at 50°C.

Analysis

Characterization of polymer has been carried out using ¹³C-nuclear magnetic resonance (NMR) Fourier transform infrared spectroscopy (FTIR), gel permeation chromatography (GPC), differential scanning calorimeter (DSC), viscometry, and X-ray diffraction (XRD). Samples for ¹³C-NMR spectra were prepared by dissolving 50 mg of polymer in 0.5 mL of C₆D₆-1,2,4-trichlorobenzene (1/5) and were measured at 120°C. The ¹³C-NMR spectra of polymers were recorded on a Varian Unity Plus 300 spectrometer operating at 75.5 MHz using tetramethylsilane as an internal standard. FTIR spectra were obtained with an ATI Mattson Genesis Series FTIR. Polymer films of 100 μm thickness were prepared for infrared (IR) examination by using a hot press (Graseby Specac Film Maker) at 160°C for 30 s. The pressure was then immediately released and the film allowed cooling down to ambient temperature. Samples were examined immediately after pressing in order to avoid the effect of room temperature annealing. Molecular weight and its distribution ($\overline{M}_w/\overline{M}_n$) were determined by GPC on a Waters 150-C at 135°C in 1,2-dichlorobenzene with a data processor, equipped with polystyrene gel col-

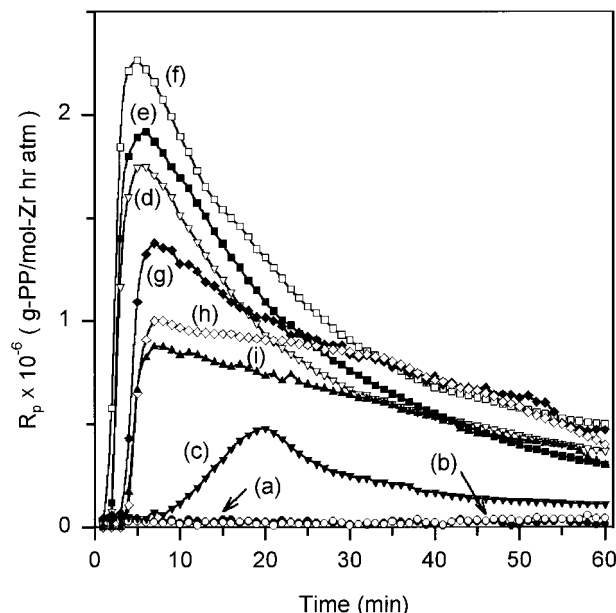


Figure 1 R_p versus time of propylene polymerizations catalyzed by 1/MAO system with $[Zr] = 80.3 \mu\text{M}$, toluene = 80 mL, $P = 1.3 \text{ atm}$, and temperature = 30°C . The $[Al]/[Zr]$ ratio is (a) 220, (b) 441, (c) 661, (d) 881, (e) 1102, (f) 1322, (g) 1762, (h) 2434, and (i) 3042.

umns. Melting and crystallization curves were recorded with a DuPont differential scanning calorimeter (DSC, Model 910) at a $10^\circ\text{C}/\text{min}$ rate. The results of the second scan are reported to eliminate differences in sample history. Powder polypropylene samples were examined by XRD at the reflection mode using Rigaku diffractometer with Ni-filtered $\text{Cu K}\alpha$ radiation at a scan rate $0.5^\circ 2\theta/\text{min}$. The intrinsic viscosity of polymers was determined in decalin at 135°C using an Ubbelohde viscometer.¹⁴

RESULTS AND DISCUSSION

Effect of MAO Concentration

The effect of MAO concentration on the kinetic profiles of propylene polymerization was investigated by using compounds **1** (Fig. 1) and **2** (Fig. 2) at 30°C . There are critical amounts of MAO below which there is negligible activity. As shown in Figure 1 and 2, the activities are very low when $[Al]/[Zr]$ ratio is below 441. For all polymerizations except very low $[Al]/[Zr]$ ratios, there is only a simple rapid rise to a maximum rate ($R_{p,\text{max}}$), followed by a decay. The polymerization profiles obtained by 2/MAO are not smoothly decayed be-

cause sticky polypropylenes are precipitated out during polymerization so that the diffusion of propylene monomer to the active sites is partially limited. At low and high $[Al]/[Zr]$ ratios, that is, $[Al]/[Zr] = 661$ and 3042 for **1**, and 596 and 5960 for **2**, the rate of formation of active sites is delayed so that there are induction periods, ranging from 3 to 8 min, which show no activity.

A remarkable effect of $[Al]/[Zr]$ ratio on polymerization rate was evident in propylene polymerization with various metallocene-MAO catalysts. The plot of average polymerization rate (\bar{R}_p) and maximum polymerization rate ($R_{p,\text{max}}$) versus $[Al]/[Zr]$ ratio for 1/MAO and 2/MAO catalysts is shown in Figure 3. Generally 2/MAO catalyst shows much higher activity than 1/MAO catalyst. The maximum activities reach at different $[Al]/[Zr]$ ratios, around 1300 for 1/MAO and around 2500 for 2/MAO. Similar dependencies of MAO concentration on activity of propylene polymerization have been reported for many catalytic systems such as $\text{rac-Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2\text{-MAO}$,¹⁵ $\text{Me}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2\text{-MAO}$,¹⁵ $\text{rac}(\text{EBTHI})\text{ZrCl}_2\text{-MAO}$,¹⁶ and $\text{Me}_2\text{C}(3\text{-MeCp})(\text{Flu})\text{ZrCl}_2\text{-MAO}$,¹⁷ even though the $[Al]/[Zr]$ ratio showing maximum activities are different each other.

