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Effect of cocatalyst on the chemical composition distribution and microstructure of ethylene-hexene copolymer produced by a metallocene/Ziegler-Natta hybrid catalyst

Hai Woong Park, Kyung Won La, Jin Suk Chung* and In Kyu Song†

School of Chemical and Biological Engineering, Institute of Chemical Processes,
Seoul National University, Shinlim-dong, Kwanak-gu, Seoul 151-744, Korea
*School of Chemical Engineering and Bioengineering, University of Ulsan, Ulsan 680-749, Korea

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Abstract−A silica-magnesium bisupport (SMB) was prepared by a sol-gel method for use as a support for metallocene/Ziegler-Natta hybrid catalyst. The SMB was treated with methylaluminoxane (MAO) prior to the immobilization of $TiCl_4$ and *rac*-Et(Ind)$_2$ZrCl$_2$. The prepared *rac*-Et(Ind)$_2$ZrCl$_2$/TiCl$_4$/MAO/SMB catalyst was applied to the ethylene-hexene copolymerization with a variation of cocatalyst species (polymerization run 1: triisobutylaluminum (TIBAL) and methylaluminoxane (MAO), polymerization run 2: triethylaluminum (TEA) and methylaluminoxane (MAO)). The effect of cocatalysts on the chemical composition distributions (CCDs) and microstructures of ethylene-hexene copolymers was examined. It was found that the catalytic activity in polymerization run 1 was a little higher than that in polymerization run 2, because of the enhanced catalytic activity at the initial stage in polymerization run 1. The chemical composition distributions (CCDs) in the two copolymers showed six peaks and exhibited a similar trend. However, the lamellas in the ethylene-hexene copolymer produced in polymerization run 1 were distributed over smaller sizes than those in the copolymer produced in polymerization run 2. It was also revealed that the *rac*-Et(Ind)$_2$ZrCl$_2$/TiCl$_4$/MAO/SMB catalyst preferably produced the ethylene-hexene copolymer with non-blocky sequence when TEA and MAO were used as cocatalysts.

Key words: Metallocene/Ziegler-Natta Hybrid Catalyst, Ethylene-Hexene Copolymer, Chemical Composition Distribution (CCD), Microstructure, Cocatalyst

INTRODUCTION

Metallocene catalysts have received considerable attention because of their high catalytic activity and excellent ability of comonomer incorporation in the olefin polymerization. Polymers produced by a metallocene catalyst show improved mechanical and optical properties compared to those produced by a Ziegler-Natta catalyst [1-5]. It is well known that the polymers produced by a metallocene catalyst have a limitation in polymer processing due to their narrow molecular weight distribution (MWD), while those produced by a Ziegler-Natta catalyst show good processability due to the broad molecular weight distribution [6,7]. The metallocene catalysts are basically homogeneous catalyst systems, while the Ziegler-Natta catalysts used in commercial polymerization processes are heterogeneous catalyst systems. Therefore, it is desirable to heterogenize the metallocene catalysts in order for use in existing commercial processes such as slurry or gas-phase processes [8,9].

For the practical application of metallocene catalysts, inorganic materials such as silica, alumina, and zeolite have been used as a support for metallocene catalysts [10,11]. A mixture of metallocene and Ziegler-Natta catalysts has been also employed in order to improve processability of the polymer produced by a metallocene component [12,13]. Another promising approach to use both metallocene and Ziegler-Natta catalysts is to hybrid these catalysts by impregnating these two components on a single support [14-19]. It was reported that a metallocene/Ziegler-Natta hybrid catalyst impregnated on a recrystallized $MgCl_2$ support produced a polymer with a bimodal molecular weight distribution, indicating the improved processability of the resulting polymer [14,15]. A silica-magnesium bisupport (SMB) prepared by a sol-gel method was also used to impregnate both metallocene and Ziegler-Natta catalysts, by taking advantage of the fact that silica and magnesium dichloride are well known supports for metallocene and Ziegler-Natta catalysts, respectively [16-19]. The existence of two different active sites in the hybrid catalyst supported on the silica-magnesium bisupport was confirmed by the observation of a bimodal molecular weight distribution and two melting temperatures of polyethylene.

