

Synthesis and properties of polyethylene and polypropylene containing hydroxylated cyclic units in the main chain

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Abstract

Polyethylene and isotactic polypropylene containing hydroxylated cyclic units were synthesized by copolymerization of ethylene or propylene and cycloolefins, dicyclopentadiene (DCPD), 5-vinyl-2-norbornene (VNB), 5-ethylidene-2-norbornene (ENB), with zirconocene catalysts and subsequent hydroboration reaction of residual unsaturated group. The resulting hydroxylated copolymers showed higher glass transition temperature (T_g) than the original and hydrogenated copolymers. Relationship between the cycloolefin content and ΔT_g (ΔT_g = difference of T_g between hydroxylated copolymer and hydrogenated copolymer) was given by a straight line independent of the structure of the comonomers. Improvement in shape memory effect was observed in the hydroxylated ethylene-VNB copolymer.

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1. Introduction

Cycloolefin copolymers (COCs) have been developed for optical materials with high glass transition temperature. These copolymers are efficiently synthesized by copolymerization of conventional olefins and cycloolefins using homogeneous transition metal catalysts, especially metallocene catalysts. The metallocene catalysts are also effective catalysts for copolymerization with cycloolefins having another unsaturated group, termed cycloolefins. Copolymerizations of ethylene and various cycloolefins, such as vinylcyclohexene, cyclopentadiene, 1,5-cyclooctadiene, 2,5-norbornadiene, 5-vinyl-2-norbornene (VNB), dicyclopentadiene (DCPD), have been investigated with various metallocene catalysts. These copolymerizations produced the corresponding copolymers having unsaturated cyclic units in the polyethylene main chain [1–8]. The unsaturated group was efficiently converted to hydroxyl group or epoxy group with following chemical reactions [1–3]. The functionalization of cyclic units in the COCs is one of the useful methods to improve the properties of COCs.

Incorporation of hydroxylated cyclic units into COCs would improve the thermal properties, especially glass transition temperature (T_g), due to the hydrogen bonding between the hydroxyl groups. In this study, we have investigated copolymerization of ethylene or propylene with cycloolefins, DCPD, VNB, 5-ethylidene-2-norbornene (ENB), with zirconocene catalysts using methylaluminumoxane (MAO) as a cocatalyst, and following hydroboration reaction of the resulting copolymer to incorporate the hydroxyl group into the unsaturated cyclic units. Effect of hydroxy group on the thermal properties and mechanical properties of the copolymers has been studied with the comparison of the properties of original and hydrogenated copolymers.

2. Experimental part

2.1. Materials

The zirconocene catalysts *rac*-ethylenebis(indenyl)zirconium dichloride (1) and *rac*-dimethylsilylbis(2-methylindenyl)zirconium dichloride (2) were commercially obtained from Aldrich and Boulder Science Co., Ltd., respectively, and used without further purification. A toluene solution of triisobutylaluminum was purchased from Wako Pure Chemical Industries, Ltd. and used without further purification. Trityl tetrakis(pentafluorophenyl)borate ($\text{Ph}_3\text{C}(\text{C}_6\text{F}_5)_4$) was commercially obtained from Boulder Science and used as

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toluene solution. DCPD (Tokyo Kasei Kogyo) (a toluene solution) was dried with CaH_2 following filtration under nitrogen atmosphere. VNB (Aldrich), and ENB (Aldrich) were dried with CaH_2 under nitrogen atmosphere. Toluene and xylene were commercially obtained and dried with CaH_2 and distilled under nitrogen atmosphere. Ethylene was commercially obtained from Sumitomo Seika and used without further purification. Propylene was kindly donated from Mitsui Chemicals and used without further purification. *p*-Toluenesulfonylhydrazide (TSH) was commercially obtained from Tokyo Kasei Kogyo and used as received. A THF solution of 9-borabicyclo[3.3.1]nonane (9-BBN) was commercially obtained from Aldrich.

