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Synthesis and crystalline structure of polyethylene containing 1,3-cylopentane units in the main chain by ring-opening metathesis copolymerization of cycloolefins following hydrogenation reaction

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Abstract

Polyethylene containing 1,3-cyclopentane units in the main chain was synthesized by ring-opening metathesis copolymerization of cyclopentene (CPE) or cyclooctene with norbornene (NB) following hydrogenation reaction. The copolymer with *cis*-1,3-cyclopentane units was obtained in good yield. The resulting copolymers showed multiple melting points. Temperature-rising elution fractionation of the copolymers elucidated a broad distribution of the copolymer composition. WAXD and FT-IR analyses of the copolymers showed existence of hexagonal crystal in hydrogenated poly(CPE-*co*-NB).

Keywords: Polyethylene; 1,3-Cylopentane unit; Ring-opening metathesis polymerization

1. Introduction

Polyolefins with cyclic structures in the main chain, so-called cycloolefin copolymers (COCs), have been developed due to their high performance, high glass transition temperature and good transparency. The copolymers are efficiently synthesized by copolymerization of conventional olefins and cycloolefins with homogeneous transition metal catalysts, such as metallocene catalyst [1]. The copolymers can be also synthesized by copolymerization of olefin with α,ω-nonconjugated diene involving intramolecular cyclization.

We have been investigating synthesis and structure of polyolefins with small cyclic units, especially cyclopentane unit, in the main chain. Polyethylenes or polypropylenes containing 1,2- or 1,3-disubstituted cyclopentane units in the main chain were successively synthesized by copolymerization of ethylene or polypropylene with cyclopentene (CPE) or 1,5-hexadiene (HD), respectively, using zirconocene catalysts [2–5]. Among these copolymers, polyethylene containing 1,3-cyclopentane units in the main chain showed a unique crystalline structure, transition from the orthorhombic cell to the hexagonal cell increasing with HD in the copolymers [6,7]. The polyethylene is the first example of the ethylene-based copolymer which shows hexagonal phase under the ambient temperature and pressure without external treatment. The hexagonal phase of polyethylene is relevant to liquid crystalline phase, as reported by Ungar, and would make possible new applications of polyolefins.

The copolymerization of ethylene with HD, however, was accompanied by crosslinking reaction, which yielded unfavorable gel fraction [4]. An alternating synthetic route of polyethylene containing 1,3-cyclopentane units is ring-opening metathesis polymerization (ROMP) of norbornene (NB) or

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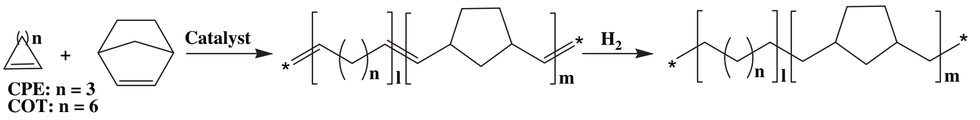
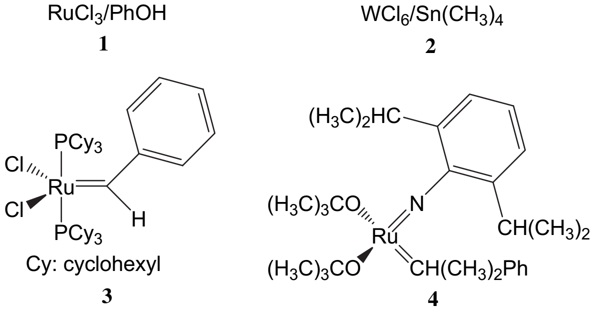


Scheme 1.



Scheme 2. Catalysts for ring-opening metathesis polymerization.

norbornene-derivatives [8] following hydrogenation reaction. This process is commercially used to synthesize amorphous cycloolefin polymers for optical materials with high performance, good transparency, high glass transition temperature, low water absorption, and so on [9–11]. We have applied this method to synthesize crystalline polyethylene containing 1,3-cyclopentane units in the main chain by means of ring-opening metathesis copolymerization of a cycloolefin and NB following hydrogenation reaction. The method should make it possible to synthesize the desired polyethylene without forming crosslinking fraction which was reported in the copolymerization of ethylene and HD. The methylene length between cyclopentane units in the copolymer can be controlled by means of copolymerization with cycloolefins of different molecular sizes.

In this study, we have investigated ring-opening metathesis copolymerization of CPE or cyclooctene (COT) and norbornene (NB) with four kinds of catalysts (Scheme 2) following hydrogenation reaction, as shown in Scheme 1 [12–18], and studied the crystalline structure and thermal properties of the resulting copolymers.

2. Experimental part

2.1. Materials

Catalysts for ring-opening metathesis polymerization, ruthenium(III) chloride *n*-hydrate (**1**), WCl_6 (**2**), benzylidene-bis(tricyclohexylphosphine)dichlororuthenium(IV) (**3**), and 2,6-diisopropylphenylimidoneophylidenemolybdenum-(VI)bis(*t*-butoxide) (**4**) (Scheme 2), were commercially obtained from Wako Pure Chemical Industries, Ltd. or Chisso Co. Ltd. and used without further purification. Phenol (Wako Pure Chemical Industries, Ltd.) and tetramethyltin (Tokyo Kasei Kogyo) were used without further purification. CPE, COT, and NB were commercially obtained from Aldrich, and dried with CaH_2 under nitrogen atmosphere. 1,4-Dioxane (dehydrated grade) and dichloromethane (dehydrated grade) were commercially obtained from Kanto Kagaku Co. Ltd. and used as received. *p*-Toluenesulfonhydrazide (TSH) was commercially obtained from Tokyo Kasei Kogyo and used as received. Xylene was commercially obtained and dried with CaH_2 and distilled under nitrogen atmosphere.

2.2. Copolymerization procedure

Copolymerizations of CPE or COT and NB with catalysts **1–4** were carried out in a 50-mL glass reactor equipped with a magnetic stirrer. Toluene was added to the reactor under nitrogen atmosphere. Further general procedures of the copolymerization with each catalyst are descried below.

*Copolymerization with catalyst **1** (run 1)*: Phenol (42.0 mmol, 4.0 g), NB (5.3 mmol, 0.50 g), and CPE (48.0 mmol, 4.5 mL) were introduced to the reactor. The copolymerization was started by introducing 16.0 mg of catalyst **1** to the reactor. The copolymerizations of different CPE/NB feed ratio or COT/NB were also conducted with the same procedure.

