Characteristics of Diether- and Phthalate-Based Ziegler-Natta Catalysts for Copolymerization of Propylene and Ethylene and Terpolymerization of Propylene, Ethylene, and 1-Butene

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ABSTRACT: Copolymerization of propylene and ethylene and terpolymerization of propylene, ethylene, and 1-butene were carried out to compare the characteristics of diether- and phthalate-based Ziegler-Natta catalysts in a reaction system of pilot scale. The ethylene incorporation with the diether-based catalyst was higher but the 1-butene incorporation was lower compared with those of the phthalate-based catalyst. In the case of copolymers from the diether-based catalyst, melting behavior, determined through differential scanning calorimetry (DSC), showed a distinct shoulder peak and lots of nuclei were formed during crystallization. The diether-based catalyst led to polymers having blockier ethylene sequences compared with those of the phthalate-based catalyst; the highly crystallizable fraction (HIS) containing blockier ethylene sequences was produced with the diether-based catalyst. These results seem to be the result of regio-irregular characteristics of the diether-based catalyst. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2013.

INTRODUCTION

Polypropylene, together with polyethylene, is one of the typical commodity polymers. The majority of polypropylene is commercially produced using a Ziegler-Natta catalyst with a cocatalyst such as an alkylaluminum and an external electron donor such as an alkylalkoxysilane. In general, a Ziegler-Natta catalyst for producing polypropylene contains titanium tetrachloride, magnesium chloride, and an internal electron donor. The role of the internal electron donor in the Ziegler-Natta catalyst system is very crucial in terms of activity, isotacticity, hydrogen response, and molecular weight distribution. It is well established that internal electron donors stabilize small primary magnesium chloride crystallite, affect the amount and distribution of titanium tetrachloride, and transform poorly stereoselective sites to highly stereoselective sites. The typical example of an internal electron donor is an aromatic diester such as dialkyl phthalate, discovered in early 1980s,[1] phthalate-based Ziegler-Natta catalysts have been widely used for the commercial production of polypropylene. There have been many efforts to develop new internal electron donors such as 1,3-diethers,[2–4] succinates,[5–7] and malonates.[8–10]

Catalysts containing 1,3-diethers as internal electron donors show unique characteristics compared with catalysts containing other components. According to previous studies,[11–19] in general, diether-based catalysts show high activity and high hydrogen response in the polymerization of propylene and yield polymers having narrow molecular weight distribution and high isotacticity even without an external electron donor. Concerning the high activity and high hydrogen response of the diether-based catalysts, it was reported that diether-based catalysts had a high content of active sites[12,13] with low regioseletivity.[14–17] Additionally, the 1,3-diethers are not easily displaced from the catalyst surface on contact with a cocatalyst such as an alkylaluminum because the 1,3-diethers show higher affinity towards magnesium chloride than to a cocatalyst, and consequently diether-based catalysts make polypropylene having comparatively high isotacticity without an external electron donor. It was also reported that when a 1,3-diether was used as an external electron donor with a phthalate-based catalyst, polymers having similar properties in terms of tacticity and regioselectivity were made with a catalyst containing a 1,3-diether as an internal electron donor.[18,19] Moreover, several studies have been done on the coordination of internal electron donors on lateral
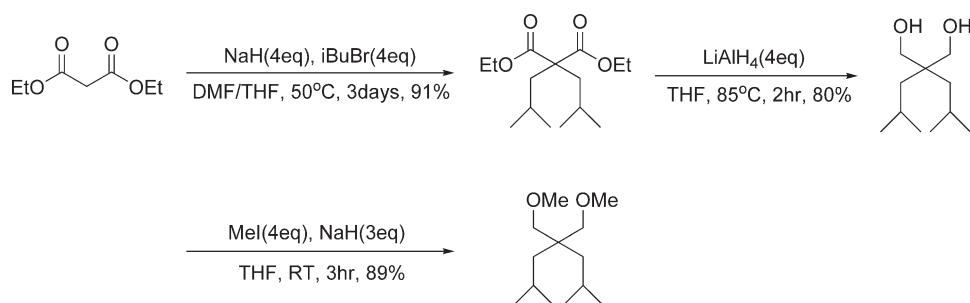
Scheme 1. Synthesis of 2,2-diisobutyl-1,3-dimethoxypropane.

faces of magnesium chloride.[20–24] According to these studies, 1,3-diethers have more preference for coordination on the (110) face of magnesium chloride than on the (100) face, while phthalates have similar preferences for coordination on both faces.

Although the above studies have provided the basic characteristics of diether-based catalysts for the polymerization of propylene, the characteristics of the catalysts for the copolymerization of propylene and other comonomers such as ethylene or 1-butene have not been much discussed yet. Busico et al.[17] investigated the regioselectivity of a diether-based catalyst using copolymerization of propylene and ethylene and Bi et al.[25] reported the results of copolymerization of propylene and 1-octene in a batch-wise polymerization system. It is difficult to maintain uniform concentration of monomers and the state of active catalyst in a batch system. In this work, in a reaction system of pilot scale under steady-state conditions, copolymerization of propylene and ethylene and terpolymerization of propylene, ethylene, and 1-butene were carried out using two Ziegler-Natta catalysts with different internal electron donors, a diether (2,2-diisobutyl-1,3-dimethoxypropane) and a phthalate (diisobutyl phthalate). It is well known that sufficient amounts of an internal electron donor in a catalyst are needed to obtain polypropylenes having high isotacticity. For this reason we prepared two catalysts having sufficient amounts of internal electron donors in the preparation step. The characterization of copolymers and terpolymers was also performed and the characteristics of the two catalysts were compared. In particular, this work was focused on the elucidation of effect of two different donors on the microstructure of copolymers and terpolymers.