2.2. Copolymerization procedure

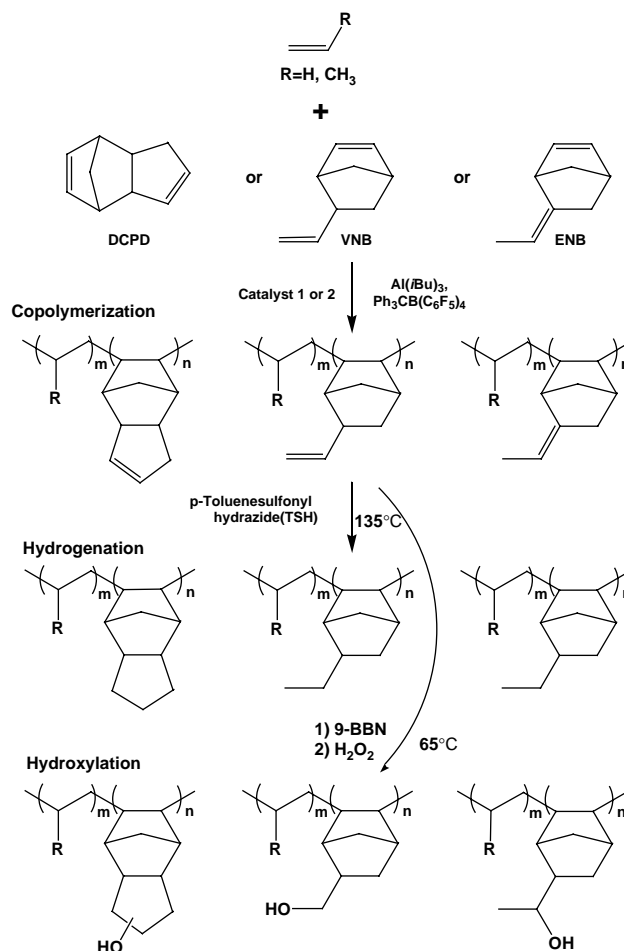
Copolymerizations of ethylene or propylene and cyclo-diolefins (DCPD, VN, or ENB) were carried out in a 100-mL glass reactor equipped with a magnetic stirrer. Toluene (50 mL) was added to the reactor under nitrogen atmosphere. Ethylene or propylene was introduced to the reactor at 40 °C under 1 atm until the solvent was saturated with the monomer, and measured amount of a cyclo-diolefin was added. A toluene solution of triisobutylaluminum and a zirconocene catalyst (2.5–10.0 μmol) were added to the reaction system (molar ratio of $[\text{Al}]/[\text{Zr}]=250$). The copolymerization was started by introducing the toluene solution of $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ to the reactor (molar ratio of $[\text{B}]/[\text{Zr}]=1.0$). The copolymerization was terminated by adding a small amount of methanol. The polymer was precipitated in a large excess of HCl acidified methanol and recovered by filtration. The copolymer obtained was washed with methanol and water. The resulting copolymer was finally washed with acetone and dried in vacuo at room temperature for 6 h.

2.3. Hydrogenation of unsaturated cyclic units

Hydrogenation of the copolymers was carried out in a 100-mL glass reactor equipped with a magnetic stirrer. A copolymer, four times molar equivalent of TSH per unsaturated units in the copolymer, and a proper quantity of xylene were added to the reactor under nitrogen atmosphere. The hydrogenation was conducted 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 acetone, and dried in vacuo at room temperature for 6 h.

2.4. Hydroxylation of unsaturated cyclic units

Hydroxylation of the copolymers was carried out in a 100-mL glass reactor equipped with a magnetic stirrer. A copolymer, toluene and THF (4:1 vol/vol) were added to the reactor under nitrogen atmosphere. The reactor was heated at 50 °C, and a THF solution of 9-BBN (5 equiv. of



Scheme 1.

9-BBN per unsaturated cyclic unit) was introduced to the reaction system. The hydroboration was conducted at 65 °C for 3 h. The reactor was cooled to 40 °C, and the reaction was terminated by adding a NaOH aqueous solution (1.5 M)

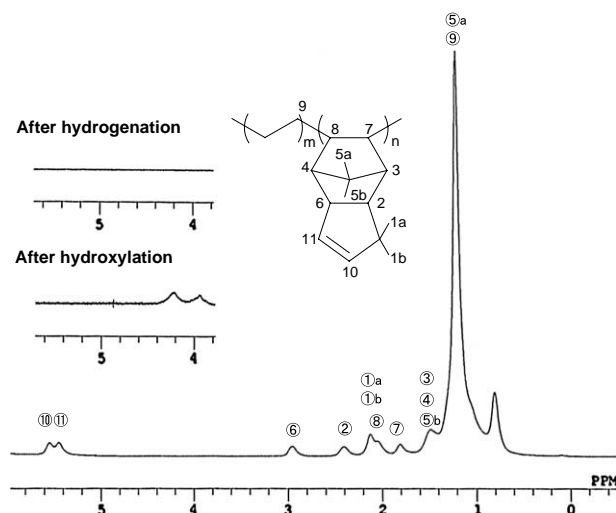


Fig. 1. ¹H NMR spectra of poly(ethylene-co-DCPD) (sample 1) and hydrogenated (sample 1-H) or hydroxylated (sample 1-OH) copolymers.

