Polymerization of Ethylene and Ethylene/1-Hexene over Ziegler–Natta/Metallocene Hybrid Catalysts Supported on MgCl₂ Prepared by a Recrystallization Method

HAN SEOCK CHO, JIN SUK CHUNG, JAE HYUCK HAN, YOUNG GWAN KO, WHA YOUNG LEE

Department of Chemical Engineering, College of Engineering, Seoul National University, Shinlim-Dong, Kwanak-Ku, Seoul 151-742, Korea

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ABSTRACT: MgCl₂ for use as a catalyst support was prepared by dissolution in methanol and recrystallization in *n*-decane, followed by vacuum-drying at 2,000 rpm. The prepared support was modified by treatment with alkylaluminum compounds. The activity profile of ethylene over the supported catalysts persisted for periods up to 1 h during the polymerization. The prepared Ziegler–Natta/metallocene hybrid catalysts exhibited the characteristics of both metallocene and Ziegler–Natta catalysts. The polymer produced by the hybrid catalysts gave bimodal peaks in differential scanning calorimetry analysis for ethylene and ethylene/1-hexene polymerization, suggesting that the polymer was composed of two different lamellar structures that were polymerized by each catalyst. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1707–1715, 1998

Key words: recrystallized magnesium dichloride support; metallocene catalyst; Ziegler–Natta catalyst; hybrid catalysts; polymerization; ethylene; ethylene/1-hexene

INTRODUCTION

In early 1980, metallocene catalyst systems, originally discovered by Kaminsky and Sinn, were focused upon as the next generation of catalysts for olefin polymerization.¹ Such systems show a high activity with respect to olefin polymerization and are capable of producing polymers with special properties which are unattainable via Ziegler–Natta catalyst systems.^{2,3} As a result, numerous studies, both industrial and academic, were initiated. The metallocene catalyst systems are basically homogeneous systems, and the majority of studies on such catalysts have concen-

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trated on solution-phase processes. However, in order for metallocene catalysts to be used in the prevailing slurry or gas-phase processes, a procedure for the preparation of a support for a metallocene catalyst is necessary. In addition, because all commercial polymerization processes which involve Ziegler–Natta catalysts are used in heterogeneous systems, the preparation of heterogeneous metallocene catalysts is a prerequisite for the existing processes. In recent papers, a variety of supports such as SiO₂,⁴ Al₂O₃,⁵ Zeolite,⁶ etc., have been used. Although metallocene catalysts have the advantages of high activity and special polymer properties, the polymers produced via these catalysts have a very narrow molecular weight distribution (MWD, M_w/M_n). In polymer processing, molecular weight and MWD are important because they determine both mechanical and rheological properties.⁷ On the one hand, polyethylenes with narrow MWD lead to products with higher impact resistance and higher resis-

Correspondence to: W. Y. Lee (wyl@plaza.snu.ac.kr).

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tance to environmental stress-cracking. On the other hand, polyethylenes with a broad MWD show greater flowability in the molten state at high shear rate, which is important for blowing and extrusion techniques.8 Therefore, it is possible that the narrow MWD via metallocene catalysts could be broadened by preparing Ziegler-Natta/metallocene hybrid catalysts because of the relatively higher molecular weight of polymers produced by the Ziegler–Natta catalyst fraction. Hybrid catalysts can take advantage of the properties of both the metallocene and Ziegler-Natta catalysts. In addition, hybrid catalysts would be expected to be utilized in prevailing processes without significant process modification and to enhance processability of the polymers. In this study, MgCl₂ was used as the support and was prepared by a recrystallization technique using methanol as the dissolution material. The new type of hybrid catalysts were prepared for the polymerization of ethylene and ethylene/1-hexene. The prepared support and the hybrid catalysts were characterized by inductively coupled plasma (ICP), thermogravimetric analysis (TGA), and gas chromatography (GC), and the polymerization of ethylene and ethylene/1-hexene was conducted in order to investigate the characteristics of the hybrid catalysts.