EXPERIMENTAL

Materials

As internal electron donors, diisobutylphthalate (99%) was supplied by Aldrich and 2,2-diisobutyl-1,3-dimethoxypropane was synthesized in the following method (Scheme 1). Diethoxy malonate (99%, Aldrich) was converted to diethoxy 2,2-diisobutyl-malonate through a reaction with sodium ethoxide (95%, Aldrich) and isobutyl bromide (99%, Aldrich) in ethanol (99.5%, Aldrich) solution. Next, diethoxy 2,2-diisobutylmalonate was transformed to 2,2-diisobutylpropane-1,3-diol under a reaction with lithium aluminum hydride (95%, Aldrich) in tetrahydrofurane (99.9%, Aldrich) solution. Finally, 2,2-diisobutyl-1,3-dimethoxypropane was formed by a reaction with 2,2-diisobutylpropane-1,3-diol, methyl iodide (99%, Aldrich), and sodium hydride (60% in mineral oil, Aldrich) in tetrahydrofur-

ane/dimethylformamide (99.8%, Aldrich) solution. The synthesized 2,2-diisobutyl-1,3-dimethoxypropane was identified by ^{1}H-NMR. Yield: 65 %, ^{1}H-NMR (400 MHz, CDCl$_3$, δ, ppm): 3.25 (s, 6H), 3.14 (s, 4H), 1.73-1.66 (m, 2H), 1.20 (d, J = 5.5 Hz, 4H), 0.87 (d, J = 6.7 Hz, 12H).

Anhydrous magnesium chloride (99.3%) was supplied by Okada Chemicals and 2-ethylhexanol (99.6%) was supplied by Aldrich. Titanium tetrachloride (99%) was obtained by Yakuri Pure Chem. n-hexane (95%, Aldrich), n-heptane (99%, Aldrich), n-decane (98%, Samchun), toluene (99.8%, Aldrich), and xylene (98.5%, Aldrich) were used after purification with a purification system (Pure Solv, Innovative Technology).

Propylene (99.6%), ethylene (99.95%), 1-butene (99.99%), and hydrogen (99.99%) were supplied by Lotte Chemical Corp. and used after passing a purification column filled with molecular sieve 4A. Triethylaluminum (96.0%) was obtained from Gulbransen and dicyclopentyldimethoxysilane (99.6%) was obtained from Shin-Etsu.

Preparation of Catalyst

Two types of catalysts were prepared: a diether-based catalyst (TiCl$_4$/2,2-diisobutyl-1,3-dimethoxypropane/MgCl$_2$) and a phthalate-based catalyst (TiCl$_4$/diisobutyl phthalate/MgCl$_2$). The catalysts were prepared with the following procedure under nitrogen atmosphere. In a 3 L glass reactor, anhydrous magnesium chloride (95.2 g, 1.0 mol), n-decane (400 mL), and 2-ethylhexanol (550 mL, 3.5 mol) were added successively. The mixture was heated to 135°C under stirring and held at that temperature for 1 h; then, an internal electron donor (0.15 mol, 2,2-diisobutyl-1,3-dimethoxypropane or diisobutyl phthalate) was added to the mixture. The mixture was held at constant temperature for 1 h and a clear solution was obtained. The clear solution was cooled to room temperature. In another 3 L glass reactor, n-hexane (700 mL), toluene (700 mL) and titanium tetrachloride (880 mL, 8.0 mol) were added successively and cooled to −20°C. The clear solution containing magnesium chloride was added to the mixture containing titanium tetrachloride during 2 h at −20°C. The mixture was heated to 75°C at a rate of 0.5°C/min and held at that temperature for 2 h. Solid catalyst was formed during the procedure. The supernatant was removed by siphoning and titanium tetrachloride (440 mL, 4.0 mol) and toluene (1500 mL) were added. Next, the reactor temperature was ramped up to 110°C and held for 2 h. After that, the supernatant was removed and the solid catalyst

was washed and siphoned with *n*-hexane (1500 mL) three times and dried under nitrogen to obtain the solid catalyst.

The content of titanium was measured by UV-vis spectrometry (UV-2450, Shimadzu) after the solid catalyst was fully dissolved in acidic water. The content of magnesium was measured by X-ray fluorescence (ZSX Primus-II, Rigaku) and the content of internal electron donor was measured by gas chromatography (HP 6890 Plus, Hewlett Packard) after the solid catalyst was fully dissolved in acidic methanol/toluene.

Polymerization

Polymerization was performed under continuous and steady-state conditions using a polymerization system with a 140 L reactor fully filled with liquid monomers as reaction medium. Monomers (propylene, ethylene, and 1-butene), hydrogen, the prepared catalyst, triethylaluminum as a cocatalyst, and dicyclopentyldimethoxysilane as an external electron donor were continuously fed to the reactor; the produced polymer was continuously discharged from the reactor. Reaction temperature was maintained at 70°C (homopolymerization and copolymerization) or 60°C (terpolymerization) and reaction pressure was maintained at 34.5 kg_f/cm^2. Total feed rate of monomers was 80 kg/h. The feed rate of the catalyst was controlled at a constant production rate of polymer (~40 kg/h) and the polymer concentration in the reactor was set at 560 g/L. The average retention time of the catalysts in the reactor was 1.5 h. The feed rate of triethylaluminum was maintained at 170 weight ppm to total monomers feed; mole ratio of triethylaluminum to dicyclopentyldimethoxysilane was maintained at 6. In the case of the copolymer, the feed rate of ethylene was controlled in the range of 4 ~ 6 mol % of ethylene contents in the obtained polymers and, in case of terpolymerization, 1-butene feed rate was controlled in the range of 3 ~ 4 mol % of 1-butene contents in the obtained polymers.