Table 1
Structure and thermal properties ethylene–cycloolefin copolymers and their derivatives

Sample	Comonomer	mol% ^a	T_m (°C)	T_g (°C)	Sample	T_m (°C)	T_g (°C)	$[\eta]$ dL/g	M_v^b	Sample	T_m (°C)	T_g (°C)	ΔT_g K	
1	DCPD	8.6	121.7	14.7	1-H	122.5	18.4	0.35	8,500	1-OH	126.9	39.1	20.7	
2		9.2	108.3	22.9	2-H	108.6	22.8			2-OH	112.0	50.0	27.2	
3		24.8	n.d ^c	65.4	3-H	n.d ^c	74.8			3-OH	n.d ^c	140.3	65.5	
4		30.5	n.d ^c	71.3	4-H	n.d ^c	83.3			4-OH	n.d ^c	145.2	61.9	
5	VNB	3.0	67.3/	−2.6	5-H	68.5/	−0.7	0.44	11,800	5-OH	77.0/	21.7	22.4	
			119.8			119.8						122.7		
6		5.0	120.5	−3.4	6-H	123.1	−2.8			6-OH	118.6	32.7	35.5	
7		7.5	122.3	3.9	7-H	122.2	6.4			7-OH	119.3	42.3	35.9	
8	ENB	10.0	119.5	11.0	8-H	121.1	14.2	0.40	10,300	8-OH	123.9	46.9	32.7	
9		1.8	100.5	−3.0	9-H	101.0	−2.0			9-OH	102.3	2.4	4.4	
10		12.6	118.0	12.0	10-H	119.7	14.2			10-OH	118.7	25.7	11.5	
11		15.6	n.d ^c	13.3	11-H	114.8	19.0			11-OH	115.5	42.6	23.6	
12		38.0	n.d ^c	41.0	12-H	n.d ^c	46.0	0.36	8,900	12-OH	n.d ^c	148.3	102.3	

^a Determined by ¹H NMR spectroscopy.

^b Viscosity–average molecular weight calculated by Mark–Houwink–Sakurada equation, $K=0.062$ (mL/g) and $\alpha=0.70$ were employed for ethylene-based copolymers.

^c Not detected.

and a mixture of H₂O₂ and THF. After further stirring for 3 h, the polymer was precipitated in a large excess of methanol. The resulting copolymer was washed with boiling methanol for 3 h, and acetone, and dried in vacuo at room temperature for 6 h.

2.5. Analytical procedures

¹H NMR and ¹³C NMR spectra of the copolymers were recorded at 110 °C on a JEOL Alpha-300 spectrometer in pulse Fourier transform mode. The sample solution was made in 1,2,4-trichlorobenzene/C₆D₆ (9:1 v/v) or 1,1,2,2-tetrachloroethane/1,1,2,2-tetrachloroethane-*d*₂ (9:1 v/v) as solvents and the resonance of C₆D₆ (7.15, 128.03 ppm) or 1,1,2,2-tetrachloroethane-*d*₂ (5.88, 74.47 ppm) was used as an internal

reference. Limiting viscosity number ($[\eta]$) of the copolymers was determined by Ubbelohde viscometer at 135 °C using decahydronaphthalene as a solvent. Thermal properties of the copolymers were investigated by a Seiko DSC220 (Seiko Instruments Inc.) at a heating rate of 10 °C/min after previous heating to 200 °C and cooling to −100 °C by 10 °C/min.

2.6. Test of shape memory effect

Test specimens were prepared by hot press at 200 °C, 20 Mpa following quenched in water at room temperature. The test specimens had the dimensions of 10 mm length, 8 mm width, and 0.85 mm thickness. The test specimen was elongated to 200% strain at 70 °C at a constant elongation rate of 10 mm/min, and subsequently cooled to −5 °C at 200% strain. The recovery was measured by maintaining the elongated sample at the recovery temperature for 5 min.

