Cationic Copolymerization Behavior of a Bicyclic Orthoester Having Hydroxy Group with Glycidyl Phenyl Ether and Volume Change on Their Copolymerization

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ABSTRACT: This article describes cationic ring-opening copolymerization of a bicyclic orthoester having hydroxy group (BOE-OH) and glycidyl phenyl ether (GPE), and the volume shrinkage behavior during the copolymerization. THF soluble polyethers [poly(BOE-OH-*co*-GPE)] were obtained by the copolymerizations at 80–180°C, while crosslinked poly(BOE-OH-*co*-GPE) was obtained by the copolymerizations at 220–250°C. This crosslinking reaction may originate from the dehydration of methylol groups in the side chain of poly(BOE-OH-*co*-GPE). The volume shrinkage during the cationic copolymerization reduced as the increase of the BOE-OH feed ratio. By contrast, the volume shrinkage on the crosslinking polymerization was almost independent on the BOE-OH feed ratio. Poly(BOE-OH-*co*-GPE)s with higher BOE-OH composition showed lower thermal weight loss temperature owing to the release of H_2O by dehydration of methylol groups. The BOE-OH component in the THF soluble poly(BOE-OH-*co*-GPE)s lowered the glass transition temperature (T_g), while that in the crosslinked poly(BOE-OH-*co*-GPE) increased the T_g probably because of the higher crosslinking density. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 1356–1361, 2006

Key words: cationic polymerization; ring-opening polymerization; crosslinking

INTRODUCTION

Shrinkage upon polymerization has been an important problem in industrial processes to construct high-performance materials including strain-free composites, resins, precision coatings, high strength adhesives, and dental fillings. Several approaches have been employed to reduce the shrinkage upon polymerization. For example, the use of high molecular materials, the additions of fillers, and the curing at low processing temperature have been attempted, although these methods are not substantial enough because of the inherent shrinkage during typical polymerizations. One of the desirable solutions for this problem is the design of monomers that show nearly zero shrinkage or expansion on their polymerizations. For example, double-ring-opening polymerizations of spiro orthoesters,[1–3] spiro orthocarbonates,[4–10] and bicyclic orthoesters (BOE)[11–15] proceed with slight shrinkage or expansion, which is ascribable to the release of their strongly constraint bicyclic structure to freely mobile open chains. Among them, BOEs are very unique monomers because they may be polymerized both via selective single- and double-ring-opening polymerizations. It should also be mentioned that BOEs have been successfully used as building blocks of dendritic macromolecules.[16,17] Recently, we have reported that the cationic ring-opening polymerization of a BOE derivative having hydroxy group (BOE-OH) may afford both soluble and crosslinked polyethers.[18] BOE-OH gave rise to a tetrahydrofuran (THF) soluble polyether [poly(BOE-OH)] by cationic ring-opening polymerization at 80–130°C. Owing to the double-ring-opening fashion, the volume shrinkage during the polymerization of BOE-OH is as less as 3.0%. By contrast, its polymerization at higher temperature (150–180°C) gave a soluble poly(BOE-OH) and insoluble product originated from the crosslinking reaction by the dehydration of methylol group in the side chain of poly(BOE-OH), which led to the considerable shrinkage (6.0%). This finding indicates that BOE-OH is a unique monomer providing crosslinking group into the polymers and decreasing the volume shrinkage in cationic copolymerization, i.e., BOE-OH is a potentially useful comonomer for curing of epoxy resins that afford easily modifiable hydroxyl groups in the resin and reduces internal strain of the resin.

Accordingly, we investigated the cationic ring-opening copolymerization behavior of BOE-OH and glycidyl phenyl ether (GPE) as the model reaction, and evaluated the volume change during the copolymerization, and the thermal properties of the obtained polymers.
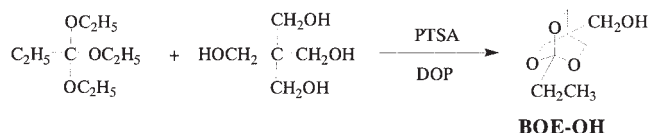

Scheme 1   Synthesis of BOE-OH.

