

Chemical composition distributions and microstructures of ethylene–hexene copolymers produced by a *rac*-Et(Ind)₂ZrCl₂/TiCl₄/MAO/SMB catalyst

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Abstract

A silica-magnesium bisupport (SMB) was prepared by a sol–gel method for use as a support for a metallocene/Ziegler–Natta hybrid catalyst. The SMB was treated with methylaluminoxane (MAO) prior to the immobilization of TiCl₄ and *rac*-Et(Ind)₂ZrCl₂. The prepared *rac*-Et(Ind)₂ZrCl₂/TiCl₄/MAO/SMB catalyst was applied to the ethylene–hexene copolymerization with variable amounts of 1-hexene used. The catalytic activity of *rac*-Et(Ind)₂ZrCl₂/TiCl₄/MAO/SMB showed a volcano feature with respect to the amount of comonomer used. The melting point attributed to the Ziegler–Natta catalyst was not changed significantly, while that attributed to the metallocene catalyst was broadened and gradually shifted to the lower temperature with increasing 1-hexene content. The number of chemical composition distribution (CCD) peaks was increased and the short chain branches were distributed over the lower temperature region with increasing 1-hexene content. The majorities of lamella distributions whose content was more than 50 wt.% shifted to the smaller lamella size with increasing 1-hexene content. The average sequence length of ethylene was steadily decreased with increasing comonomer content, while that of 1-hexene was not changed significantly. Both blocky sequence ([EHH]) and non-blocky sequence ([EHE]) were increased with increasing comonomer content. However, the increasing rate of blocky sequence formation was much higher than that of non-blocky sequence.

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1. Introduction

The mechanical and reological properties of polyethylene are generally affected by the molecular weight (M_w) and the molecular weight distribution (MWD) of the polyethylene sample. In the case of an ethylene–alpha olefin copolymer, however, the chemical composition distribution (CCD) and the identity of alpha olefin used are also important factors in determining the physical and chemical properties of the copolymer [1,2]. The chemical composition distribution (CCD) and the microstructure of the copolymer are strongly affected by the catalyst systems and/or the polymerization conditions.

Metallocene catalysts have been considered as the next generation catalysts due to their high catalytic activity and excellent ability of comonomer incorporation, compared to Ziegler–Natta catalysts [2–5]. It is well known that polymers produced by a metallocene catalyst have very narrow molecular weight distributions, and therefore, they have limitation in polymer processing [4]. However, polymers produced by a Ziegler–Natta catalyst show good processability due to their broad molecular weight distribution [6,7]. The Ziegler–Natta catalysts used in commercial polymerization processes are heterogeneous catalyst systems, while metallocene catalysts are basically homogeneous catalyst systems. Thus, metallocene catalysts need to be heterogenized on the support in order for use in the existing commercial processes such as slurry and gas-phase processes [8,9]. For this purpose, inorganic materials such as silica, alumina, and zeolite have been employed as a support for metallocene cata-

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lysts [10,11]. The hybridization of metallocene catalyst with Ziegler–Natta catalyst on a support can be an alternative choice for the practical application of a metallocene catalyst as a heterogeneous catalyst.

Mixtures of metallocene and Ziegler–Natta catalysts have been examined in order to improve the physical properties of the resulting polymers [12,13]. Another promising example for utilizing both metallocene and Ziegler–Natta catalysts is to hybrid these catalysts by impregnating these two components on a single support [14–18]. It was reported that a polyethylene produced by a metallocene/Ziegler–Natta hybrid catalyst impregnated on MgCl₂ support showed a bimodal molecular weight distribution, indicating the existence of two different active sites on the support [14,15]. A silica-magnesium bisupport (SMB) prepared by a sol–gel method was also used to impregnate both metallocene and Ziegler–Natta catalysts on the support, by taking advantage of the fact that silica and magnesium dichloride are excellent supports for metallocene and Ziegler–Natta catalysts, respectively [16,17]. In this hybrid catalyst system, the existence of two different active sites on the single support was clearly confirmed by the observation of a bimodal molecular weight distribution and two melting temperatures of polyethylene [18,19].