3. Results and discussion

3.1. Structure and properties of ethylene-based copolymers

The copolymerizations of ethylene and DCPD, VNB, or ENB were investigated with the catalyst 1 under the conditions described in Section 2. Hydrogenation and hydroxylation of the unsaturated cyclic units in the copolymers were conducted according to Section 2. The synthesis routes are summarized in Scheme 1. I will take an example Fig. 1, which shows ¹H NMR spectra of original poly(ethylene-*co*-DCPD) and hydrogenated or hydroxylated copolymers, to illustrate the structure of the copolymers. In the spectrum of original poly(ethylene-*co*-DCPD), signals derived from unsaturated group are observed at 5.4 and 5.5 ppm. Content of the DCPD was determined by ¹H NMR spectroscopy based on the signal intensity ratio of unsaturated group to the other proton signals. After the hydrogenation reaction, the signals derived from unsaturated group disappeared completely. In the spectrum of the hydroxylated polymer, the signals derived from unsaturated

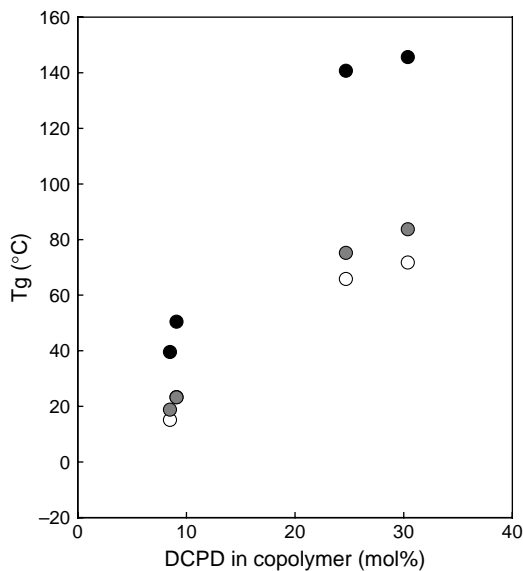


Fig. 2. Relationship between DCPD content and T_g of poly(ethylene-*co*-DCPD); original (white), after hydrogenation (gray), and after hydroxylation (black).

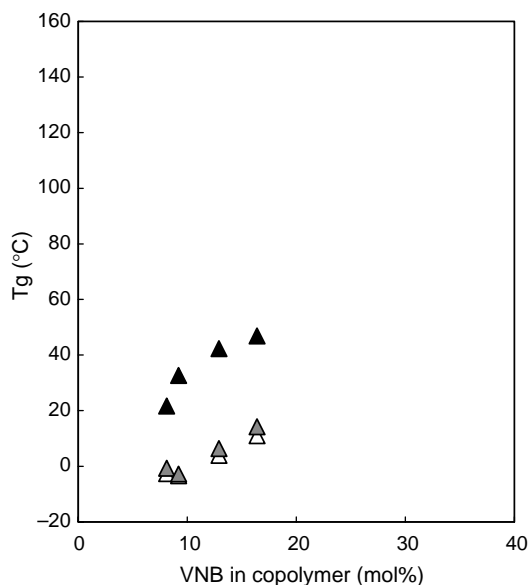


Fig. 3. Relationship between VNB content and T_g of poly(ethylene-*co*-VNB); original (white), after hydrogenation (gray), and after hydroxylation (black).

group disappeared completely, and new signals due to hydroxyl group appeared at 3.9 and 4.2 ppm. Content of the cycloolefins or completion of the hydrogenation and hydroxylation reactions of the copolymers with VNB or ENB was also confirmed by ^1H NMR spectroscopy. Structure and thermal properties of the copolymers with DCPD, VNB, and ENB are presented in Table 1 or Figs. 2–4, respectively. Melting temperature (T_m) of the copolymer with DCPD clearly decreased with increasing of DCPD content. However, a clear relationship between the VNB, ENB content of and the T_m was not found in those copolymers. This unexpected phenomenon should be derived from the heterogeneity of copolymer

