Control of Molecular Weight Distribution in Propylene Polymerization with Ziegler–Natta/Metallocene Catalyst Mixtures

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ABSTRACT: Propylene polymerization was investigated with a sequential addition of Ziegler–Natta and metallocene catalysts. From the fact that the molecular weights of polypropylene (PP) produced with Ziegler–Natta and with metallocene catalysts differ, it was possible to control the molecular weight distribution (MWD) of PP with a sequential addition of methylaluminoxane and *rac*-ethylenebis(indenyl)zirconium dichloride followed by triethylaluminum and magnesium dichloride-supported titanium tetrachloride catalyst. The obtained PP exhibited a wide MWD curve with shoulder peak. The position and height of each peak was controlled with the variation of polymerization time for each catalyst as well as the amount of each catalyst. The MWD of PP prepared with sequential addition of catalysts was much wider than that of PP obtained from each catalyst. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 67: 2213–2222, 1998

Key words: metallocene; Ziegler–Natta catalyst; sequential addition; molecular weight distribution; Flory distribution

INTRODUCTION

Currently, Ziegler–Natta catalyst is a conventional olefin polymerization catalyst used in various processes. Usually, Ziegler–Natta catalyst produces polyolefins with polydispersity indexes (M_w/M_n) of 5 to 10.[1]

Since Kaminsky's mid-1980s study, metallocene catalysts have been studied extensively from both the academical and practical points of view. Metallocene catalyst is a kind of organometallic compound composed of group 4 transition metal, σ ligand, brid-ges, and π ligand. Metallocene catalyst can produce polyolefins with various stereoregularity and average molecular weight (MW) with narrow molecular weight distribution (MWD).[2,3] Therefore, it is possible to obtain polyolefins of desired MW, MWD, and stereoregularity with the appropriate metallocene catalyst.

MW and MWD are important factors in determining the physical, mechanical, and rheological properties of polymers. While MW controls the mechanical properties of polymers, MWD mainly controls the rheological properties.[4] Therefore, it is necessary to control the MW and MWD of polymers to optimize the mechanical property and processability.

There have been three major methods of controlling the MWD of polyolefin produced. The first

Table I Propylene Polymerization Activities of MgCl₂–Ti and EIZ Catalysts with Various Cocatalysts and Properties of Obtained PP

Run No.	Catalyst	Cocatalyst	[Al]/[Metal]	Activity in kg PP/(mol-metal · mol-propylene · h)	T_m (°C)	I.I. (wt %)	M_n	M_w	M_w/M_n
1	MgCl₂–Ti	TEA	100	3,700	160.7	75.0	44,000	271,000	6.1
2	MgCl₂–Ti	TEA + MAO	40 + 60	3,000	159.8	88.0	47,000	270,000	5.8
3	MgCl₂–Ti	MAO	100	2,600	160.2	84.2	67,000	323,000	4.8
4	MgCl₂–Ti	MAO	4,000	1,600	159.0	68.8	—	—	—
5	EIZ	TEA	100	0	—	—	—	—	—
6	EIZ	TEA + MAO	300 + 1,000	0	—	—	—	—	—
7	EIZ	MAO	2,000	7,100	129.5	0	6,000	15,000	2.4
8	EIZ	MAO	4,000	12,500	130.5	0	9,000	23,000	2.6

Polymerization conditions: [Ti] = 6.18×10^{-5} mol/L, [Zr] = 3.19×10^{-5} mol/L; solvent; 200 mL toluene. I.I., isotacticity index.

method is to use a series of reactors with different polymerization conditions, such as hydrogen pressure, temperature, and polymerization time. The second is to melt-blend polymers with different MW. But these two cases are cumbersome because additional steps in process are necessary; miscibility problems can also occur because of the different melt viscosities of the polymer blend pairs. The third method is to modify the polymerization catalyst directly. This method is simple but highly advanced catalyst technology is needed.

Until now, mixtures of metallocene catalysts have been used[5,6] or metallocene catalyst was introduced as modifier into the conventional Ziegler–Natta catalyst used in current process to control MWD of polypropylene (PP).[7] But few reports have been published for the sequential addition of Ziegler–Natta and metallocene catalysts.

In this article, based upon the above background, the reactor-blended PP was obtained by using *rac*-ethylenebis(indenyl)zirconium dichloride (*rac*-ethylene(Ind)₂ZrCl₂, EIZ) catalyst and magnesium dichloride (MgCl₂)-supported titanium tetrachloride (TiCl₄)(MgCl₂–Ti) catalyst to control MWD. Propylene polymerization was performed by a sequential addition of EIZ and MgCl₂–Ti catalyst with the appropriate aluminum compound cocatalyst. The MW, MWD, thermal properties, and rheological properties of the polymers, as well as polymerization characteristics, were examined.