In this work, a silica-magnesium bisupport (SMB) was prepared by a sol–gel method for use as a support for a metallocene/Ziegler–Natta hybrid catalyst. The prepared catalyst (*rac*-Et(Ind)₂ZrCl₂/TiCl₄/MAO(methylaluminoxane)/SMB) was applied to the ethylene–hexene copolymerization with variable amounts of 1-hexene used. Chemical composition distributions and microstructures of ethylene–hexene copolymers produced by the *rac*-Et(Ind)₂ZrCl₂/TiCl₄/MAO/SMB catalyst were examined.

2. Experimental

2.1. 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 P₂O₅ (Yakuri Chemicals). Toluene (Samjun Chemicals) and 1-hexene (Aldrich) were purified by distillation over sodium metal. MgCl₂ (Junsei Chemical), colloidal SiO₂ (LUDOX HS-40, Aldrich), *rac*-Et(Ind)₂ZrCl₂ (Strem), TiCl₄ (Aldrich), methylaluminoxane (MAO, Albermale), and triethylaluminum (TEA, Aldrich) were used without further purification.

2.2. Preparation of supported hybrid catalyst

The silica-magnesium bisupport (SMB) was prepared according to a method reported in a previous study [16]. The SMB was then treated with methylaluminoxane (MAO) according to a reported method [16]. The MAO-treated SMB (MAO/SMB) (2 g) was suspended in toluene (100 ml), and it was reacted with TiCl₄ (2 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 TiCl₄/MAO/SMB. The TiCl₄/MAO/SMB was suspended in toluene (20 ml), and subsequently, it was reacted with *rac*-Et(Ind)₂ZrCl₂ dissolved in toluene (10 ml). The resulting slurry was washed seven times with toluene (100 ml), and it was finally dried under vacuum to yield *rac*-Et(Ind)₂ZrCl₂/TiCl₄/MAO/SMB.

2.3. Copolymerization of ethylene with 1-hexene

Toluene (300 ml), supported catalyst (0.04 g), and known amounts of cocatalyst (triethylaluminum (TEA) and methylaluminoxane (MAO)) were introduced into a glass reactor (1000 ml) equipped with a magnetic stirrer under a flow of nitrogen. Known amounts of 1-hexene and cocatalyst were introduced into the reactor before the initiation step. The molar ratios of cocatalyst with respect to transition metal were fixed at Al/Ti = 300 (TEA) and Al/Zr = 300 (MAO). After evacuating the nitrogen in the reactor by a 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 hydrochloric acid solution diluted with methanol. A series of ethylene–hexene copolymerizations were carried out by varying the amount of 1-hexene used from 2 to 10 ml.

2.4. Characterization of ethylene–hexene copolymer

The melting temperature (*T*_m) of the ethylene–hexene copolymer was measured using a differential scanning calorimeter (DSC, TA 2010) with a heating rate of 10 °C/min. The molecular weight (*M*_w) and molecular weight distribution (MWD) of the ethylene–hexene copolymer were determined by a gel permeation chromatography (GPC, PL-GPC 220) at 160 °C using 1,2,4-trichlorobenzene as a solvent. The GPC column was calibrated using standard polystyrene. The comonomer content and triad sequence in the ethylene–hexene copolymer were analyzed using a 100 MHz ¹³C nuclear magnetic resonance spectrometer (¹³C NMR, Avance 500) at 130 °C on the basis of the Randall method [20].

2.5. Chemical composition distribution of ethylene–hexene copolymer

A stepwise annealing procedure was conducted to analyze the chemical composition distribution (CCD) of ethylene–hexene copolymer [21–23]. As shown in Fig. 1, the 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 using a DSC with a heating rate of 10 °C/min. The lamella thickness of the fractionated ethylene–hexene copolymer was determined using the Thomson–Gibbs equation [24].