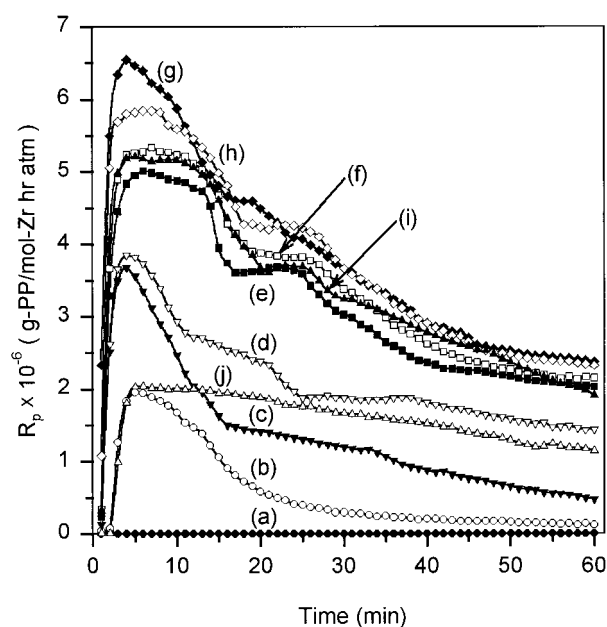


Figure 2 R_p versus time of propylene polymerizations catalyzed by 2/MAO system with $[Zr] = 65.7 \mu\text{M}$, toluene = 80 mL, $P = 1.3 \text{ atm}$, and temperature = 30°C . The $[Al]/[Zr]$ ratio is (a) 298, (b) 596, (c) 894, (d) 1193, (e) 1491, (f) 1781, (g) 2385, (h) 2981, (i) 3678, and (j) 5963.

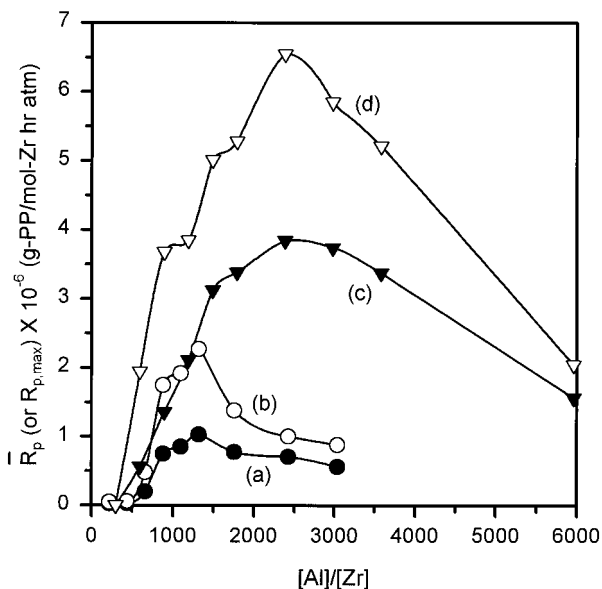


Figure 3 \bar{R}_p (a) and (c) and $R_{p,max}$ (b) and (d) versus time plot of the data in Fig. 1 (a) and (b) and Fig. 2 (c) and (d).

The reason why excess amount of MAO is required for the activation of metallocene in the olefin polymerization remains uncertain. 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 $Cp_2Zr(Me)(Cl)$, and the use of excess MAO produces Cp_2ZrMe_2 .¹⁸ It is now recognized that either methyl or chloride abstraction by Al centers in the MAO takes place.¹⁹ Though MAO undoubtedly acts to methylate metallocene, to scavenge impurities, and to act as a Lewis acid for anion abstraction from the metal-alkyl molecule, generating an electrophilic species, these cannot explain exactly the need of excess amount of MAO for the activation. It has been suggested that the high MAO concentration is required to increase the generation of cationic metallocene active sites and to prevent the formation of inactive metallocene dimer.²⁰

It is interesting to note that 1/MAO catalyst shows maximum activity at the similar [Al]/[Zr] ratio ([Al]/[Zr] \approx 1300) with $Me_2C(Cp)(Flu)ZrCl_2/MAO$ ¹⁵ catalyst, even though the former catalyst has methyl groups as a ligand. This indicates that excess amount of MAO is not needed to alkylate metallocene halide compounds. The catalytically active metallocene complex is a cation that requires an anion for charge neutralization. The

