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Electron donor-induced improvement of the microstructure of polypropene-block-poly(ethene-co-propene) synthesized by a modified stopped-flow polymerization method and correlation with its crystalline morphology

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Abstract

The influence of electron donors on the synthesis of polypropene-block-poly(ethene-co-propene) (PP-b-(PE-co-PP)) using a modified stopped-flow polymerization method was examined in terms of correlation of the microstructure of the polymer with its crystalline morphology. The results of propene homopolymerization and ethene–propene copolymerization indicated that the application of suitable internal and external donors induced an improvement in the stereoregularity of polypropene (PP) without a decrease in the initial activity and a significant change in the monomer composition and monomer sequence distribution of the poly(ethene-co-propene) (PE-co-PP). The $TiCl_4$/ethylbenzoate/$MgCl_2$ – cyclohexylmethyldimethoxysilane catalyst system was found to produce PP-b-(PE-co-PP) having highly isotactic PP segments. The resulting block copolymers were investigated by cross-fractionation chromatography and differential scannning calorimetry, suggesting that the improved stereoregularity of the PP part in the PP-b-(PE-co-PP) had an effect only on the crystallinity and crystallinity distribution but had no influence on the crystallizability and lamellar thickness of the block copolymer. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Olefin block copolymer; Modified stopped-flow polymerization method; $MgCl_2$-supported Ziegler catalyst

1. Introduction

In world production of synthetic materials, polypropene (PP) holds the first place because of its specific properties involving easy processibility, low specific gravity and low production cost [1]. The impact-modified PP, the so-called PP block-type copolymer, exhibits improvements in mechanical properties over PP homopolymer by addition of 10%–20% of poly(ethene-co-propene) (PE-co-PP) [2,3]. The commercial block-type copolymer is typically prepared in situ in a two-reactor system, in which PP is made in the first reactor and PE-co-PP is made continuously in the second reactor [2,4]. It should be noted that PE-co-PP is not chemically linked to PP in the commercial block-type copolymer which can be regarded as a complicated composite of PP, PE-co-PP and polyethene (PE) [5–8].

In our previous study [9,10], the synthesis of polypropene-*block*-poly(ethene-co-propene) (PP-b-(PE-co-PP)) could be accomplished by a modified stopped-flow polymerization method in the presence of a $MgCl_2$-supported Ziegler catalyst. The stopped-flow polymerization method can be carried out within an extremely short period (ca. 0.1 s), which is shorter than the lifetime of the growing polymer chain [11]. The results of GPC, ^{13}C NMR, cross fractionation chromatography (CFC), differential scanning calorimetry (DSC), and optical microscopic observation indicated the formation of a block copolymer having a chemical linkage between PP and PE-co-PP. The regulation of the composition of each part in the block copolymer was achieved by changing the polymerization period [9,10]. The block formation was also confirmed by the results of the morphology observation and the mechanical properties [12].

From the industrial aspect, the control of crystalline–amorphous microstructure is considered to be one of the key technologies in obtaining a polymer having excellent

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properties. PP is a typical example of a polymer whose structure and properties, such as chain conformation, crystal structure, mechanical strength, etc., are profoundly affected by stereoregularity. The stereospecificity of $MgCl_2$-supported Ziegler catalysts has been markedly improved using suitable Lewis bases as internal and external donors [13–15]. The existence of electron donors also induces variations in the chemical composition and monomer sequence distribution of PE-co-PP [16–18], which are related closely to the elastomeric properties. Thus, it seems to be of interest to synthesize the block copolymers containing highly isotactic PP segments and PE-co-PP segments with high randomness.

In the current study, we examined the influence of electron donors on the microstructure of PP-b-(PE-co-PP) obtained by the modified stopped-flow method. The resulting block copolymers were evaluated using DSC and CFC in order to elucidate the effect of the improved stereoregularity of the PP part on the crystalline morphology including crystallinity, crystallinity distribution, and lamellar thickness of the block copolymer. Propene homopolymerization and propene–ethene copolymerization with various internal and external donors were also investigated in terms of the catalyst activity, molecular weight and its distribution and microstructure.