EXPERIMENTAL

Materials

Propylene (polymerization grade; Hyosung T&C Co., Onsan, Korea) and nitrogen (99.999%; Korea

Table II Propylene Polymerization by Sequential Addition of EIZ/MAO and MgCl₂–Ti/MAO Catalyst Systems with Various [Zr]/[Ti] Ratios

Run No.	Catalyst	[Zr]/[Ti]	Activity in kg PP/(mol-metal · mol-propylene · h)	I.I. (wt %)	*mmmm*
8	EIZ	—	12,500	0.0	82.9
9	EIZ → MgCl₂–Ti	0.38	9,400	20.6	85.4
10	EIZ → MgCl₂–Ti	0.21	5,000	20.2	—
11	EIZ → MgCl₂–Ti	0.11	3,800	24.2	—
12	EIZ → MgCl₂–Ti	0.03	2,300	39.6	91.0
4	MgCl₂–Ti	—	1,600	68.8	75.8

Polymerization conditions: [Zr] = 3.19×10^{-5} mol/L for Run No. 8, [Ti] + [Zr] = 2.81×10^{-5} mol/L for Runs No. 9–12, [Ti] = 6.18×10^{-5} mol/L for Run No. 4; cocatalyst = MAO ([Al]/[M] = 4,000); solvent: 200 mL toluene; MgCl₂–Ti catalyst was added 10 min after polymerization with EIZ catalyst. I.I., isotacticity index.
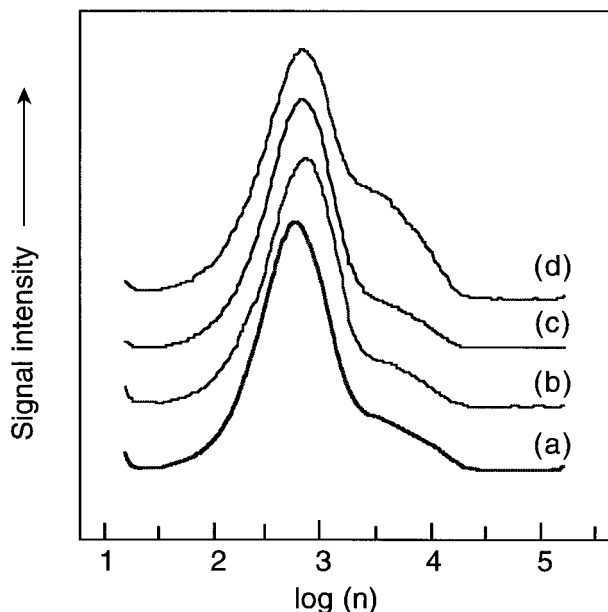
Figure 1 GPC curves for PP obtained by sequential addition of EIZ/MAO and MgCl$_2$–Ti/MAO catalyst systems: (a) Run No. 9, (b) Run No. 10, (c) Run No. 11, (d) Run No. 12; n is degree of polymerization.

(MAO, type 4 in toluene; Akzo Co., Deer Park, TX), triethylaluminum (TEA; Aldrich Chem., Milwaukee, WI), MgCl$_2$ (anhydrous, Extra Pure grade; Junsei, Tokyo, Japan), TiCl$_4$ (99.995+%; Aldrich Chem., Milwaukee, WI), diisobutylphthalate (DIBP; Tokyo Kesei, Tokyo, Japan) and cyclohexyldimethoxymethylsilane (CHDMS; polymerization grade, Mitsui Petrochem. Co., Tokyo, Japan) were used without further purification.

Catalyst

Metallocene compound EIZ was purchased from Aldrich Chem., Milwaukee, WI. Ziegler–Natta catalyst, MgCl$_2$–Ti, was prepared by ball-milling methods.[8] After measured amounts of MgCl$_2$, TiCl$_4$, DIBP, and toluene were introduced into a stainless-steel pot in a nitrogen atmosphere, the mixture was ball-milled with zirconia balls for 72 h. The resultant catalyst was washed with fresh toluene and finally suspended in a measured amount of toluene. The contents of Ti and DIBP in the obtained MgCl$_2$–Ti catalyst were 1.10 and 9.35 wt %, respectively.

Polymerization

Polymerization in toluene medium was carried out under atmospheric pressure of monomer at 40°C. In a dried glass reactor, solvent and cocatalyst were introduced successively, followed by saturation with propylene, and the polymerization was initiated by

Specialty Gases Co., Ltd., Seoul, Korea) were purified with columns of calcium chloride (CaCl$_2$, Extra Pure grade; Shinyo, Osaka, Japan), phosphorus pentoxide (P$_2$O$_5$, 98.0+%; Yakuri Pure Chemicals, Osaka, Japan), and molecular sieve 4Å. Toluene (Extra Pure grade; Yakuri Pure Chemicals, Osaka, Japan) was purified by refluxing over sodium metal and benzophenone in a nitrogen atmosphere. Modified methylaluminoxane

Table III   Propylene Polymerization by Sequential Addition of EIZ/MAO and MgCl$_2$–Ti/TEA Catalyst Systems with Various Polymerization Times

Run No.	Catalyst	Polymerization Time (min)		Activity in kg PP/(mol-metal · mol-propylene · h)	I.I. (wt %)	*mmmm*
		EIZ	MgCl$_2$–Ti			
8	EIZ	60	0	12,500	0.0	82.9
13	EIZ → MgCl$_2$–Ti	40	20	3,400	38.1	—
14	EIZ → MgCl$_2$–Ti	30	30	2,600	42.3	84.1
15	EIZ → MgCl$_2$–Ti	20	40	2,300	42.9	—
16	EIZ → MgCl$_2$–Ti	10	50	1,800	67.9	—
2	MgCl$_2$–Ti	0	60	3,000	88.0	76.6

