Influence of Electron Donors on the Initial Stage of Cyclopolymerization of 1,5-Hexadiene with $MgCl_2$-Supported Ziegler Catalysts Analyzed by Temperature Rising Elution Fractionation

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ABSTRACT: Additive effects of donors on the initial polymerization of 1,5-hexadiene with the $MgCl_2$-supported Ziegler catalysts were investigated by using the stopped-flow method, temperature rising elution fractionation (TREF) analysis, and kinetic study. The cyclopolymerization of 1,5-hexadiene proceeded within an extremely short period ($\leq$ 0.2 s) and yielded a unique poly(methylene-1,3-cyclopentane). *cis* ring content and *cis–cis* unit in meso dyad of the resulting polymer were increased by the addition of electron donors. The influence of internal and external donors was examined by the estimation of kinetic parameters and TREF analysis. Because the addition of the internal donor caused an obvious change in one of the kinetic parameters and the microstructure, an isospecific active site was considered to be formed by the addition of the internal donor. In the case of the external donor, the additive effects on the stereospecificity were weaker than those of the internal donor. It was expected from TREF measurements that the external donor modified an aspecific active site into a lower isospecific active site. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 2976–2983, 2002; DOI 10.1002/app.2326

Key words: ziegler catalyst; 1,5-hexadiene; cyclopolymer; stopped-flow method; electron donor

INTRODUCTION

In the polymerization of propene with $MgCl_2$-supported Ziegler catalyst systems, electron donors used as internal and external donors play an important role in improving the stereospecificity of the catalyst systems. The role of electron donors has been proposed by many investigators.[1–4] Zambelli et al.[3] have suggested that internal donors have no effect on isospecific active sites and inhibit the formation of aspecific active sites through titanium fixation, whereas Soga et al.[4] proposed that coordination of internal donor caused an aspecific active site to transform into an

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isospecific active site. In the case of the external donor,[1–5] it is generally accepted that the dominant role is the selective poisoning of aspecific active sites, and the other role is to change some of the potentially aspecific centers into isospecific ones. These considerations, however, are questionable because many investigations on the mechanism of donors were mainly based on the analyses of the resulting polymer. Chain-transfer and termination reactions occur during the olefin polymerization, suggesting that the polymerization behavior and the structure of the resulting polymer do not accurately reflect the nature of the active sites. To study the interaction of an electron donor with the active site, it is necessary to perform the polymerization without side reactions.

The stopped-flow polymerizations of propene and 1,5-hexadiene with an $MgCl_2$-supported Ziegler catalyst was investigated to demonstrate that the polymerization proceeded in a quasi-living stage.[6,7] In particular, it was possible to observe the initial stage of the 1,5-hexadiene polymerization with the stopped-flow method, suggesting that there were two distinct stereochemical events in the cyclopolymerization. The cyclopolymer of 1,5-hexadiene is poly(methylene-1,3-cyclopentane) having four microstructures. As shown in Scheme 1 , the enantioselectivity of the first insertion step is determined from the tacticity, whereas the diastereoselectivity of the second cyclization step is determined from the fraction rate of a *cis* or *trans* ring.[8–10] The microstructure of the resulting cyclopolymer is expected to reflect the chemical and stereochemical events only on the active sites.

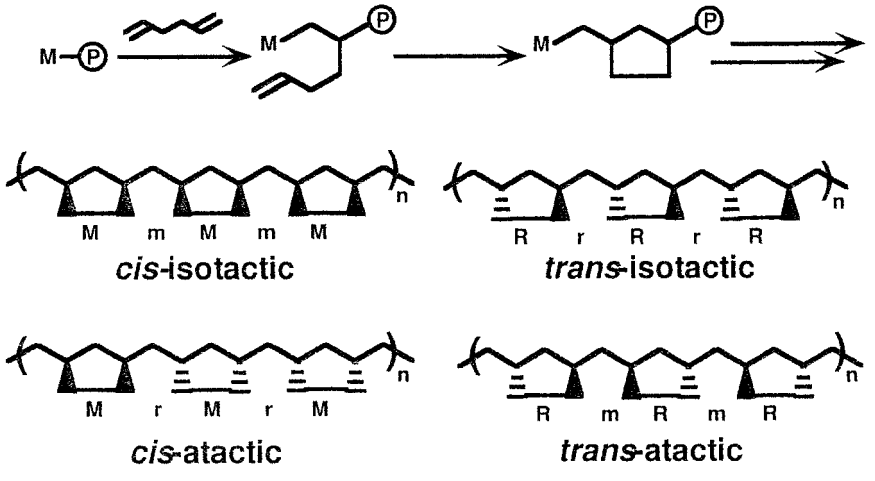
Temperature rising elution fractionation (TREF) analysis is known to separate polymer chains by stereochemistry, geometric isomerism, and molecular weight. We have previously reported that the TREF analysis of the cyclopolymer of 1,5-hexadiene obtained by the stopped-flow method had great potential as an effective tool for elucidation of the microstructural heterogeneity of polymers, which are considered to be related to the active sites and their properties.[7] Accordingly, the influence of the internal and external donor on stereospecificities is thought to be observable through the analyses of the polymer obtained at the initial polymerization stage of 1,5-hexadiene.