*Copolymerization with catalyst **2** (run 6)*: NB (10.7 mmol, 1.01 g), CPE (43.2 mmol, 3.8 mL), and dioxane (5.0 mL) were introduced to the reactor. The copolymerization was started by introducing a dioxane solution of the catalyst system, catalyst **2** (0.25 mmol, 0.10 g), tetramethyltin (0.003 mmol, 0.2 mL), and dioxane (5.0 mL), to the reactor. The copolymerizations of different CPE/NB feed ratio or COT/NB copolymerization were also conducted with the same procedure.

*Copolymerization with catalyst **3** (run 9)*: NB (17.1 mmol, 1.61 g), CPE (68.4 mmol, 6.1 mL), and dichloromethane (6.0 mL) were introduced to the reactor. The copolymerization was started by introducing a dichloromethane solution of the catalyst system, catalyst **3** (0.012 mmol, 10.0 mg) and dichloromethane (10.0 mL), to the reactor. The copolymerizations of different CPE/NB feed ratio or COT/NB were also conducted with the same procedure.

*Copolymerization with catalyst **4** (run 12)*: NB (2.1 mmol, 0.19 g) and CPE (8.4 mmol, 0.7 mL) were introduced to the reactor. The copolymerization was started by introducing 0.021 mmol (10.0 mg) of catalyst **4** to the reactor. The copolymerizations of different CPE/NB feed ratio or COT/NB were also conducted with the same procedure.

The copolymerizations were terminated by adding a small amount of methanol. The polymer was precipitated in a large excess of methanol and recovered by filtration. The copolymer obtained was dissolved in chloroform and re-precipitated in a large excess of methanol. The resulting copolymer was finally recovered by filtration and dried in vacuo at room temperature for 6 h.

2.3. Hydrogenation

Hydrogenation of the copolymers was carried out in a 50-mL glass reactor equipped with a magnetic stirrer. About 0.1 g of a copolymer, four times molar equivalent of TSH per unsaturated units in the copolymer, and 15.0 mL of xylene were added to the reactor under nitrogen atmosphere [19]. The hydrogenation proceeded at 135 °C for 4 h. The reaction was terminated by adding a small amount of water and the polymer was precipitated in a large excess of methanol. The copolymer obtained was washed with methanol, and dried in vacuo at 60 °C for 6 h.

2.4. Analytical procedures

^{1}H NMR or ^{13}C NMR spectra of copolymers were recorded on a JEOL Alpha-300 spectrometer in pulse Fourier transform mode. The sample solution of unsaturated copolymer was made in $CDCl_3$ and recorded at room temperature. The sample solution of hydrogenated copolymer was made in trichlorobenzene/C_6D_6 (4/1 v/v) and recorded at 90 °C. The resonance of $CDCl_3$ (7.15 ppm, 77.03 ppm) or C_6D_6 (7.15 ppm, 128.03 ppm) was used as an internal reference, respectively. Molecular weight and molecular weight distribution of the copolymer were measured at 40 °C by means of gel-permeation chromatography (JASCO LC-2000) using chloroform as a solvent and calibrated with standard polystyrene samples. Thermal properties of the copolymers were investigated by a Seiko DSC220 (Seiko Instruments Inc.) at a heating rate of 20 °C/min after previously heating to 200 °C/20 °C per minute and cooling to 20 °C/10 °C per minute. Temperature-rising elution fractionation (TREF) of the hydrogenated copolymers was carried out according to the following method. The copolymer (0.6 g) and xylene (100 mL) were introduced to a 200 mL flask. The copolymer was dissolved at 135 °C and left for 2 h. Sea sand (180 g) was added to the polymer solution at 135 °C and left for 2 h. The copolymer mixture was gradually cooled to room temperature and was heated to an elution temperature and left for 2 h and xylene solution of the copolymer was collected by filtration using a ball filter. The fractionated polymer was precipitated in methanol, recovered by filtration and dried in vacuo at 60 °C for 6 h.

Samples of WAXD measurement were melted at 200 °C and pressed under 10 MPa pressure, followed by quenching in water of room temperature. WAXD patterns of the copolymers were acquired on a Rigaku Rad-C using Cu Kα radiation. Samples for FT-IR spectroscopy were melted at 200 °C and pressed under 10 MPa pressure, followed by gradual cooling to room temperature. Infrared spectra were measured using JASCO FT-IR-460 Plus. Attenuated Total Reflection method was employed at 256-times scan with a spectral resolution of 1 cm^{-1}.

3. Results and discussion

3.1. Ring-opening metathesis copolymerization of CPE and NB

Ring-opening metathesis copolymerization of CPE and NB was conducted with catalysts **1–4**. The results are presented in Table 1. NB content in the copolymer linearly increased with increasing of NB concentration in the feed. The reactivity of NB is much higher than that of CPE, and the copolymers with high NB content (more than 39 mol%) were obtained in the experiment. The catalyst nature did not affect the monomer reactivity of the copolymerization.

3.2. Structure and thermal properties of hydrogenated poly(CPE-co-NB)

Hydrogenation of the unsaturated units in the ring-opening metathesis copolymerized poly(CPE-*co*-NB) was conducted according to Section 2. Completion of the hydrogenation reaction was confirmed by ^{1}H NMR spectroscopy of the resulting

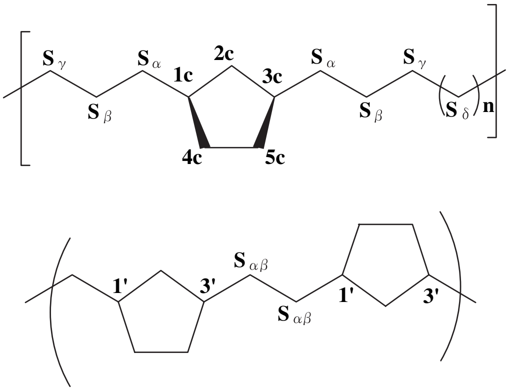
Table 1
Ring-opening metathesis copolymerization of CPE and NB

Sample	Catalyst	Time (h)	Yield (g)	Activity (kg/mol M h)	NB in feed (mol%)	NB in copolymer[a] (mol%)	M_n[b] ($\times10^{-5}$)	M_w/M_n[b]
1	**1**	24	0.26	0.67[c]	10	61	1.9	2.5
2	**1**	24	0.49	1.27[c]	15	70	4.3	1.6
3	**1**	24	0.63	1.65[c]	25	78	2.8	2.2
4	**2**	1.5	0.51	1.68	10	55	0.8	2.7
5	**2**	0.4	0.48	4.74	15	63	0.9	2.8
6	**2**	0.5	0.51	4.04	20	87	3.4	2.3
7	**3**	0.2	0.32	78.1	10	39	0.3	1.8
8	**3**	0.2	0.43	105	15	59	0.4	1.9
9	**3**	0.2	0.46	114	20	76	0.5	1.9
10	**3**	0.1	0.34	169	40	92	0.6	2.8
11	**4**	16	0.11	0.20	10	49	0.5	3.9
12	**4**	16	0.10	0.18	20	63	0.5	2.7
13	**4**	16	0.27	0.51	40	91	1.1	2.1
14	**4**	16	0.35	0.64	100	100	1.1	3.5

[a] Determined by ^{1}H NMR.