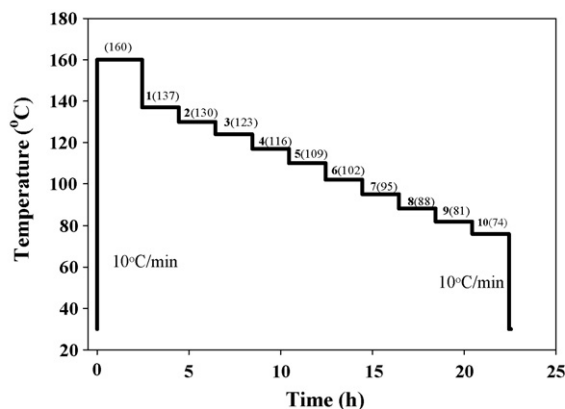


Fig. 1. Stepwise annealing procedure for chemical composition distribution analysis of ethylene–hexene copolymer.

3. Results and discussion

3.1. Catalytic activities and physical properties of ethylene–hexene copolymer

Table 1 shows the catalytic activities of *rac*-Et(Ind)₂ZrCl₂/TiCl₄/MAO/SMB and physical properties of ethylene–hexene copolymer with variable amounts of 1-hexene used. The catalytic activity of the *rac*-Et(Ind)₂ZrCl₂/TiCl₄/MAO/SMB showed a volcano feature with respect to the amount of comonomer used. The maximum catalytic activity was observed when 6 ml of 1-hexene was used. Excessive amounts of comonomer were not favorable for the catalytic activity of the *rac*-Et(Ind)₂ZrCl₂/TiCl₄/MAO/SMB. Fig. 2 shows the catalytic activity profiles of *rac*-Et(Ind)₂ZrCl₂/TiCl₄/MAO/SMB with time on stream. The catalytic activity was high at the initial stage and then steadily decreased with time on stream. However, the catalytic activity was not changed significantly when 10 ml of 1-hexene was used. As expected, the comonomer content was increased with increasing the amount of 1-hexene used.

Fig. 3 shows the DSC profiles of ethylene–hexene copolymers produced with variable amounts of 1-hexene used. The melting temperatures (T_m) of ethylene–hexene copolymers are also summarized in Table 1. As shown in Fig. 3, two melting temperatures (T_m) of ethylene–hexene copolymers were observed within a temperature window of 99–132 °C. One melting point appearing at around 130 °C was attributed to active sites of the Ziegler–Natta catalyst, and it was not changed significantly with respect to the amount of comonomer used. It is interesting to note that the other melting point in the low temperature region, which

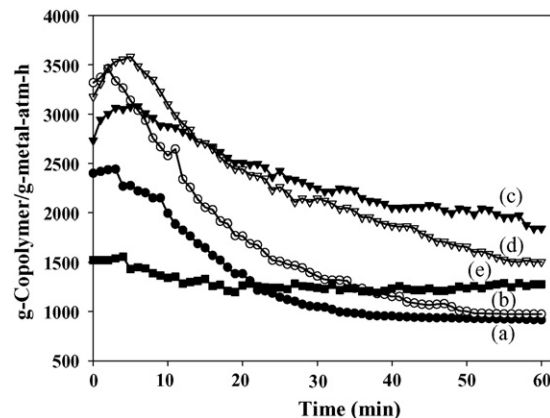


Fig. 2. Catalytic activity profiles of *rac*-Et(Ind)₂ZrCl₂/TiCl₄/SMB with time on stream in the ethylene–hexene copolymerization with variable amounts of 1-hexene used: (a) 2 ml, (b) 4 ml, (c) 6 ml, (d) 8 ml, (e) 10 ml; ethylene pressure = 1.3 atm, hydrogen pressure = 0.2 atm, Al/Zr = 300 (MAO), Al/Ti = 300 (TEA), polymerization temperature = 55 °C, polymerization time = 60 min, solvent = toluene (300 ml).