anion must be a noncoordinating ion in order not to compete with the propylene monomer for binding to the metallocene. MAO is known to be an effective anion to stabilize the resulting cationic active species by functioning as a noncoordinating anion, even though the structure of the anion formed from the MAO is poorly defined. As shown in Figure 1 and 2, the polymerizations carried out with small amount of MAO, [Al]/[Zr] = 661 for 1/MAO catalyst and [Al]/[Zr] = 596 and 894 for 2/MAO catalyst, deactivate very fast after reaching maximum rates. The rate of deactivation in polymerizations cocatalyzed by intermediate concentration of MAO ([Al]/[Zr] = 881, 1102, and 1322 in Figure 1, and [Al]/[Zr] = 1193 to 3678 in Figure 2) is second order to the concentration of the active catalytic species. However, the first order of deactivation is recorded at higher concentration of MAO ([Al]/[Zr] = 2434 and 3042 in Figure 1 and [Al]/[Zr] = 5963 in Figure 2). These results demonstrate that MAO not only produces the cations but also stabilizes the anion and that the concentration of MAO needed to stabilize the anion is very high. If not stabilized, the anion can attack the metallocene cation nucleophilically. In order to demonstrate the charge stabilization, one equivalent of $[Ph_3C][B(C_6F_5)_4]$ was injected during polymerization by using 1/MAO at very low concentration of MAO ([Al]/[Zr] = 441) (Fig. 4). Immediately after injecting the noncoordinating

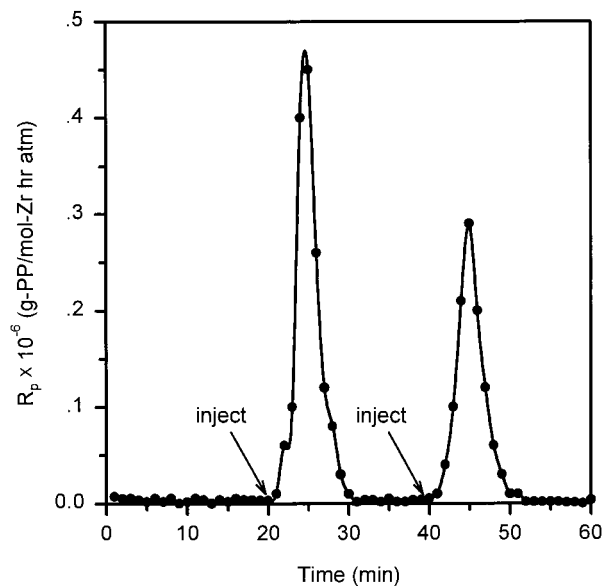


Figure 4 Rate curve obtained by injecting 80.3 μM of $[Ph_3C][B(C_6F_5)_4]$ after 20 and 40 min of polymerization by the condition of Fig. 1(b).

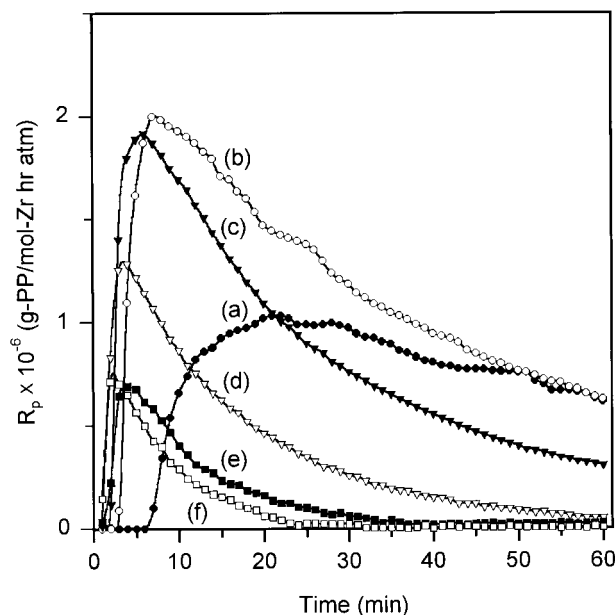


Figure 5 R_p versus time of propylene polymerizations catalyzed by 1/MAO system with $[Zr] = 80.3 \mu\text{M}$, $[Al]/[Zr] = 881$, toluene = 80 mL, and $P = 1.3 \text{ atm}$. Polymerization temperature is (a) 10, (b) 20, (c) 30, (d) 40, (e) 50, and (f) 60°C.

anion into the reactor, the polymerization activity is recovered considerably due to the charge stabilization by the incoming anions. This result indicates that the cationic active species, which are not sufficiently stabilized by an excess MAO, deactivate to permanently inactive species or remain dormant sites. The dormant sites can be reactivated by injecting stabilizing anions, such as $[B(C_6F_5)_4]^-$ (Fig. 4). However, the resulting cationic species formed by injecting $[B(C_6F_5)_4]^-$ are not so stable that they are easily deactivated to inactive species. Repetitive injection of $[B(C_6F_5)_4]^-$ recovers the polymerization rate again, but the active species are not stable enough to retain recovered polymerization rate.

