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Structure of cyclopentene unit in the copolymer with propylene obtained by stereospecific zirconocene catalysts

Naofumi Naga*, Yukio Imanishi

Graduate School of Materials Science, Nara Institute of Science and Technology, 8916-5, Takayama, Ikoma, Nara 630-0101, Japan

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Abstract

Copolymerization of propylene and cyclopentene (CPE) was carried out using as a catalyst isospecific *rac*-ethylenebis(indenyl)zirconium dichloride (**1**), *rac*-dimethylsilylenebis(indenyl)zirconium dichloride (**2**), *rac*-dimethylsilylenebis(2-methylindenyl)zirconium dichloride (**3**), or syndiospecific diphenylmethylene(cyclopentadienyl)(9-fluorenyl)zirconium dichloride (**4**) with methylaluminoxane as a cocatalyst. Isospecific zirconocene catalysts **1**–**3** produced copolymers having narrow molecular weight distribution, while syndiospecific catalyst **4** effected propylene homopolymerization. Microstructures of the copolymers were studied by ^{13}C NMR and distortionless enhancement of polarization transfer (DEPT) spectroscopy. CPE was found to be incorporated in the copolymer preferentially via 1,2-insertion mechanism in the copolymerization with the catalyst **3**. The catalyst **1** and **2** gave copolymers containing CPE units formed by either 1,2-insertion or 1,3-insertion mechanism. The proportion of 1,3-insertion units increased with increasing CPE content in the copolymers. The isomerization reaction from 1,2-insertion to 1,3-insertion CPE units was discussed on the basis of kinetic parameters. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Zirconocene catalysts; Copolymer; Propylene

1. Introduction

Cycloolefin copolymer (COC) has been well known as useful material with high transparency and heat resistance. Copolymerizations of ethylene or propylene with cycloolefins have been conducted with homogeneous metallocene catalysts. Especially, ethylene–norbornene copolymerization with a variety of metallocene catalysts has been investigated to develop useful optical material [1–12]. Other ethylene-based COCs have been synthesized, and the structure and property of the copolymers have been investigated [13–15]. Copolymerizations of propylene and cycloolefins have also been conducted to synthesize polypropylene with specific properties [16–18].

We were interested in diverse modes of cyclopentene (CPE) incorporation in polymers and copolymers (Scheme 1). In the homopolymerization with zirconocene catalysts, CPE is polymerized preferentially via 1,3-insertion mechanism [19–21]. Kaminsky and Spiehl investigated copolymerization of ethylene and CPE with typical bridged-zirconocene catalysts, and found that CPE was copolymerized preferentially via 1,2-insertion mechanism [14]. Müller and coworkers conducted the copolymerization with a specific zirconocene catalyst, *rac*-dimethylsilylene(ferroceno [2,3]indenyl) (cyclopentadienyl)zirconium dichloride, and observed the occurrence of both 1,2-insertion and 1,3-insertion CPE units in the copolymer [15]. Copolymerization of propylene with CPE was conducted with a zirconocene catalyst by Kaminsky and coworkers [16] and Köller and coworkers [17]. However, little is known about the effect of catalyst structure on the microstructure of resulting copolymer. Control of the structure of CPE units should be essential for precise synthesis of poly(propylene-*co*-CPE) with deserved properties.

In this study, we carried out copolymerization of propylene and CPE with stereospecific metallocene catalysts, *rac*-ethylenebis(indenyl)zirconium dichloride (**1**), *rac*-dimethylsilylenebis(indenyl)zirconium dichloride (**2**), *rac*-dimethylsilylenebis(2-methylindenyl)zirconium dichloride (**3**), and diphenylmethylene(cyclopentadienyl)(9-fluorenyl)-zirconium dichloride (**4**), to investigate microstructure of the copolymers and the mechanism of CPE polymerization (Scheme 2).

2. Experimental part

2.1. Materials

Zirconocene complexes were commercially available

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* Corresponding author. Tel.: +81-783-72-6043; fax: +81-743-72-6049.
E-mail address: naga@ms.aist-nara.ac.jp (N. Naga).