Polymerization conditions: [Zr] = 3.19×10^{-5} mol/L for Run No. 8, [Zr] = 6.06×10^{-6} mol/L and [Ti] = 1.52×10^{-4} mol/L for Runs No. 13–16, [Ti] = 6.18×10^{-5} mol/L for Run No. 2; cocatalyst = MAO ([Al]/[Zr] = 4,000) and TEA ([Al]/[Ti] = 100) for Runs No. 8 and 13–16, TEA + MAO {([Al] of TEA + [Al] of MAO)/[Ti] = 40 + 60} for Run No. 2; solvent: 200 mL toluene. I.I., isotacticity index.
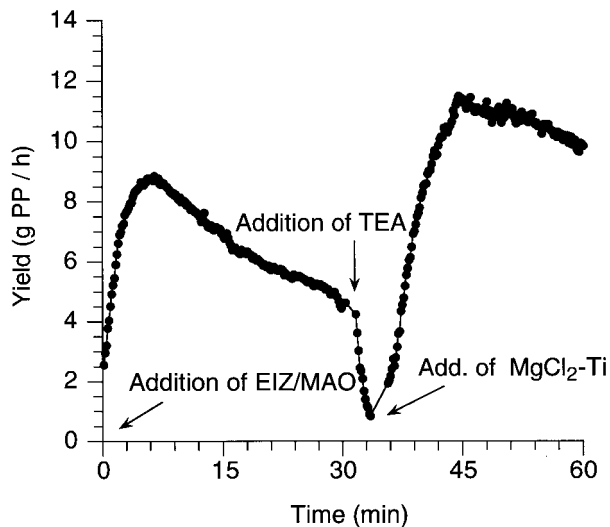
Figure 2 Propylene polymerization rate profile for sequential addition of EIZ/MAO and $MgCl_2-Ti/TEA$ catalyst systems (Run No. 14).

the injection of catalysts. If necessary, external electron donor (CHDMS) was added just before the injection of catalysts. With continuous flow of propyl-

ene, the consumption rate of monomer was recorded with a Mass Flow Controller (MFC, 5850E, Brooks Instrument Div., U.S.A.). Polymerization was terminated by injection of ethanol after 1 h. The obtained polymer was washed with acidified methanol (5 wt % HCl in methanol) and fresh methanol, successively.

Analytical Procedures

The content of metals in the supported catalyst was determined by inductively coupled plasma (Shimadzu ICPQ-1000, Tokyo, Japan). Isotacticity index (I.I.) was determined by the weight percent of boiling heptane insolubles. The extraction experiment was performed in a Soxhlet extractor for 5 h. The *mmmm* pentad composition of PP was determined by integrating the individual peak in the methyl carbon region obtained with carbon-13 nuclear magnetic resonance (Jeol JNM-EX400, Tokyo, Japan) apparatus. MW and MWD of polymer were determined by a high-temperature gel permeation chromatography (GPC; Polymer Laboratory PL-210, U.S.A.) with Waters' Styrogel col-

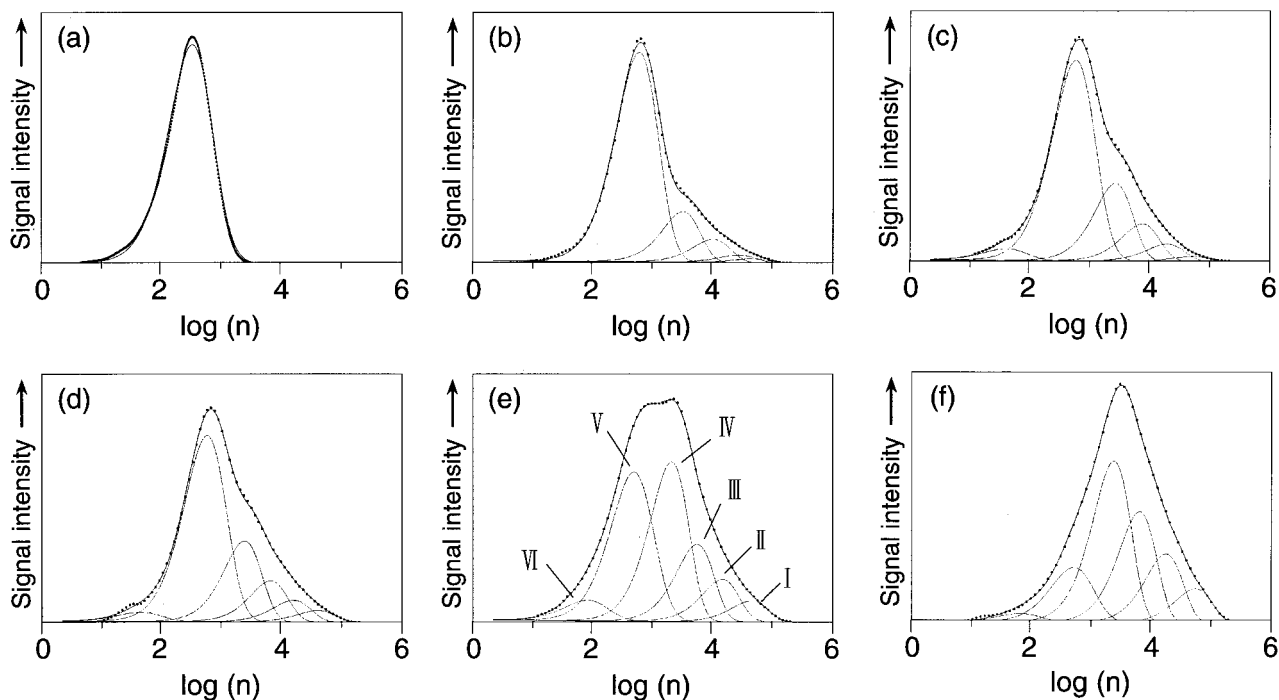**Figure 3** GPC curves for PP obtained by EIZ, $MgCl_2-Ti$ alone, and sequential addition of EIZ/MAO and $MgCl_2-Ti/TEA$ catalyst systems: (a) Run No. 8, (b) Run No. 13, (c) Run No. 14, (d) Run No. 15, (e) Run No. 16, (f) Run No. 2; original GPC curves (· · ·); Flory component and simulated GPC curves (——); n is degree of polymerization.