2. Experimental

2.1. Materials

$MgCl_2$ (11 m^2/g) and cyclohexylmethyldimethoxysilane (CMDMS) were kindly supplied by Toho Titanium Co., Ltd., Japan. Ethylbenzoate (EB), di-*n*-butylphthalate (DBP) (Wako Pure Chemical Industries, Ltd., Japan) and CMDMS were dried over molecular sieves 13X under a nitrogen atmosphere. $TiCl_4$ (Wako Pure Chemical Industries, Ltd., Japan) was used without further purification. Ethene and propene donated by Chisso Corp., Japan, were of research grade and were used without further purification. Triethylaluminum ($Al(C_2H_5)_3$, TEA, Tosoh Akzo Corp., Japan) was used as a toluene solution. Toluene was purified by passage through a molecular sieves 13X column.

2.2. Catalysts preparation

Two types of supported catalysts having different internal donors and an internal donor-free supported catalyst were used in this study. In all cases, the catalysts were used as a toluene slurry for polymerization.

A monoester-type supported catalyst ($TiCl_4/EB/MgCl_2$) was prepared by the reaction of the co-ground product of $MgCl_2$ and EB with $TiCl_4$ followed by washing with *n*-heptane. The catalyst was finally washed with toluene and stored as a toluene slurry [9,10]. The Ti content of the monoester-type catalyst was 0.33 mmol-Ti/g-cat.

A diester-type supported catalyst ($TiCl_4/DBP/MgCl_2$) was prepared as follows: $MgCl_2$ (36 g) and DBP (7.8 ml) were placed in a 1.2-L stainless steel vibration mill pot with 55 balls (25 mm diameter) under nitrogen and ground for 30 h at room temperature. The ground product (80 g) was allowed to interact with $TiCl_4$ (400 ml) in a 1-L three-necked flask at 90°C for 2 h with stirring under nitrogen, followed by washing with toluene. The Ti content of the diester-type catalyst was 0.38 mmol-Ti/g-cat.

An internal donor-free $MgCl_2$-supported Ziegler catalyst ($TiCl_4/MgCl_2$) was obtained in a manner similar to that reported previously [19, 20]. The catalyst was prepared by co-grinding $MgCl_2$, $TiCl_4$, and heptane, followed by the reaction with $TiCl_4$. Finally, the catalyst was washed with toluene. The Ti content of the internal donor-free catalyst was 0.39 mmol-Ti/g-cat.

2.3. Homo- and copolymerization using the stopped-flow technique

The stopped-flow polymerization was carried out according to the previously reported method [10,19,20]. The homopolymerization of propene was performed with a catalyst (0.47 mmol-Ti) and $Al(C_2H_5)_3$ (14 mmol, Al/Ti mole ratio = 30) in toluene at 30°C for 0.1–0.2 s. The propene concentration (0.71 mol/L) in toluene at 30°C was determined by gas chromatography (Yanaco G6800-CS-FS-G, Japan) with a porous polymer packed column (Waters Porapak® Q, 50–80 mesh, 1.5 m, USA).

The ethene–propene copolymerization was performed in a manner similar to that for the homopolymerization of propene mentioned earlier. A mixed gas was supplied into the vessels at atmospheric pressure for 60 min using a mass-flow controller. The composition of monomer feeds (ethene/propene mole ratio = 0.11) was adjusted to be the same as used in the synthesis of the block copolymer.

When EB or CMDMS was employed as an external donor, it was introduced into one of the vessels with $Al(C_2H_5)_3$. In our previous stopped-flow study [19], the effect of the pre-treatment of CMDMS with TEA with a variety of Al/donor mole ratios on the stereospecificity of the $MgCl_2$-supported catalyst was investigated in terms of the catalyst activity, microtacticity, and kinetic parameters. The results for propene polymerization after the pre-treatment of the TEA with CMDMS indicated that a maximum isotacticity with minor catalyst deactivation was obtained at an Al/donor mole ratio of 20. On the basis of these results, the polymerization of propene was carried out at an Al/donor mole ratio of 20 by the stopped-flow polymerization method.