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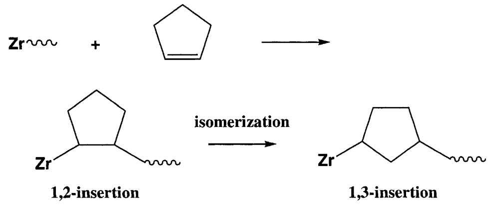
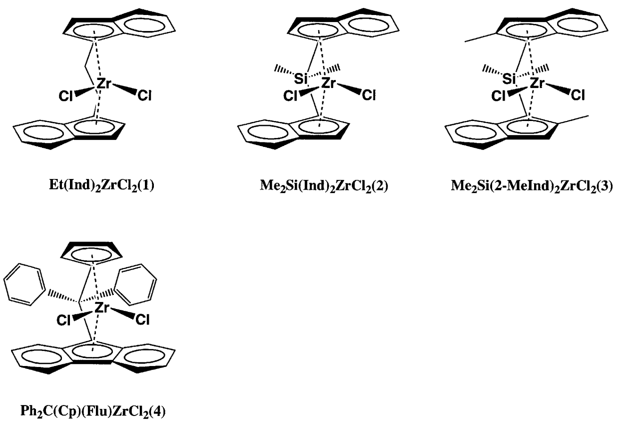


Scheme 1. Mechanism of propagation reaction of CPE being accompanied by isomerization reaction.

from Aldrich Co. Ltd and Boulder Science Co. Ltd, and used without further purification. Toluene solution of methylaluminoxane (MAO) was donated from Tosoh Akzo Co. Ltd and used without further purification. CPE (Tokyo Kasei) and toluene (Wako Chemicals) were dried with CaH_2 and distilled under nitrogen atmosphere before use. Propylene (Takachiho Chemicals) was purified by passing it through columns of NaOH, P_2O_5 and molecular sieves 3A.



Scheme 2. Zirconocene catalysts used in the present investigation.

2.2. Copolymerization

Copolymerization of propylene with CPE was carried out in a 100 ml glass reactor equipped with a magnetic stirrer. Toluene was added to the reactor under nitrogen atmosphere. Propylene was introduced to toluene in the reactor at 40 °C under 1 atm until the solvent was saturated with propylene, and a measured amount of CPE was added. A toluene solution of MAO and a zirconocene catalyst were mixed in a 50 ml glass flask at 25 °C for 5 min. Polymerization was started by introducing the catalyst solution into the reactor. After a requisite time of reaction, the polymerization was terminated by adding a small amount of ethanol. The polymer was precipitated in a large excess of ethanol and recovered by filtration. The polymer obtained was extracted with boiling *o*-dichlorobenzene to remove residual catalyst. The solution of extracted polymer was concentrated by evaporation and precipitated in a large excess of ethanol. The precipitate was recovered by filtration and dried in vacuo at 60 °C for 6 h.

2.3. Analytical procedures

Molecular weight and molecular weight distribution of the copolymer were measured at 140 °C by means of gel permeation chromatography (Tosoh HLC-8121 GPC/HT) using *o*-dichlorobenzene as a solvent and calibrated with standard polystyrene samples. ^1H NMR, ^{13}C NMR and DEPT spectra were recorded at 130 °C on a JEOL Lambda-400 Fourier transform NMR spectrometer in 5 wt% *o*-dichlorobenzne/benzne-d_6 (9/1, v/v) solution.

3. Results and discussion

Copolymerization of propylene and CPE was carried out

Table 1
Propylene/cyclopentene(CPE) copolymerization with zirconocene/MAO catalyst (polymerization conditions: [Zr], 0.1 mmol/l (runs 4, 8, and 12, 0.2 mmol/l); molar ratio of (MMAO)Al/Zr, 1000; propylene, 1.0 atm; polymerization temperature, 40 °C)

Run	Catalyst	CPE (mol/l)	t^a (min)	Polymer yield (kg/molZr h)	CPE in copolymer[b] (mol%)	1,3-insertion CPE units[c] (%)	$M_n{}^d$ ($\times 10^{-4}$)	$M_w/M_n{}^d$
1	**1**	0.57	15	2380	2.0	51.6	1.1	1.7
2	**1**	1.14	15	2260	3.6	54.8	0.78	1.8
3	**1**	2.27	60	570	5.8	56.5	0.45	1.8
4	**1**	5.68	60	310	10.1	62.4		
5	**2**	0.57	10	2700	1.4	22.8	1.8	1.9
6	**2**	1.14	30	1040	3.7	24.8	1.2	1.7
7	**2**	2.27	30	910	5.3	27.5	0.80	1.9
8	**2**	5.68	360	18	7.8	31.5		
9	**3**	0.57	15	2200	1.5	0.0	3.0	1.8
10	**3**	1.14	15	1900	2.1	0.0	2.7	1.9
11	**3**	2.27	15	1360	4.1	0.0	1.8	2.1
12	**3**	3.42	30	350	6.1			
13	**4**	2.27	30	760	0.0		8.4	1.7

[a] Polymerization time.
[b] Determined by ^1H NMR spectroscopy.
[c] Determined by ^1H and ^{13}C NMR spectroscopy.
[d] Molecular weight and molecular weight distribution determined by GPC using polystyrene standard.