EXPERIMENTAL

Measurements

^1H and ^{13}C NMR spectra were recorded on a JEOL EX-270 spectrometer, using tetramethylsilane (TMS) as internal standard in chloroform-d at 27°C. FTIR spectra were recorded with a Jasco FTIR 470 Plus instrument. Molecular weight of BOE-OH was measured with gas chromatography mass spectrometer on a SHIMADZU GCMS-QP5050A equipped with a polysiloxane column (FRONTIER LAB, UA5–30M-0.25D). Molecular weights and their distributions (MWD; M_w/M_n) of polymers were estimated by gel permeation chromatography (GPC) on a Viscotek TDA MODEL301 system equipped with four consecutive polystyrene gel columns (TSKgel, GMHXL, G2500H, G3000H, and G4000H) and a refractive index detector. Tetrahydrofuran was used as an eluent (flow rate, 1.0 mL/min) and polystyrene standards were employed for calibration. Ten percent weight loss temperatures (T_d^{10}s) of polymers were determined by SEIKO TG/DTA-6200 and EXSTAR-6000 system with a data processor under N_2 atmosphere, at the heating rate of 10°C/min. Gas transition temperatures (T_gs) of polymers were determined by SEIKO DSC-220 and EXSTAR-6000 system with a data processor, under N_2 atmosphere, at the scanning rate of 10°C/min and by means of a second scan. The measurement range was from −50 to 100°C. Specific gravities of polymers were measured with a SHIMADZU Accupyc 1330–03 micromeritics gas pycnometer.

Materials

GPE (TOKYO KASEI CO., Tokyo, Japan) and boron trifluoride etherate (BF₃OEt₂, TOKYO KASEI, Tokyo, Japan) were distilled under reduced pressure before use. Pentaerythritol, triethyl orthopropionate, p-toluenesulfonic acid (TOKYO KASEI), di-2-ethylhexyl phthalate (DOP, TOKYO KASEI), THF, and n-hexane were used as received.

Synthesis of 1-ethyl-4-hydroxymethyl-2,6,7-trioxabicyclo[2.2.2]-octane [BOE-OH][11]

To a 300-mL three-neck flask equipped with a Dean-Steark trap, pentaerythritol (13.6 g, 0.10 mol), triethyl orthopropionate (17.6 g, 0.10 mol), and a trace amount of anhydrous p-toluenesulfonic acid were added and

dissolved into 100 mL of DOP. The solution was heated at 140°C for 3 h under nitrogen atmosphere. After the theoretical amount of ethanol was collected in the trap, the reaction was stopped and the precipitate was removed by filtration. Volatile substances were evaporated and the residue was distilled to obtain 15.2 g (87%) of BOE-OH (bp 100°C/50 Pa) (Scheme 1).

^1H NMR (CDCl₃, TMS): δ = 4.02 (6H, s, C—CH₂—O), 3.47 (2H, s, C—CH₂—OH), 1.71 (2H, q, J = 7.0 Hz, CH₃—CH₂—C), 0.96 (3H, t, J = 7.0 Hz, CH₃—) ppm. ^{13}C NMR (CDCl₃, TMS): δ = 109.6 (C—(O)₃), 69.1 (C—CH₂—O), 60.9 (C—CH₂—OH), 35.5(C—CH₂—OH), 29.5 (CH₃—CH₂—C), 7.15 (CH₃—) ppm. IR (NaCl): 3472 (—OH), 1273, 1046 (C—O—C) cm^{-1}. Mass (M⁺) 173. ELEM. ANAL.: Calcd, C : 55.16, H : 8.10, O : 36.74; Found, C : 55.83, H : 8.66, O : 35.51.

Cationic ring-opening copolymerization of BOE-OH and GPE

A typical procedure is shown as follows. BOE-OH (535 mg, 3.07 mmol) and GPE (482 mg, 3.21 mmol) were added into a thoroughly dried test tube under nitrogen atmosphere. After injection of BF₃OEt₂ (23.0 μL, 0.18 mmol), the test tube was heated at 80°C for 24 h. The resulting mixture was dissolved in THF and poured into n-hexane. The precipitate was collected and dried under vacuum to obtain the viscous poly-(BOE-OH₄₈-co-GPE₅₂) in 80% yield (798 mg).