[b] Determined by GPC calibrated using polystyrene standard samples.

[c] kg/g cat h.



Scheme 3. Structure of hydrogenated poly(CPE-*co*-NB) or poly(COT-*co*-NB).

copolymers. The hydrogenated copolymer formed polyethylene containing 1,3-cyclopentane units in the main chain as shown in Scheme 3. Fig. 1 shows ^{13}C NMR spectrum of hydrogenated poly(CPE-*co*-NB), and indicates that the 1,3-cyclopentane units in the copolymer main chain forms *cis*-structure [4].

DSC melting curves of the hydrogenated copolymers (samples 1H–3H) obtained with catalyst **1** are shown in Fig. 2(1) and the thermal properties are summarized in Table 2. Multiple melting peaks were detected in all the copolymers. A clear relationship between the content of cyclopentane unit and the ΔH_m was not found in those copolymers. These unexpected results should be derived from the heterogeneity of the copolymer composition. The main melting peaks at around 117 °C were observed in all the copolymers, and whose temperatures were almost independent of the NB (1,3-cyclopentane unit) content in the copolymer. Small melting peaks were detected at around 73 and 133 °C. A hydrogenated ring-opening metathesis polymerized NB obtained with catalyst **4** (sample 14H), poly(ethylene-1,3-cyclopentane), showed the melting peaks at 131.2 and 144.2 °C (Table 5). Intensity of the higher melting peak of hydrogenated poly(CPE-*co*-NB), which should be derived from NB-rich (co)polymer, increased with increasing NB content in the copolymer. These results indicate heterogeneity of composition of the copolymer obtained with catalyst **1**.

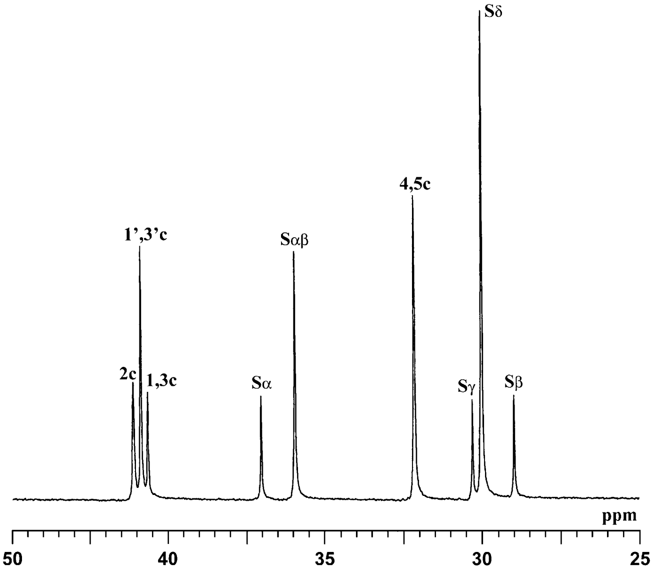


Fig. 1. ^{13}C NMR spectrum of hydrogenated poly(CPE-*co*-NB) obtained with catalyst **4** (sample 12H: NB in copolymer 63 mol%).

TREF of the copolymers was investigated to elucidate the composition distribution of the copolymers. TREF diagrams of the copolymers (samples 1H and 3H) are shown in Fig. 3 (1). The initial and final elution temperatures of the copolymer slightly decreased with increasing of the NB (1,3-cyclopentane unit) content in the copolymer. The TREF diagrams of the copolymers indicated existence of 10 wt% of the high temperature elution fraction. Thermal properties of the eluted fractions of samples 1H and 3H are also summarized in Table 2 [20]. Two compositions with different melting temperatures of 70–80, 115 °C were detected in the fractions eluted lower than 55 °C. The compositions with higher melting temperature of 130 °C were eluted more than 60 °C. The results cleared the existence of three compositions with different melting temperatures, about 70–80, 115, 130 °C, in samples 1H and 3H.

DSC melting curves of the hydrogenated copolymers (samples 4H–6H) obtained with catalyst **2** are shown in Fig. 3 (2) and the thermal properties are summarized in Table 3. Sample 4H showed one melting peak at 115 °C, while the copolymer with higher NB (1,3-cyclopentane unit) content (samples 5H and 6H) showed multiple melting peaks from 80 to 135 °C. TREF diagrams of the copolymers obtained with catalyst **2** (samples 5H and 6H) are shown in Fig. 3 (2). Thermal properties of the eluted fractions of samples 5H and 6H are summarized in Table 3 [20]. The TREF diagram of sample 5H indicated that distribution of the copolymer composition was almost homogeneous. On the other hand, sample 6H was eluted wide range of the temperature, indicating broad distribution of copolymer composition. Sample 5H was composed with the composition whose melting temperature was about 115 °C with small amount of a low melting temperature fraction whose melting temperature was about 80 °C. The results of the elution of 6H cleared the existence of four kinds of compositions with different melting temperatures of about 80, 100–120, 130 and 160 °C. Addition of NB in the feed should induce the heterogeneity of the active species for the metathesis copolymerization.

DSC melting curves of the hydrogenated copolymers (samples 7H–10H) obtained with catalyst **3** are shown in Fig. 2 (3) and the thermal properties are summarized in Table 4. All the copolymers showed the main melting peak from 115 to 125 °C with the small peaks from 79 to 97 °C. The melting temperature of the main peaks roughly increased with increasing NB (1,3-cyclopentane unit) content in the copolymer. TREF diagrams of the copolymers obtained with catalyst **3** (samples 8H and 10H) are shown in Fig. 3 (3). The TREF diagrams of the copolymers indicated existence of 30 wt% of the low temperature elution fraction. Thermal properties of the eluted fractions of samples 8H and 10H are summarized in Table 4 [20]. These samples contained two kinds of compositions, whose melting temperatures were about 75–95 °C and 110–120 °C.