2.4. Synthesis of block copolymer using the modified stopped-flow method

The synthesis of the block copolymer using the modified stopped-flow method was conducted according to the method reported previously [9,10]. The synthesis of the block copolymer was carried out with the catalyst

(0.47 mmol-Ti) and $Al(C_2H_5)_3$ (14 mmol, Al/Ti mole ratio = 30) in toluene at 30°C. When an external donor was used, it was introduced into one of the vessels with $Al(C_2H_5)_3$ to avoid unfavorable interaction of the external donor with the catalyst before the polymerization. The polymerization time of each block part was adjusted to be less than 0.10 s to avoid unfavorable chain transfer reactions. The propene and ethene concentrations in each vessel at 30°C were 0.71 and 0.15 mol/L, which were determined by gas chromatography. The polymerization was quenched in an ethanol/HCl solution as a quenching agent; the polymer obtained was then washed with distilled water and dried in vacuo.

2.5. Characterization of resulting polymers

The molecular weight and molecular weight distribution of the polymers obtained in this study were determined by gel permeation chromatography (GPC, Senshu SSC-7100, Japan) with polystyrene gel columns (Tosoh TSK-GEL G3000HHR and TSK-GEL G5000HHR, Japan) at 140°C using *o*-dichlorobenzene containing 2,6-di-*tert*-butyl-*p*-cresol (0.03 wt.%) as an antioxidant. The molecular weight was calculated by a standard procedure based on the universal calibration curve of PP.

^{13}C NMR spectra were recorded with a Varian Gemini-300 spectrometer operated at 75 MHz with proton decoupling at 120°C. The pulse interval was 5.2 s, the acquisition time was 0.8 s, the pulse angle was 90°, and the number of transients accumulated was 10,000. The polymer solutions were prepared by dissolving ca. 20% (w/v) of polymers in a mixture of 1,2,4-trichlorobenzene with 2,6-di-*tert*-butyl-*p*-cresol (0.03 wt.%). 25% (v/v) Benzene-d_6 was added as an internal lock and a small amount of hexamethyldisiloxane was used for internal chemical shift reference (2.03 ppm). The meso pentad fraction (*mmmm*) of the PP homopolymer was determined according to the method reported previously [21,22]. The monomer composition and monomer sequence distribution of PE-co-PP were estimated according to standard techniques [23,24]. The reactivity ratio products ($r_E \cdot r_P$) and the number-average sequence length of the ethene units were calculated from dyads and triads, respectively [25,26].

2.6. Cross fractionation chromatography

The crystallinity distribution of polymer samples obtained in this study was determined by cross-fractionation chromatography (CFC T-150A, Mitsubishi Petrochemical Co., Japan) with *o*-dichlorobenzene as an extraction solvent. Approximately 2 mg of sample (0.3 wt.% *o*-dichlorobenzene) was loaded onto a column of insert packing with slow cooling, followed by stepwise elution from the column at 0°C, 10°C, 20°C, 30°C, 40°C, 50°C, 60°C, 64°C, 68°C, 72°C, 76°C, 80°C, 84°C, 88°C, 92°C, 96°C, 100°C, 103°C, 106°C, 109°C, 112°C, 115°C, 120°C, 140°C at a flow rate of 1.0 ml min^{-1}. Each eluted polymer solution was automatically sent to the GPC section (Shodex AD-806NS, Showa Denko K. K., Japan) of the CFC system equipped with an infrared detector.

2.7. Thermal analysis

The melting temperature (T_m) and enthalpy of fusion (ΔH_f) of the polymer samples were measured by DSC (METTLER-TOLEDO calorimeter DSC 820, USA.) under the following conditions: heated from 50°C to 230°C at a heating rate of 10°C min^{-1}, held for 10 min, cooled to −100°C at a cooling rate of 1.0°C min^{-1}, held for 10 min, and heated from −100°C to 230°C at a scanning rate of 10°C min^{-1} (measurement of T_m) under a nitrogen atmosphere. The degree of crystallinity of PP (χ_c) was determined by the following equation [27,28],