^1H NMR (CDCl₃, TMS): δ = 7.24 (2 × 0.52H, —Ph), 6.88 (3 × 0.52H, —Ph), 4.2–3.85 (2 × 0.48H, C—CH₂—OCO, 4 × 0.52H, C—CH₂—O), 3.85–3.20 (1 × 0.52H, CH—CH₂—O, 2 × 0.48H, C—CH₂—OH, 6 × 0.48H, C—CH₂—O), 2.31 (2 × 0.48H, CH₃—CH₂—C), 1.12 (3 × 0.48H, CH₃—) ppm. IR (NaCl): 3495 (—OH), 1739 (—COO—), 1600 (—Ph), 1498 (—Ph), 1193 (—COO—), 1084 (C—O—C), 756 (—Ph) cm^{-1}. GPC: M_n, 1360; M_w/M_n, 1.85. ELEM. ANAL. : Calcd, C : 63.57, H : 7.41, O : 29.03; Found, C : 63.22, H : 7.54, O : 29.24.

Cationic crosslinking ring-opening copolymerization of BOE-OH and GPE

A typical procedure is shown as follows. BOE-OH (538 mg, 3.09 mmol) and GPE (459 mg, 3.06 mmol) were added into a thoroughly dried test tube under

TABLE I
Cationic Copolymerization of BOE-OH and GPE[a]

Run	Feed ratio (BOE-OH/GPE) (mol %)	Poly(BOE-OH-*co*-GPE)		
		Yield (%)	Composition[b] (BOE-OH/GPE)	M_n (M_w/M_n)[c]
1	100/0	84.4	100/0	1140 (7.10)
2	90/0	90.5	90/10	1320 (8.36)
3	75/25	77.3	72/28	2040 (2.68)
4	60/40	86.3	61/39	2150 (2.66)
5	50/50	78.6	48/52	1490 (2.89)
6	40/60	85.9	42/58	1920 (1.96)
7	25/75	78.2	25/75	2100 (1.69)
8	10/90	82.6	14/86	1980 (1.83)
9	0/100	68.7	0/100	1790 (2.26)

[a] Conditions: temperature, 130°C; time, 6 h.
[b] Determined by ^{1}H-NMR spectroscopy (270 MHz, CDCl$_3$).
[c] Estimated by GPC (polystyrene standard, THF).

nitrogen atmosphere. After injection of BF$_3$OEt$_2$ (23.6 μL, 0.18 mmol), the test tube was heated at 220°C for 24 h. The resulting mixture was separated into THF soluble poly(BOE-OH-*co*-GPE) (165.5 mg (17%)) and THF insoluble crosslinked polymer (368.9 mg (64%)).
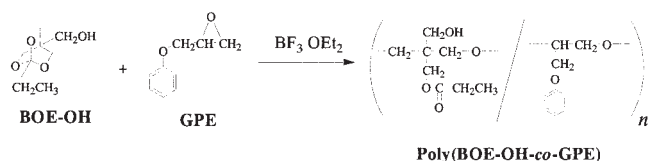
IR(KBr): 3470 (—OH), 1739 (—COO—), 1600 (—Ph), 1497 (—Ph), 1193 (—COO—), 1082 (C—O—C), 754 (—Ph) cm^{-1}. ELEM. ANAL.: Calcd, C : 65.08, H : 7.32, O : 27.6; Found, C : 65.53, H : 7.36, O : 27.11.

RESULTS AND DISCUSSION

Cationic copolymerization of BOE-OH and GPE

The cationic copolymerization of BOE-OH and GPE initiated by BF$_3$OEt$_2$ was carried out under various feed ratios. (Table I, Scheme 2) The composition of the obtained poly(BOE-OH-*co*-GPE) was determined by ^{1}H NMR spectroscopy. The copolymers have ester moiety in the side chain in the same manner with the polymer obtained by cationic homopolymerization of BOE-OH,[18] indicating that BOE-OH copolymerized with GPE via double-ring-opening polymerization. The copolymer compositions agreed well with the feed ratios. All the GPC profiles of these copolymers showed single modal elution peaks, and no THF insoluble polymers were produced.