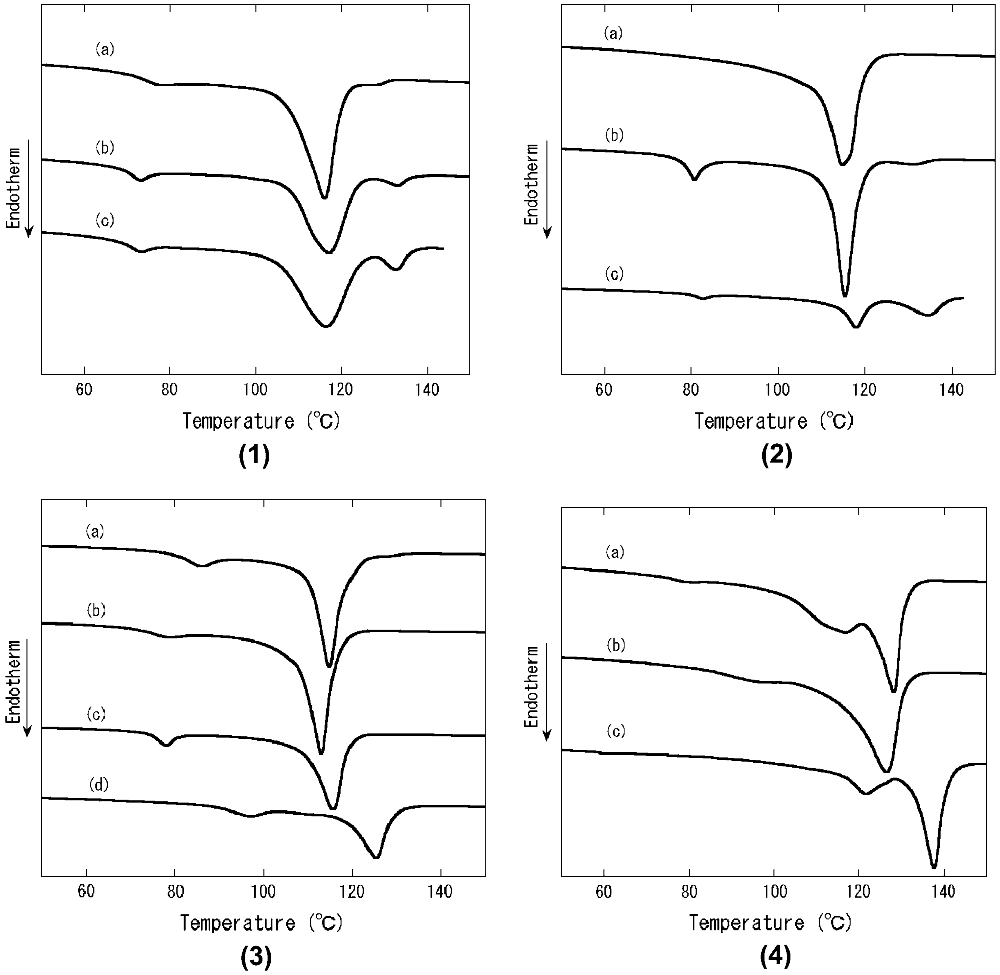


Fig. 2. DSC melting curves of hydrogenated poly(CPE-*co*-NB) obtained with catalyst **1** (1): (a) sample 1H; (b) sample 2H; (c) sample 3H, catalyst **2** (2): (a) sample 4H; (b) sample 5H; (c) sample 6H, catalyst **3** (3): (a) sample 7H; (b) sample 8H; (c) sample 9H; (d) sample 10H, catalyst **4** (4): (a) sample 11H; (b) sample 12H; (c) sample 13H.

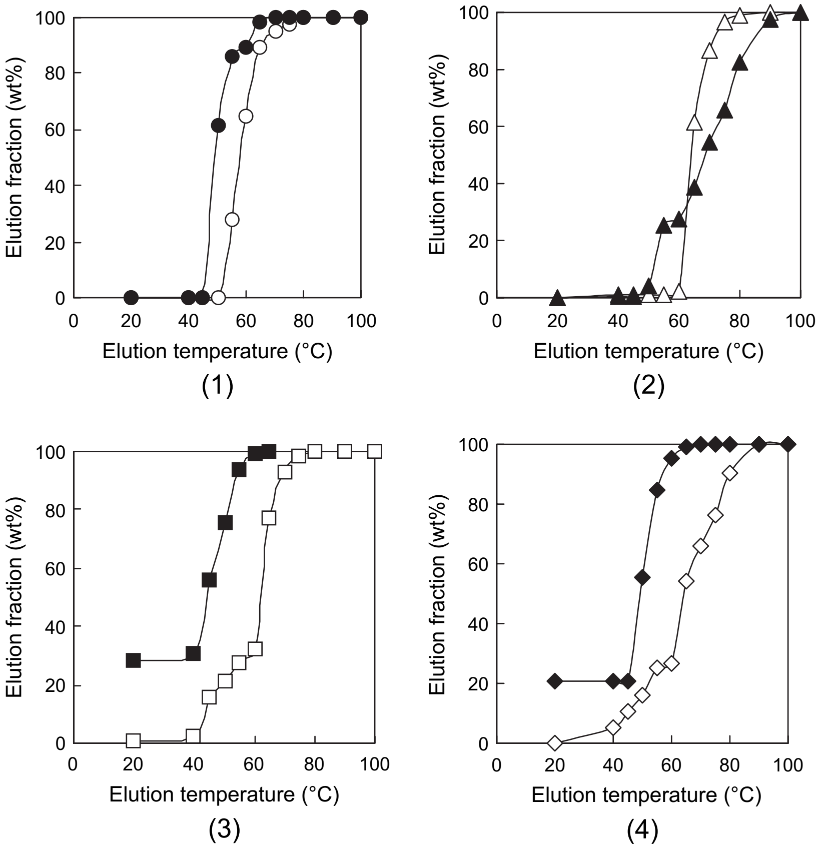
DSC melting curves of the hydrogenated copolymers (samples 11H–13H) obtained with catalyst **4** are shown in Fig. 2 (4) and the thermal properties are summarized in Table 5. All the copolymers showed multiple and/or broad melting peaks. TREF diagrams of the copolymers obtained with catalyst **4** (samples 12H and 13H) are shown in Fig. 3 (4). The diagrams of the copolymers indicated the existence of 20–25 wt% of the low temperature elution fraction. Thermal properties of the eluted fractions of samples 12H and 13H are summarized in Table 5 [20]. These samples contained two or three kinds of compositions, whose melting temperatures ranged from 110 to 135 °C.