Characterization of Polymers

Molecular weight and molecular weight distribution of polymer were measured by gel permeation chromatography (PL-GPC220, Polymer Laboratories) at 160°C with 1,2,4-trichlorobenzene as a solvent. Data were calibrated using polystyrene standards (M_w 10,000 ~ 12,000,000, Polymer Laboratories) and polypropylene standards (M_w 10,000 ~ 200,000, American Polymer Standards).

Differential scanning calorimetry (DSC) measurement was carried out with a thermal analysis system (Q200, TA Instruments). DSC scan was obtained by heating from 20°C to 200°C, cooling from 200°C to 20°C, and then reheating from 20°C to 200°C, at a rate of 10°C/min.

^{13}C-NMR spectra of the obtained polymer was measured to obtain the content of incorporated ethylene and the microstructure of the polymer using a Bruker Avance 400 spectrometer at 100°C with 1,2,4-trichlorobenzene as a solvent.

Crystallization behavior of the obtained polymer was investigated using optical microscopy (Vanox-AHMT3, Olympus) in the following manner. Polymer film (2 micrometer thickness) was prepared and melted on a heating stage. Temperature was ramped to 200°C at the rate of 10°C/min and maintained at

that temperature in order to remove thermal history. After that, the molten film was cooled to the given crystallization temperature at the rate of 10°C/min; then, crystallization behavior was checked at that temperature.

To check the more detailed monomer sequence of the polymer chain, the obtained polymer was fractionated into three parts (HIS: boiling *n*-heptane insoluble fraction, XIS: xylene insoluble fraction, and XS: xylene soluble fraction) in the following manner (Scheme 2). First, *n*-heptane insoluble and soluble parts were separated by Soxhlet extraction of polymer sample by boiling *n*-heptane. *n*-Heptane insoluble part was obtained by drying the insoluble solid and *n*-heptane soluble part was obtained by evaporating *n*-heptane from the extracted *n*-heptane solution. Then, *n*-heptane soluble part was dissolved in xylene at 135°C and cooled down to room temperature. Xylene insoluble part was obtained by drying the precipitated solid; xylene soluble part was obtained by evaporating xylene from the remaining solution. The fractionated polymers were also characterized with gel permeation chromatography, differential scanning calorimetry, and ^{13}C-NMR.

RESULTS AND DISCUSSION

The composition of the prepared catalysts and results of polymerization of propylene are given in Table I. The donor content of the diether-based catalyst is higher than that of the phthalate-based catalyst, although the two catalysts were prepared using the same quantities of donors in the preparation step. However, the prepared catalysts showed very high and similar stereo-regularity in the polymerization of propylene. As can be seen in Table I, the xylene solubles (XS) of the two catalysts were 0.8 and 1.0 wt %, respectively, showing that the two catalysts provide very high stereoselectivity in the polymerization of propylene. The other results, as discussed below, are in agreement with those of previous studies.[2–4] Hydrogen feed rate of the diether-based catalyst was lower than that of the phthalate-based catalyst (H_2 Feed rate = 1,290 vs. 2,120 wppm). This implies that the hydrogen response of the diether-based catalyst is better. The molecular weight distribution of the polymer with the diether-based catalyst was narrower (M_w/M_n = 4.1) than that with the phthalate-based catalyst (M_w/M_n = 4.1 vs. 5.6).
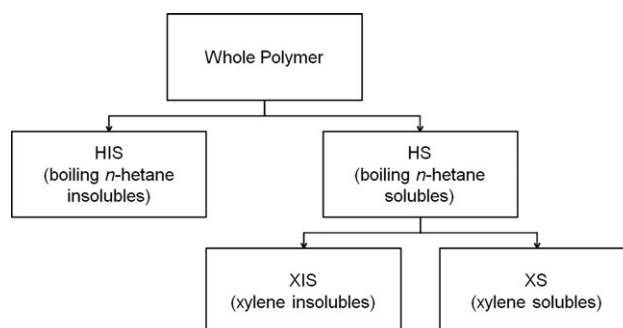
Scheme 2. Fractionation of polymer into boiling *n*-heptane insoluble fraction (HIS), xylene insoluble fraction (XIS), and xylene soluble fraction (XS).

Table I. Composition of the Prepared Catalysts and Results of Polymerization of Propylene

Catalyst	Catalyst composition			Polymerization results				
	Ti (wt %)	Mg (wt %)	Donor (wt %)	H_2 Feed (wppm)	M_w (g/mol)	MWD (M_w/M_n)	T_m (°C)	XS (wt %)
Diether-based	2.6	17.0	16.8	1,290	200,600	4.1	163.8	0.8
Phthalate-based	2.3	17.0	10.1	2,120	183,400	5.6	163.0	1.0

Polymerization conditions: temperature = 70°C, pressure = 34.5 kg$_f$/cm^2, average retention time = 1.5 h.

According to a review by Soares,[26] the chemical composition distribution of copolymer becomes broader with decreasing molecular weight and increasing blockiness. In this study, the average molecular weights of the polymers were controlled to keep them at a similar level by controlling the feed rate of hydrogen in order to remove the molecular weight effect on the chemical composition distribution. The results of the copolymerization of propylene and ethylene with the diether- and phthalate-based catalysts are shown in Table II. The results of copolymerization were similar to the results of the polymerization of propylene in terms of the hydrogen response and molecular weight distribution. The feed rates of hydrogen of the diether-based catalyst were ~60% of those of the phthalate-based catalyst, which allowed us to obtain copolymers having similar molecular weights. The copolymers with the diether-based catalyst had narrower molecular weight distribution ($M_w/M_n = 4.0 \sim 4.4$ vs. $5.6 \sim 6.0$). The ethylene incorporation of the diether-based catalyst was slightly higher than that of the phthalate-based catalyst. Actually, the ratios of incorporated ethylene to ethylene feed with the diether-based catalyst were 2.32 (D1) and 2.04 (D2), while the ratios with the phthalate-based catalyst were 1.74 (P1) and 1.90 (P2), respectively.