EXPERIMENTAL

Materials

High-purity N2 and ethylene (Sinyang Gas Products, Seoul, Korea) were further purified prior to use by sequentially passing them through columns containing 5 Å molecular sieves (Kokusan Chemical Works, Tokyo, Japan), anhydrous P₂O₅ (Yakuri Pure Chemicals, Osaka, Japan), and RI-DOX, an oxygen scavenger (Fischer Scientific, New Jersey). The molecular sieves were regenerated at 2-mo intervals by treatment with a stream of N₂ at 250°C, and the oxygen scavenger was activated by treatment with a stream of H_2 at 250°C. Toluene (Oriental Chemical Industry, Seoul, Korea) which was used as a solvent for the catalyst preparation and polymerization, was purified by distillation over elemental sodium under an N₂ atmosphere to remove residual traces of moisture and oxygen. 1-Hexene as a comonomer was also purified by reflux over elemental sodium. MgCl₂ (Aldrich Chemical Company, Milwaukee, WI), CH₃OH (Farmitalia Carlo Erba, Milano, Italy),

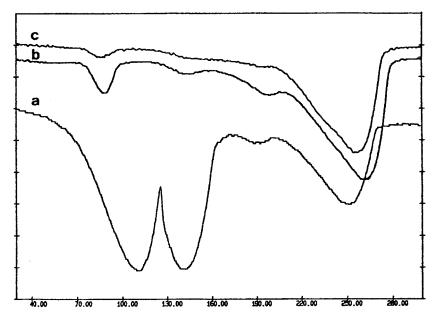
 Cp_2ZrCl_2 (Strem Chemicals, Newburyport, MA), TiCl₄(Aldrich), triisobutylaluminum (TiBAL; Aldrich), triethylaluminium (TEA; Aldrich), trimethylaluminum (TMA; Aldrich), and methylaluminoxane, type 4 (MAO; Akzo Chemicals, Illinois) were used without further purification.

Preparation of Support and Catalyst

Anhydrous MgCl₂, 0.10 mol (9.52 g), was introduced into a glass reactor equipped with a magnetic stirrer and 100 mL of methanol was added. The mixture was heated to 60°C and stirred until the MgCl₂ dissolved completely. A total of 100 mL of *n*-decane was then added to this homogeneous solution and the final mixture was stirred at 2,000 rpm under vacuum at 80°C. MgCl₂ particles were slowly precipitated in the *n*-decane medium as the methanol evaporated. The resulting MgCl₂ particles were washed four times with toluene to remove residual *n*-decane and then dried under vacuum to remove the toluene. Thus the recrystallized $\rm MgCl_2~(\rm MgCl_2~\cdot~nCH_3OH)^{9-10}$ was obtained. A total of 5 g of support was introduced into a 500-mL flask equipped with a water-cooled reflux condenser and a magnetic stirrer. The alkylaluminum compound (1M) was then added to the flask according to the methanol and methoxy contents in the support, and 100 mL of toluene was added as a diluent. The mixture was stirred at 0, 20, 40, and 60°C for 30 min each and then stirred at 80°C for 2 h to complete the reaction. The mixture was then washed six times to remove the unreacted alkylaluminum and finally dried under vacuum to yield the alkylaluminum/MgCl₂. The washed supports (2 g) were suspended in 100 mL of toluene, reacted with 0.10 g Cp_2ZrCl_2 at 50°C for 2 h, and then washed in the same manner. After polymerization of this metallocene-supported catalyst, 20 mL of TiCl₄ was introduced into the catalyst and the mixture was stirred for 2 h at 80°C. After the reaction, the mixture was washed six times with toluene to give the final Ziegler-Natta/metallocene hybrid catalysts. These hybrid catalysts, denoted as TiCl₄/Cp₂ZrCl₂/alkylaluminum compound/ MgCl₂, were suspended in 100 mL of toluene and used as catalysts.

Characterization

To determine the methanol and methoxy contents in the recrystallized $MgCl_2$, GC (Yanaco G1700, Porapak Q column) and TGA (Perkin-



Temperature (\mathcal{C})

Figure 1 DTG thermograms of supports: (a) recrystallized MgCl₂; (b) MgCl₂, 100°C; (c) MgCl₂, 200°C.