Table 2
Thermal properties of hydrogenated poly(CPE-*co*-NB) obtained with catalyst **1**

Sample	NB in copolymer (mol%)	Elution temperature (°C)	T_m[a] (°C)	ΔH_m[a] (J/g)
1H	61		78.0/116.0	65.0
1H50		50	76.1/113.8	77.3
1H55		55	77.1/114.7	64.6
1H60		60	76.2/112.9/129.4	60.6
2H	70		73.0/117.4/133.4	59.8
3H	78		73.5/116.5/132.2	64.6
3H50		50	69.0/113.3	61.9
3H55		55	69.0/115.5	55.6
3H60		60	115.1/132.5	44.7
3H65		65	112.9/134.3	33.4

[a] Determined by DSC.

The molecular weight distribution of the copolymers was narrow, heterogeneity of the copolymer composition has been, however, observed in all the hydrogenated copolymers independent of the catalysts used. In particular, catalysts **3** and **4** have been known as homogeneous catalysts for ring-opening metathesis polymerization of cycloolefins. We have confirmed reproducibility of the composition distribution of the hydrogenated copolymers. We concluded that the unexpected results derived not from the technical problems in the experiment but from the nature of the active species. The increase of NB in the feed broadened the composition distribution of copolymer. The catalysts with an NB ligand have not been isolated, although it seems likely that the NB-coordination to the active sites caused the active sites of multiple monomer reactivity, and give rise to the composition distribution of the copolymers. A similar phenomenon was observed



(1)
(2)
(3)
(4)

Fig. 3. Relationship between elution temperature and summation of elution fraction of hydrogenated poly(CPE-*co*-NB) obtained with catalyst **1** (1): ○ sample 1H (NB, 61 mol%); ● sample 3H (NB, 78 mol%), catalyst **2** (2): △ sample 5H (NB, 63 mol%); ▲ sample 6H (NB, 87 mol%), catalyst **3** (3): □ sample 8H (NB, 59 mol%); ■ sample 10H (NB, 92 mol%), catalyst **4** (4): ◇ sample 12H (NB, 63 mol%); ◆ sample 13H (NB, 91 mol%).

in the vinyl-type copolymerization of ethylene and NB with zirconocene catalysts [21].

3.3. Crystalline structure of hydrogenated poly(CPE-co-NB)

WAXD patterns of hydrogenated poly(CPE-*co*-NB) are shown in Fig. 4 (1–4) obtained with catalysts **1**–**4**, respectively. In the case of typical crystalline polyethylene, reflection peaks due to (110) and (200) crystal planes of orthorhombic cell at $2\theta = 21°$ and 23.5°, respectively, are observed in the WAXD pattern. These reflection peaks were detected in the WAXD patterns of samples 4H (Fig. 4 (2) (a)) and 11H–13H (Fig. 4 (4) (a–c)), obtained with catalysts **2** and **4**, respectively. A diffraction peak at $2\theta = 19.7$–20.0° was observed in most of the copolymers. The reflection should be due to the (100) plane of hexagonal cell of polyethylene containing 1,3-cyclopentane units in

Table 3
Thermal properties of hydrogenated poly(CPE-*co*-NB) obtained with catalyst **2**

Sample	NB in copolymer (mol%)	Elution temperature (°C)	T_m[a] (°C)	ΔH_m[a] (J/g)
4H	55		115.2	105.9
5H	63		80.6/115.6	101.7
5H60		60	79.7/115.5	85.5
5H65		65	79.3/115.1	85.7
5H70		70	79.3/115.5	74.1
6H	87		82.7/117.8/134.6	42.3
6H50		50	76.1/101.2	26.9
6H55		55	81.6/118.2	74.5
6H65		65	116.0/131.2/158.9	29.3
6H70		70	132.1/158.9	27.5
6H75		75	129.0/158.9	33.9

[a] Determined by DSC.

Table 4
Thermal properties of hydrogenated poly(CPE-*co*-NB) obtained with catalyst **3**

Sample	NB in copolymer (mol%)	Elution temperature (°C)	T_m[a] (°C)	ΔH_m[a] (J/g)
7H	39		86.4/115.1	109.9
8H	59		78.8/113.3	122.3
8H40		40	112.0	99.4
8H45		45	112.0	97.8
8H50		50	76.2/111.5	170.0
8H55		55	77.5/112.4	137.5
8H60		60	78.4/112.4	106.9
8H65		65	113.8	122.6
8H70		70	113.4	161.5
9H	76		78.1/115.7	77.5
10H	92		97.3/125.4	47.3
10H20		20	95.8/113.8	9.8
10H45		45	116.9	40.2
10H50		50	87.4/119.2	38.4
10H55		55	92.3/123.6	52.3

[a] Determined by DSC.

Table 5
Thermal properties of elution fraction of hydrogenated poly(CPE-*co*-NB) obtained with catalyst **4**

Sample	NB in copolymer (mol%)	Elution temperature (°C)	T_m [a] (°C)	ΔH_m [a] (J/g)
11H	49		117.4/127.7	96.4
12H	63		126.8	79.4
12H40		40	112.0/122.7	104.8
12H50		50	113.7/123.6	87.6
12H60		60	114.2	106.0
12H65		65	114.2/122.2	73.8
12H70		70	115.1/122.2	111.6
12H80		80	121.8	146.0
12H90		90	127.2	173.9
13H	91		121.8/137.5	58.9
13H20		20	111.5	17.9
13H50		50	116.0	42.0
13H55		55	116.0/126.7	44.7
13H60		60	112.9/133.0	39.0
13H65		65	118.3/134.8	38.9
14H	100		131.2/144.2	55.3

[a] Determined by DSC.

the main chain [6,7], which was formed by hydrogenated poly(CPE-*co*-NB). Reflection peaks at $2\theta = 18°$ and 19° were attributed to the diffraction from co-existed hydrogenated NB-based copolymer [22]. The DSC analysis supports the result.