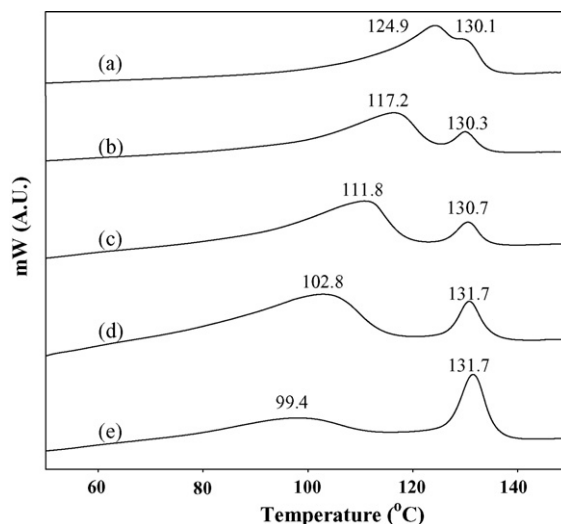


Fig. 3. DSC profiles of ethylene–hexene copolymers produced with variable amounts of 1-hexene used: (a) 2 ml, (b) 4 ml, (c) 6 ml, (d) 8 ml and (e) 10 ml.

was attributed to active sites of the metallocene catalyst, gradually shifted from 124.9 to 99.4 °C with increasing the amount of 1-hexene used. These results are due to the large difference in the ability of comonomer incorporation between Ziegler–Natta and metallocene catalysts. Judging from the fact that the melting point of the copolymer caused by the metallocene catalyst shifted to the lower temperature and was broadened with increas-

Table 1

Catalytic activities of *rac*-Et(Ind)₂ZrCl₂/TiCl₄/MAO/SMB and physical properties of ethylene–hexene copolymer with variable amounts of 1-hexene used

1-Hexene used (ml)	Al/Zr	Al/Ti	Catalytic activity (g copolymer/g metal atm h)	T_m (°C)	Comonomer content (mol%)
2			1470	124.9/130.1	4.0
4			1700	117.2/130.3	6.5
6	300 (MAO)	300 (TEA)	2750	111.8/130.7	7.2
8			2570	102.8/131.7	8.4
10			890	99.4/131.7	9.5

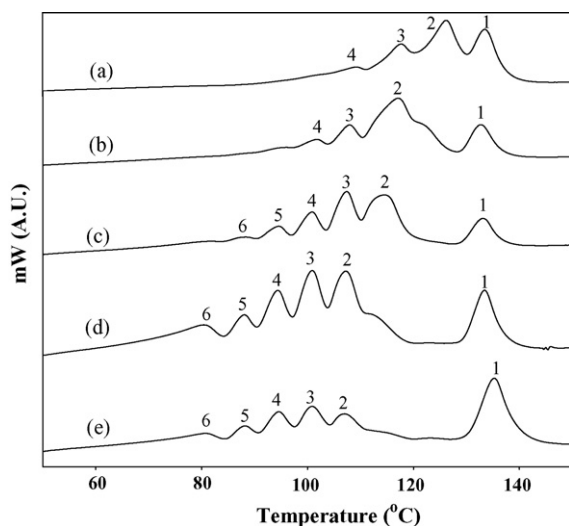


Fig. 4. Chemical composition distributions of ethylene-hexene copolymers analyzed by a stepwise crystallization method: (a) 2 ml, (b) 4 ml, (c) 6 ml, (d) 8 ml and (e) 10 ml.

ing the amount of 1-hexene used, it is likely that the crystallinity of the copolymer produced by the metallocene active sites was decreased with increasing the amount of 1-hexene used.

The molecular weights (M_w) of ethylene-hexene copolymers produced by *rac*-Et(Ind)₂ZrCl₂/TiCl₄/SMB were in the order of ca. 1.0×10^4 g/mol, and the molecular weight distributions of ethylene-hexene copolymers were in the range of 3.0–5.0.