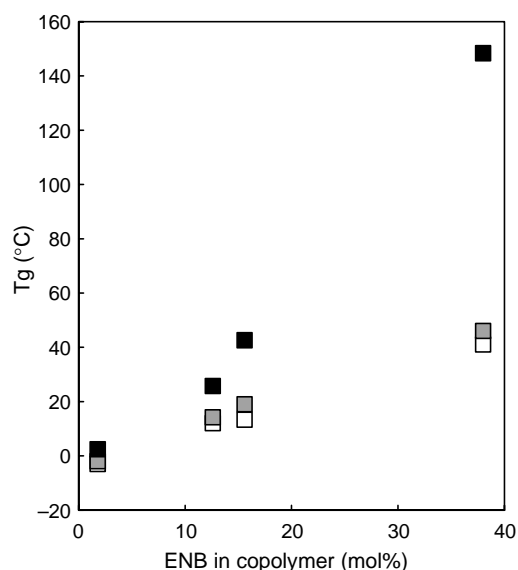


Fig. 4. Relationship between ENB content and T_g of poly(ethylene-*co*-ENB); original (white), after hydrogenation (gray), and after hydroxylation (black).

composition, as previously reported in ethylene–norbornene copolymer prepared by typical zirconocene catalysts [9]. Glass transition temperatures (T_g s) of all the copolymers increased with increasing of the cycloolefins in the copolymers. The copolymer with DCPD showed higher T_g than the other copolymers. The hydrogenated copolymers showed the T_g s as same as those of the original copolymers with the exception of the copolymers with DCPD. The T_g s of hydrogenated poly(ethylene-*co*-DCPD)s were higher than those of the original poly(ethylene-*co*-DCPD)s. One explanation for this phenomenon may be that the hydrogenated DCPD units reinforce entanglement of the polymer chains or stacking between cyclic units. There is room for further investigation. Remarkable increase in T_g s was observed in all the hydroxylated copolymers. The hydrogen bonding derived from the introduced OH groups should raise the T_g of the hydroxylated copolymers. The relationship between comonomer content and ΔT_g , (T_g of hydroxylated copolymer)–(T_g of hydrogenated copolymer), is illustrated in Fig. 5. The ΔT_g value linearly increased with increasing of comonomer content, independent of nature of the copolymerized cycloolefins. The slope of the plots is 2.4 K/(mol of comonomer).

3.2. Structure and properties of propylene-based copolymers

The copolymerizations of propylene and DCPD, VNB, or ENB with the catalyst 2, and the hydrogenation and hydroxylation of the unsaturated cyclic units in the copolymers were investigated according to Section 2 as shown in Scheme 1. Fig. 6 shows ^1H NMR spectra of original poly(propylene-*co*-DCPD) and hydrogenated or hydroxylated copolymers. Signals derived from unsaturated group are observed at 5.4 and 5.6 ppm. After the

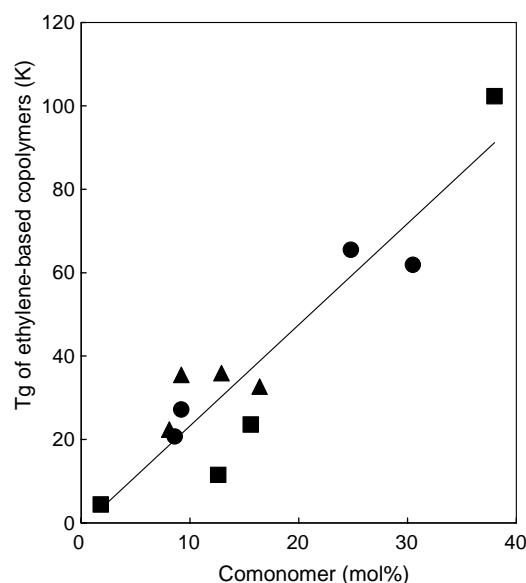


Fig. 5. Relationship between comonomer content and ΔT_g of ethylene-based copolymers with DCPD (●), VNB (▲), and ENB (■).