Differential scanning calorimetry (DSC) measurement was carried out to investigate the melting behavior of the copolymers by the two catalysts. As can be seen in Figure 1, the copolymers formed by the diether-based catalyst have shoulder peaks in the upper region from the peak melting temperature; this phenomenon is clear in the case of the copolymer with higher ethylene content (D2). These results indicate that the copolymers formed using the diether-based catalyst have structurally diverse polymer chains compared with those formed using the phthalate-based catalyst. Isothermal crystallization behavior was also observed using optical microscopy. The crystallization behavior was detected at a given temperature from the molten state; Figure 2 shows the results. Copolymers formed with the two catalysts showed quite different crystallization patterns. Copolymers formed using the diether-based catalyst had higher numbers of nuclei in the initial stage and, finally, smaller spherulites than those formed using the phthalate-based catalyst. According to the results of gel permeation chromatography (Table II), it is clear that the diether-based catalyst produces copolymers having narrower molecular weight distribution; however, in terms of microstructure the melting or crystallization behaviors show that the diether-based catalyst may produce copolymers having diverse polymer chains.

^{13}C-NMR measurement was carried out to verify the monomer sequence of the copolymers; the results are given in Table III. A noticeable difference is that the triad "EEE" portions of the diether-based catalyst are higher than those of the phthalate-based catalyst. The "EEE" portions in the total ethylene of D1 and D2 are 22.7% and 15.1%, respectively, while the "EEE" portions in the total ethylene of P1 and P2 are only 7.5% and 7.3%, respectively. The values of the reactivity ratio ($r_1 \times r_2$) are also quite different between the two catalysts. The ratios of D2 and P2 are 5.8 and 3.8, respectively; the ratio for the diether-based catalyst is much higher. From these results it can be seen that it is highly probable that the diether-based catalyst produces a blockier copolymer in the copolymerization of propylene and ethylene.

For more detailed analysis, the copolymers (D2 and P2) were fractionated into three parts: hardly crystallizable fraction (XS), moderately crystallizable fraction (XIS), and highly crystallizable fraction (HIS). Table IV shows the properties of each fraction.

Table II. The Results of Copolymerization of Propylene and Ethylene Using the Diether- and Phthalate-Based Catalysts

Catalyst	Sample code	Feed condition		Polymer analysis					Ratio of incorporation ($C_2^=$)
		$C_2^=$ (mol %)	H_2 (wppm)	$C_2^=$ (mol %)	Mw (g/mol)	MWD (M_w/M_n)	T_m (°C)	XS (wt %)	
Diether-based	D1	1.9	1720	4.4	180,400	4.4	147.4	3.3	2.32
	D2	2.6	1820	5.3	181,700	4.0	143.2	4.6	2.04
Phthalate-based	P1	2.3	2710	4.0	193,900	6.0	148.4	3.1	1.74
	P2	2.9	3340	5.5	205,000	5.6	143.5	4.9	1.90

Polymerization conditions: temperature = 70°C, pressure = 34.5 kg$_f$/cm^2, average retention time = 1.5 h.
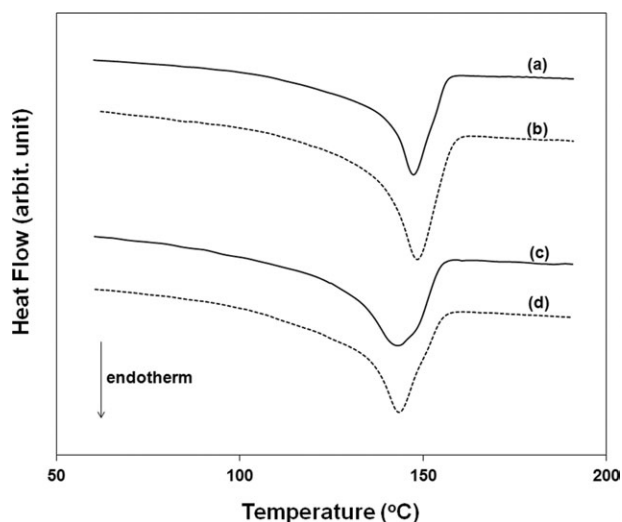
Figure 1. The melting behaviors of copolymers by diether- and phthalate-based catalysts. (a) D1 (diether), (b) P1 (phthalate), (c) D2 (diether), and (d) P2 (phthalate).

The hardly crystallizable fraction (XS) had higher ethylene content and lower molecular weight; the highly crystallizable fraction (HIS) had lower ethylene content and higher molecular weight in both catalysts. The difference of molecular weight among the three fractions was smaller in the case of the diether-based catalyst; this result was in agreement with the narrower molecular weight distribution of the whole copolymer. The DSC peaks of melting and crystallization were slightly different between the two catalysts. Especially in the highly crystallizable fraction (HIS), the peak temperatures of melting and crystallization of the diether-based catalyst are higher than those of the phthalate-based catalyst, although the peak melting temperatures of whole copolymers are almost the same (Table I). These results may comply with the DSC melting curve, which has a shoulder peak and more copolymer nuclei with the diether-based catalyst (Figures 1 and 2).