In this work, a silica-magnesium bisupport (SMB) prepared by a sol-gel method was used for the preparation of *rac*-Et(Ind)$_2$ZrCl$_2$/TiCl$_4$/MAO(methylaluminoxane)/SMB catalyst. The prepared catalyst was applied to the ethylene-hexene copolymerization with a variation of cocatalyst species, and the effect of cocatalysts on the catalytic activities and physical properties of ethylene-hexene copolymers was investigated. Chemical composition distributions (CCDs) and microstructures [20,21] of ethylene-hexene copolymers produced by a *rac*-Et(Ind)$_2$ZrCl$_2$/TiCl$_4$/MAO/SMB catalyst were extensively examined.

EXPERIMENTAL

1. Materials

High purity ethylene (World Gas) and nitrogen (Daesung Gas) were further purified by sequential passage through columns containing molecular sieve 5A (Kokusan Chemical Works) and anhydrous P_2O_5 (Yakuri Chemicals). Toluene (Samjun Chemicals) and

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[†] To whom correspondence should be addressed.
E-mail: inksong@snu.ac.kr

1-hexene (Aldrich) were purified by distillation over sodium metal. $MgCl_2$ (Junsei Chemical), colloidal SiO_2 (LUDOX HS-40, Aldrich), *rac*-Et(Ind)$_2$ZrCl$_2$ (Strem), $TiCl_4$ (Aldrich), methylaluminoxane (MAO, Albermale), triethylaluminum (TEA, Aldrich), and triisobutylaluminum (TIBAL, Aldrich) were used without further purification.

2. Preparation of Silica-Magnesium Bisupport (SMB) Treated with MAO

Silica-magnesium bisupport (SMB) treated with methylaluminoxane (MAO) was prepared according to a similar method in a previous report [16]. $MgCl_2$ was dissolved in distilled water (100 ml), and pH of the solution was adjusted at 6.4 by adding H_2SO_4. The solution was introduced into corn oil (2.5 liter) and stirred at 2,000 rpm for uniform dispersion. Colloidal silica (80 ml) was then introduced into the mixed solution of corn oil and $MgCl_2$. The agglomerated particles separated from the solution were washed seven times with toluene, and they were dried at 110 °C in a nitrogen stream to yield silica-magnesium bisupport. The silica-magnesium bisupport (SMB) (6 g) was suspended in toluene (100 ml), and then methylaluminoxane (MAO, 10 wt% in toluene) (100 ml) was introduced into the slurry for 2 h at 0 °C. The mixture was stirred at 0 °C, 20 °C, 40 °C, and 60 °C for 30 min each, and then finally at 80 °C for 2 h. The MAO-treated SMB (MAO/SMB) was washed seven times with toluene and dried under vacuum.

3. Preparation of Supported Catalyst

The MAO-treated SMB (MAO/SMB, 5 g) was suspended in toluene (100 ml), and it was reacted with $TiCl_4$ (5 ml) at 50 °C for 2 h. The resulting slurry was washed seven times with toluene (100 ml), and then it was dried under vacuum to obtain $TiCl_4$/MAO/SMB. The $TiCl_4$/MAO/SMB was further reacted with *rac*-Et(Ind)$_2$ZrCl$_2$ (0.5 g) dissolved in toluene (20 ml). The resulting slurry was washed seven times with toluene (100 ml), and it was finally dried under vacuum to yield *rac*-Et(Ind)$_2$ZrCl$_2$/TiCl$_4$/MAO/SMB.

4. Ethylene Copolymerization with 1-Hexene

Toluene (300 ml), supported catalyst (0.04 g), 1-hexene (6 ml), and known amounts of cocatalyst mixture (polymerization run 1: triisobutylaluminum (TIBAL) and methylaluminoxane (MAO), polymerization run 2: triethylaluminum (TEA) and methylaluminoxane (MAO)) were introduced into a glass reactor (1,000 ml) equipped with a magnetic stirrer under nitrogen flow. The molar ratios of cocatalyst with respect to transition metal were fixed at Al/Ti=300 (TIBAL or TEA) and Al/Zr=300 (MAO). After nitrogen in the reactor was evacuated by vacuum pump, hydrogen was fed into the reactor at a pressure of 0.2 atm. The polymerization was initiated by introducing ethylene at a constant pressure of 1.3 atm. The copolymerization of ethylene with 1-hexene was conducted at 55 °C for 60 min. The copolymerization was terminated by adding an excess amount of a HCl solution diluted with methanol.