Table IV Parameters of Flory Component Respresenting MWD of PP Obtained by MgCl$_2$–Ti Catalyst and Sequential Addition of Catalysts

	Component					
	← Higher Molecular Weight Component					
	I	II	III	IV	V	VI
(a) PP obtained by MgCl$_2$–Ti catalyst (Run No. 2)						
b	0.00274	0.00282	0.00305	0.00375	0.00882	0.0293
Fraction (%)	7.6	15.2	24.6	36.5	13.9	2.2
(b) PP obtained by sequential addition of catalysts (Run No. 16)						
b	0.00275	0.00285	0.00310	0.00390	0.00910	0.0262
Fraction (%)	4.1	8.4	15.5	32.9	34.4	4.7
(c) PP obtained by sequential addition of catalyst with external electron donor: CHDMS (Run No. 18)						
b	0.00274	0.00283	0.00307	0.00396	0.00992	0
Fraction (%)	5.3	19.6	24.0	30.8	20.3	0

umn at 160°C in 1,2,4-trichlorobenzene. The MW was estimated by using a polystyrene calibration curve. The sample used in GPC analysis and Soxhlet extraction was treated with 0.1 wt % of Irganox 1010 as thermal stabilizer. Resolution of the GPC chromatograms into components was performed with a commercial software system (Peakfit; Jandel Scientific, U.S.A.). The melting temperature (T_m) and glass transition temperature (T_g) of polymer were determined from the peaks of the second scanning curve obtained with differential scanning calorimetry (DSC; Perkin–Elmer DSC 7, Norwalk, CT) at the heating rate of 20°C/min. Rheological property was investigated using a rheometrics mechanical spectrometer with parallel plate at 190°C and strain of 15% in dynamic mode.

RESULTS AND DISCUSSION

Propylene Polymerization by EIZ and MgCl$_2$–Ti Catalyst with Various Cocatalysts

Propylene polymerization by EIZ or MgCl$_2$–Ti catalyst with various alkylaluminum compounds such as TEA, MAO, and a mixture of TEA and MAO (TEA+MAO) was performed and the results are shown in Table I.

The activity of MgCl$_2$–Ti catalyst with TEA ([Al]/[Ti] = 100) was 3,700 (kg PP/mol-Ti·mol-propylene·h). When TEA+MAO {([Al of TEA] + [Al of MAO])/[Ti] = 40 + 60) or MAO ([Al]/[Ti] = 100 or 4000)} was used as cocatalyst, activity

gradually became lower. The T_m of PP obtained from MgCl$_2$–Ti catalyst was around 160°C. I.I. was 70–90, which was a little lower than that of commercial PP because no external electron donor was used in Run Nos. 1–4. M_w of PP was about 300,000 and M_w/M_n was about 6.

EIZ did not polymerize propylene when TEA was used as a cocatalyst as shown in Run Nos. 5 and 6 in Table I. When MAO was used as cocatalyst, the activity increased with [Al]/[Ti] increase, but T_m of PP was almost unchanged.[9] The T_m of PP obtained from EIZ catalyst was 130°C because of the regioirregularity, 1,3-misinsertion.[9,10] I.I. was 0 due to regioirregularity. M_w was less than 30,000 and M_w/M_n was about 2.

Propylene Polymerization by Sequential Addition of EIZ/MAO and MgCl$_2$–Ti/MAO Catalyst Systems

Propylene polymerization was performed by the sequential addition of EIZ and MgCl$_2$–Ti catalysts in the presence of MAO cocatalyst because only MAO can activate both EIZ and MgCl$_2$–Ti catalyst. MgCl$_2$–Ti catalyst was added 10 min after the injection of EIZ catalyst and the polymerization results are shown in Table II.