Elmer TGA7) were used, and the temperature at which methanol and methoxy desorbed was examined by a differentiating TGA thermogram. Scanning electron microscopy (SEM) (JEOL JSM-840A) was used to observe the morphology of the support and the catalyst. The titanium and zirconium contents of the catalysts were measured using inductively coupled plasma (ICP) (VG PQ2-Turbo, VG elemental). The differential scanning calorimetry (DSC) (Dupont V 4.0B) was carried out under a nitrogen atmosphere at a heating rate of 10°C/min. The molecular weight and molecular weight distribution of polyethylene were measured by gel permeation chromatography (GPC) (PL-210; Polymer Laboratories Ltd.) at 160°C with 1,3,5trichlorobenzene as the solvent. The 1-hexene contents in the ethylene/1-hexene copolymer were measured by Fourier transform infrared spectroscopy (Nicolet Impact-410).¹¹

Polymerization of Ethylene and Ethylene/1-Hexene

A total of 300 mL of toluene and cocatalyst (MAO or alkylaluminum compound) were introduced into a 1-L glass reactor (equipped with a

	GC (wt %)	TGA	(wt %)
Support	$\begin{array}{ll} Methanol \ + \ Methoxy \\ (CH_{3}OH) & (Mg\text{-}OCH_{3}) \end{array}$	$\begin{array}{c} Methanol^{a} \\ (CH_{3}OH) \end{array}$	$\begin{array}{c} Methoxy^{b} \\ (Mg\text{-}OCH_{3}) \end{array}$
Recrystallized $MgCl_2$ ($MgCl_2$)	57.9	38.6	16.4
MgCl ₂ , 100°C MgCl ₂ , 200°C	30.4 23.8	9.2 4.5	$18.1 \\ 17.5$

 Table I
 Methanol and Methoxy Contents in the Supports

^a Weight reduction from 30°C to 200°C.

^b Weight reduction from 200°C to 300°C.

Catalysts	Zr (wt %)	Ti (wt %)	
Cp ₂ ZrCl ₂ /MgCl ₂	_	_	
Cp ₂ ZrCl ₂ /TiBAL/MgCl ₂	1.109		
Cp ₂ ZrCl ₂ /TiBAL/MgCl ₂ -100°C	0.012		
Cp ₂ ZrCl ₂ /TiBAL/MgCl ₂ -200°C	_		
Cp ₂ ZrCl ₂ /TiBAL/MgCl ₂	1.11	_	
Cp ₂ ZrCl ₂ /TEA/MgCl ₂	0.44	_	
Cp ₂ ZrCl ₂ /TMA/MgCl ₂	0.056	_	
TiCl ₄ /Cp ₂ ZrCl ₂ /TiBAL/MgCl ₂	0.97	2.09	
$TiCl_4/Cp_2ZrCl_2/TMA/MgCl_2$	0.41	1.57	
$TiCl_4/Cp_2ZrCl_2/TEA/MgCl_2$	0.051	3.85	

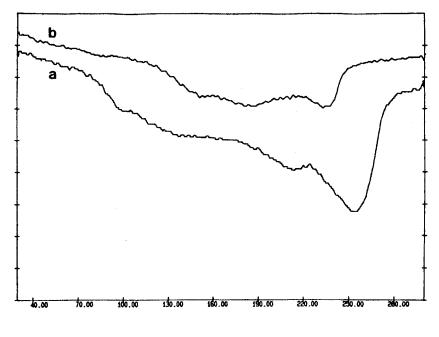
Table IIElemental Analysis of the SupportedCatalysts

magnetic stirrer) under a stream of dry N_2 , and then evacuated to remove the N_2 . Ethylene was then fed at a constant pressure of 1.3 bar containing a hydrogen partial pressure of 0.2 bar. In the copolymerization, ethylene was continuously supplied to a toluene solution containing 1-hexene. The polymerization was initiated by introducing the catalyst suspension into the reactor with a syringe. After a 50-min reaction time, the polymerization was terminated by adding an excess of dilute hydrochloric acid solution in methanol, and the polymer was isolated and dried. The polymerization rate was determined from the amount of consumed ethylene, measured with a mass flowmeter.