$$\chi_c = \frac{\Delta H_f}{\Delta H_f^0}, \tag{1}$$

where ΔH_f is the enthalpy of fusion obtained for a given PP, as measured by DSC. ΔH_f^0 (209 J/g) denotes the folded-chain PP crystal [29,30]. In contrast, the enthalpy of fusion of the PP part in the PP-b-(PE-co-PP) ($\Delta H_{f,\,pp}$) is described by the following equation,

$$\Delta H_{f,pp} = \frac{Y_b}{Y_h} \cdot \Delta H_{f,block}, \tag{2}$$

where Y_h and Y_b are the yields of PP homopolymer corresponding to the PP part in the block copolymer and the PP-b-(PE-co-PP), respectively. $\Delta H_{f,\,block}$ is the enthalpy of fusion obtained for a given overall PP-b-(PE-co-PP). The degree of crystallinity was then also calculated using Eq. (1).

3. Results and discussion

Stereoregularity can be regarded as the most important factor in determining the crystalline morphology and the end-use properties of PP. In this work, our attention was focused on the influence of electron donors on the microstructure of the resulting PP-b-(PE-co-PP). Prior to investigating the block copolymer, the effect of donors on PP homopolymer and PE-co-PP was investigated using the stopped-flow method. The control of the crystalline–amorphous microstructure of the PP-b-(PE-co-PP) is thought to be attained by choosing suitable electron donors and appropriate polymerization conditions.

3.1. Influence of catalyst type on propene polymerization

Much effort has been devoted by many research groups to finding the best catalyst system including internal electron donors [31–33]. With this in mind, three different types of $MgCl_2$-supported Ziegler catalysts were used in this study. The propene polymerization was carried out with a variety of $MgCl_2$-supported catalysts in toluene at 30°C for ca. 0.1 s using the stopped-flow polymerization method. The results

Table 1
Results of propene polymerization with a variety of $MgCl_2$ supported Ziegler catalysts[a]

Catalyst	Activity (g mol-Ti^{-1} s^{-1})	$\overline{M}_n$[b]	$\overline{M}_w/\overline{M}_n$[b]	*mmmm*[c] (%)
$TiCl_4/MgCl_2$[d]	4100	5600	3.2	57.8
$TiCl_4$/EB[e]/$MgCl_2$	5000	9500	3.0	87.8
$TiCl_4$/DBP[f]/$MgCl_2$	200	7800	3.2	94.0

[a] Propene polymerization was conducted with the catalyst with $Al(C_2H_5)_3$ (Al/Ti = 30) at 30°C for ca. 0.1s.

[b] Molecular weight and its distribution were determined by GPC.

[c] Meso pentad fraction (*mmmm*) was determined by ^{13}C NMR.

[d] Internal donor-free catalyst.

[e] Ethylbenzoate (EB).

[f] Di-*n*-butylphthalate (DBP).

are summarized in Table 1. The catalytic activity was observed to decrease in the following order: $TiCl_4/EB/MgCl_2 > TiCl_4/MgCl_2 > TiCl_4/DBP/MgCl_2$. The molecular weight of PP obtained with the $TiCl_4/EB/MgCl_2$ catalyst system was apparently higher than those with other catalyst systems. In all cases, the molecular weight distributions were almost the same. The catalyst preparation procedure for $TiCl_4/EB/MgCl_2$ leads to high activity sufficient for the production of PP having high isotacticity even at the initial polymerization stage. Thus, $TiCl_4/EB/MgCl_2$ is considered to be the most suitable for the synthesis of the block copolymer, because of its higher initial activity and stereospecificity.

3.2. Influence of external donor on the stereoregularity of PP

A suitable combination of internal and external donors is required to improve the stereospecificity effectively [31]. In this section, the effect of an external donor on the improvement of the stereoregularity of PP was investigated in the stopped-flow polymerization with the $TiCl_4/EB/MgCl_2$-TEA catalyst system. The typical Lewis bases, EB and cyclohexylmethyl dimethoxysilane (CMDMS), were employed as external donors.