The polymerization activity increased and I.I. decreased with [Zr]/[Ti] ratio. The *mmmm* pentad value of PP obtained by the sequential addition of catalyst systems was higher than that of PP by EIZ or MgCl$_2$–Ti catalyst alone, which might be due to the modification effect of metallocene compounds on the Ti active center.[11,12]

Table V   Properties of Polypropylene Obtained by Sequential Addition of EIZ/MAO and MgCl$_2$–Ti/TEA Catalyst Systems

| | | | | | | | Total | Total | Fraction of PP Prepared from MgCl$_2$–Ti (wt %) | | |
| | | | | | | | | | | Calculated | |
Run No.[a]	M_n	M_w	M_w/M_n	T_g (°C)	T_m (°C)		ΔH_m (J/g)	X_c[b] (%)	Estimated[c]	from GPC[d]	from Polymerization Rate Profiles[e]
8	9,000	23,000	2.6	−15.0	130.0		78.6	41.8	0.0	0.0	0.0
13	22,000	122,000	5.5	−10.5	133.8	157.2	74.3	39.5	75.0	32.6	37.4
14	18,000	133,000	7.4	−9.0	136.5	157.4	59.8	31.8	85.8	47.6	57.2
15	22,000	166,000	7.5	−11.7	131.8	156.9	67.7	36.0	92.4	52.4	60.3
16	22,000	201,000	9.2	−9.7		158.5	66.3	35.3	96.8	78.1	89.7
2	47,000	270,000	5.8	−11.2		159.8	70.2	37.3	100.0	100.0	100.0

[a] Polymerization conditions are same as shown in Table III.

[b] Crystallinity from heat of fusion: X_c (%) = $100 \times (\Delta H_m/\Delta H_m^*)$, $\Delta H_m^* = 188$ J/g.

[c] Estimated from the catalyst concentration and activity of each catalyst.

[d] Calculated from the fraction of each peak in Figure 3. The contribution from MgCl$_2$–Ti in peak V was obtained based upon the ratio of fraction of peak IV and peak V in Figure 3(f).

[e] Calculated by the integration of individual curve as shown in Figure 2.

Figure 1 shows the GPC curve for PP obtained by the sequential addition of EIZ/MAO and MgCl$_2$–Ti/MAO. All the GPC curves exhibited wide MWD with shoulder peaks because the MW of PP prepared from EIZ or MgCl$_2$–Ti catalyst was much different from each other, as shown in Table I. As the amount of MgCl$_2$–Ti increased, the height of the peak at MW of 300,000 increased. This result indicates that the MWD of PP can be controlled by the variation of the [Zr]/[Ti] ratio.

Propylene Polymerization by Sequential Addition of EIZ/MAO and MgCl$_2$–Ti/TEA Catalyst Systems

In case of sequential addition of EIZ/MAO and MgCl$_2$–Ti/MAO catalyst systems, a large amount of expensive MAO was necessary and the activity of MgCl$_2$–Ti became low using MAO instead of TEA. In addition, it was not simple to control the amount of PP prepared from each catalyst by simple variation of [Zr]/[Ti] ratios because EIZ polymerized propylene continuously even after MgCl$_2$–Ti catalyst was introduced, and the activity of EIZ was much higher than that of MgCl$_2$–Ti catalyst. In order to eliminate these disadvantages, the propylene polymerization was performed by the sequential addition of EIZ/MAO and MgCl$_2$–Ti/TEA catalyst systems with differ-

ent polymerization times for each catalyst; the results are shown in Table III.

As the polymerization time for EIZ catalyst increased, the total polymerization activity increased. I.I. of PP obtained with long EIZ polymerization time became smaller because PP prepared from EIZ has chemical inversion.[9] On the other hand, *mmmm* pentad composition of PP obtained by sequential addition of catalyst systems was a little higher than that of PP prepared from EIZ or MgCl$_2$–Ti catalyst alone.

The propylene polymerization rate profile for the sequential addition of the catalysts ("Run No." 14 in Table III) is shown in Figure 2.

When EIZ/MAO ([Al]/[Zr] = 4,000) was introduced as catalyst system, the polymerization was initiated with typical decay characteristics. With introduction of TEA ([Al]/[Zr] = 2,500) after 30 min, the propylene polymerization activity of EIZ catalyst decreased dramatically because EIZ cannot polymerize propylene with TEA cocatalyst as shown in "Run Nos." 5 and 6 in Table I. But the propylene polymerization was reinitiated remarkably by the injection of MgCl$_2$–Ti catalyst ([Al in TEA]/[Ti] = 100) because MgCl$_2$–Ti catalyst has high activity even with TEA+MAO cocatalyst mixture, as shown in "Run No." 2 in Table I. Therefore it was possible to control the amount of PP produced by each catalyst not only with the

Table VI   Propylene Polymerization by Sequential Addition of EIZ/MAO and MgCl₂–Ti/TEA Catalyst Systems Without and With External Electron Donor (CHDMS)