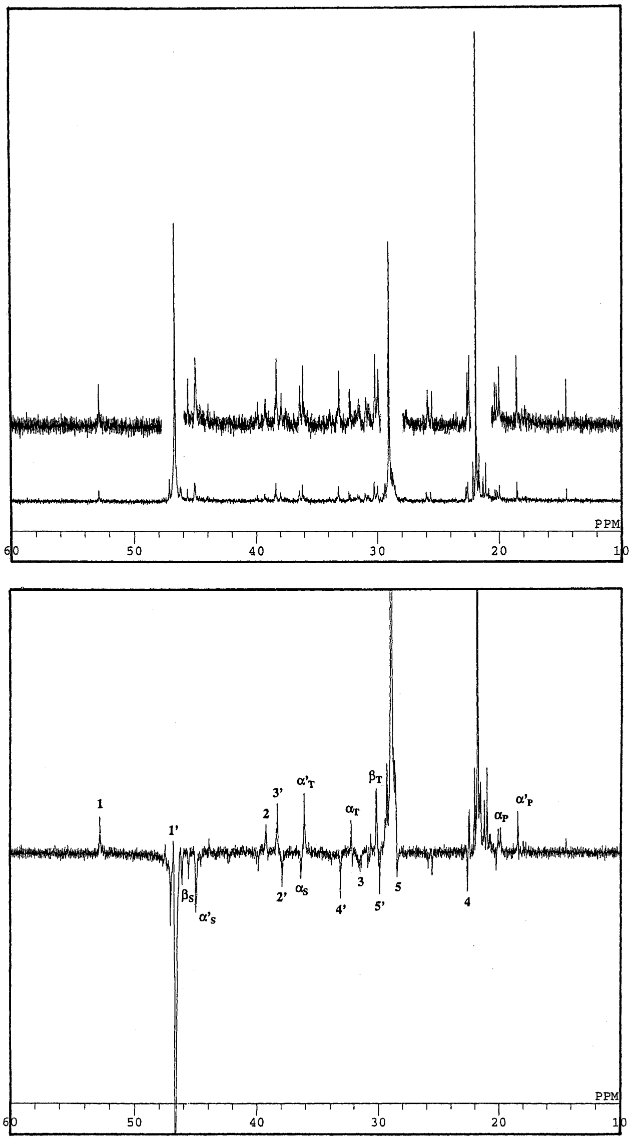


Fig. 1. ^{13}C NMR spectra (top) and DEPT spectrum (bottom) of poly(propylene-*co*-CPE) obtained with **1** (run 3).

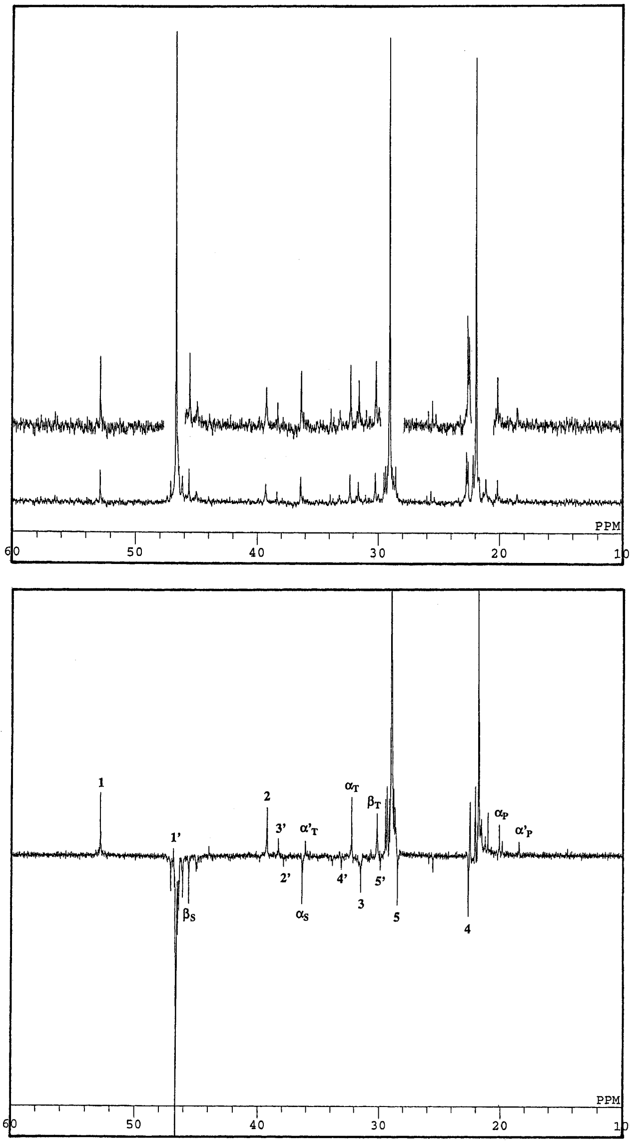


Fig. 2. ^{13}C NMR spectra (top) and DEPT spectrum (bottom) of poly(propylene-*co*-CPE) obtained with **2** (run 7).