The propene polymerizations were conducted with and without an external donor in toluene at 30°C for ca. 0.1 s by stopped-flow polymerization. The improvement of the stereospecificity accompanied by slight catalyst deactivation was observed in the presence of CMDMS or EB to the catalyst system, as shown in Table 2. The molecular weight and its distribution were not sensitive to the presence of external donors. The higher value of the microtacticity of the resulting PP was achieved in the case of the polymerization with CMDMS (*mmmm* = ca. 96%). It was clear that the $TiCl_4/EB/MgCl_2$–CMDMS catalyst system showed excellent performance with regard to the improvement in the stereoregularity of PP and the high activity at the initial polymerization stage. Therefore, it is apparent that this catalyst system is the most suitable for the synthesis of tailor-made crystalline–amorphous olefin block copolymers by using the modified stopped-flow polymerization technique.

3.3. Effect of external donor on ethene–propene copolymerization

The effect of an external donor on the monomer composition and monomer sequence distribution of PE-co-PP was also investigated, the results of which are summarized in Table 3. The values of the triads distribution in the PE-co-PP obtained with and without CMDMS were found to be almost the same. Further, there is no significant differences in the ethene content, the reactivity ratio products ($r_E \cdot r_P$), and the number-average sequence length of the ethene units (n_E). A minor influence of CMDMS on the molecular weight and molecular weight distribution of the copolymer was observed, which is a tendency similar to that in the case of the homopolymerization of propene. Thus, the addition

Table 2
Influence of external donor on propene polymerization with $TiCl_4/EB/MgCl_2$ catalyst[a]

Code	External donor	Yield (g/mol-Ti)	$\overline{M}_n$[b]	$\overline{M}_w/\overline{M}_n$[b]	*mmmm*[c] (%)
P-1	—	500	9500	3.0	87.8
P-2	EB[d]	470	9000	3.2	90.0
P-3	CMDMS[e]	420	10000	3.4	95.7

[a] Propene polymerization was conducted with the catalyst with $Al(C_2H_5)_3$ (Al/Ti = 30) at 30°C for 0.1 s after the pre-treatment of an external donor with TEA (Al/donor = 20) for 20 min.

[b] Molecular weight and its distribution were determined by GPC.

[c] Meso pentad fraction (*mmmm*) was determined by ^{13}C NMR.

[d] Ethylbenzoate (EB).

[e] Cyclohexylmethyldimethoxysilane (CMDMS).

Table 3
Influence of external donor on monomer composition and monomer sequence distribution of PE-co-PP obtained with $TiCl_4/EB/MgCl_2$ catalyst[a]

External donor	Triad sequence distribution (mol%)[b]						Ethene content (mol%)[b]	$r_E \cdot r_P$ [c]	n_E [d]
	PPP	PPE	EPE	PEP	PEE	EEE			
None[e]	22.6	19.0	8.9	10.4	13.8	25.3	49.5	3.7	2.9
CMDMS[f]	24.0	20.0	8.2	8.9	14.4	24.5	47.8	3.5	3.0

[a] Ethene–propene copolymerization was conducted with the catalyst and TEA (Al/Ti = 33) at 30°C for ca. 0.1 s.
[b] Triad sequence distribution and ethene content were determined by ^{13}C NMR.
[c] Reactivity ratio products was calculated from dyads.
[d] The number-average sequence length of ethene units was calculated from triads.
[e] Activity (g mol-Ti^{-1} s^{-1}) = 5500, $\overline{M}_n = 9700$, $\overline{M}_w/\overline{M}_n = 3.3$.
[f] Activity (g mol-Ti^{-1} s^{-1}) = 4600, $\overline{M}_n = 10,000$, $\overline{M}_w/\overline{M}_n = 2.5$.

of CMDMS to the $TiCl_4/EB/MgCl_2$ catalyst system had an effect predominantly on the improvement in stereospecificity but had scarcely any effect on the reactivity of ethene and propene during the initial polymerization stage. Hence, the stopped-flow polymerization with the $TiCl_4/EB/MgCl_2$–CMDMS catalyst system is considered to be applicable to the synthesis of the block copolymer having controlled crystalline–amorphous microstructure and excellent properties.