Effect of Temperature

Propylene was polymerized by 1/MAO and 2/MAO at polymerization temperature (T_p) ranging from 10 to 90°C, and the results are shown in Figures 5 and 6. Polymerizations at low temperatures, that is, 10 and 20°C, have induction periods ranging from 2 to 6 min, followed by increase of R_p to maximum rates in 30 min. Increasing T_p above 30°C, the induction period is eliminated, and the time to reach maximum rate becomes very short. In the 1/MAO catalyst, deactivation

rate becomes faster as T_p increases; however, the decay-rate profiles show complicated behavior by changing T_p in 2/MAO catalyst. At low T_p ranging from 10 to 30°C, the polymerization rates deactivate by a second order. The deactivation rates become slower when T_p is 40 and 50°C; and, on the contrary, the polymerizations at 60 and 70°C show accelerating rate profiles. Polymerizations at high T_p , 80 and 90°C, are again changed to decay rate profiles. Generally, 2/MAO catalyst is much more thermally stable and more active than 1/MAO catalyst. The Arrhenius plots (Fig. 7) of \bar{R}_p and $R_{p,\text{max}}$ are not linear over the entire range of polymerization temperature for the 2 catalytic systems. The 1/MAO catalyst shows maximum activity between 20 and 30°C, while the 2/MAO catalyst shows maximum activity around 80°C.

It is not clear why a simple alteration of the bridge, replacement of isopropylidene group by an ethyl group, brings about a big difference in catalytic activity and in temperature dependence on polymerization. It is possible to explain with steric and electronic factors, but the subject deserves a more in-depth investigation before any statement can be made. Since the $\text{Et}(\text{Cp})\text{-(Flu)ZrCl}_2$ compound has 2 carbon atoms in the bridge, the cyclopentadienyl and fluorenyl moi-

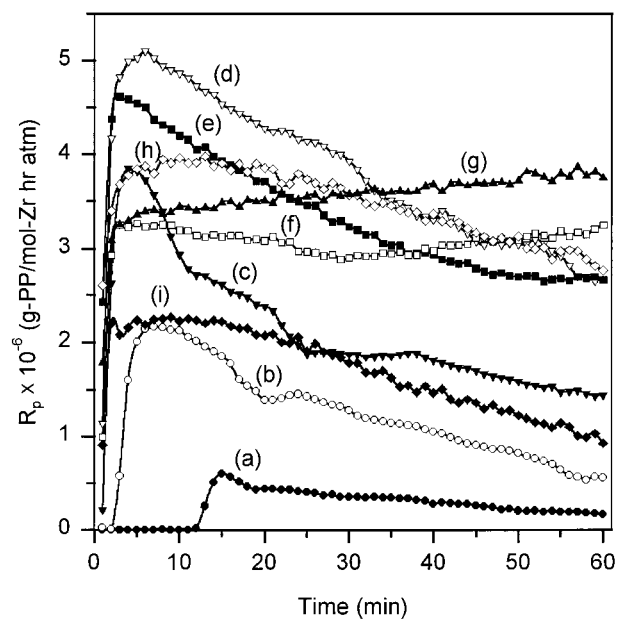


Figure 6 R_p versus time of propylene polymerizations catalyzed by 2/MAO system with $[Zr] = 65.7 \mu\text{M}$, $[Al]/[Zr] = 1193$, toluene = 80 mL, and $P = 1.3 \text{ atm}$. Polymerization temperature is (a) 10, (b) 20, (c) 30, (d) 40, (e) 50, (f) 60, (g) 70, (h) 80, and (i) 90°C.

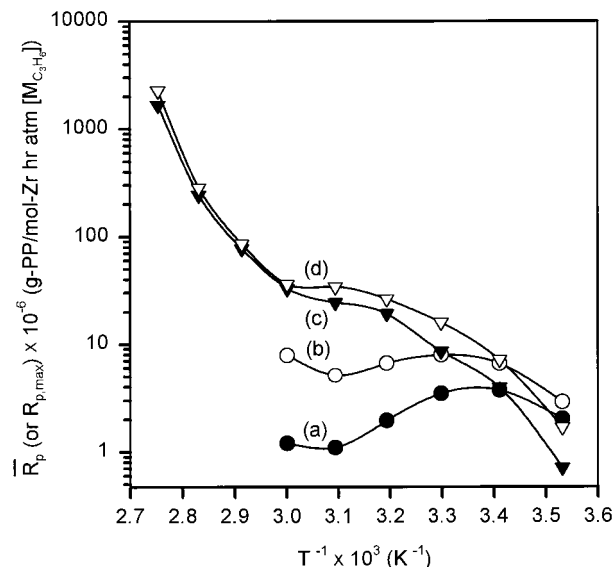


Figure 7 Arrhenius plot of \overline{R}_p (a) and (c) and $R_{p,\max}$ (b) and (d). Profiles (a) and (b) are obtained by **1**/MAO, and (c) and (d) by **2**/MAO.

eties are pushed further away and adopt a more parallel position. As a result, the centroid–Zr–centroid angle is increased. According to the single crystal XRD study,^{10–13} in the crystal structure of pseudo- C_s symmetric Et(Cp)(Flu)ZrCl₂ exists 2 types of molecules, which are 2 conformers (δ - and λ -conformer). The interatomic bond angles and distances of these conformers are different enough to be considered as 2 structurally different molecules.^{10–12} Two conformers interconvert quickly enough to be indistinguishable in the NMR time scale.^{10–12} However, the mobility of their cationic active species activated by excess amount of MAO should be restricted due to contact ion pairing between zirconium alkyl cations and MAO anions. Different from Et(Cp)(Flu)ZrCl₂, neutral *i*Pr(Cp)(Flu)ZrCl₂, is characterized by the prochirality and bilateral symmetry (exact C_s symmetry), and its cationic active species have a S,R-enantiomeric nature.^{5,6} Since we can safely assume that the structures of **1** and **2** are same as those of corresponding metallocene chlorides, the difference in the activity according to polymerization temperature is expected to be deeply related to these structural differences, especially in solution. These structural differences is also expected to influence the resulting polymer structure (*vide infra*).