FT-IR measurement of polyethylene gives us useful information about the structural transformation from orthorhombic to hexagonal cell. Fig. 5 (1–4) shows the FT-IR spectra in the frequency region of the methylene rocking vibration (710–740 cm^{-1}) of hydrogenated poly(CPE-*co*-NB) obtained with catalysts **1**–**4**, respectively. In the case of typical crystalline polyethylene, the absorption bands of the methylene rocking vibration due to orthorhombic cell are observed at 719 and 730 cm^{-1}. On the other hand, an absorption band due to the hexagonal cell appeared at 723 cm^{-1}, as observed in poly(ethylene-*co*-HD) [7]. No absorption band was detected from 700 to 730 cm^{-1} in the FT-IR spectrum of hydrogenated metathesis polymerized NB [23]. In the FT-IR spectra of samples 4H (Fig. 5 (2) (a)) and 11H (Fig. 5 (4) (a)), the absorption bands due to orthorhombic cell were detected at 719 and 730 cm^{-1}.

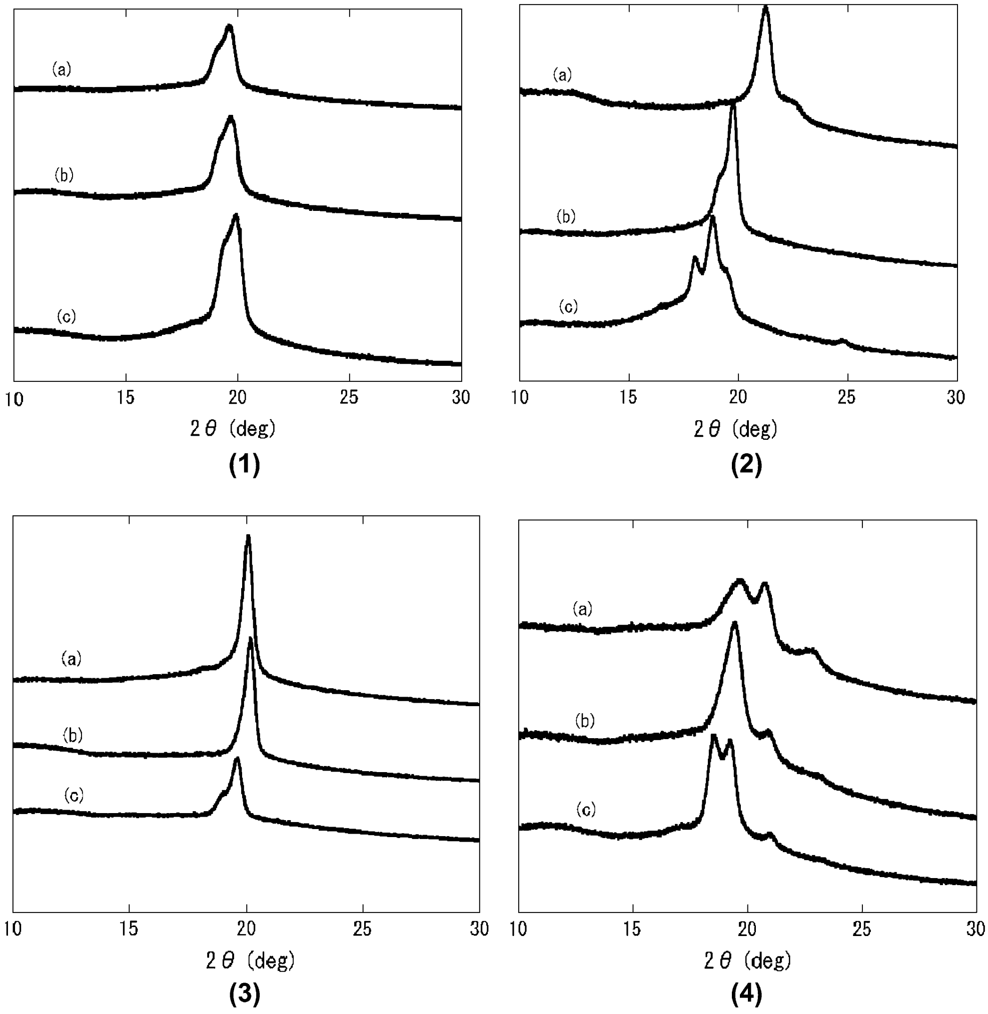


Fig. 4. WAXD patterns of hydrogenated poly(CPE-*co*-NB) obtained with catalyst **1** (1): (a) sample 1H; (b) sample 2 H; (c) sample 3H, catalyst **2** (2): (a) sample 4H; (b) sample 5H; (c) sample 6H, catalyst **3** (3): (a) sample 7H; (b) sample 8H; (c) sample 9H, catalyst **4** (4): (a) sample 11H; (b) sample 12H; (c) Sample 13H.