3.4. Synthesis of polypropene-block-poly(ethene-co-propene) using modified stopped-flow polymerization method

The synthesis of PP-b-(PE-co-PP) was conducted with the $TiCl_4/EB/MgCl_2$–CMDMS catalyst system at 30°C for an extremely short period (0.1–0.2s). The PP-b-(PE-co-PP)s were also synthesized without an external donor as a comparison. A slight catalyst deactivation was observed with the addition of CMDMS, while the influence on the molecular weight and its distribution in the block copolymer was negligibly small, as can be seen in Table 4. This behavior is similar to the case of propene homopolymerization and ethene–propene copolymerization using the stopped-flow method described in the previous section. Irrespective to the presence of CMDMS, the polymer yield and the molecular weight of the block copolymer increased with time. The values of the molecular weight distribution were almost the same, independent on the polymerization time in both cases. On the basis of the results, it may be reasonable to consider that the polymerization proceeds without unfavorable chain-transfer and termination reactions and that the states of the active sites on the catalyst are constant under the conditions used for the synthesis of the block copolymers. This means that the formation of a block copolymer having a chemical linkage between PP and PE-co-PP occurs, independently of whether or not CMDMS is present as an external donor. Therefore, the synthesis of PP-b-(PE-co-PP) including the high isotactic PP segment was considered to be achieved using the $TiCl_4/EB/MgCl_2$–CMDMS catalyst system. The chain length of each kind of block could be controlled by changing the polymerization time. The possibility of design and synthesis of controlled crystalline–amorphous olefin block copolymer using the modified stopped-flow polymerization method was verified in this study.

3.5. Characterization of resulting block copolymers

The crystalline morphology, including crystallinity, crystallinity distribution, and lamellar thickness of the PP

Table 4
Synthesis of PP-b-(PE-co-PP) by the modified stopped-flow polymerization method[a]

Sample	External donor	Polym. time (s)		Yield (g/mol-Ti)	$\overline{M}_n$ [b]	$\overline{M}_w/\overline{M}_n$ [b]
		PP	PE-co-PP			
B-1	None	0.05	0.05	650	6500	3.2
B-2		0.05	0.10	1050	9000	3.1
B-3		0.10	0.05	900	12,000	3.1
B-4		0.10	0.10	1300	14,000	3.0
B-5	CMDMS[c]	0.05	0.05	550	7000	3.3
B-6		0.05	0.10	890	9000	3.4
B-7		0.10	0.05	760	12,000	3.1
B-8		0.10	0.10	1100	14,000	3.3

[a] Synthesis of block copolymer was conducted with $TiCl_4/EB/MgCl_2$ catalyst and TEA (Al/Ti = 30) at 30°C for 0.1–0.2 s.
[b] Molecular weight and its distribution were determined by GPC.
[c] Synthesis of block copolymer was carried out after the pretreatment of CMDMS with TEA (Al/donor ratio = 20) for 20 min.