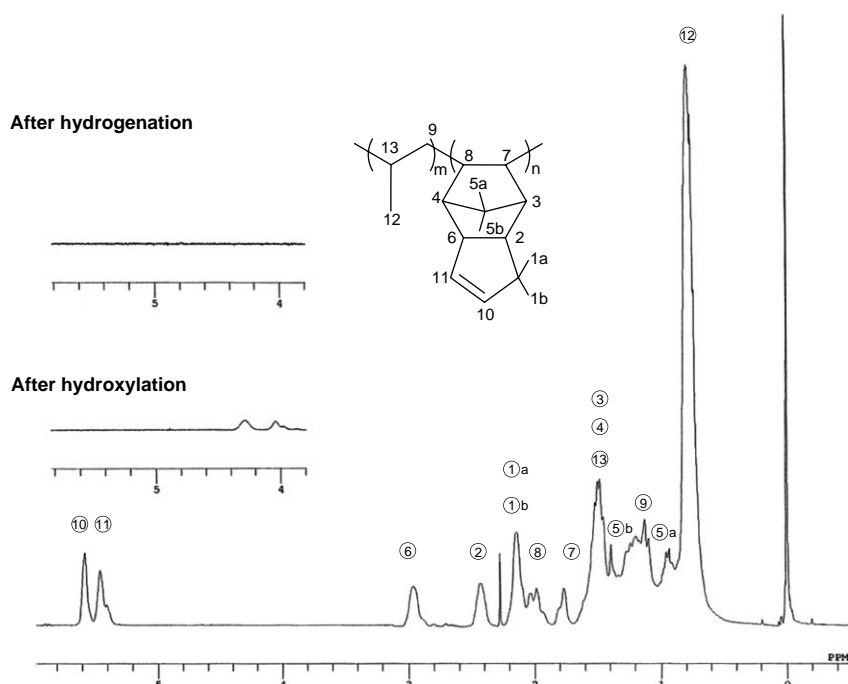


Fig. 6. ^1H NMR spectra of poly(propylene-co-DCPD) (sample 15) and hydrogenated (sample 15-H) or hydroxylated (sample 15-OH) copolymers.

hydrogenation reaction, the signals derived from unsaturated group disappeared completely. In the spectrum of the hydroxylated copolymer, the signals derived from unsaturated group disappeared completely, and new signals due to hydroxyl group appeared at 4.0 and 4.3 ppm. Completion of the hydrogenation and hydroxylation reactions of other copolymers was also confirmed by ^1H NMR spectroscopy. Chemical shift of the signal derived from methyl carbon of propylene sequence in the copolymer was observed at 22 ppm in the ^{13}C NMR spectroscopy, indicating that the propylene sequence in the copolymer formed isotactic sequence. Structure and thermal properties of the copolymers with DCPD, VNB, and ENB are presented in Table 2 or Figs. 7–9, respectively. The copolymer with DCPD showed higher T_g than the other copolymers. The hydrogenated

copolymers showed the T_g s as same as those of the original copolymers with the exception of the copolymers with DCPD. The T_g s of all the hydroxylated copolymers were higher than those of the original copolymers. These results are much the same as those observed in the ethylene-based copolymers. Relationship between comonomer content and ΔT_g is illustrated in Fig. 10. The ΔT_g value linearly increased with increasing of comonomer content, independent of the structure of cyclodiolefin, as observed in the ethylene-based copolymers. The slope of the plots is 2.5 K/(mol of comonomer). This value is almost the same that of the ethylene-based copolymers. The result indicates that structure of the copolymer backbone, ethylene linkage or propylene linkage, does not affect the formation of hydrogen bonding between the hydroxyl groups.

Table 2
Structure and thermal properties propylene–cyclodiolefin copolymers and their derivatives

Sample	Comonomer	mol% ^a	T_m (°C)	T_g (°C)	Sample	T_m (°C)	T_g (°C)	$[\eta]$ dL/g	M_v^b	Sample	T_m (°C)	T_g (°C)	ΔT_g K
13	DCPD	2.4	156.8	−1.3	13-H	156.3	0.6			13-OH	n.d ^c	2.0	1.4
14		14.8	n.d ^c	49.3	14-H	n.d ^c	52.8	0.094	5,200	14-OH	n.d ^c	88.0	35.2
15		24.8	n.d ^c	62.2	15-H	n.d ^c	85.1	0.085	4,600	15-OH	n.d ^c	144.2	59.1
16	VNB	2.3	n.d ^c	−3.4	16-H	n.d ^c	−4.7			16-OH	n.d ^c	1.0	5.7
17		6.3	n.d ^c	−1.1	17-H	n.d ^c	0.1	0.25	17,700	17-OH	n.d ^c	18.4	18.3
18		10.4	n.d ^c	2.1	18-H	n.d ^c	6.1	0.24	16,800	18-OH	n.d ^c	30.9	24.8
19	ENB	3.1	103.6	−2.0	19-H	102.3	0.0			19-OH	104.8	2.9	2.9
20		5.2	n.d ^c	8.4	20-H	n.d ^c	5.9			20-OH	n.d ^c	9.8	3.9
21		6.2	n.d ^c	10.4	21-H	n.d ^c	6.5	0.26	18,600	21-OH	n.d ^c	23.0	16.5
22		21.4	n.d ^c	21.4	22-H	n.d ^c	24.3	0.16	10,100	22-OH	n.d ^c	60.6	36.3

^a Determined by ^1H NMR spectroscopy.