Monomer sequence analysis of the fractions was carried out using ^{13}C-NMR; the results are given in Table V. In the highly crystallizable fraction (HIS), the triad "EEE" portion of the diether-based catalyst is 0.8 mol % while that of the phthalate-based catalyst is 0.2 mol %. On the other hand, the triad "EEE" portion of the diether-based catalyst in the hardly crystallizable fraction (XS) was lower than that of the phthalate-based catalyst (2.0 vs. 3.7 mol %). In addition, in the case of the diether-based catalyst, the reactivity ratio ($r_1 \times r_2$) of the highly crystallizable fraction (HIS) was 9.9; this value was very high compared with those of the other fractions. Figure 3 shows the triad "EEE" portions in the total incorporated ethylene of each fraction. As can be seen in Figure 3, the highly crystallizable fraction (HIS) of the diether-based catalyst had a much higher triad "EEE" portion (22.3%) in the total incorporated ethylene than that
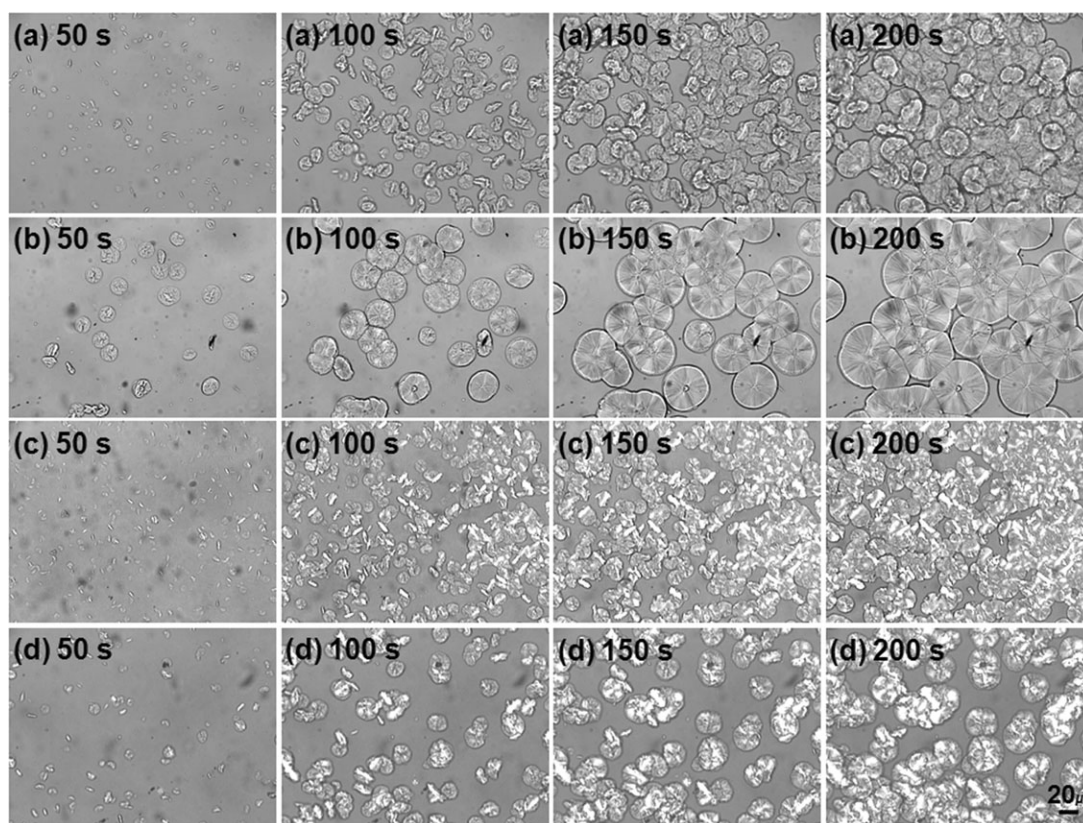

Figure 2. The picture of isothermal crystallization using optical microscopy after 50, 100, 150, and 200 seconds at the crystallization temperature, ((a) and (b): 124°C, (c) and (d): 120°C). (a) D1 (diether), (b) P1 (phthalate), (c) D2 (diether), and (d) P2 (phthalate).

Table III. The Monomer Sequence of Copolymers Measured with ^{13}C-NMR

Catalyst	Sample code	monad (mol %)		triad (mol %)						$r_1 \times r_2$
		P	E	PPP	PPE	EPE	PEP	EEP	EEE	
Diether-based	D1	95.6	4.4	89.5	6.0	0.2	2.9	0.4	1.0	11.2
	D2	94.7	5.3	86.7	7.8	0.3	3.8	0.6	0.8	5.8
Phthalate-based	P1	96.0	4.0	89.6	6.2	0.3	3.2	0.5	0.3	3.9
	P2	94.5	5.5	85.8	8.2	0.5	4.1	0.9	0.4	3.8

Table IV. The Properties of Copolymer Fractions with the Diether- and Phthalate-Based Catalysts

Catalyst	Sample code	Fraction (wt %)	$C_2^=$ (mol %)	M_n (g/mol)	M_w (g/mol)	MWD (M_w/M_n)	T_m (°C)	T_c (°C)
Diether-based	D2	XS 4.6	19.1	3,700	41,000	11.1	77.1	28.0
		XIS 36.0	5.8	36,700	128,100	3.5	136.8	98.0
		HIS 59.4	3.6	48,300	180,500	3.7	146.0	100.6
Phthalate-based	P2	XS 4.9	22.4	3,100	24,100	7.8	78.6	39.2
		XIS 32.9	5.4	30,600	136,700	4.5	137.5	98.2
		HIS 62.2	3.4	65,100	211,500	3.2	144.6	97.6

(5.9%) of the phthalate-based catalyst. On the contrary, the hardly crystallizable fraction (XS) of the diether-based catalyst had a lower triad "EEE" portion (10.5%) than that (16.5%) of the phthalate-based catalyst. From these results it can be said that the diether-based catalyst forms a highly crystallizable fraction (HIS) with a blockier monomer sequence; this fraction seems to affect the blockier monomer sequence of the whole copolymer. In addition, it is likely that this fraction leads the above melting and crystallization behavior of the copolymer formed by the diether-based catalyst to be different from those behaviors when using the phthalate-based catalyst.