In this article, we have studied the effect of donors on the kinetic parameters and the microstructural heterogeneities of the resulting cyclopolymers, with the aim of clarifying interactions of electron donors with the $MgCl_2$-supported Ziegler catalysts. Our approach was based on the fractionation of the resulting polymers using TREF, combined with the stopped-flow polymerization technique. The TREF analysis of the cyclopolymers obtained by the stopped-flow method is thought to provide reliable information on the active sites just after the formation. Therefore, it is considered that the use of these methods is a promising approach to elucidate the changes in the states of the active sites by interaction with an electron donor and their influence on the stereoregulating cyclopolymerization behavior.

EXPERIMENTAL

Materials

1,5-Hexadiene (purchased from Tokyo Chemical Industry, Japan) was refluxed and distilled over CaH_2 (purchased from Nacalai Tesque, Inc., Kyoto, Ja-



Scheme 1 Cyclopolymerization of 1,5-hexadiene.

pan). $MgCl_2$ and cyclohexylmethyldimethoxysilane (CMDMS) were kindly donated by Toho Titanium Co., Ltd. (Japan). Ethyl benzoate (EB) (Wako Pure Chemical Industries, Ltd., Japan) and CMDMS were dried over molecular sieves 13× Wako) under a nitrogen atmosphere. Triethyl aluminum (TEA, donated by Tosoh Akzo Corp., Japan) and CMDMS were used as a toluene (Wako) solution. Toluene was purified by passing it through a column of molecular sieve 13×.

Catalysts Preparation

Two types of highly active $MgCl_2$-supported Ziegler catalysts were employed in this study to clarify the effect of the catalyst type on the formation and deactivation of the active sites. The monoester-type catalyst ($TiCl_4$/EB/$MgCl_2$, A) was prepared by cogrinding $MgCl_2$ and EB, followed by the reaction with $TiCl_4$ according to the method previously reported.[11] The catalyst was used as a toluene slurry, and the Ti content of the catalyst was 0.35 mmol-Ti/g-cat.

An internal donor-free catalyst ($TiCl_4$/$MgCl_2$, B) was prepared according to the method previously reported.[12] $MgCl_2$ (36 g), $TiCl_4$ (108 mL), and toluene (108 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 (200 mL) was treated with $TiCl_4$ (200 mL) in a 1-L three-necked flask at 90°C for 2 h with stirring under nitrogen, followed by washing with heptane. The catalyst was used as a toluene slurry, and the Ti content of the catalyst was 0.38 mmol-Ti/g-cat.

Cyclopolymerization of 1,5-Hexadiene and Estimation of Kinetic Parameters

The stopped-flow polymerization and estimation of kinetic parameters were carried out according to the method reported previously.[11–16] The stopped-flow polymerization of 1,5-hexadiene was conducted with each of the catalysts (A: 1.3 g; B: 1.2 g; 0.47 mmol-Ti) and TEA (70 mM, Al/Ti mol ratio = 30) in toluene at 30°C in a manner similar to the previously reported method.[6,7] The toluene slurry (100 mL) of the catalyst and TEA solution in toluene (100 mL), including 1,5-hexadiene ([M] = 1.0*M*), were placed in the respective vessels. The slurry and the solution were forced to flow simultaneously through a Teflon tube from the vessels into a flask containing a quenching agent under a small pressure of nitrogen. The polymerization occurred in the Teflon tube from the contact point with the catalyst and cocatalyst to the quenching point in the flask. The polymerization time was adjusted to 0.1–0.2 s. The polymer obtained was washed with distilled water and dried *in vacuo* at 60°C for 2 h.