Keeping in mind that the cationic ring-opening copolymerization of BOE-OH is accompanied by the

crosslinking at high temperature, we copolymerized BOE-OH and GPE (feed molar ratio, 50/50) at various temperature. Figure 1 shows the relationship between the yields of crosslinked poly(BOE-OH-*co*-GPE) versus the polymerization time. The copolymerizations at 80–180°C gave a THF soluble poly(BOE-OH-*co*-GPE)s selectively without accompanying the formation of any crosslinked products, whereas those at 220–250°C resulted in giving the mixture of both soluble and crosslinked poly(BOE-OH-*co*-GPE). The yields of the crosslinked polymers increased with the reaction time and reached up to 60%.

BOE-OH and GPE were copolymerized cationically under several feed ratios (Fig. 2). Table II shows the yields of THF soluble and crosslinked poly(BOE-OH-*co*-GPE) on the cationic copolymerization of BOE-OH and GPE for 24 h at 250°C. The yield of crosslinked poly(BOE-OH-*co*-GPE) increased with the increase of
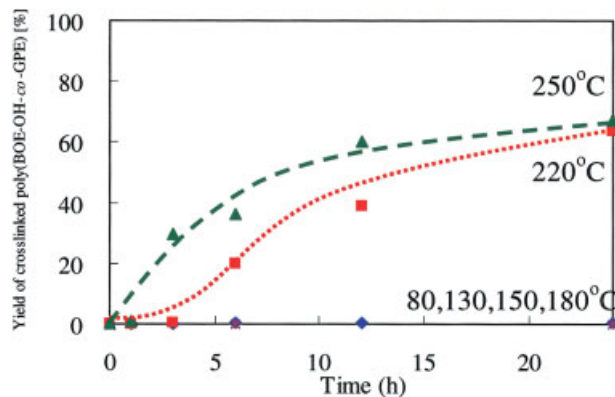

Figure 1 Time versus yield of crosslinked poly(BOE-OH-*co*-GPE) in cationic copolymerization of BOE-OH and GPE at various temperature (Conditions:, bulk polymerization,; [BOE-OH]$_0$/[GPE]$_0$, = 50/50;, Initiator:, BF$_3$OEt$_2$ 3.0 mol % vs. monomers). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

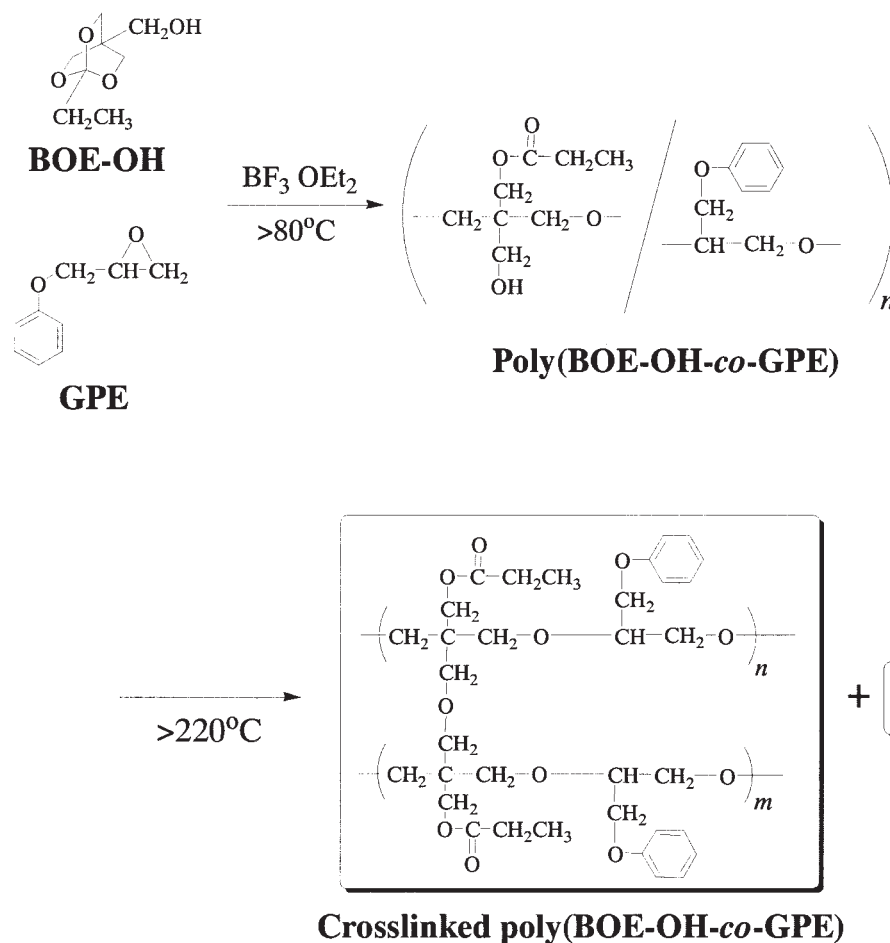**Scheme 2** Cationic ring-opening copolymerization of BOE-OH and GPE.