RESULTS AND DISCUSSION

Effect of Support Pretreatment on Impregnation of Metallocene Catalyst

In the recrystallized MgCl₂, methanol used as a dissolution material coexists with methoxy groups $(Mg-OCH_3)$ bonded to the Mg. Because the methanol in the support serves as a deactivation material (that is, a Lewis base) for the metallocene catalyst, it should be eliminated or reduced to the lowest possible level. Two methods are generally used to accomplish this. The first involves physically heating under a N2 atmosphere to reduce the methanol content and the second involves a chemical reaction between methanol and alkylaluminum compounds such as TEA, TMA, and TiBAL. For this reason, supports were prepared having different methanol contents by heating one under a N₂ atmosphere, followed by reaction with the alkylaluminum compounds based on the contents of methanol and methoxy groups, to give



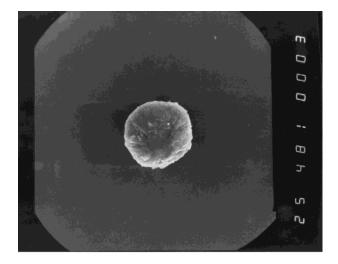
Temperature (\mathcal{C})

Figure 2 DTG thermograms of catalysts: (a) $Cp_2ZrCl_2/TiBAL/MgCl_2$; (b) $TiCl_4/Cp_2ZrCl_2/TiBAL/MgCl_2$.

an acceptable number of impregnation sites. To examine the desorption temperature of methanol and methoxy groups, the support was scanned from 30 to 300°C by TGA under an N2 atmosphere, and DTG thermograms were obtained by differentiating TGA thermograms. Figure 1 shows the DTG thermograms of the supports, which were prepared at various temperatures. The methanol contents decreased drastically with increasing treatment temperature, but the level of methoxy groups desorbed at about 250°C remained constant. Table I shows the methanol and methoxy contents as analyzed by GC and TGA. The contents of methanol plus methoxy are nearly the same for both GC and TGA analyses. Table II shows the impregnated zirconium contents of the catalyst. As the methanol content in the support increases, the impregnated zirconium content increases as well. However, the support which was treated by physically heating at 100 and 200°C, followed by reaction with alkylaluminum compounds based on the residual methanol and methoxy groups, is impregnated with relatively smaller amounts of zirconium. This suggests that the Cp_2ZrCl_2 is impregnated at the sites where methanol and alkylaluminum compounds reacted. Thus, it is believed that these chemical complex sites produced by the reaction between methanol and alkylaluminum create the impregnation sites for Cp₂ZrCl₂.

Effect of Methanol and Methoxy Groups on Supporting Ziegler–Natta/Metallocene Hybrid Catalysts

As seen in Table II, it was necessary for the support to be pretreated with an alkylaluminum compound in order to create an appropriate impregnation site. When an alkylaluminum compound is used as a pretreatment reagent, TiBAL is effective for impregnating Cp₂ZrCl₂ catalyst to create potential catalytic sites, suggesting that TiBAL reacts well with the methanol in the support. After the support was impregnated with Cp2ZrCl2, the Ziegler-Natta/ metallocene hybrid catalysts were prepared by reacting the metallocene-supported catalyst with $TiCl_4$. To evaluate the influence of methanol and methoxy groups on catalyst impregnation, the catalyst was scanned by TGA under an N2 atmosphere. Figure 2 shows that the methoxy contents in the impregnated Cp₂ZrCl₂ catalyst remained constant but decreased during the reaction with TiCl₄. This is due to the fact that methoxy groups originally existing in the recrystallized MgCl₂, and



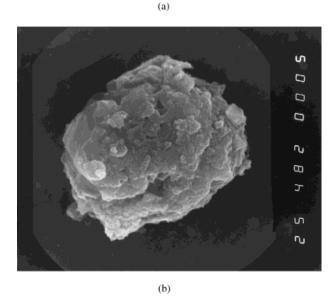


Figure 3 SEM photographs of support and catalyst: (a) recrystallized MgCl₂; (b) Cp₂ZrCl₂/TiBAL/MgCl₂.

also produced by reaction between methanol in the support and TiBAL, create the impregnation sites for TiCl₄. Collectively, these data indicate that methanol and methoxy contents in the recrystal-lized MgCl₂ are an important factor in catalyst impregnation. Consequently, the methanol content of the support affects the impregnation of Cp₂ZrCl₂, and the methoxy groups affect that of TiCl₄ in the hybrid catalysts.