The propagation rate constant (k_p) and active sites concentration ([C^*]) were determined by:

$$\bar{M}_n = M_0 \frac{k_p[M]t}{1 + k_{tr}t} \quad (1)$$

$$Y = k_p[M][C^*]t \quad (2)$$

where $\bar{M}_n$, M_0, [M], t, Y, and k_{tr} are the number-average molecular weight of the polymer, the molecular weight of the monomer, the monomer concentration, the polymerization time, the polymer yield, and the transfer rate constant, respectively.

Temperature Rising Elution Fractionation Analysis

TREF analysis was performed with an on-line system (Senshu SSC-7300) with *o*-dichlorobenzene (ODCB) containing 0.03 wt % of 2,6-di-*tert*-butyl-*p*-cresol as an antioxidant. The fraction column, 10 mm in diameter and 30 cm in length, loaded with Chromosorb (Celite Corp.) was used for the characterization to obtain the TREF profile. Based on the results, the fractionation of the samples was conducted by using a wider column (diameter: 30 mm; length: 30 cm) in the system. About 70 mg polymer was dissolved in 10 mL ODCB at 140°C, and a part of the solution (6 mL, ~ 7 mg/mL) was eluted through the fraction column in the case of the characterization. For the fractionation of the polymers, ~ 1.5–1.6 g of sample was dissolved in 60–70 mL of ODCB at 140°C, and a part of the solution (50 mL, ~ 24 mg/mL) was eluted through the wider column; the column was then slowly cooled (6.7°C/h) to 10°C for polypropene and 20°C for the cyclopolymer. Elution with ODCB (1500 mL/h) was first carried out at 10 or 20°C for 2–3 h to obtain the ODCB-soluble fraction. The column was heated in incremental steps of temperature (20, 38, 51, 68, 100°C for the cyclopolymer, and 10, 50, 100, 107, 140°C for polypropene) and eluted with ODCB. At each step, the elution temperature slowly increased for a period of 2 h and then remained constant for several hours until the peak of the sample disappeared in the refractive index detector. The polymers of each fraction were recovered by evaporating the ODCB solvent. The sample was then washed several times with acetone, filtered with a

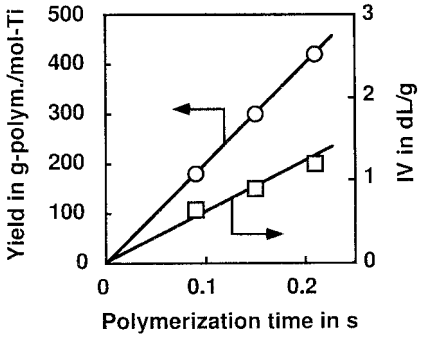


Figure 1 Dependence on polymerization time of polymer yield (○), intrinsic viscosity (IV, □) of resulting cyclopolymer obtained with the monoester-type catalyst by the stopped-flow polymerization of 1,5-hexadiene.

1-μm polytetrafluoroethylene (PTFE) filter (Advantec, T100A047A), and dried *in vacuo* at 60°C.

Measurements

A gel permeation chromatography (GPC, Senshu SSC-7100)–viscometry (viscometer detector H502B, Viscotek) module was used for the characterization of the resulting polymers. The intrinsic viscosity of the cyclopolymer of 1,5-hexadiene was determined by the module at 140°C by using ODCB as a solvent. The GPC section was equipped with a polystyrene gel column (Jordi-Gel DVB Mixed Bed). The intrinsic viscosity of the cyclopolymer was converted to M_n by using a calibration curve with a standard polystyrene.