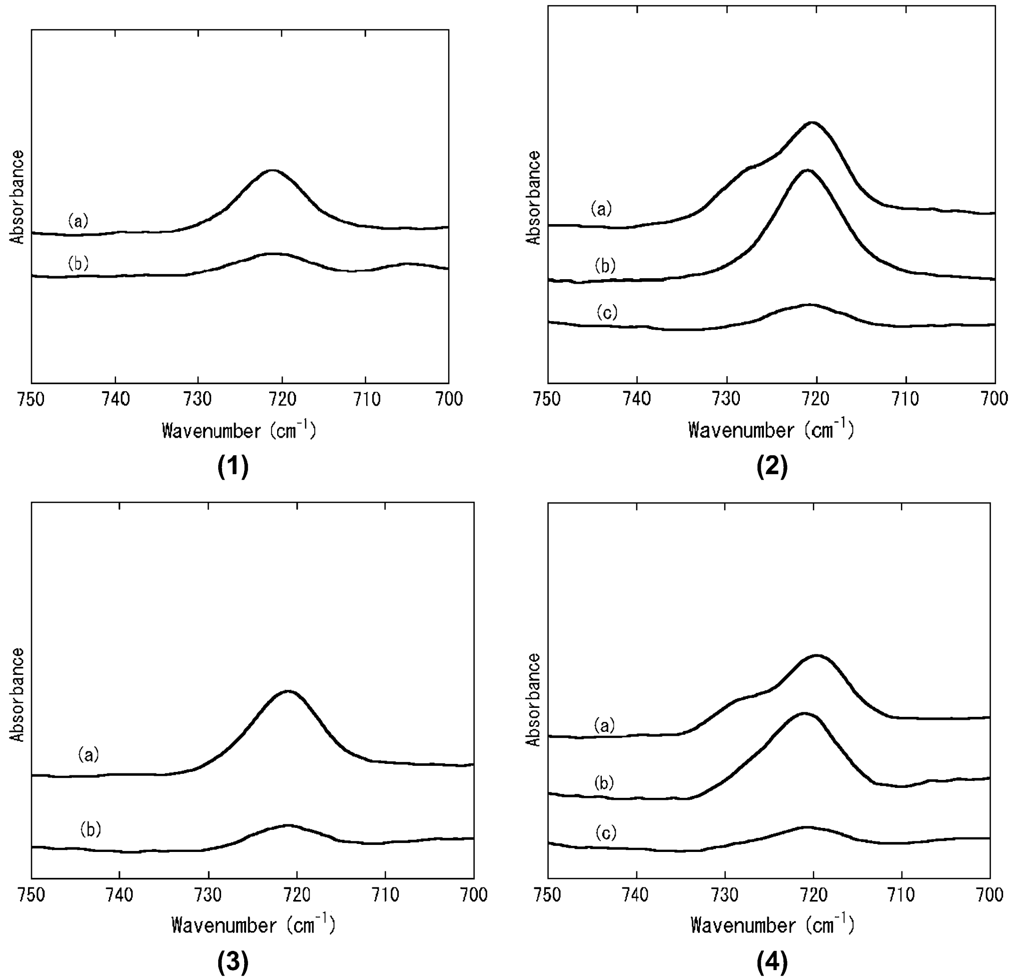


Fig. 5. FT-IR spectra of hydrogenated poly(CPE-*co*-NB) obtained with catalyst **1** (1): (a) sample 1H; (b) sample 3H, catalyst **2** (2): (a) sample 4H; (b) sample 5H; (c) sample 6H, catalyst **3** (3): (a) sample 8H; (b) sample 10H, catalyst **4** (4): (a) sample 11H; (b) sample 12H; (c) sample 13H.

The FT-IR spectra of the other samples showed an absorption band at 723 cm^{-1}, indicating formation of the hexagonal cell.

WAXD and FT-IR measurements of hydrogenated poly(CPE-*co*-NB) cleared, with all but some contamination of orthorhombic cell and/or co-existed hydrogenated NB-rich copolymer, existence of hexagonal cell due to polyethylene containing 1,3-cyclopentane units in the main chain.

3.4. Ring-opening metathesis copolymerization of COT and NB

Ring-opening metathesis copolymerization of COT and NB was conducted with catalysts **1**–**4**. The results are presented in Table 6. NB content in the copolymer linearly increased with increasing NB concentration in the feed. The incorporation of NB in the copolymerization with COT was lower than that in the copolymerization with CPE. The catalyst nature affected the monomer reactivity of the copolymerization, and the incorporation of NB decreased in the following order; **2** > **4** > **3** > **1**. Molecular weights of the copolymers were higher than those of poly(CPE-*co*-NB), and increased with increasing NB in the copolymer. Molecular weight distributions of the copolymers were narrow.

3.5. Thermal properties of hydrogenated poly(COT-co-NB)

Hydrogenation of the unsaturated units in the ring-opening metathesis copolymerized poly(COT-*co*-NB) was conducted to obtain the polyethylene containing 1,3-cyclopentane units in the main chain. Thermal properties of hydrogenated poly(COT-*co*-NB) are summarized in Table 7. A clear relationship between the NB (1,3-cyclopentane unit) content and the ΔH_m was not found in those copolymers. DSC melting curves of some hydrogenated copolymers (samples 16H, 19H, 24H, and 25H) obtained with catalysts **1**–**4**, respectively, are shown in Fig. 6. Multiple melting peaks were detected in the DSC curves. The melting peaks ranging from 130 to 145 °C should be derived from NB-rich copolymer [20]. These results indicate the heterogeneity of the copolymer composition,

Table 6
Copolymerization of COT with NB and properties of the copolymer

Sample	Catalyst	Time (h)	Yield (mg)	Activity (kg/mol M h)	NB in feed (mol%)	NB in copolymer[a] (mol%)	M_n[b] ($\times10^{-5}$)	M_w/M_n[b]
15	**1**	20	283	1.76[c]	15	8	5.8	1.4
16	**1**	20	380	2.38[c]	20	19	6.5	1.3
17	**1**	20	578	3.61[c]	30	38	10.0	1.2
18	**2**	0.5	119	1.83	5	4	1.0	1.5
19	**2**	0.8	247	2.37	10	23	1.9	1.6
20	**2**	0.4	164	3.15	20	56	5.0	1.5
21	**2**	0.1	700	5.38	30	89	3.9	1.7
22	**3**	0.1	385	631	15	21	5.8	1.3
23	**3**	0.1	840	1377	20	27	8.1	1.2
24	**3**	0.1	917	1530	30	31	6.7	1.4
25	**4**	0.2	82	40.0	15	37	2.1	2.5
26	**4**	0.1	130	42.0	20	49	4.6	1.6
27	**4**	0.2	46	22.3	30	61	6.9	1.4

[a] Determined by ^{1}H NMR.
[b] Determined by GPC using polystyrene standard.
[c] kg/g cat h.

Table 7
Thermal properties of hydrogenated poly(COT-*co*-NB)

Sample	Catalyst	NB in copolymer[a] (mol%)	T_m[b] (°C)	ΔH_m[b] (J/g)
15H	**1**	8	88.3/133.5	38.9
16H	**1**	19	93.2/134.8	47.9
17H	**1**	38	121.1/143.1	35.0
18H	**2**	4	126.3/133.9	74.4
19H	**2**	23	126.8/139.7	72.3
20H	**2**	56	145.6	38.1
21H	**2**	89	141.0	31.0
22H	**3**	21	136.1	34.9
23H	**3**	27	123.5	64.0
24H	**3**	31	121.9/134.8	45.9
25H	**4**	37	130.7/142.9	86.1
26H	**4**	49	131.4	58.5
27H	**4**	61	129.9/141.5	24.2
14H	**4**	100	131.2/144.2	55.3

[a] Determined by ^{1}H NMR.
[b] Determined by DSC.

which was generated of necessity, independent of the catalysts used.