Terpolymerizations of propylene, ethylene, and 1-butene with the two catalysts were carried out; the results are given in Table VI. Similar to that of the copolymer, the molecular weight distribution of the terpolymer with the diether-based catalyst was narrower than that with the phthalate-based catalyst. The ethylene reactivity of the diether-based catalyst was also slightly higher than that of the phthalate-based catalyst; the ratios of incorporated ethylene to fed ethylene were 2.05 (diether) and

1.71 (phthalate), respectively. These results are in line with the results of copolymerization. However, the 1-butene reactivity of the diether-based catalyst was slightly lower than that of the phthalate-based catalyst; the ratios of incorporated 1-butene to fed 1-butene were 0.57 (diether) and 0.63 (phthalate), respectively. It might be inferred from these results that, for the insertion of smaller monomers, the diether-based catalyst is preferred to the phthalate-based catalyst. Monomer sequence analysis of the terpolymers was also carried out using ^{13}C-NMR; the results are given in Table VII. Similar to the case of the copolymer, the triad "EEE" portions of the diether-based catalyst are two times higher than those of the phthalate-based catalyst (1.0 vs. 0.5 mol %). This means that the diether-based catalyst also produced a blockier sequence in the terpolymerization.

The terpolymers were also fractionated into three parts: hardly crystallizable fraction (XS), moderately crystallizable fraction (XIS), and highly crystallizable fraction (HIS). Table VIII shows the properties of each fraction. Similar to the case of the copolymers, the hardly crystallizable fraction (XS) had higher

Table V. The Monomer Sequence of Copolymers Fractions Measured with ^{13}C-NMR

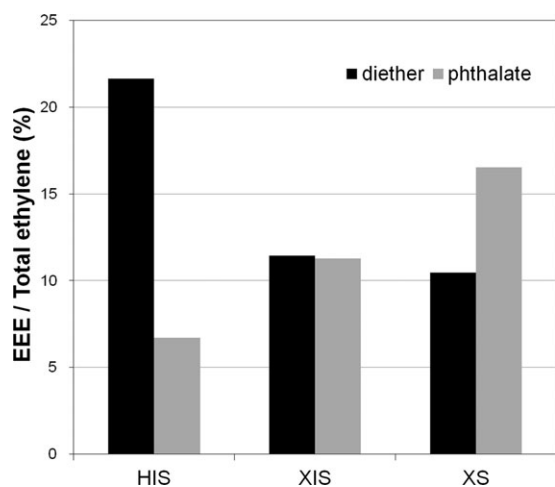| Catalyst	Sample code	Fraction	monad (mol %)		Triad (mol %)						$r_1 \times r_2$
			P	E	PPP	PPE	EPE	PEP	EEP	EEE	
Diether-based	D2	XS	80.9	19.1	55.2	22.0	3.6	11.8	5.3	2.0	1.5
		XIS	94.2	5.8	84.7	9.3	0.2	4.5	0.6	0.7	3.9
		HIS	96.4	3.6	91.0	5.4	0.1	2.6	0.1	0.8	9.9
Phthalate-based	P2	XS	77.6	22.4	51.9	21.0	5.0	11.6	6.9	3.7	1.9
		XIS	94.6	5.4	86.1	8.2	0.4	4.1	0.6	0.6	4.1
		HIS	96.6	3.4	90.8	5.7	0.1	2.8	0.3	0.2	4.3

Figure 3. The triad "EEE" portion in total incorporated ethylene of copolymer fractions.

ethylene content and lower molecular weight, and the highly crystallizable fraction (HIS) had lower ethylene content and higher molecular weight in both two catalysts. However, the contents of 1-butene in the three fractions were similar. The difference of molecular weight among the three fractions was smaller and the peak temperatures of melting and crystallization of the highly crystallizable fraction (HIS) were also higher in the case of the diether-based catalyst. These results are in line with the results for the copolymers.

Monomer sequence analysis of the fractions was carried out using ^{13}C-NMR; the results are given in Table IX. In the highly crystallizable fraction (HIS), the triad "EEE" portion of the diether-based catalyst is 1.1 mol % while that of the phthalate-based catalyst is only 0.1 mol %. On the other hand, the triad "EEE" portion of the diether-based catalyst in the hardly crystallizable fraction (XS) is lower than that of the phthalate-based catalyst (2.7 vs. 5.2 mol %). These results are in agreement with the results for the copolymers and confirm that the diether-based catalyst forms a highly crystallizable fraction (HIS) with a blockier ethylene sequence.

In previous studies,[14–16] diether-based catalysts have shown more preference for 2,1-insertion (regio-irregular insertion) of propylene on growing polymer chains than have phthalate-based catalysts. The 2,1-insertion lowered the polymerization rate of propylene; the active site after 2,1-insertion became

dormant. Chain transfer with smaller hydrogen molecules after the 2,1-insertion can occur, and, consequently, diether-based catalysts showed hydrogen response higher than that of phthalate-based catalysts. Busico et al.[17] confirmed the higher regio-irregularity of diether-based catalysts by investigating copolymers of propylene and ethylene-[1-^{13}C]; they reported that, in the case of a diether-based catalyst, ethylene-[1-^{13}C] units adjacent to the 2,1-inserted propylene unit were found with more frequency.

As for our results in this study, higher ethylene incorporation and lower 1-butene incorporation in the case of the diether-based catalyst can be elucidated by the regio-irregular characteristics caused by 2,1-insertion errors of propylene. The active site after 2,1-insertion becomes sterically hindered and it is difficult to insert propylene. Smaller molecules than propylene, like hydrogen or ethylene, are more easily able to approach the sterically hindered active site; this made it possible to show increased ethylene reactivity in the copolymerization and terpolymerization. On the contrary, 1-butene, a larger molecule than propylene, is not easily inserted into the sterically hindered active site and 1-butene reactivity in the terpolymerization decreases as a result.