with isospecific or syndiospecific zirconocene catalyst at 40 °C. The results are summarized in Table 1. The isospecific catalysts (**1**–**3**) produced copolymers. The yield of polymer linearly decreased with increasing proportion of CPE in the feed monomer. Molecular weight of the copolymer decreased with increasing CPE content in the copolymer. In the copolymerization with the syndiospecific catalyst **4**, polymerization of propylene without incorporation of CPE occurred. These results do not agree with previous reports of various propylene/α-olefin or α,ω-diolefin copolymerizations. It has been reported in the copolymerization of propylene/1-hexene [22] and propylene/1,5-hexadiene or 1,7-octadiene [23] that the syndiospecific catalysts, such as isopropylidene(cyclopentadienyl)(9-fluorenyl) zirconium dichloride and **4**, took α-olefin or α,ω-diolefin in copolymer more than isospecific catalyst **1** or **2**. In addition, the catalyst **4** gave copolymers containing high amount of CPE units in ethylene/CPE copolymerization.[1] These results mean that CPE cannot react with the propagating chain ends composed of the catalyst **4** and propylene due to steric hindrance.

The structure of poly(propylene-*co*-CPE) was investigated by ^{13}C NMR and distortionless enhancement of polarization transfer (DEPT) (135°), as shown in Figs. 1–3 for the copolymers obtained with the isospecific catalysts **1** (run 3), **2** (run 7) and **3** (run 11), respectively. For the assignment of signals, refer to Scheme 3. A larger number of signals appeared in Figs. 1 and 2 compared to Fig. 3. The signals

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[1] Copolymerization of ethylene and CPE was conducted with zirconocene catalysts under the same conditions as in the present copolymerization. The catalyst **4** copolymerized as much CPE as the catalyst **2** [24].