Morphology of Support and Catalyst

Figure 3 shows SEM photographs of recrystallized $MgCl_2$ and the metallocene-supported catalyst. When anhydrous $MgCl_2$ was recrystallized

Catalyst	Cocatalyst	Al/[M]	Activity	$T_m~(^{\circ}\mathrm{C})$	Crystallinity $X_c \ (\%)$	$M_w \ (imes 10^{-4})$	MWD
Cp ₂ ZrCl ₂	MAO	1,000	51.03	125.8	79.6	1.29	2.10
Cp ₂ ZrCl ₂ /	MAO	500	26.93				
TiBAL/MgCl ₂		1,000	47.37	127.5	74.9	4.33	4.64
0 2		2,000	61.48				
TiCl ₄ /Cp ₂ ZrCl ₂ /	MAO	1,000	31.81	126.2, 135.6	67.7	56.4	9.07
TiBAL/MgCl ₂	TMA	100	8.23	132.1	66.9		
0 2	TEA	100	12.28	132.3	65.4		
	TiBAL	100	10.88	133.1	67.0		
TiCl ₄ / TiBAL/MgCl ₂	MAO	1,000	30.23	134.8	62.0	42.7	5.19

Table III Analytical Data on the Ethylene Produced by Cp₂ZrCl₂ Catalyst Systems

 X_c (%) = 100 ($\Delta H_m / \Delta H_m^*$), ΔH_m^* = 282.84 J/g.¹¹ Polymerization conditions: $T = 70^{\circ}$ C, $P_{C2H4} = 1.3$ atm, $P_{H2} = 0.2$ atm. Activity: kg-high-density polyethylene/g-[M] · atm · h.

under vacuum at 2,000 rpm, the support was spherical in shape, as was shown in our previous paper.¹² However, after pretreatment with TiBAL the support becomes porous, suggesting that methanol in the support is removed by reaction with TiBAL. Such impregnation sites produced by the reaction of methanol with TiBAL are essential for impregnating the metallocene catalyst, and TiBAL is effective for this reaction, as shown in Table II.

Polymerization of Ethylene and Ethylene/1-Hexene

Table III shows the results of ethylene polymerization over the metallocene catalyst (Cp_2ZrCl_2) , the metallocene-supported catalyst (Cp₂ZrCl₂/TiBAL/ MgCl₂), the hybrid catalysts (TiCl₄/Cp₂ZrCl₂/ TiBAL/MgCl₂), and the Ziegler-Natta-supported catalyst (TiCl₄/TiBAL/MgCl₂). In comparing the activities of the metallocene catalyst with those of the Ziegler-Natta-supported catalyst with the MAO cocatalyst, the activity decreases in an orderly manner due to the relatively low activity characteristics of the Ziegler-Natta catalyst. However, when the activities of the metallocene catalyst and the metallocene-supported catalyst are compared, there is not a great deal of difference between the two. The main reason for this behavior is probably due to the increase in the stability of the supported catalyst during the polymerization, as shown in Figure 4. Figure 4 shows that the activity of the metallocene catalyst drastically decreases after 15 min, but that of the metallocene-supported catalyst remains high for periods of up to 1 h. Also, generally speaking, the reduction in activity with time is a characteristic of MgCl₂-supported Ziegler-Natta catalysts.¹³ However, the activity profile of hybrid catalysts continues in contrast to the conventional Ziegler–Natta catalyst. It is conceivable that the previously supported metallocene catalyst plays a role in dispersing TiCl₄, which prevents agglomeration during impregnation and thus increases the stability of the TiCl₄. For the case of the copolymerization of ethyl-

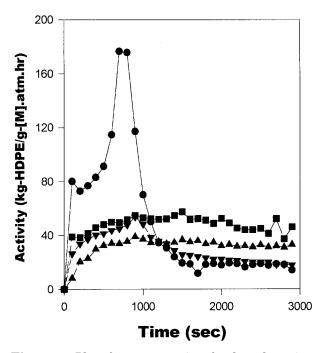


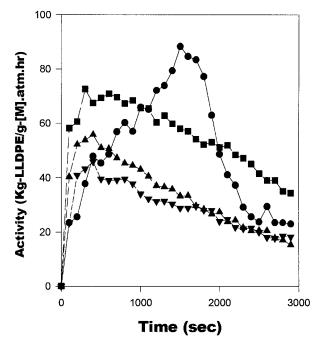
Figure 4 Plot of rate versus time for the polymerization of ethylene over Cp₂ZrCl₂ catalyst systems: (•) Cp₂ZrCl₂; (•) Cp₂ZrCl₂/TiBAL/MgCl₂; (•) TiCl₄/Cp₂ZrCl₂/TiBAL/MgCl₂; (•) TiCl₄/TiBAL/MgCl₂. Polymerization conditions: $T_p = 70^{\circ}$ C; $P_{C2H4} = 1.3$ atm; $P_{H2} = 0.2$ atm; Al/[M] = 1,000.