Figure 2 Plausible mechanism of cationic crosslinking copolymerization of BOE-OH with GPE.

the feed ratio of BOE-OH. Especially, the yields of the crosslinked product increased significantly across the equimolar feed ratio, probably owing to the sufficient amount of the hydroxyl group as the crosslinking group.

TABLE II
Cationic Copolymerization and Crosslinking of BOE-OH and GPE[a]

		Yield (%)	
Run	Feed ratio (BOE-OH/GPE) (mol %)	Crosslinked poly(BOE-OH-co-GPE)	Poly(BOE-OH-co-GPE)
1	100/0	82.5	3.9
2	90/0	75.0	6.0
3	75/25	95.0	0.7
4	60/40	80.7	6.7
5	50/50	69.5	19.6
6	40/60	58.7	25.9
7	25/75	59.9	23.0
8	10/90	56.7	25.0
9	0/100	—	46.9

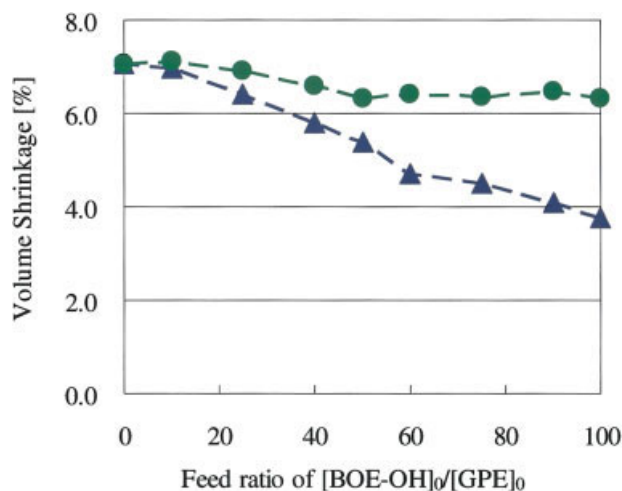[a] Conditions: temperature, 250°C; time, 24 h.

Figure 3 Volume shrinkage on cationic polymerization and crosslinking reaction under various feed ratio of BOE-OH and GPE. Volume shrinkage on polymerization at 80°C. and volume shrinkage on crosslinking polymerization at 250°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
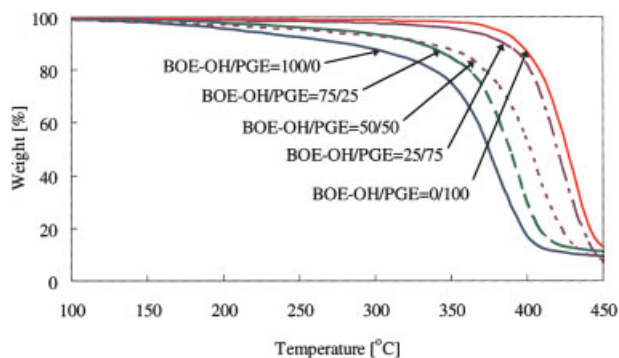
Figure 4 TGA thermograms of poly(BOE-OH-*co*-GPE)s. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Volume change on cationic polymerization and crosslinking