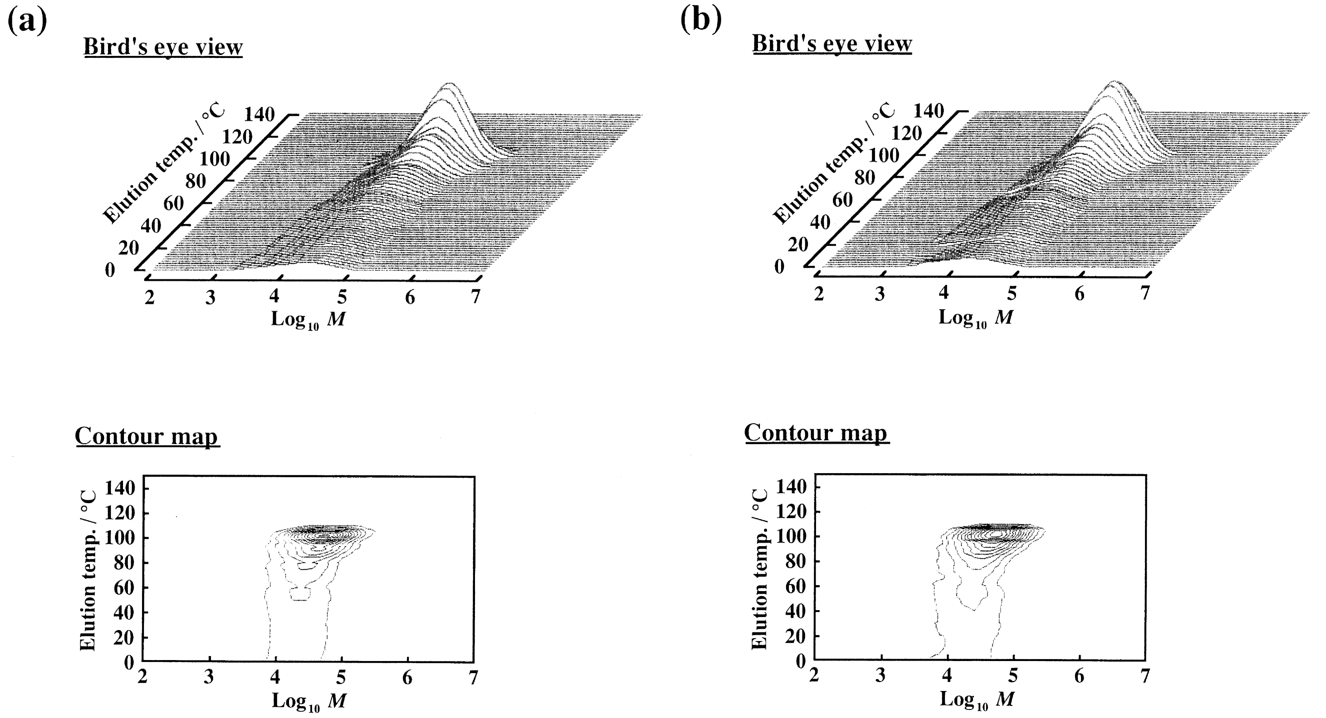

Fig. 1. Bird’s eye view (differential-type) and the corresponding contour maps of PP-b-(PE-co-PP)s obtained without (a, sample: B-4) and with CMDMS (b, sample: B-8) by CFC.

homopolymer, is mainly dependent upon the stereoregularity [34]. In the previous section, it was found that the addition of an external donor to the catalyst system induces an improvement in the stereoregularity of the PP part in the block copolymer. Here, the question arises regarding whether the improved stereoregularity of the PP part in PP-b-(PE-co-PP) affects the crystalline morphology. The arrangement of the block copolymer obtained in this study is expected to be complicated because of the crystalline PP part and the co-existence of the amorphous PE-co-PP part that are chemically linked. In order to clarify this point, the resulting block copolymers were characterized by CFC and DSC.

The CFC technique is considered to be suitable for the evaluation of the crystallinity, crystallinity distribution, and crystallizability of the block copolymer. A comparison of the structural heterogeneity between the block copolymers obtained with and without CMDMS was made by means of CFC. Fig. 1 shows a bird’s eye view (differential-type) of PP-b-(PE-co-PP)s obtained by CFC, and the corresponding contour maps. These figures clearly show that PP-b-(PE-co-PP)s eluted at each temperature region between 0°C and 120°C are mainly composed of a unified component. The bird’s eye view and the contour maps of the resulting PP-b-(PE-co-PP)s remained the same, regardless of the presence of CMDMS. This result suggests that the addition of

Table 5
Characterization of fractionated block copolymers obtained with and without CMDMS

Elution temp (°C)	Without CMDMS[a]			With CMDMS[b]		
	Wt. Fraction[c] (%)	$\overline{M}_n$[d]	$\overline{M}_w/\overline{M}_n$[d]	Wt. Fraction[c] (%)	$\overline{M}_n$[d]	$\overline{M}_w/\overline{M}_n$[d]
0–30	42.1	10,000	2.4	37.2	8800	2.3
30–45	5.4	14,000	2.1	6.0	13,000	2.0
45–82	16.8	17,000	1.8	17.5	17,000	1.7
82–96	13.7	27,000	1.8	16.0	26,000	1.7
96–112	22.0	38,000	1.8	23.3	38,000	1.7

[a] Sample: B-4, see Table 4.