Catalyst	Cocatalyst	Al/[M]	Activity	T_m (°C)	$\begin{array}{c} \text{Crystallinity} \\ X_c \ (\%) \end{array}$	M_w (×10 ⁻⁴)	MWD	1-Hexene Content (mol %)
Cp_2ZrCl_2	MAO	1,000	56.10	115.9	68.1	1.42	2.15	4.3
Cp ₂ ZrCl ₂ /	MAO	500	27.68					
TiBAL/MgCl ₂		1,000	55.32	122.1	57.1	2.04	2.95	3.7
		2,000	75.99					
TiCl ₄ /Cp ₂ ZrCl ₂ /	MAO	1,000	29.99	121.7, 125.6	39.6	25.0	5.65	3.2
$TiBAL/MgCl_2$	TMA	100	6.52	122.0	38.4			
	TEA	100	14.63	122.7	46.3			
	TiBAL	100	13.93	121.9	41.9			
TiCl ₄ / TiBAL/MgCl ₂	MAO	1,000	33.24	125.1	46.8	24.6	3.95	2.9

Table IVAnalytical Data on the Ethylene/1-Hexene Copolymer Producedby Cp2ZrCl2 Catalyst Systems

 X_c (%) = 100 ($\Delta H_m / \Delta H_m^*$), ΔH_m^* = 291.7 J/g.¹¹ Polymerization conditions: 1-Hexene = 5 cc, T = 70°C, P_{C2H4} = 1.3 atm, P_{H2} = 0.2 atm. Activity: kg-linear-low-density polyethylene/g-[M] \cdot atm \cdot hr.

ene/1-hexene, Table IV shows that the activity is slightly higher than that for ethylene polymerization. Particularly, in Figure 5, all supported catalysts except the metallocene catalyst (Cp_2ZrCl_2) consume considerable amounts of ethylene in the early stage of ethylene/1-hexene copolymerization, but Cp_2ZrCl_2 consumes smaller amounts compared with the others. This suggests that the ethylene/1hexene copolymerization over Cp_2ZrCl_2 is initially well polymerized, with the result that the insertion of 1-hexene into the growing ethylene chain is more effective than for any other supported catalyst. In



() a b b c d d 120 140 160 Temperature (°C)

Figure 5 Plot of rate versus time for the polymerization of ethylene/1-hexene over Cp₂ZrCl₂ catalyst systems: (**●**) Cp₂ZrCl₂; (**■**) Cp₂ZrCl₂/TiBAL/MgCl₂; (**▲**) TiCl₄/Cp₂ZrCl₂/TiBAL/MgCl₂; (**▼**) TiCl₄/TiBAL/MgCl₂. Polymerization conditions: 1-Hexene = 5 cc; $T_p = 70^{\circ}$ C; $P_{C2H4} = 1.3$ atm; $P_{H2} = 0.2$ atm; Al/[M] = 1,000.

Figure 6 DSC thermograms of polyethylene prepared via the Cp_2ZrCl_2 catalyst systems: (a) Cp_2ZrCl_2 ; (b) $Cp_2ZrCl_2/TiBAL/MgCl_2$; (c) $TiCl_4/Cp_2ZrCl_2/TiBAL/MgCl_2$; (d) $TiCl_4/TiBAL/MgCl_2$.

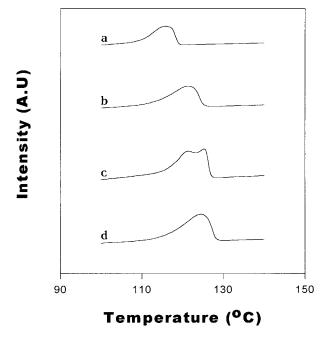


Figure 7 DSC thermograms of ethylene/1-hexene prepared via the Cp₂ZrCl₂ catalyst systems: (a) Cp₂ZrCl₂; (b) Cp₂ZrCl₂/TiBAL/MgCl₂; (c) TiCl₄/Cp₂ZrCl₂/TiBAL/MgCl₂; (d) TiCl₄/TiBAL/MgCl₂.