^{13}C-NMR spectra were recorded on a Varian Gemini-300 spectrometer at 120°C on 20% (w/v) solution in 1,2,4-trichlorobenzene (pulse width = 90°; delay time = 5 s). Ten percent (w/v) benzene-d_6 was added as an internal lock, and hexamethyldisiloxane was used as an internal chemical shift reference (2.03 ppm). The microstructure of the cyclopolymer was determined by using a procedure similar to that described in the preceding article.[17]

RESULTS AND DISCUSSION

The initial polymerization stage of 1,5-hexadiene with $MgCl_2$-supported Ziegler catalysts was examined on the basis of the microstructural heterogeneity of the cyclopolymers, which are considered to be related to the active sites on the catalyst. The cyclopolymerization of 1,5-hexadiene is thought to have an advantage in investigating the nature and distribution of the active sites, because the microstructure of the resulting cyclopolymer is affected not only by the enantioselectivity for insertion but also by the diastereoselectivity for cyclization. The microstructures of the cyclopolymer obtained at the initial polymerization stage of 1,5-hexadiene by means of the stopped-flow method were thought to be affected by the nature of active sites on the $MgCl_2$-supported Ziegler catalysts just after their formation. Accordingly, the influence of the internal and external donors on stereospecificities is considered to be observable through the analysis of the polymer obtained at the initial polymerization stage of 1,5-hexadiene. As mentioned in the introduction, our attention was focused on the multiplicity of the active sites and their interaction with the electron donors.[1]

Change in Kinetic Parameters on Cyclopolymerization of 1,5-Hexadiene by Addition of Internal Donor

The effect of the internal donor on the polymerization behavior was examined with $MgCl_2$-supported Ziegler catalysts. Cat. A and B, having different stereospecificities, were required in this study to evaluate more obviously the change in the kinetic parameters and the microstructures of the cyclopolymer. The cyclopolymerization was carried out in toluene at 30°C by using the stopped-flow method with two types of $MgCl_2$-supported Ziegler catalysts, the results of which are shown in Figures 1 and 2 and Table I. The yield and intrinsic viscosity of the cyclopolymer obtained with both catalysts were apparently proportional to polymerization time up to about 0.2 s.

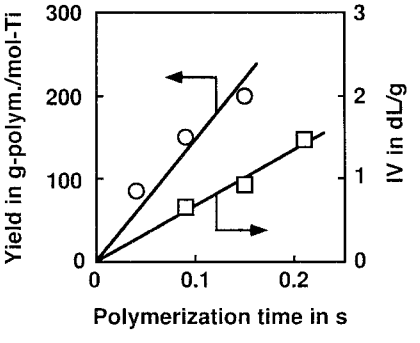


Figure 2 Dependence on polymerization time of polymer yield (○), intrinsic viscosity (IV, □) of resulting cyclopolymer obtained with the internal donor-free catalyst by the stopped-flow polymerization of 1,5-hexadiene.

Table I Stopped-Flow Polymerization of 1,5-Hexadiene with $MgCl_2$-Supported Ziegler Catalysts and $Al(C_2H_5)_3$ in Toluene at 30°C[a]

Cat. Type	External Donor	Yield (g/mol-Ti)	IV[b] (dL/g)	*cis*[c] (%)	*c–c*[d] (%)	*t–t*[e] (%)
$TiCl_4/EB/MgCl_2$	—	300	0.96	58	37	27
	EB	310	0.91	59	39	21
	CMDMS	320	0.89	64	38	22
$TiCl_4/MgCl_2$	—	200	0.93	45	26	34
	EB	190	0.86	47	34	28
	CMDMS	190	0.88	49	35	26

[a] Polymerization conditions; [Al], 70 mmol/L; Al/Ti, 30; Al/D, 20, polymerization time, 0.15 s.
[b] Intrinsic viscosity (IV) was determined by GPC-viscometry module (ODCB, 140°C).
[c] Determined by ^{13}C-NMR.
[d] *cis–cis* unit in meso dyad.
[e] *trans–trans* unit in meso dyad.

The results indicate that the cyclopolymerization proceeds without chain transfer and termination reactions and that the states of the active sites on the catalysts have not changed, regardless of the catalyst system. Additionally, there was no induction period, indicating that the formation of the polymerization center is rapid, which is completed within 0.01 s. The polymerization yields the crystalline polymer, in which all of the monomer units approximately cyclized within an extremely short period (< 0.2 s). Thus, it is considered that the cyclization is faster than propagation. As shown in Table I, the stereospecificity of cat. A was superior to that of cat. B. (The stereoselectivities of the cyclopolymers obtained with both catalysts were significantly different. The value of the *cis* ring content and the *cis–cis* unit increased with the addition of an internal donor. On the other hand, the *trans–trans* unit decreased with the addition of an internal donor.)