5. Characterization of Ethylene-Hexene Copolymer

The melting temperature (T_m) of ethylene-hexene copolymer was measured by using a differential scanning calorimeter (DSC, TA 2010) with a heating rate of 10 °C/min. The molecular weight (Mw) and molecular weight distribution (MWD) were determined by gel permeation chromatography (GPC, PL-GPC 220) at 160 °C using 1,2,4-trichlorobenzene as a solvent. The GPC column was calibrated by using standard polystyrene. The comonomer content and triad sequence in the ethylene-hexene copolymer were analyzed with a 100 MHz ^{13}C nuclear magnetic resonance spectrometer (^{13}C NMR, Avance 500) at 130 °C on the basis of the Randall method [22]. The chemical composition distribution (CCD) of ethylene-hexene copolymer was determined by a stepwise annealing method [23-26]. As shown in Fig. 1, temperature was increased to 160 °C at a rate of 10 °C/min and maintained for 2 h for complete melting. The melted polymer was slowly cooled at 137, 130, 123, 116, 109, 102, 95, 88, 81, and 74 °C for 2 h, respectively, and was finally cooled to 30 °C at a rate of 10 °C/min. The chemical composition distribution of ethylene-hexene copolymer was determined by using a DSC with a heating rate of 10 °C/min. The lamella thickness of fractionated ethylene-hexene copolymer was calculated by the Thomson-Gibbs equation [27].

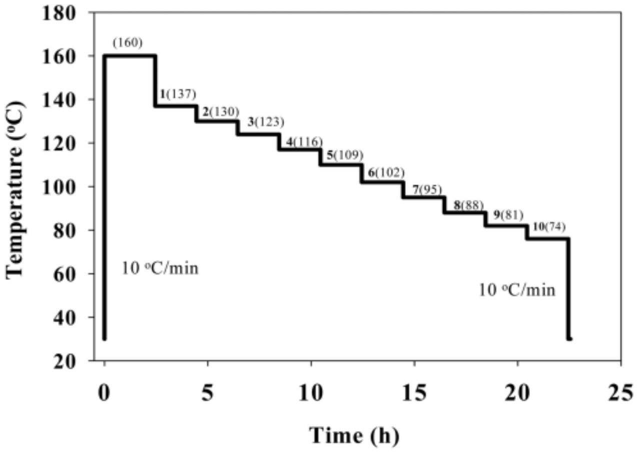

Fig. 1. Stepwise annealing procedure for chemical composition distribution analysis of ethylene-hexene copolymer.

RESULTS AND DISCUSSION

1. Catalytic Activities and Physical Properties of Copolymers

Fig. 2 shows the activity profiles of *rac*-Et(Ind)$_2$ZrCl$_2$/TiCl$_4$/MAO/SMB catalyst in the ethylene-hexene copolymerization with a vari-

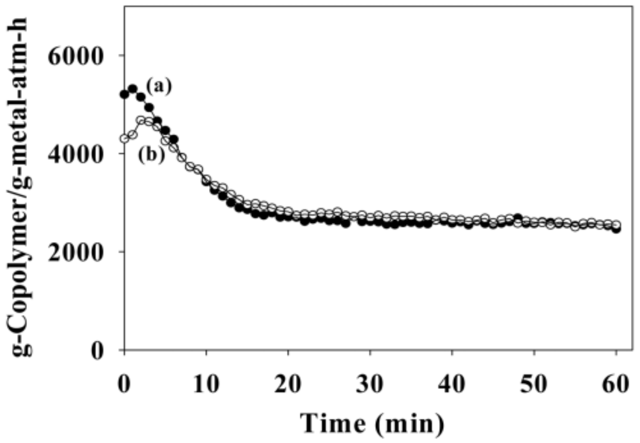

Fig. 2. Activity profiles of *rac*-Et(Ind)$_2$ZrCl$_2$/TiCl$_4$/MAO/SMB catalyst in the ethylene-hexene copolymerization with a variation of cocatalyst species: (a) TIBAL and MAO, (b) TEA and MAO.