CHARACTERIZATION OF SPP

In Table I, the properties of sPP obtained by **1**/MAO and **2**/MAO at various polymerization temperatures are summarized. The molecular weight of polymer decreases monotonically as T_p increases. The melting point (T_m) and crystallinity (X_c) of polymer are also decreased as T_p increases. The decrease of molecular weight of polymer with T_p is a typical phenomenon found in the olefin polymerizations by metallocene–MAO catalyst. Since a normal activation energy of termination by β -H elimination, which is the most important chain termination with metallocene catalysts, is somewhat higher than for propagation, T_p is one of the dominating factors to control molecular weight of resulting polymers. In fact, the decrease of molecular weight with increasing T_p is one of weak points of metallocene catalyst in comparison with conventional Ziegler–Natta Catalysts. Since many commercial polyolefin plants are operated at high T_p , if metallocenes are to be used in these operations, it is frequently difficult to produce commercially useful polymers at high T_p .

Ewen et al.²¹ reported that the molecular weight of PP made with *rac*-(EBI)HfCl₂, *rac*-(EBTHI)HfCl₂, and the corresponding titanocenes showed a decrease in \overline{M}_v with increasing T_p . A subsequent article reported that the \overline{M}_n of *i*PP obtained with *rac*-(EBI)ZrCl₂/MAO catalyst decreased from 5500 when the polymerization was carried out at -10°C to 2000 at 50°C .²² The decrease of \overline{M}_n of *i*PP was also reported for the propylene polymerization by the *rac*-MeCH(Me₄Cp)(Ind)TiCl₂–MAO catalyst.²³

The sPPs obtained by **1**/MAO system are characterized by narrow molecular weight distribution, which is the great promise of metallocene catalyst. As shown in Table I, $\overline{M}_w/\overline{M}_n$ (MWD) values of all polymers investigated in this study are in the range of 1.8–2.4, approaching the Poisson distribution. The narrow MWD is indicative of uniform active species present in **1**/MAO system. There are many published results supporting that the MWD of sPP produced by *i*Pr(Cp)(Flu)ZrCl₂/MAO catalyst is slightly changed by increasing T_p .^{5,6,9} However, the MWD values of sPP obtained by **2**/MAO catalyst change greatly according to T_p , as shown in Table I and Figure 8. At low T_p , say 10, 30, and 50°C , MWD values are small; however, the values increase as T_p increases. The MWD value ranging from 4.43 to 6.38 is hardly attainable in the metallocene catalysts because the catalytically active sites formed

Table I Properties of sPP Obtained by 1/MAO and 2/MAO Catalysts at Various Polymerization Temperatures.

Run No.	Catalyst	[Al]/[Zr]	Temp. (°C)	$\bar{R}_p^a \times 10^{-6}$	$R_{p,max}^a \times 10^{-6}$	rrrr% by NMR	$\bar{M}_v^b \times 10^{-4}$	$\bar{M}_w^c \times 10^{-4}$	MWD ^c	A_{867}/A_{975} by IR	T_m (°C)	Crystallinity (%)	
Figure 5(a)	1/MAO	881	10	0.73	1.03	94.01	15.79	14.02	1.74	1.04	139.9, 148.0	50.69	
Figure 5(b)			20	1.15	2.00	90.00	10.50	12.47	2.12	.97	135.2, 142.8	46.23	
Figure 5(c)			30	0.86	1.92	83.78	6.78	—	—	—	.83	119.0, 135.0	41.41
Figure 5(d)			40	0.88	1.29	82.70	5.82	—	—	—	.81	118.4, 128.1	35.07
Figure 5(e)			50	0.15	0.69	68.00	3.20	—	—	—	.62	111.6	24.17
Figure 5(f)			60	0.11	0.71	65.38	2.66	—	—	—	.56	93.4	18.91
Figure 6(a)	2/MAO	1193	10	0.25	0.60	78.78	20.25	26.79	2.41	.79	126.8	30.38	
Figure 6(b)			20	1.20	2.16	72.00	14.43	—	—	—	.71	114.4	27.14
Figure 6(c)			30	2.12	3.85	70.00	10.30	—	—	—	.68	118.4	10.04
Figure 6(d)			40	3.72	5.10	50.00	4.21	—	—	—	.37	—	—
Figure 6(e)			50	3.29	4.62	37.38	2.31	—	—	—	.15	—	—
Figure 6(f)	60	3.00	3.27	—	2.08	—	—	—	—	—	—		
Figure 6(g)	70	3.49	3.87	18.99	1.77	—	—	—	—	—	—		
Figure 6(h)	80	3.41	3.98	—	1.31	—	—	—	—	—	—		
Figure 6(i)	90	1.67	2.27	15.01	1.09	—	—	—	—	—	—		

Polymerization conditions are indicated in corresponding figures in the run no.