3.2. Chemical composition distribution and lamella thickness of ethylene-hexene copolymer

Fig. 4 shows the chemical composition distributions of ethylene-hexene copolymers analyzed by a stepwise crystallization method. Four peaks were observed in the ethylene-hexene copolymers when 2 ml and 4 ml of 1-hexene were used. Two additional peaks were observed in the ethylene-hexene copolymers when the amount of 1-hexene was increased from 6 to 10 ml. It is noteworthy that the peak temperatures shifted to the lower temperature region with increasing the amount of 1-hexene used. It can be summarized that the number of CCD peaks was increased from 4 to 6 and the short chain branches of ethylene-hexene copolymer were distributed over the lower temperature region with increasing the amount of 1-hexene incorporated.

Table 2 shows the lamella thickness of fractionated ethylene-hexene copolymer and its distribution determined on the basis of the Thomson-Gibbs equation [24]. The copolymer produced with 2 ml of 1-hexene showed a lamella with a thickness of 131 Å, which was not found in the other copolymers. Over 50 wt.% of the lamellas in the ethylene-hexene copolymers produced with 4 and 6 ml of 1-hexene were distributed in the range of 59–84 Å, while lamellas between 87 and 131 Å were found to be over 50 wt.% in the copolymer produced with 2 ml of 1-hexene. On the other hand, ca. 50 wt.% of the lamellas in the copolymer produced with 8 ml of 1-hexene were distributed in the range of 50–60 Å. This implies that the more

Table 2

Lamella thickness of fractionated ethylene-hexene copolymer and its distribution

1-Hexene used (ml)	Peak number	Lamella thickness (Å)	wt.%
2	1	263	27.7
	2	131	41.5
	3	87	22.3
	4	63	8.50
4	1	236	16.9
	2	84	58.4
	3	61	14.6
	4	51	10.1
6	1	241	14.4
	2	76	36.7
	3	59	24.4
	4	50	12.2
	5	43	8.9
	6	38	3.4
8	1	263	17.0
	2	60	30.8
	3	50	20.7
	4	43	15.1
	5	38	8.2
	6	34	8.2
10	1	274	36.4
	2	60	22.2
	3	50	16.2
	4	43	13.1
	5	38	7.1
	6	33	5.0

1-hexene was used, the smaller sizes of lamellas were produced. In other words, the majorities of lamella distributions whose content was more than 50 wt.% shifted to the smaller lamella size with increasing the amount of 1-hexene used; 87–131, 59–84, and 50–60 Å for 2, 4–6, and 8 ml of 1-hexene, respectively. The copolymers produced with 8 ml and 10 ml of 1-hexene showed lamellas below 40 Å, which were not found in the copolymers produced with 2 and 4 ml of 1-hexene. Although the amount of small lamellas was increased with increasing the amount of 1-hexene used, 36.4 wt.% of the lamellas retained a thickness of 274 Å in the copolymer produced with 10 ml of 1-hexene.

3.3. Comonomer content, average sequence length, and triad sequence

Table 3 shows the comonomer content, average sequence length (\bar{n}_E , \bar{n}_H), and triad sequence in ethylene-hexene copolymer evaluated by the Randall method [20]. 4.0–9.5 mol% of comonomer was incorporated in the ethylene-hexene copolymer when the amount of 1-hexene was increased from 2 to 10 ml. It was observed that the average sequence length of ethylene (\bar{n}_E) was steadily decreased with increasing comonomer content, while that of 1-hexene (\bar{n}_H) was not changed significantly. It was also found that the blocky sequence ([EHH]) was increased from 2.4 to 6.9 mol% with increasing comonomer content, while the non-blocky sequence ([EHE]) was increased from 1.6 to 2.6 mol%. Fig. 5 shows the variation of [H] content,

Table 3
Comonomer content, average sequence length, and triad sequence in ethylene–hexene copolymer