Table 1. Catalytic activities of *rac*-Et(Ind)$_2$ZrCl$_2$/TiCl$_4$/MAO/SMB and physical properties of ethylene-hexene copolymers

Polymerization run	Al/Zr	Al/Ti	1-Hexene added	Catalytic activity (g-Copolymer/g-metal-atm-h)	T$_m$ (°C)	Comonomer content (mol%)
1	300 (MAO)	300 (TIBAL)	6 ml	3,350	110.3 130.7	7.2
2	300 (MAO)	300 (TEA)		2,730	111.8 130.8	7.3

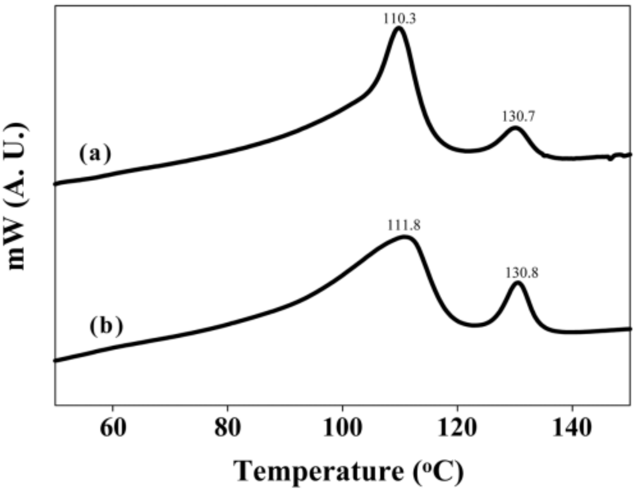

Fig. 3. DSC profiles of ethylene-hexene copolymers produced with a variation of cocatalyst species: (a) TIBAL and MAO, (b) TEA and MAO.

ation of cocatalyst species. The catalytic activity in polymerization run 1 (the polymerization with TIBAL and MAO) was a little higher than that in polymerization run 2 (the polymerization with TEA and MAO), as also summarized in Table 1. This is because the catalytic activity in polymerization run 1 was higher than that in run 2 at the initial stage (during the initial 5 min). However, there was no significant difference in the activity profiles with time on stream in both polymerizations after 5 min.

Fig. 3 shows the DSC profiles of ethylene-hexene copolymers produced with a variation of cocatalyst species. The melting temperatures of ethylene-hexene copolymer produced in polymerization run 1 were 110.3 °C and 130.7 °C, while those of copolymer produced in polymerization run 2 were found to be 111.8 °C and 130.8 °C (Table 1). There was no great difference in melting temperatures in both cases. An important point is that the ethylene-hexene copolymers showed two melting temperatures in both cases. This clearly indicates that both metallocene and Ziegler-Natta components contributed to the ethylene-hexene copolymerization. The melting point appearing at around 110 °C was attributed to active sites of metallocene catalyst, while that appearing at around 130 °C was due to active sites of Ziegler-Natta catalyst. It is noteworthy that the T$_m$ peak attributed to metallocene catalyst in the polymerization run 1 was narrower and sharper than that in run 2. The molecular weights (Mw) of ethylene-hexene copolymers produced by a *rac*-Et(Ind)$_2$ZrCl$_2$/TiCl$_4$/SMB catalyst were on the order of ca. 1.0×10^4 g/mol. The molecular weight distributions of ethylene-hexene copolymers were approximately 5.5 in both cases.

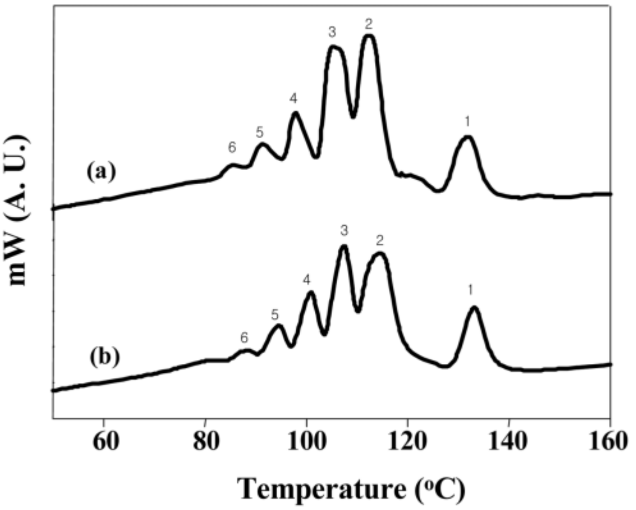

Fig. 4. Chemical composition distributions of ethylene-hexene copolymers produced with a variation of cocatalyst species: (a) TIBAL and MAO, (b) TEA and MAO.