^a Unit of activity is g-PP/(mol-Zr·hr·atm).

^b Viscosity-average molecular weight.

^c Measured by GPC.

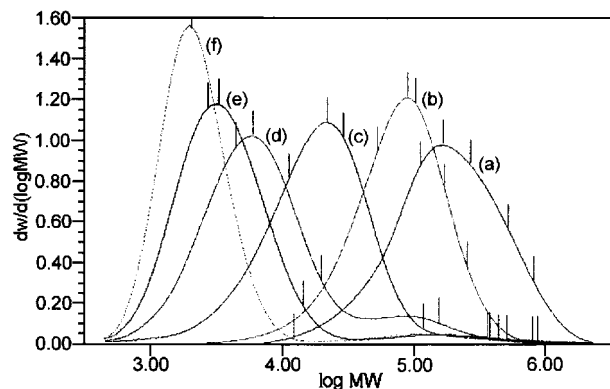
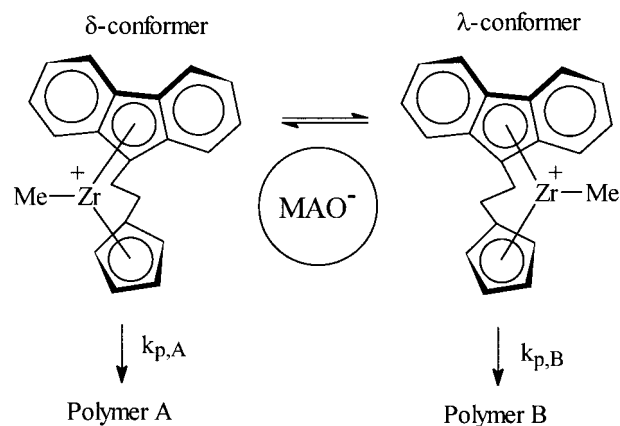


Figure 8 GPC curves for the total polymers produced by **2**/MAO at various temperatures. Polymerization temperature is (a) 10, (b) 30, (c) 50, (d) 70, (e) 80, and (f) 90°C.

by the reaction of metallocenes and MAO are generally uniform over the entire T_p range. One patent²⁴ described the production of sPP with MWD of 4.2 by using $i\text{Pr}(\text{Cp})(\text{Flu})\text{ZrCl}_2/\text{MAO}$ catalyst; however, this broad MWD was attained by conducting the polymerization at 2 temperatures (20°C for 10 min, followed by 50°C for 50 min).

It follows from the Shultz–Flory equation that for a single site type catalyst, the expected MWD should have values around 2. This has been observed generally for polymers produced in homogeneous catalysis with metallocene without regard to the stereospecificity of the catalytic systems. Large deviations from this value are indicative for the existence of more than one active species in the polymerization medium. As discussed before, there are 2 ion-paired conform-

ers in the polymerization medium by **2**/MAO catalyst^{10–12}:



At low T_p , most of the polymer produced is due to $k_{p,A}$ (assuming that δ -conformer is the form produced upon activation or that $k_{p,A} \gg k_{p,B}$). As T_p increases above 50°C, significant amounts of δ -conformer are converted to λ -conformer, and this results in polymers that are growing with the rate constant $k_{p,B}$. These conformational isomeric species have different receptivity towards agostic interaction and produce chains of different length. Polymerizations occurring at 2 different rates broaden the MWD.

Since the **2**/MAO catalyst very much resembles a multisite system other than **1**/MAO, the **2**/MAO catalyst produces polymers having much lower $[rrrr]$ pentad values than **1**/MAO at the similar polymerization conditions (Table I). Above T_p of

Table II Fractionation of sPP Samples Obtained by **1**/MAO and **2**/MAO Catalysts at $T_p = 10^\circ\text{C}$

Catalyst	Fraction	Wt % of sPP		
		Dissolved	T_m (°C)	Crystallinity (%)
1 /MAO	Total polymer	100	139.9, 148.0	50.69
	ether	0.46	—	—
	<i>n</i> -Pentane	1.34	—	—
	<i>n</i> -Hexane	7.35	137.5, 149.5	47.39
	<i>n</i> -Heptane	90.85	136.7, 148.1	35.18
2 /MAO	Total polymer	100	126.8	30.38
	ether	14.50	nd	nd
	<i>n</i> -Pentane	7.80	101.7	15.55
	<i>n</i> -Hexane	29.04	124.7	24.68
	<i>n</i> -Heptane	25.00	128.3	24.60
	Remained	23.66	127.1	19.48