Kinetic parameters, propagation rate constant (k_p), and active sites concentration ([C^*]) were estimated from the polymer yield and number-average molecular weight of the resulting polypropene using eqs. (1) and (2). The kinetic parameters of cat. A were $[C^*]_A$ = 0.7 mol % and k_{pA} = 3700 L mol/s. In the case of cat. B, the kinetic parameters were $[C^*]_B$ = 0.4 mol % and k_{pB} = 3600 L mol/s, respectively. The addition of the internal donor caused an increase in [C^*] ($[C^*]_A/[C^*]_B$ = 1.8), but the k_p was almost constant (k_{pA}/k_{pB} = 1.0). In our previous study, the propene polymerization with cat. A showed an increase in k_p (k_{pA}/k_{pB} = 2.5) and a decrease in [C^*] ($[C^*]_A/[C^*]_B$ = 0.5), compared with cat. B.[12,13] In general, it was suggested that the active sites on the catalyst surface have vacant sites and that the stereospecificity of the catalyst is generated on the basis of the number of the vacant sites.[4] In propene polymerization, it is regarded that the active sites having two vacant sites produce the atactic polymer, and the other active sites having one vacant site produce the isotactic polymer. The internal donor seems to exist in the vicinity of the vacant sites on the $MgCl_2$ surface and to transform an aspecific active site into an isospecific active site. The two-step mechanism of the propagation reaction, which involves olefin coordination on a transition metal and insertion of a coordinated olefin into the metal-carbon bond via a four-center transition state, is widely accepted.

In this study, it is proposed that the insertion of 1,5-hexadiene occurs as follows. The cyclopolymerization of 1,5-hexadiene proceeds when only one double-bond of 1,5-hexadiene coordinates to a vacant site (Scheme 1). However, it is considered that the cyclopolymerization of 1,5-hexadiene cannot proceed when both double bonds of 1,5-hexadiene coordinate simultaneously to the vacant sites of one or two active sites. In this case, it seems that an active site on the $MgCl_2$ surface is deactivated by a 1,5-hexadiene monomer. As mentioned above, it is considered that the kinetic parameters for each catalyst were influenced by a specific insertion mechanism of the 1,5-hexadiene monomer and the formation of a cyclopolymer having intricate microstructures.

Change in Microstructural Heterogeneity of the Cyclopolymer of 1,5-Hexadiene by Addition of Internal Donor

The crystallinity of the cyclopolymer of 1,5-hexadiene is sensitive to the *cis*/*trans* stereochemistry of the rings and the relative stereochemistry be-

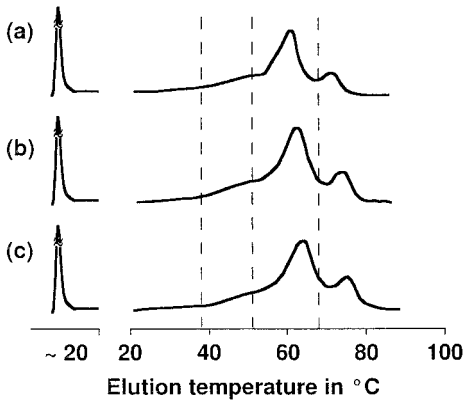


Figure 3 TREF curves of cyclopolymers of 1,5-hexadiene obtained by the stopped-flow method in the presence of external donor [(a) none; (b) EB; (c) CMDMS].

tween the rings. Therefore, the microstructural heterogeneity of the cyclopolymer is considered to be clearly detected by TREF analysis. To clarify these points, in our previous article, the stopped-flow polymerization of 1,5-hexadiene was performed, and the microstructure of the resulting cyclopolymer was investigated by TREF analysis.[7] The result suggested the existence of a distribution of the active sites having different selectivities for insertion and cyclization, which are closely related to the microstructural heterogeneity of the resulting cyclopolymer. In this article, the active sites and their interaction with an electron donor are considered to be observable through the analysis of the cyclopolymer obtained at the initial polymerization stage by using both the stopped-flow method and TREF analysis.