1-Hexene used (ml)	Comonomer content (mol%)		Average sequence length (\bar{n})		Triad sequence (mol%)					
	[E]	[H]	\bar{n}_E	\bar{n}_H	[EHE]	[EHH]	[HHH]	[HEH]	[HEE]	[EEE]
2	96.0	4.0	33.6	1.4	1.6	2.4	0	0	5.7	90.3
4	93.5	6.5	22.5	1.6	1.8	4.7	0	0	8.4	85.1
6	92.8	7.2	19.4	1.5	2.3	4.9	0	0	9.5	83.3
8	91.6	8.4	16.7	1.5	2.5	5.9	0	0	10.9	80.7
10	90.5	9.5	15.0	1.6	2.6	6.9	0	0	12.1	78.4

[E]: ethylene, [H]: 1-hexene.

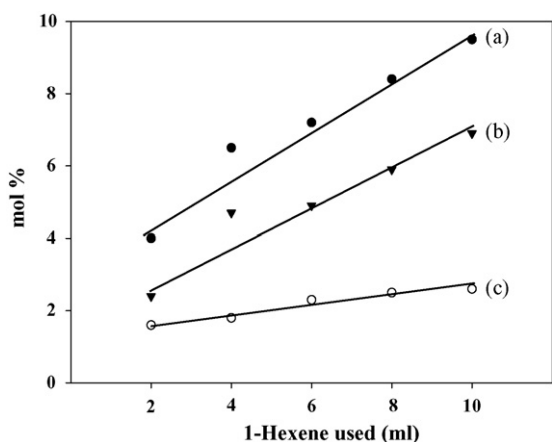


Fig. 5. Variation of [H] content, [EHH] sequence, and [EHE] sequence in the copolymers as a function of 1-hexene used: (a) [H] content, (b) [EHH] sequence and (c) [EHE] sequence.

[EHH] sequence, and [EHE] sequence in the copolymers as a function of 1-hexene used. One again, it was clearly observed that the increasing rate of blocky sequence ([EHH]) formation was much higher than that of non-blocky sequence ([EHE]), indicating that the comonomer was preferably incorporated into the ethylene–hexene copolymer as a blocky sequence form over the *rac*-Et(Ind)₂ZrCl₂/TiCl₄/MAO/SMB catalyst.

4. Conclusions

A silica-magnesium bisupport (SMB) was prepared by a sol–gel method, and it was used as a single support for a metallocene/Ziegler–Natta hybrid catalyst. The prepared catalyst (*rac*-Et(Ind)₂ZrCl₂/TiCl₄/MAO/SMB) was applied to the ethylene–hexene copolymerization with variable amounts of 1-hexene used. It was found that the catalytic activity of *rac*-Et(Ind)₂ZrCl₂/TiCl₄/MAO/SMB showed a volcano feature with respect to the amount of comonomer used. The maximum catalytic activity was observed when 6 ml of 1-hexene was used. It was also observed that the melting point attributed to the Ziegler–Natta catalyst was not changed significantly while that attributed to the metallocene catalyst was broadened and gradually shifted to the lower temperature with increasing the amount of 1-hexene used. The number of CCD peaks was increased from 4 to 6 and the short chain branches were distributed over the

lower temperature region with increasing comonomer content. The majorities of lamella distributions whose content was more than 50 wt.% shifted to the smaller lamella size with increasing 1-hexene content. The average sequence length of ethylene (\bar{n}_E) was steadily decreased with increasing comonomer content, while that of 1-hexene (\bar{n}_H) was not changed significantly. Both blocky sequence ([EHH]) and non-blocky sequence ([EHE]) were increased with increasing comonomer content. However, the increasing rate of blocky sequence ([EHH]) formation was much higher than that of non-blocky sequence ([EHE]). This indicates that the comonomer was preferably incorporated into the ethylene–hexene copolymer in the form of a blocky sequence.

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