Run No.	Catalyst	Polym. Time (min) EIZ	MgCl₂–Ti	Activity in kg PP/(mol-metal · mol-propylene · h)	I.I. (wt %)	M_n	M_w	M_w/M_n
(a) Without external electron donor								
15	EIZ → MgCl₂–Ti	20	40	2,300	42.9	22,000	166,000	7.5
16	EIZ → MgCl₂–Ti	10	50	1,800	67.9	22,000	201,000	9.2
2	MgCl₂–Ti	0	60	3,000	88.0	47,000	270,000	5.8
(b) With external electron donor								
17	EIZ → MgCl₂–Ti	20	40	2,200	74.6	12,000	202,000	16.5
18	EIZ → MgCl₂–Ti	10	50	1,700	81.8	32,000	332,000	10.3
19	MgCl₂–Ti	0	60	2,600	100	75,000	517,000	6.9

Polymerization conditions: [Zr] = 6.06 × 10⁻⁶ mol/L, [Ti] = 1.52 × 10⁻⁴ mol/L; cocatalyst = MAO ([Al in MAO]/[Zr] = 4,000) and TEA ([Al in TEA]/[Ti] = 100) for Runs No. 15–18, TEA+MAO {([Al] of TEA + [Al] of MAO)/[Ti] = 40 + 60} for Runs No. 2 and 19; [CHDMS]/[Al] = 0.2; solvent: 200 mL toluene. I.I., isotacticity index.

amount of each catalyst used but also with the polymerization time for each catalyst.

The MWD curve of the samples was obtained with GPC and is shown in Figure 3. All the MWD curves for the sequential addition of catalyst systems exhibited broad distribution. The peak that appeared at the lower MW region originated from the PP obtained from the EIZ/MAO catalyst system, and the peak at the higher MW region was due to PP from MgCl₂–Ti catalyst. It was possible to prepare PP of wide MWD with shoulder peak by controlling the height of each peak with the variation of the polymerization time for each catalyst.

The Flory distribution function can represent the "most probable distribution" to be obtained from a random polymerization process using homogeneous catalyst in which one growing chain produces one dead chain. The Flory distribution function in GPC coordinates can be expressed as follows[13,14]:

$$a^2 \exp\{4.6 \log(n)$$
$$- a \exp[2.3 \log(n)]\} \text{ versus } \log(n) \quad (1)$$

$$a = \Sigma R_t / R_p \quad (2)$$

where n is the degree of polymerization, a is the probability of the chain termination reaction, ΣR_t is the sum of the chain termination rates, and R_p is the chain propagation rate.

However, in most cases, GPC chromatograms are noticeably broadened because of the limited resolution power of the GPC methods. In addition to

the mathematical models which have been proposed to describe the shape of such peaks,[15,16] the empirical equations, such as eq. (3), which imitate the mathematical models were developed to make the experimental curve-fitting procedure easy.[13]

$$Kb^2 \exp\{4.6 \log(n) - E[b - F \log(n)]$$
$$\times \exp[2.3 \log(n)]\} \text{ versus } \log(n) \quad (3)$$

where b is the modified value of a, E and F are two experimental peak-broadening parameters, and K is the normalization coefficient. The values of E, F, and K depend on particular conditions of GPC measurement, and both E and F are functions of b.

It is known that metallocene catalyst contains single active center.[10] Therefore, polyolefins from metallocene catalyst can be characterized by a single Flory distribution function such as eq. (3).[13] In our experiment, PP with different MW was prepared from EIZ catalyst by the variation of polymerization temperature. The MWD curves for each PP were curve-fitted using one Flory distribution function, eq. (3), to determine the dependence of E and F on b.

Finally, the broadened Flory distribution function, eq. (6), for our GPC experiment was obtained with the following dependence of E and F on b:

$$E = 6.7158 + 2.6153 \log b \qquad r^2 = 0.97981 \quad (4)$$
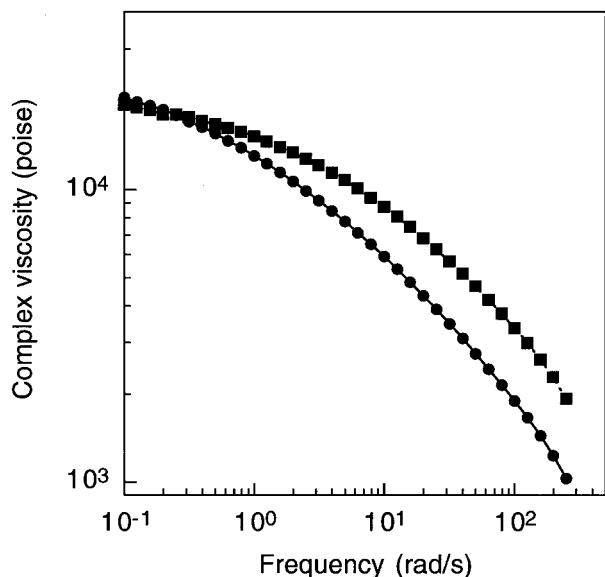$$F = -0.00075 + 0.2944 b \qquad r^2 = 0.99957 \quad (5)$$

Figure 4 Complex viscosity versus frequency for commercial and prepared PP: commercial PP (M_w = 222,000, M_w/M_n = 5.2) (— ■ —); prepared PP of Run No. 17 (M_w = 202,000, M_w/M_n = 16.5) (— ● —).