The cyclopolymerization was conducted with the $MgCl_2$-supported Ziegler catalysts and TEA; the results are shown in Table I. The TREF profile of the resulting cyclopolymer obtained with cat. A for 0.15 s is shown in Figure 3. Because two main peaks at 63 and 73°C were observed in the profile, the microstructure was found to be heterogeneous. The GPC and ^{13}C-NMR analysis of the each fraction eluted at a different temperature suggests the distribution of the active sites having different selectivities for the insertion and cyclization. On the other hand, the cyclopolymerization with cat. B using the stopped-flow method gave a low crystallinity cyclopolymer, resulting in most of that part being eluted below 20°C. It is assumed that the cyclopolymer eluted below 20°C corresponds to an ata-polymer (*cis*–ata, *trans*–ata). The comparison of the TREF analysis of the cyclopolymers obtained with two types of catalysts apparently indicated that the stereospecificity of the cyclopolymers was drastically changed by whether an internal donor is present in the catalyst. The existence of nonuniform active sites with different selectivities for the insertion and cyclization was confirmed by the TREF results of the cyclopolymer of 1,5-hexadiene obtained by using the stopped-flow technique. Thus, the microstructure of the cyclopolymer obtained was influenced by the conformational preferences of the incipient ring and the interaction of that ring with the nature of the active sites on the catalyst.

Change in Microstructural Heterogeneity of the Cyclopolymer of 1,5-Hexadiene by Addition of External Donor

The stereospecificity of Ziegler–Natta catalysts was markedly improved by the addition of the suitable external donor.[1–5] Because the advantages of the external donors became evident in the early 1980s, many investigations were performed to understand the relationship between their structure and the performance of the catalytic system. In this study, the influence of an external donor was examined in terms of the microstructure of the cyclopolymer obtained by the stopped-flow method. The efficiency of the catalyst system is known to be dependent on the appropriate choice of the donors. EB is commonly cited as an example of good internal and external donors. The more efficient external donors are known to be alkoxysilane derivatives containing at least one bulky alkyl group, such as CMDMS, which are the most commonly used external donors in modern industrial processes.

The results of cyclopolymerization with different catalyst systems, where different external donors were added, are shown in Table I. The selectivities of the insertion and the cyclization were increased by the addition of EB and CMDMS as an external donor. It was well indicated that the selectivity for cyclization is sensitive to the nature of the active sites on the $MgCl_2$ surface. The *cis* ring is formed on the sterically hindered active sites[8]; therefore, it was thought the external donors directly acted on the active sites and increased the steric hindrance in the vicinity of the active sites. Furthermore, the addition of EB and CMDMS affected the diastereoselectivity for the resulting cyclopolymers because the interactions of TEA with the external donor were changed according to the kind of donor. The difference in the diastereoselectivity for the cyclopolymer can be explained from the interactions of TEA with the external donor as follows. The mixture of mo-

Table II TREF Results of Cyclopolymers of 1,5-Hexadiene Obtained by Stopped-Flow Polymerization Methods[a]

	$TiCl_4/EB/MgCl_2$					$TiCl_4/EB/MgCl_2/CMDMS$				
Temp. (°C)	Weight (%)	IV[b] (dL/g)	*cis*[c] (%)	*c–c*[d] (%)	*t–t*[e] (%)	Weight (%)	IV[b] (dL/g)	*cis*[c] (%)	*c–c*[d] (%)	*t–t*[e] (%)
20	42	0.45	49	40	34	33	0.40	51	33	26
20–38	6	0.73	57	47	22	9	0.68	52	34	26
38–51	9	0.81	63	37	21	16	0.78	63	44	15
51–68	35	0.99	68	45	15	34	0.98	69	54	11
68–100	8	1.38	75	56	13	8	1.25	74	65	7

[a] Polymerization condition; [Al], 70 mmol/L; Al/Ti, 30; Al/D, 20, polymerization time, 0.15 s.
[b] Intrinsic viscosity (IV) was determined by GPC-viscometer module (ODCB, 140°C).
[c] Determined by ^{13}C-NMR.
[d] *cis–cis* unit in meso dyad.
[e] *trans–trans* unit in meso dyad.

noester and TEA causes the formation of TEA derivatives in the reaction of TEA with EB.[18,19] On the other hand, the alkoxysilane/TEA mixture causes the formation of TEA and the alkoxysilane/TEA 1 : 1 complex.[19,20] In our research group, it was reported previously that the addition of CMDMS effectively improved the tacticity of the resulting polymer in an extremely short period.[21]