[b] Sample: B-8, see Table 4.

[c] Weight fraction of each eluted polymer was estimated from the data of temperature rising electron fractionation section of CFC system.

[d] Molecular weight and its distribution were determined by the GPC section of the CFC system.

Table 6
Thermal properties and crystallinity of PPs and PP-b-(PE-co-PP)s

Sample[a]	T_m (°C)[b]	ΔH_f (J/g)		χ_c[d] (wt.%)
		obs.[b]	calc.[c]	
P-1	158	123	—	59
B-4	154	33	86	41
P-3	159	135	—	65
B-8	154	39	102	49

[a] See Tables 2 and 4.

[b] Melting temperature (T_m) and heat of fusion (ΔH_f) of polymers were observed by DSC.

[c] Heat of fusion of PP part in the PP-b-(PE-co-PP)s was calculated from Eq. (2), see Section 2.

[d] Crystallinity (χ_c) was calculated from Eq. (1), see Section 2.

CMDMS to the catalyst system has no influence on the crystallizability of the block copolymer obtained. As shown in Table 5, it turns out that each fraction possesses a narrow molecular weight distribution ($\overline{M}_w/\overline{M}_{n\approx 2}$) with a different molecular weight. There were no significant differences between the block copolymers in the values of the molecular weight eluted at each temperature. However, the weight of the fraction eluted at 30°C–112°C was found to increase in the case of the block copolymer obtained with CMDMS. These results suggest that the improvement of the stereoregularity of the PP part affected only the crystallinity distribution but had no influence on the crystallizability of the block copolymer.

The crystallizability of a polymer chain is a critical factor which governs lamellar thickness. As is well-known, the melting temperature (T_m) is related to the lamellar thickness, and the enthalpy of fusion (ΔH_f) depends on the degree of crystallinity. Thus, these values of resulting block copolymer and PP homopolymer were determined from DSC measurements, the results of which are presented in Table 6. The PP-b-(PE-co-PP)s exhibit a lower melting temperature, compared with that of PP homopolymers. It is suggested that the depressing of the recrystallization or rearrangement process of the PP crystal occurs because of the chemically linked PE-co-PP part to give a thinner crystal [12]. No difference in the melting temperatures between the polymers prepared with and without CMDMS was observed, whereas the addition of CMDMS to the catalyst system was found to induce an increase in ΔH_f of the PP-b-(PE-co-PP) and PP. Further, the degree of crystallinity of the PP part in the block copolymer obtained with CMDMS was apparently higher than that without an external donor. These results suggest that the addition of CMDMS to the catalyst system had an effect only on the crystallinity and crystallinity distribution but had no influence on the crystallizability and lamellar thickness during the melt-crystallized process in this study. This means that the improvement in the stereoregularity of the PP part reduces the amorphous layer thickness without a change in the lamellar crystal thickness in the block copolymer.

4. Conclusions

In this article, the application of electron donors for the synthesis of PP-b-(PE-co-PP) using a modified stopped-flow polymerization method is introduced as a part of our program of developing a technique for the design and synthesis of novel polyolefins having a well-defined structure and excellent properties. It was substantiated that the $TiCl_4$/EB/$MgCl_2$–CMDMS catalyst system was suitable for the improvement of the stereoregularity of the PP part in the block copolymer without a significant change in the monomer composition and monomer sequence distribution in the PE-co-PP part. The results from CFC and DSC measurements indicated that the improved stereoregularity of the PP part had an effect only on the crystallinity and crystallinity distribution, but had no influence on the crystallizability and lamellar thickness of the block copolymer. Therefore, the correlation of the catalyst systems including electron donors with the microstructure and crystalline morphology of the resulting block copolymers has been clarified by the present study. This finding has great importance from the scientific viewpoint and industrial application, such as exploiting the state-of-the-art crystalline-amorphous olefin block copolymer.

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