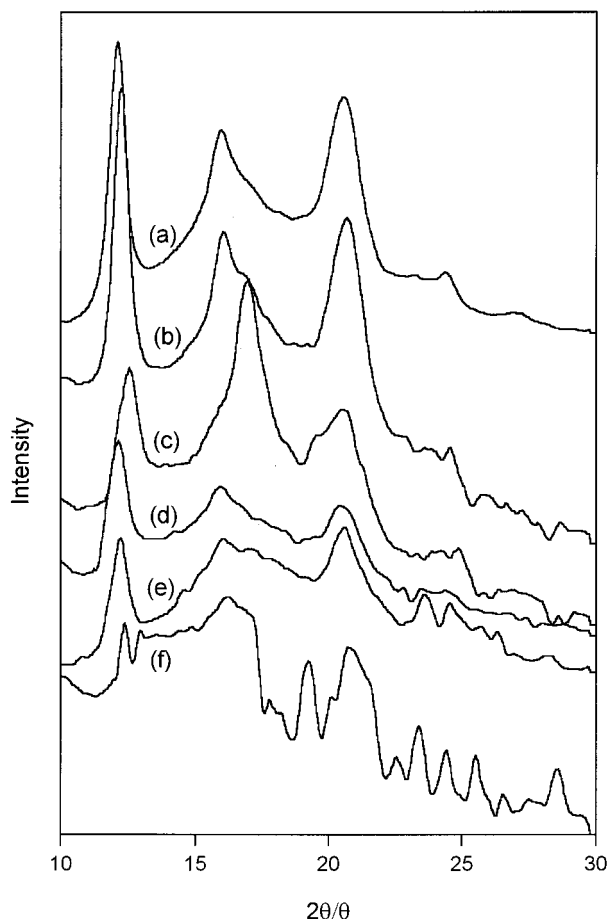


Figure 9 X-ray diffractograms of sPP samples obtained with **1**/MAO at T_p : (a) 10, (b) 20, (c) 30, (d) 40, (e) 50, and (f) 60°C.

50°C, **2**/MAO catalyst produces amorphous polymers, which contain large portion of atactic pentads. The lower stereoregularity of **2**/MAO is expected to be caused by the increase of centroid-Zr-centroid angle. The lower probability of α -agostic interaction that is caused by the increase of the bond angle and an increased structural flexibility of the catalyst framework explain the lower stereoregularity of **2**/MAO catalyst.

The fractionation of the polymer by using various solvents showing different boiling points gives information on the type of active species of catalyst and the structural defects present in resulting polymers. Two sPP samples obtained with **1**/MAO and **2**/MAO at $T_p = 10^\circ\text{C}$ were fractionated by extraction with refluxing solvents of different boiling point. The fractionation results summarized in Table II show 2 samples to contain fairly different amount of stereoirregular macromolecules. The sPP obtained by **1**/MAO is almost

insoluble in ether and pentane, and slightly soluble in hexane. Most of the sample (90.9%) is soluble in heptane. These fractionation results are frequently found in homogeneous catalysis with metallocene. The sPP obtained by **2**/MAO is soluble in various solvents, and it contains the fraction insoluble, even in heptane, demonstrating that the sample is composed of a different chain length and has many structural defects. Such characteristics of sPP sample are sure to be induced by the multiple-site feature of **2**/MAO catalyst.

Figures 9 and 10 are XRD patterns for the sPP powders obtained at different T_p using **1**/MAO and **2**/MAO catalysts, respectively. As shown in Figure 9, all sPP contain only broad peaks, indicating very small size crystallites of different kinds of unit cells. The peaks become broader as T_p increases, and the sample obtained at 60°C shows a XRD pattern appeared in amorphous

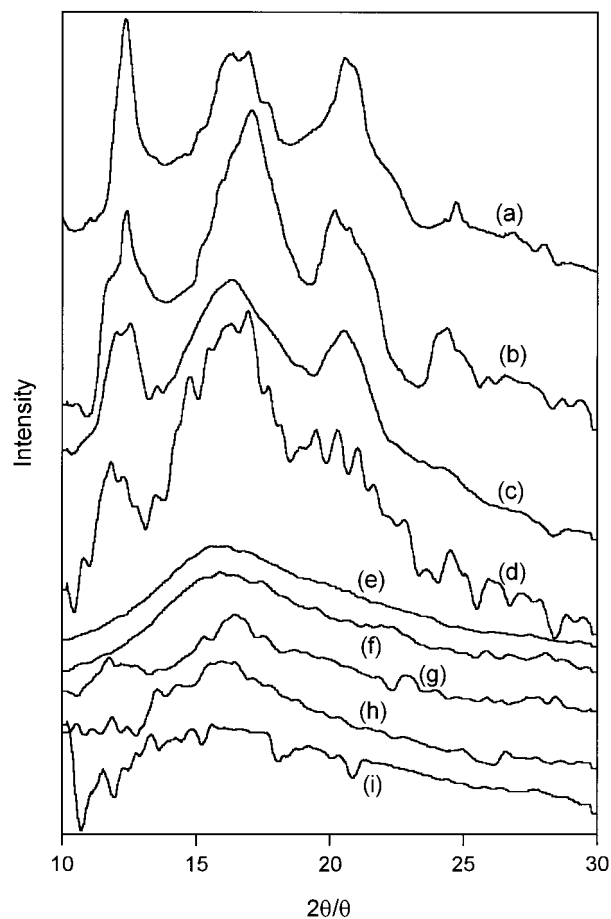


Figure 10 X-ray diffractograms of sPP samples obtained with **2**/MAO at T_p is (a) 10, (b) 20, (c) 30, (d) 40, (e) 50, (f) 60, (g) 70, (h) 80, and (i) 90°C.