The TREF profile of the cyclopolymer obtained by the addition of the external donor is shown in Figure 3. The cyclopolymerization of 1,5-hexadiene catalyzed by cat. A and CMDMS induced an increase in the crystalline part from 58 to 66%. Thus, it can be understood that the addition of the external donor caused an increase in the crystallinity of the resulting cyclopolymer. On the other hand, the cyclopolymerization with cat. B with the addition of an external donor produced a low crystallinity cyclopolymer, in which most of that part was eluted below 20°C. The highly crystalline polymer could not be obtained by the addition of an external donor in the absence of an internal donor. Thus, irrespective of the existence of the external donor, cat. B did not show the ability to form the isopolymer during the cyclopolymerization of 1,5-hexadiene. This means that the external donor hardly interacted with the complete aspecific species. On the basis of these results, the fractionation of the cyclopolymer obtained by the stopped-flow polymerization with cat. A was conducted to divide it into five fractions (~ 20, 20–38, 38–51, 51–68, and 68–100°C). Each fraction eluted at a different temperature was analyzed by ^{13}C-NMR and a GPC-Viscometry module; the results are shown in Table II and Figure 4. Fractions eluted at each temperature showed different selectivities. The contents of both of the microstructures, *cis* and *cis–cis*, increased with the increasing elution temperature. The values of *cis* and *cis–cis* were the highest in the fraction between 68 and 100°C; therefore, the crystallinity of the cyclopolymer obtained depended on the ratio of the *cis–iso* polymer. Furthermore, it is thought that the active sites of each fraction have a different reactivity with the electron donor because the weight of each fraction depends on the catalyst. In the cyclopolymerization of 1,5-hexadiene with cat. A, the addition of CMDMS into the system as the external donor was found to have no effect on the weight the fraction of 68–100°C, whereas that of the fraction eluted below 20°C

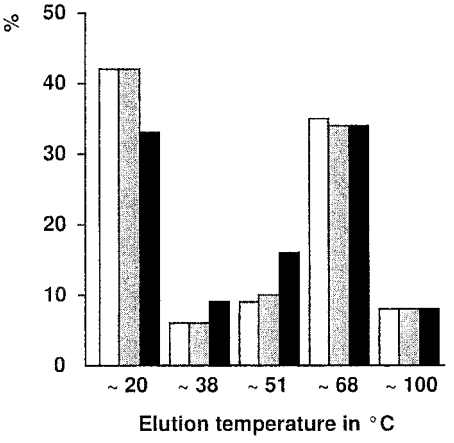


Figure 4 TREF fractions of cyclopolymers of 1,5-hexadiene obtained by the stopped-flow method in the presence of external donor (□, none; ▨, EB; ■, CMDMS).

decreased and that of the fraction of 38–51°C increased. As a result, it is considered that the external donor inhibited the extensive removal of the internal donor because of complexation or reaction with the TEA and changed some of the potentially aspecific active sites into low isospecific ones. Furthermore, our research group reported the same tendency in the case of polypropene.[16] Consequently, regardless of the kind of monomers, the external donor sterically affects one coordination vacancy of each aspecific species and transfers it into the low isospecific active site.

CONCLUSION

In this article, the nature and the distribution of the active sites on $MgCl_2$-supported Ziegler catalysts were investigated through the influence of the direct interaction of the catalyst with an electron donor on the stereospecificity and the kinetic parameters at the initial stage of the cyclopolymerization of 1,5-hexadiene. The stopped-flow polymerization of 1,5-hexadiene proceeded without side reactions and variation of the active sites, suggesting that the microstructure of the resulting cyclopolymer is affected by the nature and the distribution of the active sites just after their formation. The cyclopolymerization behavior of 1,5-hexadiene by the addition of an internal donor was influenced by an aspecific insertion mechanism of the monomer and the formation of a cyclopolymer having intricate microstructure. We conclude that the coordination of the internal donor causes an aspecific active site to transform into an isospecific active site. The addition of external donor modified some of the aspecific active sites into low isospecific active sites. The external donor sterically affects one coordination vacancy of each aspecific titanium species and consequently transfers it into a low isospecific active site. These results suggest that the microstructural heterogeneities of the cyclopolymer of 1,5-hexadiene are mainly influenced by the internal donor. From this point of view, it is concluded that the kinetic study and TREF analysis of the cyclopolymer obtained by the stopped-flow method has great potential as an effective tool for understanding the interaction of electron donors with the active sites on the $MgCl_2$-supported Ziegler catalysts.

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