^b Viscosity–average molecular weight calculated by Mark–Houwink–Sakurada equation, $K=0.010$ (mL/g) and $\alpha=0.80$ were employed for propylene-based copolymers.

^c Not detected.

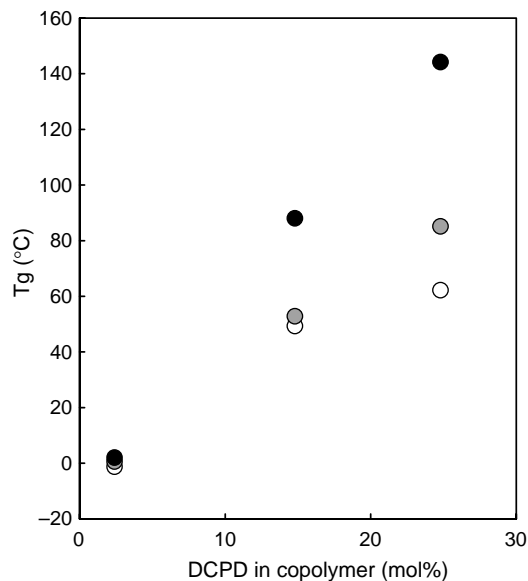


Fig. 7. Relationship between DCPD content and T_g of poly(propylene-*co*-DCPD); original (white), after hydrogenation (gray), and after hydroxylation (black).

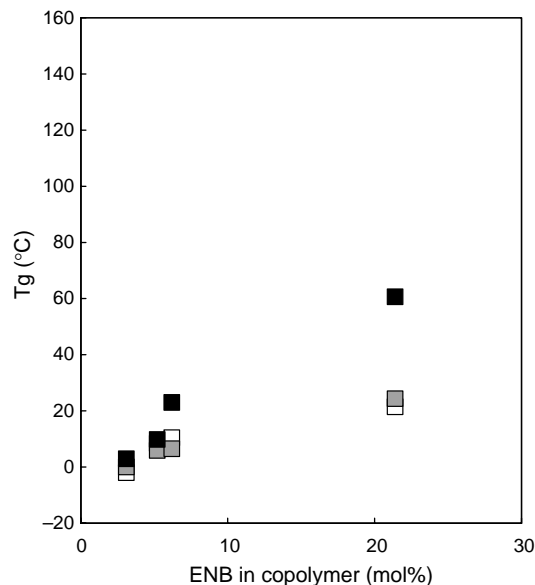


Fig. 9. Relationship between ENB content and T_g of poly(propylene-*co*-ENB); original (white), after hydrogenation (gray), and after hydroxylation (black).

3.3. Shape memory effect

The shape memory effect of hydroxylated poly(ethylene-*co*-VNB), hydrogenated poly(ethylene-*co*-VNB) and polyethylene was investigated under the conditions of Section 2. The results are summarized in Fig. 11. The recovery rate was increased with increasing the test temperature. The recovery rate of the hydrogenated copolymer (sample 5-H) and polyethylene were 91% and 85% at 100 °C, respectively. The recovery rate of hydrogenated poly(ethylene-*co*-VNB) was

higher than those of the original poly(ethylene-*co*-VNB). One explanation for this phenomenon may be that the hydrogenated VNB units reinforce entanglement of the polymer chains. The hydroxylated copolymer (samples 5-OH and 6-OH) showed 100% of recovery at 100 °C. The recovery rate of sample 6-OH was slightly higher than those of sample 5-OH at 70 or 85 °C, indicating increase in hydroxylated units improved the recovery rate. Improvement in shape memory effect in the hydroxylated copolymer should be derived from hydrogen bonding between the OH groups.