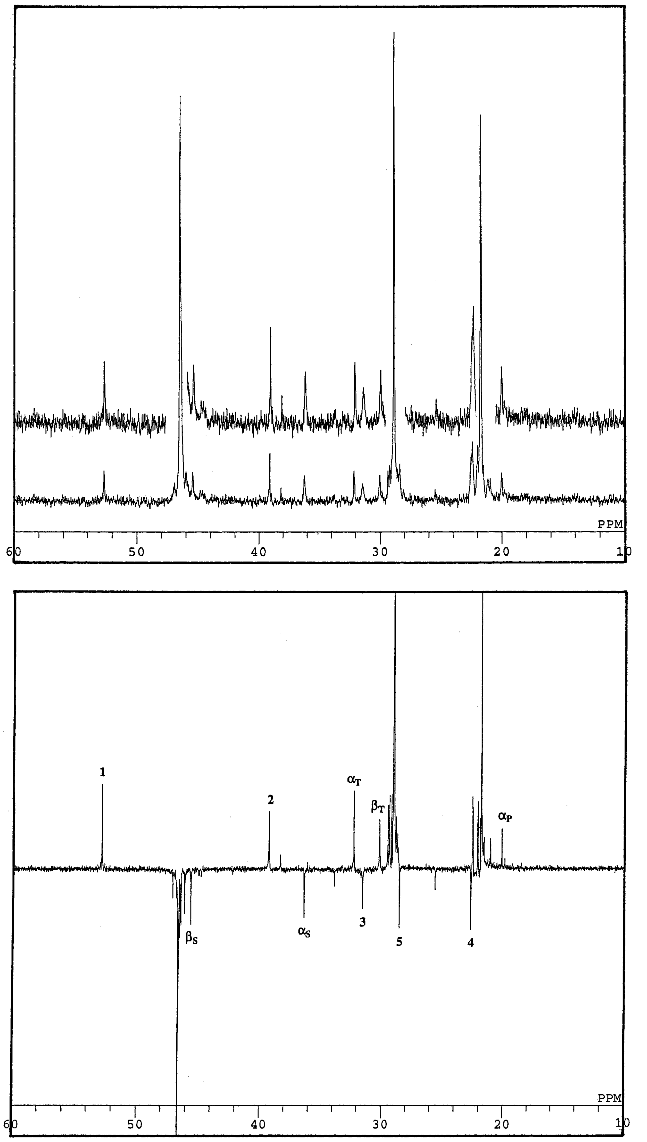
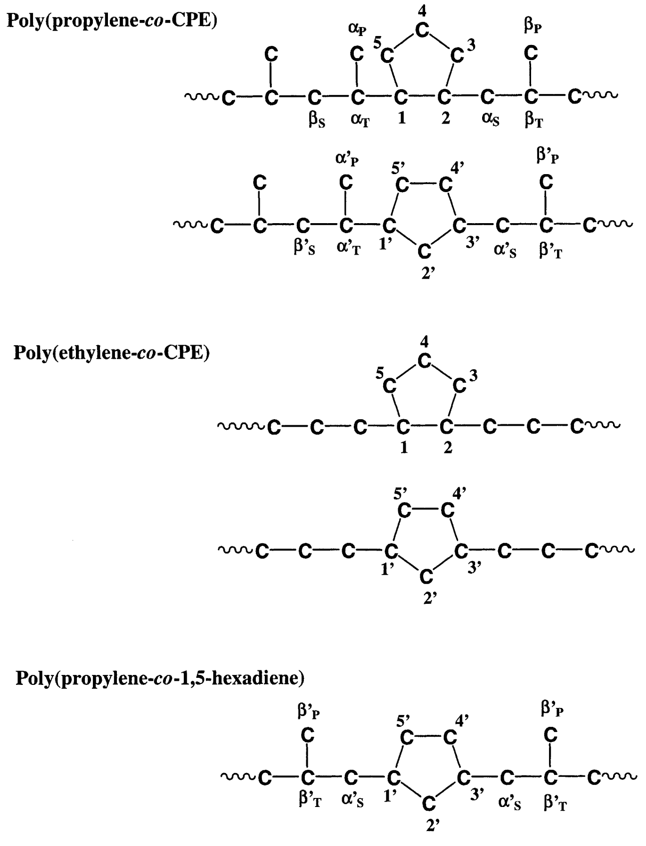


Fig. 3. ^{13}C NMR spectra (top) and DEPT spectrum (bottom) of poly(propylene-*co*-CPE) obtained with **3** (run 11).

of poly(propylene-*co*-CPE) were assigned using assignment of poly(propylene-*co*-1,5-hexadiene) [23] and poly(ethylene-*co*-CPE) [14,15]. The assignment, observed and calculated chemical shift [25] of the signals of the copolymers and reference copolymers are summarized in Table 2. Taking the chemical shift (relative intensity) into account, the signals at 22.6 (4), 28.5 (5), 31.5 (3), 39.3 (2) and 52.8 (1) ppm are assignable to 1,2-substituted cyclopentane units due to 1,2-insertion of CPE. These signals were observed in all ^{13}C NMR spectra of the copolymers. The other signals at 30.0 (5′), 33.1 (4′), 38.0 (2′), 38.3 (3′) and 46.8 (1′) ppm are observed in the ^{13}C NMR and DEPT spectra of the copolymers obtained with the catalysts **1** and **2** (Figs. 1 and 2). These signals can be assigned to the 1,3-substituted cyclopentane units due to 1,3-insertion of CPE. The diad sequence of CPE was not detected in any ^{13}C NMR spectra, and the CPE units in the copolymers should be isolated.



Scheme 3. Symbolizing carbon atoms of polypropylene and polyethylene containing 1,2- or 1,3-substituted cyclopentane structure.

The cyclopentane units in the copolymers should take either *cis*- or *trans*-structure. In the ethylene/CPE copolymerization, CPE units were found to take preferentially *cis*-structure in both 1,2-insertion and 1,3-insertion mechanisms. From the chemical shift of carbon 4 (Scheme 3) of the 1,2-substituted cyclopentane structure in an ethylene sequence (*cis*, 23.0 ppm, *trans*, 24.5 ppm) [26], *cis*-structure is expected to occur in the poly(propylene-*co*-CPE) (Scheme 4). In the case of 1,3-substituted cyclopentane structure, stereochemistry of 4′ carbon adjacent to propylene unit was defined according to a literature on poly(propylene-*co*-1,5-hexadiene) [23]. The shift value of the 4′ carbon (33.1 ppm) indicated *cis*-m structure of 1,3-substituted cyclopentane structure (Scheme 4). There are, however, some unassignable signals in the ^{13}C NMR and DEPT spectra. The signals at 14.5(P), 20.1(S), 26.0(S), 30.6(S), 32.1(S), 39.9(S) and 44.0(T) ppm are observed in the spectra of relatively low molecular weight copolymers obtained with the catalysts **1** and **2** (Figs. 1 and 2), where P, S and T are primary, secondary and tertiary carbons. These signals are assignable to a saturated chain end of *n*-propyl [14.5(tp1 and 1′), 20.1(tp2 and 2′), 32.1(tp3′), 39.9(tp3) and 44.0(tp4′ or tc1) ppm] and cyclopentyl [26.0(tc3), 30.6(tc2) and 44.0(tc1 or tp4′) ppm] groups, where tp and tc represent *n*-propyl and cyclopentyl terminal group, respectively, as shown in Scheme 5. These groups were formed upon