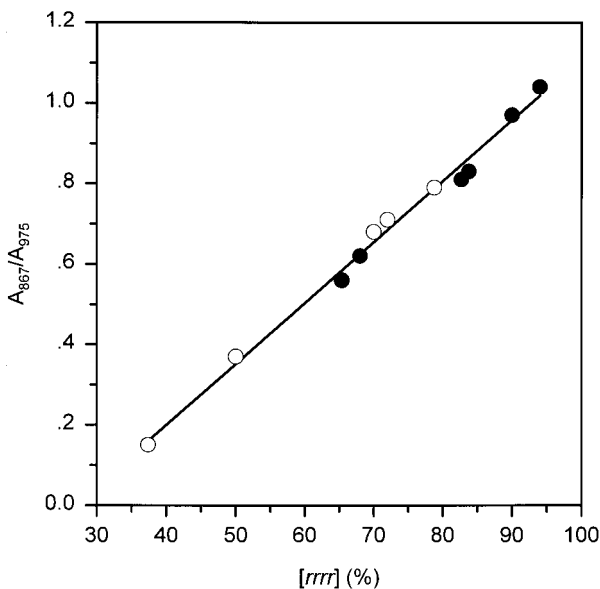


Figure 11 Relationship between IR absorption ratio (A_{867}/A_{975}) and $[rrrr]$ pentad value: (●) samples produced by 1/MAO; (○) samples prepared by 2/MAO.

polymer. Three unit cell packing models for $(t_2, g_2)_2$ chains have been proposed for sPP.^{25–28} Structure A has an orthorhombic C-centered unit cell of C222₁ space group, which requires all the chains to be of the same hand.²⁵ Structure B^{26–28} corresponds to space group Pca2₁ with chains of opposite hand along *a*. Structure C^{26–28} corresponds to space group I*bca* with a doubling of the *b*-axis in structure B. According to this classification of structure of sPP, all sPP samples obtained by 1/MAO catalyst most likely contain a C crystal structure. The sPP samples obtained at low T_p (10–40°C) by using 2/MAO are characterized by very broad XRD peaks (Fig. 10), even though the position of the peaks [(200), (020), (121), and (400)] is the same with those of sPP samples by 1/MAO. This broad XRD peaks demonstrate that the samples are composed of very small crystallite of less defined structure. These structural differences of sPP seem to be deeply related to 2 melting transitions for the samples obtained by 1/MAO and single T_m for the samples obtained by 2/MAO (Tables I and II). The samples obtained above 50°C of T_p by using 2/MAO are completely amorphous (Fig. 10).

The IR spectra provide a good opportunity to distinguish the type of stereoregularity and to make quantitative measurements. In the IR spectrum of sPP, crystalline helix bands are at 1005, 977, and 867 cm^{-1} .²⁹ Amorphous sPP has 2

bands, 975 and 962 cm^{-1} , that belong to the helix segments with TTGG conformation and chain segments with the planar TT conformation.²⁹ The presence of the intense 867 cm^{-1} band in the spectra of predominantly syndiotactic polypropylene was used for the measurement of syndiotacticity by comparing with amorphous 975 cm^{-1} band. Figure 11 shows A_{867}/A_{975} ratio versus $[rrrr]$ pentad values (by ¹³C-NMR) of sPP samples obtained by 1/MAO and 2/MAO catalysts at different T_p . There is a good linear relationship between A_{867}/A_{975} ratio and $[rrrr]$ pentad value expressed as

$$A_{867}/A_{975} = 0.015[rrrr] - 0.407$$

This simple expression is valid for the rough estimation of macrotacticity of sPP by IR method.

CONCLUSION

The C_s symmetric metallocene **1** and pseudo- C_s symmetric metallocene **2** show fairly different kinetic behaviors. At the similar polymerization conditions using MAO as a cocatalyst, 2/MAO catalyst is more active than 1/MAO by about 3 times. The activity of both catalytic systems is very sensitive to the concentration of MAO. The 1/MAO and 2/MAO catalysts record maximum activity when [Al]/[Zr] ratio is around 1300 and 2500, respectively. The large amount of MAO is needed to attain high activity because MAO not only produces the cationic active species but also stabilizes the anion.

The activity and degree of stereochemical control are also sensitive to T_p . The 2/MAO catalyst is much more thermally stable than 1/MAO catalyst; the former shows maximum activity at 80°C, while the latter at 20°C. The cationic active species generated by 2/MAO is not so stereorigid as those by 1/MAO. In 2/MAO catalyst, there exist 2 fluxional conformers that can be interconverted at high T_p so that the catalyst produces sPP of broad MWD and low stereospecificity at high T_p . When T_p is above 50°C, 2/MAO catalyst produces completely atactic polypropylene. The results of fractionation of sPP samples produced by 1/MAO and 2/MAO demonstrate that 1/MAO catalyst is characterized by uniform active sites but 2/MAO is characterized by multiple active sites. There is a good linear relationship between IR absorption ratio (A_{867}/A_{975}) and $[rrrr]$ pentad value (by ¹³C-NMR).

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