The phenomenon pertaining to the blockier ethylene sequence of copolymers from the diether-based catalyst can be also interpreted as an effect of the sterically indered active site after 2,1-insertion of propylene. An active site [Scheme 3(a)] after 2,1-insertion of propylene followed by ethylene can still be hindered sterically compared with an active site [Scheme 3(b)] after regio-regular insertion of propylene followed by ethylene; the former type of site can lead to the insertion of a small molecule (ethylene) more easily than that of a large molecule like propylene. According to previous studies,[14,17] regio-irregular defects in polymers formed using diether-based catalysts were found throughout polymer fractions regardless of their isotacticity. For example, in the case of a diether-based catalyst, a highly stereoregular fraction has a considerable number of the regio-irregular defects (0.15 mol %) compared with those of a stereo-irregular fraction (0.5 mol %). In the case of a phthalate-based catalyst, by contrast, the number of regio-irregular defects from a highly stereo-regular fraction is very much lower (0.078 mol %) than that from a stereo-irregular fraction (ca. 1.0 mol %). These results imply that, for diether-based catalysts, the difference throughout polymer fractions is smaller in terms of regio-regularity. In our study, the diether-based catalyst formed a highly

Table VI. The Results of Terpolymerization of Propylene, Ethylene, and 1-Butene Using the Diether- and Phthalate-Based Catalysts

Catalyst	Feed ratio		Polymer analysis						Ratio of incorporation ($C_2^=$)	Ratio of incorporation ($C_4^=$)
	$C_2^=$ (mol %)	$C_4^=$ (mol %)	$C_2^=$ (mol %)	$C_4^=$ (mol %)	M_w (g/mol)	MWD (M_w/M_n)	T_m (°C)	XS (wt %)		
Diether-based	2.2	6.0	4.5	3.4	255,200	4.2	129.2	6.2	2.05	0.57
Phthalate-based	2.4	5.6	4.1	3.5	264,400	5.4	129.4	8.0	1.71	0.63

Polymerization conditions: temperature = 60°C, pressure = 34.5 kg$_f$/cm^2, average retention time = 1.5 h.

Table VII. The Monomer Sequence of Terpolymers Measured with ^{13}C-NMR

Catalyst	Monad (mol %)			Triad (mol %)						
	P	E	B	PPP	PPE	EPE	PEP	EEP	EEE	XBX[a]
Diether-based	92.1	4.5	3.4	86.0	5.9	0.2	2.6	0.9	1.0	3.4
Phthalate-based	92.4	4.1	3.5	85.8	6.3	0.3	2.7	1.0	0.5	3.5

[a] X: ethylene, propylene, or 1-butene.

Table VIII. The Properties of Terpolymer Fractions with the Diether- and Phthalate-Based Catalysts

Catalyst	Fraction (wt %)	$C_2^=$ (mol %)	$C_4^=$ (mol %)	M_n (g/mol)	M_w (g/mol)	MWD (M_w/M_n)	T_m (ºC)	T_c (ºC)
Diether-based	XS 6.2	15.4	3.4	3,500	45,800	13.2	-	–
	XIS 37.9	3.8	3.6	64,400	221,100	3.4	128.3	85.1
	HIS 55.9	4.0	3.2	69,700	277,900	4.0	129.8	94.2
Phthalate-based	XS 8.0	24.1	3.4	6,200	74,200	11.9	-	–
	XIS 31.8	3.8	3.9	46,200	154,100	3.3	123.7	83.8
	HIS 60.2	2.4	3.3	109,800	354,500	3.3	127.3	90.5

crystallizable fraction (HIS) with blockier ethylene sequence compared that formed by the phthalate-based catalyst; these results seem to derive from the higher content of 2,1-inserted propylene and the lower difference of regio-irregularity among the three fractions in the polymers formed using the diether-based catalyst in contrast to the case of the phthalate-based catalyst.

CONCLUSIONS

In the copolymerizations of propylene and ethylene, a diether-based catalyst showed higher hydrogen response and ethylene incorporation than did a phthalate-based catalyst. Copolymers formed using the diether-based catalyst had narrower molecular weight distribution, similar to polymer produced with propylene only; however, these copolymers showed DSC melting curves with distinct shoulder peaks and many nuclei during crystallization. Analysis of the monomer sequence of the copolymers indicated that, compared with the phthalate-based catalyst, the diether-based catalyst led to copolymers having a blockier ethylene sequence. From an analysis of the fractionated parts (HIS: the highly crystallizable fraction, XIS: the moderately crystallizable fraction, and XS: the hardly crystallizable fraction), the diether-based catalyst produced a HIS fraction with a blockier ethylene sequence; this fraction seems to affect the melting and crystallization behaviors of polymers. In the case of the terpolymerizations of propylene, ethylene, and 1-butene, the diether-based catalyst showed higher incorporation of ethylene, as was the case in the copolymerization, but lower incorporation of 1-butene. Thus, it seems reasonable to conclude that the diether-based catalyst is preferred for the insertion of smaller monomers in polymerization. Analysis of the monomer sequence of the terpolymers and fractionated parts indicated that the diether-based catalyst also led to polymers having blockier ethylene sequences, especially in the highly crystallizable fraction (HIS). Proceeding from what has been said above, it can be concluded that, in copolymerization and terpolymerization, the diether-based catalyst makes polymers with blockier ethylene sequences compared with those formed using the phthalate-based catalyst. The above phenomena seem to

Table IX. The Monomer Sequence of Terpolymer Fractions Measured with ^{13}C-NMR

Catalyst	Fraction	Monad (mol %)			Triad (mol %)						
		P	E	B	PPP	PPE	EPE	PEP	EEP	EEE	XBX[a]
Diether-based	XS	81.1	15.4	3.4	61.6	17.4	2.2	7.9	4.8	2.7	3.4
	XIS	92.6	3.8	3.6	87.2	5.4	0.0	2.3	0.6	0.9	3.6
	HIS	92.8	4.0	3.2	87.7	5.1	0.0	2.3	0.6	1.1	3.2
Phthalate-based	XS	72.4	24.1	3.4	61.9	6.8	3.8	11.3	7.7	5.2	3.4
	XIS	92.3	3.8	3.9	85.7	6.4	0.2	2.8	0.6	0.4	3.9
	HIS	94.4	2.4	3.3	89.6	4.8	0.0	2.1	0.3	0.1	3.3