3.6. Crystalline structure of hydrogenated poly(COT-co-NB)

WAXD patterns of some hydrogenated poly(COT-*co*-NB) are shown in Fig. 7. Broad reflection peaks at $2\theta = 18°$ and $19°$, which were attributed to the diffraction from co-existed hydrogenated NB-rich copolymer, were observed in all the WAXD patterns. In the WAXD patterns of samples 19H, 24H, and 25H obtained with catalysts **2**, **3**, and **4**, respectively, the reflection peaks due to orthorhombic cell of polyethylene at $2\theta = 21°$ and $23.5°$ were observed. These reflection peaks indicate that the poly(COT-*co*-NB)s are composed of mixtures of COT-rich and NB-rich copolymers.

Fig. 8 shows the FT-IR spectra in the frequency region of the methylene rocking vibration (710–740 cm^{-1}) of some hydrogenated poly(COT-*co*-NB). The spectrum of sample 16H,

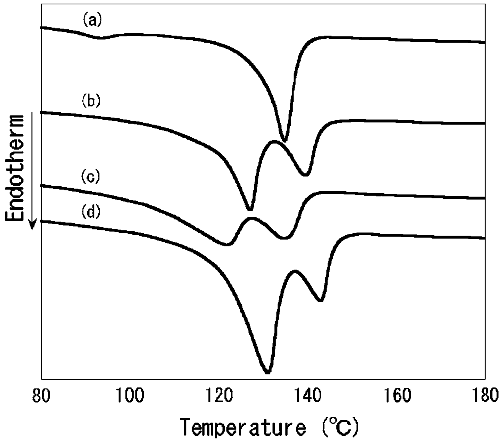


Fig. 6. DSC melting curves of hydrogenated poly(COT-*co*-NB) obtained with catalyst **1**: (a) sample 16H, catalyst **2**: (b) sample 19H, catalyst **3**: (c) sample 24H, catalyst **4**, (d) sample 25H.

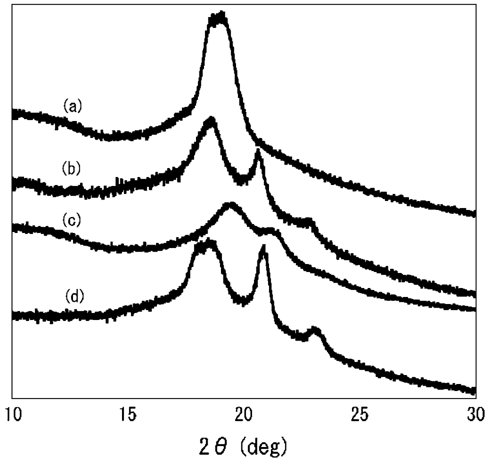


Fig. 7. WAXD patterns of hydrogenated poly(COT-*co*-NB) obtained with catalyst **1**: (a) sample 17H, catalyst **2**: (b) sample 19H, catalyst **3**: (c) sample 24H, catalyst **4**: (d) sample 25H.

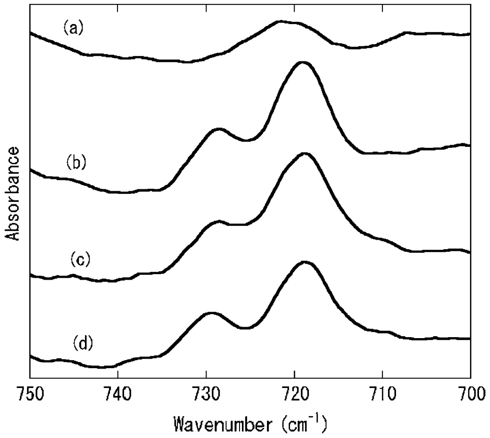


Fig. 8. FT-IR spectra of hydrogenated poly(COT-*co*-NB) obtained with catalyst **1**: (a) sample 15H, catalyst **2**: (b) sample 18H, catalyst **3**: (c) sample 23H, catalyst **4**: (d) sample 25H.

obtained with catalyst **1**, showed an absorption band at 723 cm^{-1} due to the hexagonal cell [7]. On the other hand, in the FT-IR spectra of samples 19H, 24H, and 25H, obtained with catalysts **2**, **3**, and **4**, respectively, the absorption bands due to orthorhombic cell were detected at 719 and 730 cm^{-1}.

WAXD and FT-IR measurements of hydrogenated poly(COT-*co*-NB) cleared that the copolymers obtained with catalyst **1** formed hexagonal cell, however, the other copolymers formed the orthorhombic cell, like the typical polyethylene. These results indicate that poly(COT-*co*-NB) obtained with catalysts **2**–**4** were composed of COT-rich copolymer and NB-rich copolymer mixtures.

With all its composition distribution, hydrogenated poly(CPE-*co*-NB) showed hexagonal phase in the crystal independent of the metathesis catalysts used. On the other hand, hydrogenated poly(COT-*co*-NB)s which were obtained with catalysts **2**–**4** formed the orthorhombic phase. The difference should be derived from their width of the composition distribution. Hydrogenated poly(CPE-*co*-NB) contains some ingredients of polyethylene with 1,3-cyclopentane units in the main chain which forms hexagonal phase, whereas, poly(COT-*co*-NB) should be composed with bimodal fractions of COT-rich and NB-rich copolymers.

4. Conclusion

Polyethylene containing 1,3-cyclopentane units in the main chain was successively synthesized by ring-opening metathesis copolymerization of CPE or COT with NB following hydrogenation reaction using TSH. The 1,3-cyclopentane units preferentially formed *cis*-structure. DSC, TREF, WAXD, and FT-IR analyses of the resulting copolymers elucidated, however, broad distribution of the copolymer composition.

In the case of hydrogenated poly(CPE-*co*-NB), the copolymers contained the hexagonal crystals. A hydrogenated poly(COT-*co*-NB) obtained with catalyst **1** also had the hexagonal crystals. While, the other hydrogenated poly(COT-*co*-NB) samples showed the WAXD patterns derived from the orthorhombic cell of ethylene-based polymer and hydrogenated ring-opening metathesis polymerized NB-based (co)polymer.

The ring-opening metathesis copolymerization of monocyclic cycloolefin and NB following hydrogenation should be one of the effective methods to synthesize polyethylene containing *cis*-1,3-cyclopentane units in the main chain. No crosslinking fraction, which could be formed by intermolecular reaction of polymer chains, was obtained. The thermal properties and crystalline structure of hydrogenated copolymers obtained with a classical catalyst **1** indicated comparative homogeneous active species in the copolymerizations. Some truly homogeneous catalyst for the metathesis copolymerizations should be developed in the next step.

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[23] FT-IR spectrum of hydrogenated ring-opening metathesis polymerized NB obtained with catalyst 4 is available in Supporting information.