Table 2
^{13}C NMR chemical shifts in the isotactic poly(propylene-*co*-CPE) and reference copolymers

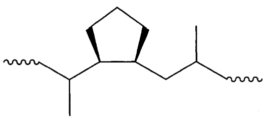
Poly(propylene-*co*-CPE)				Poly(ethylene-*co*-CPE)		Poly(propylene-*co*-1,5-hexadiene)	
Assignment[a]	Type[b]	Chemical shift (ppm)		Chemical shift (ppm)		Chemical shift (ppm)	
		Observed	Calculated[c]	*cis*	*trans*	*cis*	*trans*
1	T	52.8	49.7	43.1	46.4		
2	T	39.3	39.7–40.0	43.1	46.4		
3	S	31.5	34.9–35.4	31.0	35.8		
4	S	22.6	27.4	23.0	24.5		
5	S	28.5	30.3–31.1	31.0	35.8		
α_P	P	20.0–20.2	19.1–19.4				
α_S	S	36.3	37.9–38.3				
α_T	T	32.3	33.5				
β_S	S	45.6	43.2				
β_T	T	30.2	29.7–30.5				
$1'$	T	46.8	45.5	40.7	39.4	38.4	37.0
$2'$	S	38.0	37.0	41.2	39.5	44.3	41.7
$3'$	T	38.3	37.6	40.7	39.4	38.4	37.0
$4'$	S	33.1	33.7	32.2	33.4	32.4–34.2	33.6–34.2
$5'$	S	30.0	31.5	32.2	33.4	32.4–34.2	33.6–34.2
α'_P	P	18.5	18.7–19.0				
α'_S	S	45.0	39.6–40.0			45.1	45.1
α'_T	T	36.0	35.2				

[a] Corresponding structures are show in Scheme 3.

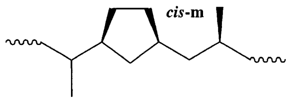
[b] P, S and T represent primary, secondary and tertiary carbons.

[c] Calculated from Lindeman and Adams relationship [24].

initiation of copolymerization. On the other hand, unsaturated chain end groups were not detected by the ^{13}C NMR spectroscopy. In expanded ^{1}H NMR spectra of the copolymers obtained with the catalysts **1** and **2**, we found a signal at 5.6 ppm, which is attributable to 2-H of 1-substituted cyclopentenyl structure, as shown in Scheme 4. It indicated that chain transfer reaction occurs preferentially at the CPE-carrying propagating chain ends. The other unassignable signals in the ^{13}C NMR and DEPT spectra, at 25.5(S), 33.8(S) and 38.2(T) ppm are found even in the spectra of high molecular weight copolymers obtained with the catalyst **3**, eliminating a possibility that these signals are due to chain end structures. It is possible that the signals are derived from 1,2-substituted cyclopentane structure with different steric configuration relative to neighboring propylene units or *trans*-1,2-cyclopentane structure.



***cis*-1,2-substituted cyclopentane**



***cis*-1,3-substituted cyclopentane**

Scheme 4. Steric configuration of 1,2- or 1,3-substituted cyclopentane structure involved in polypropylene.