[a] X: ethylene, propylene, or 1-butene.
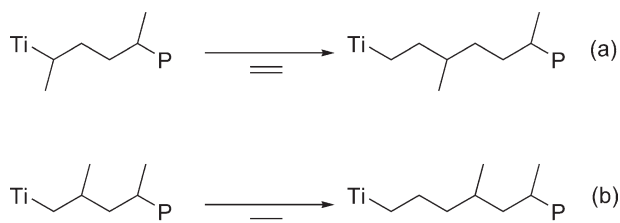
Scheme 3. Ethylene incorporation after (a) 2,1-insertion of propylene and (b)1,2-insertion of propylene.

result from the regio-irregular characteristics of the diether-based catalyst, namely the fact that sterically-hindered active sites formed by 2,1-insertion error of propylene. This work is important in that it provides practical data for commercial production because all polymerizations were performed in a reaction system of pilot scale similar to commercial production conditions.

REFERENCES

1. Albizzati, E.; Parodi, S.; Barbe, P. C. (Montedison and Mitsui Petrochemical). European Patent *86*,473, November 11, **1995**.

2. Albizzati, E.; Barbe, P. C.; Noristi, L.; Scordamaglia, R.; Barino, L.; Giannini, U.; Morini, G. (Himont). U.S. Patent 4,971,937, November 20, **1990**.

3. Morini, G.; Albizzati, E.; Balbontin, G.; Baruzzi, G.; Cristofori, A. (Basell). U.S. Patent 7,049,377, May 23, **2006**.

4. Cui, N.; Ke, Y.; Li, H.; Zhang, Z.; Guo, C.; Lu, Z.; Hu, Y. *J. Appl. Polym. Sci.* **2006**, *99*, 1399.

5. Morini, G.; Balbontin, G.; Gulevich, Y.; Kelder, R.; Duijghuisen, H.; Klusener, P.; Korndorffer, F. (Basell). European Patent 1,088,009, August 2, **2006**.

6. Matsunaga, K.; Hashida, H.; Tsutsui, T.; Yamamoto, K.; Shibahara, A.; Shinozaki, T. (Mitsui Chemicals). U.S. Patent 7,888,438, February 15, **2011**.

7. Wen, X.; Ji, M.; Yi, Q.; Niu, H.; Dong, J. *J. Appl. Polym. Sci.* **2010**, *118*, 1853.

8. Morini, G.; Balbontin, G.; Gulevich, Y.V. (Basell). European Patent 1,042,372, July 14, **2004**.

9. Yabunouchi, I.; Sadashima, T.; Funabashi, H. (Idemitsu Kosan). U.S. Patent 7,081,427, July 25, **2006**.

10. Tanase, S.; Katayama, K.; Yabunouchi, N.; Sadashima, T.; Tomotsu, N.; Ishihara, N. *J. Mol. Catal. A: Chem.* **2007**, *273*, 211.

11. Morini, G.; Albizzati, E.; Balbontin, G.; Mingozzi, I.; Sacchi, M.C.; Forlini, F.; Tritto, I. *Macromolecules* **1996**, *29*, 5770.

12. Yaluma, A. K.; Tait, P. J. T.; Chadwick, J. C. *J. Polym. Sci. Part A: Polym. Chem.* **2006**, *44*, 1635.

13. Yaluma, A. K.; Chadwick, J. C.; Tait, P. J. T. *Macromol. Symp.* **2007**, *260*, 15.

14. Chadwick, J. C.; Morini, G.; Albizzati, E.; Balbontin, G.; Mingozzi, I.; Cristofori, A. *Macromol. Chem. Phys.* **1996**, *197*, 2501.

15. Chadwick, J. C. *Macromol. Symp.* **2001**, *173*, 21.

16. Chadwick, J. C.; Morini, G.; Balbontin, G.; Camurati, I.; Heere, J. J. R.; Mingozzi, I.; Testoni, F. *Macromol. Chem. Phys.* **2001**, *202*, 1995.

17. Busico, V.; Chadwick, J. C.; Cipullo, R.; Ronca, S.; Talarico, G. *Macromolecules* **2004**, *37*, 7437.

18. Sacchi, M. C.; Forlini, F.; Tritto, I.; Locatelli, P.; Morini, G.; Noristi, L.; Albizzati, E. *Macromolecules* **1996**, *29*, 3341.

19. Chadwick, J. C.; Morini, G.; Balbontin, G.; Mingozzi, I.; Albizzati, E. *Macromol. Chem. Phys.* **1997**, *198*, 1181.

20. Barino, L.; Scordamaglia, R. *Macromol. Theory Simul.* **1998**, *7*, 407.

21. Correa, A.; Piemontesi, F.; Morini, G.; Cavallo, L. *Macromolecules* **2007**, *40*, 9181.

22. Andoni, A.; Chadwick, J. C.; Niemantsverdriet, H. J. W.; Thüne, P. C. *J. Catal.* **2008**, *257*, 81.

23. Stukalov, D. V.; Zakharov, V. A.; Potapov, A. G.; Bukatov, G. D. *J. Catal.* **2009**, *266*, 39.

24. Taniike, T.; Terano, M. *J. Catal.* **2012**, *293*, 39.

25. Bi, F.; He, A.; Li, H.; Hu, Y.; He, Z.; Han, C.C. *Polym. Int.* **2011**, *60*, 1167.

26. Soares, J. B. P. *Chem. Eng. Sci.* **2001**, *56*, 4131.