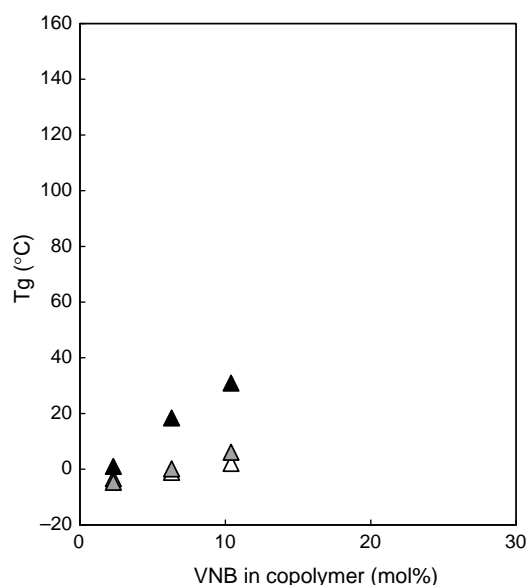


Fig. 8. Relationship between VNB content and T_g of poly(propylene-*co*-VNB); original (white), after hydrogenation (gray), and after hydroxylation (black).

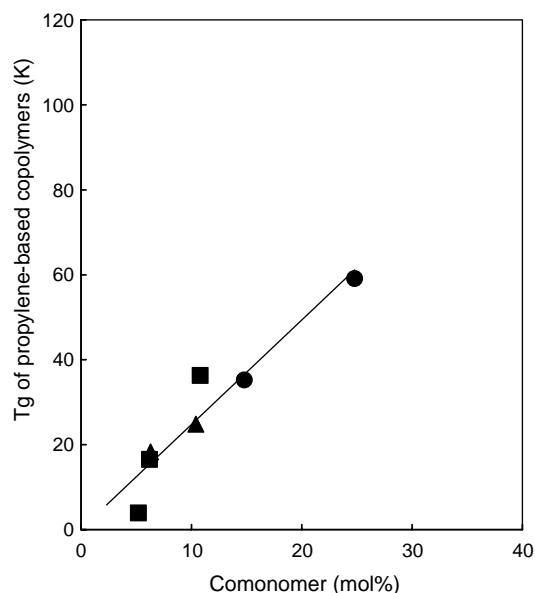


Fig. 10. Relationship between comonomer content and ΔT_g of propylene-based copolymers with DCPD (●), VNB (▲), and ENB (■).

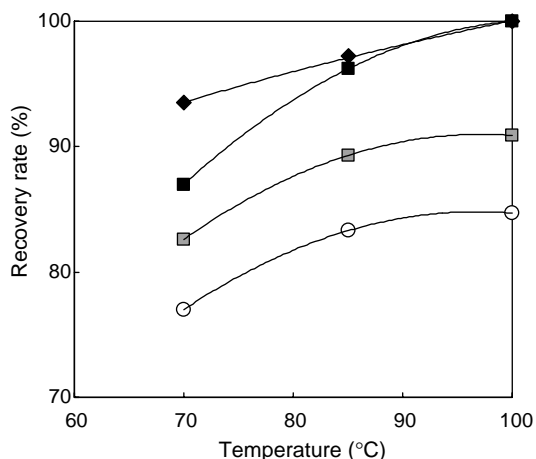


Fig. 11. Relationship between temperature and recovery rate of polyethylene (white circle), poly(ethylene-co-VNB) after hydrogenation (sample 5-H; gray square), and poly(ethylene-co-VNB) after hydrogenation (sample 5-OH; black square, sample 6-OH; black diamond).

4. Conclusion

Polyethylene and isotactic polypropylene containing hydroxylated cyclic units were efficiently synthesized by copolymerization of ethylene or propylene with cycloolefins, (DCPD, VNB, or ENB), using zirconocene catalysts following hydroboration reaction with 9-BBN. The incorporation of hydroxyl group generated the remarkable increase in T_g of

the copolymers. The rate of T_g increase was 2.4–2.5 K per 1 mol% of hydroxylated cyclic units independent of the copolymer structure. The incorporation of hydroxyl group not only raises the T_g but also improves the shape memory effect of the copolymer.

Incorporation of polar group into polyolefin has been known to be one of the effective methods to improve the printability and adhesive property. We investigated the incorporation of hydroxylated cyclic units into polyethylene and polypropylene and achieved improvements in the T_g and the shape memory effect. The selection of the cyclic structures, control of cycloolefin content in the copolymers, and following hydroxylation of residual unsaturated group are effective methods to control the thermal property as well as mechanical property of the COCs.

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