Table 2. Lamella thickness of fractionated ethylene-hexene copolymer and its distribution

Polymerization run	Cocatalyst	Peak number	Lamella thickness (Å)	wt%
1	Al/Ti=300	1	233	11.8
	(TIBAL)	2	71	32.4
	Al/Zr=300	3	57	28.5
	(MAO)	4	47	12.6
		5	41	9.8
		6	36	4.9
2	Al/Ti=300	1	241	14.4
	(TEA)	2	76	36.7
	Al/Zr=300	3	59	24.5
	(MAO)	4	50	12.2
		5	43	8.9
		6	38	3.3

2. Chemical Composition Distribution and Lamella Thickness of Copolymers

Fig. 4 shows the chemical composition distributions (CCDs) of ethylene-hexene copolymers analyzed by a stepwise crystallization method. Six peaks were observed in the ethylene-hexene copolymers in both cases, regardless of the cocatalysts used. Furthermore, both the ethylene-hexene copolymers showed a similar trend in the CCD peak positions. However, it was observed that the intensity of peak 2 was higher than that of peak 3 in the polymerization run

Table 3. Comonomer content, triad sequence, and average sequence length in the ethylene-hexene copolymer

Polymerization run	Cocatalyst	Comonomer contents (mol%)		Average sequence length		Triad sequence (mol%)					
		[E]	[H]	$\tilde{n}_E$	$\tilde{n}_H$	[EHE]	[EHH]	[HHH]	[HEH]	[HEE]	[EEE]
1	TIBAL MAO	92.8	7.2	16.1	1.5	2.3	4.9	0	0	9.5	83.3
2	TEA MAO	92.7	7.3	19.4	1.3	4.2	3.1	0	0	11.5	81.2

[E]=Ethylene, [H]=Hexene

1, while the intensity of peak 3 was higher than that of peak 2 in the run 2.

Table 2 shows the lamella thickness of fractioned ethylene-hexene copolymer and its distribution determined on the basis of the Thomson-Gibbs equation [27]. 44.2 wt% of lamellas in the ethylene-hexene copolymer produced in polymerization run 1 were observed in the range of 71-233 Å, while 51.1 wt% of lamellas in the copolymer produced in polymerization run 2 were distributed in the range of 76-241 Å. On the other hand, 27.3 wt% of lamellas in the copolymer produced in polymerization run 1 were observed in the range of 36-47 Å, while 24.4 wt% of lamellas in the copolymer produced in polymerization run 2 were distributed in the range of 38-50 Å. These results indicate the lamellas in the ethylene-hexene copolymer produced in polymerization run 1 were distributed over the smaller sizes than those in the copolymer produced in run 2.

3. Comonomer Content, Average Sequence Length, and Triad Sequence

Table 3 shows the comonomer content, average sequence length ($\tilde{n}_E$, $\tilde{n}_H$), and triad sequence of ethylene-hexene copolymer evaluated by the Randall method [22]. It was observed that almost the same amount of hexene was incorporated into the ethylene-hexene copolymer (7.2 mol% in polymerization run 1 and 7.3 mol% in polymerization run 2). What is noticeable is that 2.3 mol% of non-blocky sequence ([EHE]) was observed in the ethylene-hexene copolymer produced in polymerization run 1, while 4.2 mol% of non-blocky sequence was observed in polymerization run 2. Furthermore, the difference in blocky sequence ([EHH]) content between the two copolymers was considerable even though they contained a similar amount of comonomer (hexene). The average sequence lengths of ethylene ($\tilde{n}_E$) in the copolymers were determined to be 16.1 and 19.4 in polymerization run 1 and run 2, respectively. The above results indicate that the *rac*-Et(Ind)$_2$ZrCl$_2$/TiCl$_4$/MAO/SMB catalyst preferably produced the ethylene-hexene copolymer with non-blocky sequence when TEA and MAO were used as cocatalysts.

CONCLUSIONS

A silica-magnesium bisupport (SMB) was prepared by a sol-gel method, and it was used as a support for metallocene/Ziegler-Natta hybrid catalyst. The prepared catalyst was applied to the ethylene-hexene copolymerization with a variation of cocatalyst species (polymerization run 1: TIBAL and MAO, polymerization run 2: TEA and MAO). The catalytic activity of *rac*-Et(Ind)$_2$ZrCl$_2$/TiCl$_4$/MAO/SMB in polymerization run 1 was a little higher than that in run 2. The chemical composition distributions (CCDs) in the two copolymers showed six peaks and exhibited a similar trend. However, the lamellas in the ethylene-hexene copolymer produced in polymerization run 1 were distributed over the smaller sizes than those in the copolymer produced in run 2. It was found that the hybrid catalyst preferably produced the ethylene-hexene copolymer with non-blocky sequence when TEA and MAO were used as cocatalysts.

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