IF {[$b - F \log(n)$] < 0.002, 0, 1}

$\times Kb^2\exp\{4.6 \log(n) - E$ ABS[$b - F \log(n)$]

$\times \exp[2.3 \log(n)]\}$ versus $\log(n)$ (6)

IF (condition, $n1$, $n2$) (if the condition is satisfied then $n1$; if not then $n2$) and ABS(n) (absolute value of n) functions were adopted to eliminate mathematical abnormality.

McLaughlin and Hoeve[17] and Vickroy and colleagues[14] reported that it was possible to separate polyolefin GPC curves into Flory distributions, each of which was attributed to an active center. In addition, Kissin[18] used MWD deconvolution to determine the kinetic parameters in ethylene polymerization; and Soares and Hamielec[19] examined the theory and statistics of deconvolution of PP MWD.

GPC curves of PP from EIZ, MgCl$_2$–Ti, and sequential addition of catalyst systems were deconvolved into various curves of Flory distribution function using eq. (6); the results are shown in Figure 3.

In the case of PP obtained with EIZ catalyst, only one Flory distribution curve was enough to describe the MWD curve better than 99.9% of degree of fit, as shown in Figure 3(a).

For PP prepared from MgCl$_2$–Ti, six individual Flory distribution curves were enough, as shown

in Figure 3(f). This probably means that there are at least six distinct catalyst sites in MgCl$_2$–Ti catalyst.[14]

In the case of PP prepared from sequential addition of catalyst systems [Fig. 3(b–e)], the abrupt increase of the height of peak V by the contribution of PP originated from EIZ catalyst was clearly seen. It was possible to vary the fraction of this peak effectively with the polymerization time for each catalyst.

In order to find the effect of the existence of EIZ on the individual activity site of MgCl$_2$–Ti catalyst, the b and fraction of each component in MWD curves from Run Nos. 2 and 16 [Fig. 3(f) and (e), respectively] were summarized and are shown in (a) and (b) of Table IV.

Table IV shows that the b values of the polymer's individual components were almost the same. This good match can provide an assertion that Flory function is suitable for the MWD description of polymers produced with catalysts with single active sites. Addition of EIZ increased the fraction of peak V by a large amount, as mentioned above. Addition of EIZ also affected the relative activity of active centers of MgCl$_2$–Ti catalyst. In the presence of EIZ catalyst, the fraction of the component with higher MW (Table IV, columns I, II, III) was reduced more seriously than the lower one (IV, VI). This result intimates that the activity of the active center of MgCl$_2$–Ti catalyst that produces higher MW was more easily affected by EIZ.

The details of MW and polydispersity data are shown in Table V. The MW of polymers was between that of PP prepared from EIZ or MgCl$_2$–Ti catalyst alone, but the M_w/M_n was much higher than that of PP prepared from each catalyst alone. From the above results, it could be concluded that the MWD of PP becomes wider by sequential addition of the EIZ/MAO catalyst system, followed by TEA and MgCl$_2$–Ti catalyst.

Thermal properties of the prepared PP are also shown in Table V. The T_g, total heat of fusion, and degree of crystallinity were not so different from those of PP prepared from EIZ or MgCl$_2$–Ti catalyst alone. The PP obtained by the sequential addition of catalyst systems exhibited two T_ms, one at around 130°C and the other at around 160°C. The T_ms at 130 and 160°C were the characteristic melting peaks of PP prepared from EIZ and MgCl$_2$–Ti catalysts, respectively, as shown in Table I. Based upon the twin melting behavior, it can be seen that the obtained polymer is a mix-

ture of PP prepared from EIZ and $MgCl_2$–Ti catalysts, separately.

The fraction of PP obtained from each catalyst was calculated from GPC chromatograms or polymerization rate profiles. The GPC chromatogram was separated into Flory distributions as shown in Figure 3, and the fraction of Flory distributions from EIZ (peak V) and $MgCl_2$–Ti catalyst (peaks I–VI) was obtained. In the case of peak V, Flory distributions from EIZ and $MgCl_2$–Ti catalyst were mixed. Therefore, the contribution from $MgCl_2$–Ti catalyst in peak V was obtained based upon the ratio of fractions of peaks IV and V (from $MgCl_2$–Ti catalyst alone) in Figure 3(f). The fraction of PP from EIZ or $MgCl_2$–Ti catalyst was also calculated by the integration of individual curves in polymerization rate profiles as shown in Figure 2; the results appear in Table V. The calculated fraction of PP from $MgCl_2$–Ti catalyst was much lower than the estimated one. This indicates that the activity of $MgCl_2$–Ti catalyst is certainly lowered by EIZ catalyst. This might be due to the selective poisoning or active center modification effect of EIZ on $MgCl_2$–Ti catalyst, as can be seen in the trend of *mmmm* pentad composition in Tables II and III and the fraction of individual Flory component in Table IV(a, b).

Because the external electron donor is usually used to control the stereoregularity of PP, CHDMS was added with $MgCl_2$–Ti catalyst; the activity and MW results are shown in Table VI.

Addition of silane decreased the activity but increased I.I. by at least 20%. Kissin[13] and Soga and associates[20] reported that addition of the silane compound, apart from decreasing the yield of the atactic material, also affected the activity of different isospecific centers: the activity of activite centers with lower MW was reduced, and that with higher MW was increased. The effect of silane compound on each active center is also confirmed in Table IV: as seen in Table IV(b, c), the fraction of components with higher MW (I, II, III) increased with the addition of silane donor while that with lower MW (IV, VI) decreased.[13] This change resulted in an increase of MW and M_w/M_n of polymers as shown in Table VI.