Table IV, the results of 1-hexene contents in the copolymer correlate with this activity profile.

In DSC analyses, the crystallinity (X_c) decreases from metallocene to Ziegler-Natta-supported catalyst for ethylene polymerization because TiCl₄ produces irregular, long-chain polyethylenes. The melting temperature increases in proportion to the higher molecular weight which is the characteristic of the Ziegler-Natta catalyst. Figure 6 shows DSC thermograms for ethylene polymerization. The polymer produced on the hybrid catalysts gives bimodal peaks which partly overlap the region of the metallocene catalyst and partly that of the Ziegler-Natta catalyst, suggesting that the polymer is composed of two lamellar structures, each of which is polymerized by one of the catalysts. In comparison with ethylene polymerization, the ethylene/1-hexene copolymer has a low degree of crystallinity due to the insertion of 1-hexene in the polymer chain and to a low melting temperature. Figure 7 also shows that the copolymer produced by hybrid catalysts has two melting temperatures. Similar to the tendency of ethylene polymerization, the copolymers produced by Cp₂ZrCl₂ exist with those produced by the Ziegler-Natta catalyst. It is conceivable that the two copolymers differ in their structures

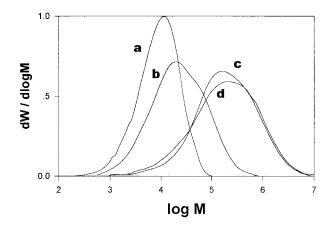


Figure 8 Molecular weight distributions of polyethylene prepared via the Cp₂ZrCl₂ catalyst systems: (a) Cp₂ZrCl₂; (b) Cp₂ZrCl₂/TiBAL/MgCl₂; (c) TiCl₄/Cp₂ZrCl₂/ TiBAL/MgCl₂; (d) TiCl₄/TiBAL/MgCl₂.

based on the contents of 1-hexene produced by each catalyst, as is shown in Table IV.

GPC analysis indicates that the molecular weight increases from metallocene to hybrid catalysts because of the characteristics of the Ziegler– Natta catalyst. GPC curves of the metallocene-supported catalyst, compared with the metallocene catalyst, showed a broad distribution. Also, hybrid catalysts, compared with the Ziegler–Natta-supported catalyst, showed a broad distribution. However, as opposed to the DSC thermograms for ethylene and ethylene/1-hexene polymerization, the GPC curves via hybrid catalysts showed a monomodal distribution, as shown in Figures 8 and 9. It is conceivable that a portion of the metallocene was embedded in a portion of the Ziegler–Natta cata-

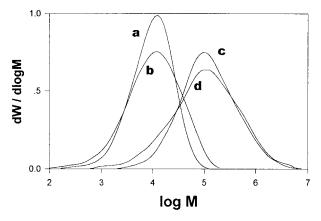


Figure 9 Molecular weight distributions of ethylene/ 1-hexene prepared via the Cp₂ZrCl₂ catalyst systems: (a) Cp₂ZrCl₂; (b) Cp₂ZrCl₂/TiBAL/MgCl₂; (c) TiCl₄/ Cp₂ZrCl₂/TiBAL/MgCl₂; (d) TiCl₄/TiBAL/MgCl₂.

lyst. It is especially noteworthy that the molecular weight and molecular weight distribution of polymers produced by the hybrid catalysts were higher and broader than any of the other polymers. These results correlate with the stability of TiCl_4 as shown in the activity profile, Figure 4. Namely, it is clear that the activity of TiCl_4 dispersed on hybrid catalysts is more stable than that of the TiCl_4 contained by the Ziegler–Natta-supported catalyst.

CONCLUSIONS

A recrystallized MgCl₂ support was prepared by using a methanol as the dissolution material. The contents of methanol and methoxy in the support are an important factor in hybrid catalyst impregnation. In terms of the treatment of the prepared support, TiBAL was an excellent pretreatment material. The produced polymer showed two different melting points, suggesting that the hybrid catalysts acted as individual active species on the supports. GPC analysis indicated that the molecular weight and molecular weight distribution of polymers produced by the hybrid catalysts were higher and broader than any other polymers for the polymerization of ethylene and ethylene/1hexene. Consequently, both catalysts appear to be compatible on recrystallized MgCl₂ and to produce a blend of polymers.

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