The 1,3-insertion of CPE in the copolymerization with the catalyst **1** and **2** can be explained by 1,2-insertion accompanying isomerization reaction. The isomerization reaction occurs more frequently in the copolymerization with the catalyst **1** than with the catalyst **2**. The 1,3-insertion has been reported in polymerization of propylene with isospecific zirconocene catalysts [27–30]. The 1,3-insertion of propylene is possible by isomerization reaction of the propagating chain of 2,1-inserted propylene via β-H elimination followed by re-entry. Resconi and coworkers reported regioirregular units (2,1- and 1,3-insertion) in the polypropylene obtained with isospecific zirconocene catalysts with decreasing amount of the units in the order of **1** > **2** > **3** [31]. This order is in agreement with the extent of 1,3-insertion of CPE in the propylene/CPE copolymerization. We found that the 1,3-insertion of CPE took place in the ethylene/CPE copolymerization with the catalyst **1**, and that the proportion of 1,3-insertion CPE was lower (20–30%) than that in propylene/CPE copolymerization.[2] Furthermore, the catalyst **2** induced a preferential 1,2-insertion of CPE in the copolymerization with ethylene. The difference can be explained in terms of different propagation rate of used olefins, ethylene or propylene. The reaction rate of propylene with a propagating chain end of 1,2-insertion CPE is lower than that of ethylene. This difference results in higher

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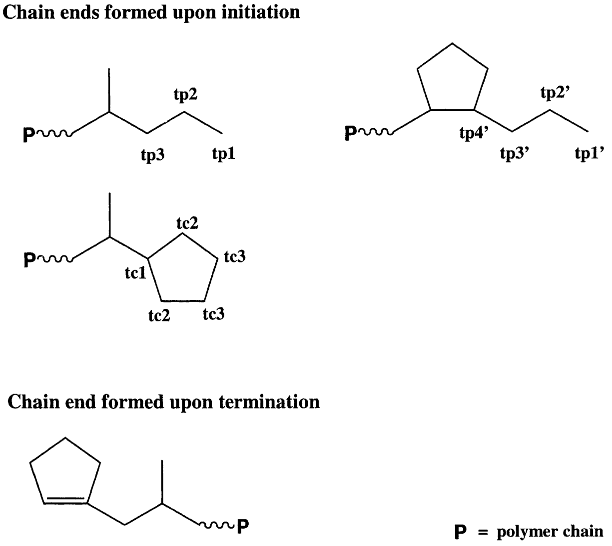
[2] Copolymerization of ethylene and CPE was conducted with **1** under the same conditions as in the present copolymerization, and 1,2-insertion CPE units were detected in the resulting copolymer [24].



Scheme 5. Possible terminal structures of propylene/CPE copolymers.

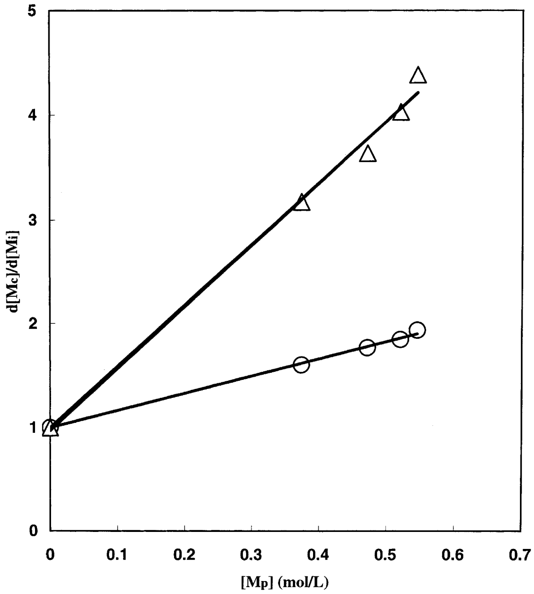


Fig. 4. Relationship between $d[M_c]/d[M_i]$ and $[M_p]$; copolymerization with **1** (○) and **2** (△).

1,3-insertion ratio in propylene/CPE copolymerization than in ethylene/CPE copolymerization.

The propagation and isomerization reaction in the copolymerization of propylene and CPE with the catalysts **1** and **2** are described by Eqs. (1)–(7), assuming that the propagation reaction obeys the first-order Markovian process and the isomerization the Bernoullian process.

Rate of reaction

$$M_p^* + M_p \xrightarrow{k_{pp}} M_p^* \qquad k_{pp}\left[M_p^*\right][M_p] \tag{1}$$

$$M_p^* + M_c \xrightarrow{k_{pc}} M_c^* \qquad k_{pc}\left[M_p^*\right][M_c] \tag{2}$$