Rheological Properties

In order to investigate the effect of MWD on rheological properties, the complex viscosity behavior of prepared PP was investigated and the results

are shown in Figure 4. As a reference, a commercial PP ($M_w = 222,000$, $M_w/M_n = 5.2$) was used.

With similar MW, the wider the MWD of PP was, the more apparent was the shear thinning observed.[21] This suggests that the polymer with wider MWD obtained by the sequential addition of catalyst systems can be processed more easily.[22]

CONCLUSION

It was possible to control MWD of PP by sequential addition of Ziegler–Natta and metallocene catalysts with the appropriate combination of catalyst and cocatalyst. In the propylene polymerization by sequential addition of EIZ/MAO and $MgCl_2$–Ti/TEA catalyst systems, it was possible to control the amount of PP produced by each catalyst not only with the amount of each catalyst used but also with the polymerization time for each catalyst. PP obtained was the reactor blend material of PP prepared from each catalyst separately. In GPC analysis, the obtained PP exhibited wide MWD curves with shoulder peaks. The height of each peak was controlled with the variation of polymerization time for each catalyst as well as the amount of each catalyst. The M_w/M_n of PP obtained from sequential addition of catalyst systems was much higher than that of PP from each catalyst alone. It was possible to deconvolve the MWD curve of PP obtained from sequential addition of catalyst systems and $MgCl_2$–Ti catalyst into six individual Flory distributions. There was some selective poisoning or active center modification effect of EIZ on $MgCl_2$–Ti catalyst. By the addition of EIZ catalyst, the fraction of the Flory component with higher MW in the GPC curve was reduced more seriously than that with lower MW. Addition of silane compound with $MgCl_2$–Ti catalyst as external electron donor decreased the activity but increased I.I. by at least 20%. PP with wider MWD prepared from sequential addition of catalyst systems exhibited more apparent shear thinning.

REFERENCES

1. Y. V. Kissin, *Isospecific Polymerization of Olefins with Heterogeneous Ziegler–Natta Catalysts,* Springer-Verlag, New York, 1985, p. 347.
2. W. Kaminsky, M. Miri, H. Sinn, and R. Woidt, *Makromol. Chem., Rapid Commun.,* **4,** 417 (1983).

3. A. Zambelli, C. Pellecchia, and L. Oliva, *Makromol. Chem., Macromol. Symp.,* **48/49,** 297 (1991).

4. U. Zucchini and G. Checchin, *Adv. Polym. Sci.,* **51,** 101 (1983).

5. A. Ahlers and W. Kaminsky, *Makromol. Chem., Rapid Commun.,* **9,** 457 (1988).

6. D. Lee, K. Yoon, S. Noh, S. Kim, and W. Huh, *Macromol. Rapid Commun.,* **17,** 639 (1996).

7. S. Shamshoum, M. J. Elder, B. R. Reddy, and D. J. Rauscher, U.S. Pat. 5,395,810 (1995).

8. L. Norsiti, P. C. Barbe, and G. Baruzzi, *Makromol. Chem.,* **192,** 1115 (1991).

9. B. Rieger, X. Mu, D. T. Mallin, M. D. Rausch, and J. C. W. Chien, *Macromolecules,* **23,** 3559 (1990).

10. H. H. Britzinger, D. Fischer, R. Mlhaupt, B. Rieger, and R. M. Waymouth, *Angew. Chem. Int. Ed. Engl.,* **34,** 1143 (1995).

11. K. Soga, T. Uozumi, and T. Shiono, *Makromol. Chem., Rapid Commun.,* **10,** 293 (1989).

12. K. Soga, T. Uozumi, and H. Yanagihara, *Makromol. Chem.,* **190,** 31 (1989).

13. Y. V. Kissin, *J. Polym. Sci., Part A: Polym. Chem. Ed.,* **33,** 227 (1995).

14. V. V. Vickroy, H. Schneider, and R. F. Abbott, *J. Appl. Polym. Sci.,* **50,** 551 (1993).

15. M. Hess and R. F. Kratz, *J. Polym. Sci.,* **A-2, 4,** 731 (1966).

16. E. M. Rosen and T. Provder, *J. Appl. Polym. Sci.,* **15,** 1687 (1971).

17. K. W. McLaughlin and C. J. Hoeve, *Transition Metal Catalyzed Polymerization,* R. P. Quirk, editor, Cambridge University Press, Cambridge, 1988, p. 337.

18. Y. V. Kissin, *Makromol. Chem., Macro. Symp.,* **66,** 83 (1993).

19. J. B. P. Soares and A. E. Hamielec, *Polymer,* **36,** 2257 (1995).

20. K. Soga, T. Shiono, and Y. Doi, *Makromol. Chem.,* **189,** 1531 (1988).

21. W. Minoshima, J. L. White, and J. E. Spruiell, *Polym. Eng. Sci.,* **20,** 1166 (1980).

22. M. Shida and L. V. Cancio, *Polym. Eng. Sci.,* **11,** 124 (1971).