$$M_c^* + M_p \xrightarrow{k_{cp}} M_p^* \qquad k_{cp}[M_c^*][M_p] \tag{3}$$

$$M_c^* + M_c \xrightarrow{k_{cc}} M_c^* \qquad k_{cc}[M_c^*][M_c] \tag{4}$$

$$M_c^* \xrightarrow{k_i} M_i^* \qquad k_i[M_c^*] \tag{5}$$

$$M_i^* + M_p \xrightarrow{k_{ip}} M_p^* \qquad k_{ip}[M_i^*][M_p] \tag{6}$$

$$M_i^* + M_c \xrightarrow{k_{ic}} M_c^* \qquad k_{ic}[M_i^*][M_c] \tag{7}$$

where M_p^*, M_c^* and M_i^* represent the active centers with terminal propylene, 1,2-substituted CPE, and isomerized (1,3-substituted) CPE units, respectively, $[M_p]$ and $[M_c]$, the concentrations of propylene and CPE, respectively, and k_{pp}, k_{pc}, k_{cp}, k_{cc}, k_i, k_{ip} and k_{ic} are the rate constants of propylene addition to a propylene terminal, CPE addition to a propylene terminal, propylene addition to a 1,2-substituted CPE terminal, CPE addition to a 1,2-substituted CPE terminal, isomerization of 1,2-substituted CPE to a 1,3-substituted CPE, propylene addition to a 1,3-substituted CPE terminal and CPE addition to a 1,3-substituted CPE terminal, respectively. The amount of polymerized CPE ($d[M_c]$) relative to the amount of isomerized CPE units in the copolymer ($d[M_i]$) can be expressed by Eq. (8)

$$d[M_c]/d[M_i] = \left\{k_{pc}\left[M_p^*\right][M_c] + k_{cc}[M_c^*][M_c] + k_{ic}[M_i^*][M_c]\right\}/k_i[M_c^*] \tag{8}$$

Assuming a steady-state concentration of each propagating species, the following equations are derived

$$k_{cp}[M_c^*][M_p] + k_{ip}[M_i^*][M_p] = k_{pc}\left[M_p^*\right][M_c] \tag{9}$$

$$k_{pc}\left[M_p^*\right][M_c] + k_{ic}[M_i^*][M_c] = k_{cp}[M_c^*][M_p] + k_i[M_c^*] \tag{10}$$

$$k_i[M_c^*] = k_{ip}[M_i^*][M_p] + k_{ic}[M_i^*][M_c] \tag{11}$$

Eq. (12) is derived from Eqs. (8) and (10)

$$d[M_c]/d[M_i] = 1 + [M_c]/K_i + [M_p]/K_i' \tag{12}$$

where $K_i = k_i/k_{cc}$ and $K_i' = k_i/k_{cp}$.

The absence of CPE sequence in the copolymer means that $1/K_i = 0$, and Eq. (12) can be written as Eq. (13)

$$d[M_c]/d[M_i] = 1 + [M_p]/K_i' \tag{13}$$

Fig. 4 shows the linear relationship between $d[M_c]/d[M_i]$ and $[M_p]$. According to Eq. (13), the K_i' values are determined from the slope, and are summarized in Table 3, together with the monomer reactivity ratio of propylene ($r_p = k_{pp}/k_{pc}$) determined by the Fineman–Ross plot. The K_i' value of the copolymerization with the catalyst **1** is 3.6 times as much as that with the catalyst **2**, indicating that

Table 3
Kinetic parameters of propylene/CPE copolymerization with zirconocene catalysts

Catalyst	K_i[a] (mol/l)	r_p[b]
1	0.64	45.5
2	0.17	72.0
3	0	51.2

[a] $K_i' = k_i/k_{cp}$.
[b] $r_p = k_{pp}/k_{pc}$.

propylene is more reactive with M_c^* involving the catalyst **2** than with M_c^* involving the catalyst **1**. This trend agrees with the order of r_p values.

4. Conclusion

The copolymerization of propylene and CPE with isospecific zirconocene catalysts successfully produced poly(propylene-*co*-CPE). The ^{13}C NMR and DEPT spectroscopy of the copolymers gave useful information of structure of CPE units in the copolymers. Highly isospecific zirconocene catalyst **3** preferentially produced the copolymers involving 1,2-substituted cyclopentane units. On the other hand, 1,3-substituted cyclopentane units, which resulted from isomerization reaction of 1,2-substituted CPE, were detected in the copolymers obtained with the catalysts **1** and **2**. Kinetic treatment enabled us to estimate the reaction parameter of the isomerization reaction. The results indicate that the substituent on the indenyl ligand and the bridged structure of the zirconocene catalyst deeply influence the propagation/isomerization ratio of CPE in the copolymerization with propylene.

Isotactic polypropylene forms 3/1 helix in the crystalline state. Cyclopentane structure introduced in the main chain of isotactic polypropylene may affect the crystalline structure and consequently physical properties of the copolymer. The effect of cyclopentane structure on the crystalline structure of propylene-based copolymers is an exciting target of the future investigation. Crystalline structure and thermal property of the obtained copolymers will be reported elsewhere.

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