It has been reported that cationic polymerization of GPE is accompanied by 8% volume shrinkage,[19] and this shrinkage may be expected to be suppressed in this copolymerization involving double-ring-opening of BOE-OH. Accordingly, we evaluated the volume shrinkage in the cationic copolymerization of BOE-OH and GPE. The volume change was calculated from the densities of the monomers and the polymers measured by a micromeritics gas pycnometer. As expected, the volume shrinkage on the cationic copolymerization was reduced with the increase of the BOE-OH feed ratio as shown in Figure 3, owing to the double ring-opening polymerization of BOE-OH. On the other hand, the volume shrinkage on the crosslinking polymerization at 250°C is almost independent on the monomer feed ratio, although higher BOE-OH feed ratio slightly reduced the shrinkage. However, the differences between the volume shrinkage of the copolymerizations at 80 and 250°C, which can be ascribed to the volume shrinkage by crosslinking, increased with the BOE-OH feed ratio. For example, the shrinkage difference for polymerizations of BOE-OH and copolymerization with $[BOE-OH]_0/[GPE]_0$ equal to 50/50 was 2.5% and 0.9%, respectively. The increased volume shrinkage on the crosslinking is as-

cribable to a lot of the crosslinked units originated from the condensation of methylol group, which may be supported by the thermal behavior of the polymers (discussed later).

Thermal properties of poly(BOE-OH-*co*-GPE) and crosslinked poly(BOE-OH-*co*-GPE)

We evaluated the thermal properties of poly(BOE-OH-*co*-GPE) and crosslinked poly(BOE-OH-*co*-GPE). Figure 4 shows the TGA thermograms of poly(BOE-OH-*co*-GPE). The onsets of the weight loss of poly-(BOE-OH-*co*-GPE) lowered with the increase of the BOE-OH composition in the copolymers. The decrease of the thermal gravity may have originated from the elimination of H_2O that is formed by the dehydration of methylol groups in the side chain. Table III shows the $T_d{}^{10}$s and T_gs of poly(BOE-OH-*co*-GPE)s and crosslinked poly(BOE-OH-*co*-GPE)s. Both $T_d{}^{10}$ and T_g of crosslinked poly(BOE-OH-*co*-GPE) were higher than those of poly(BOE-OH-*co*-GPE) obtained by the copolymerization with the same feed ratio. Interestingly, higher BOE-OH composition made the T_g of THF soluble poly(BOE-OH-*co*-GPE) lower, whereas the T_g of crosslinked poly(BOE-OH-*co*-GPE) higher. For example, the T_gs of poly(BOE-OH) and poly(BOE-OH$_{25}$-*co*-GPE$_{75}$) were -12 and 4.0°C, respectively, while the T_gs of their crosslinked polymers were 47 and 23°C, respectively. The higher T_gs of crosslinked poly(BOE-OH-*co*-GPE)s may be ascribed to the decrease of the mobility of the polymer chain by crosslinking, which will be proportional to the methylol groups in the BOE-OH component. That is, the BOE-OH component may be served as a softening moiety in the soluble polymers, but as a strangling moiety in the crosslinked polymers.

SUMMARY

A bicyclic orthoester having hydroxyl group (BOE-OH) cationically copolymerized with GPE via double-ring-opening fashion to give both a THF-soluble poly-ether [poly(BOE-OH-*co*-GPE)] at 80–180°C, and at

TABLE III
DSC and TG/DTA Measurement of Copolymers from BOE-OH and GPE

Feed ratio (BOE-OH / GPE)	100/0	90/10	75/25	60/40	50/50	40/60	25/75	10/90	0/100
Poly(BOE-OH-*co*-GPE)									
$T_d{}^{10}$ [a] (°C)	280	310	330	324	336	341	385	393	395
T_g [b] (°C)	−12	−5	3.0	1.0	1.0	3.0	4.0	8.0	20
Crosslinked poly(BOE-OH-*co*-GPE)									
$T_d{}^{10}$ [a] (°C)	351	363	365	364	371	372	383	385	
T_g [b] (°C)	47	45	43	33	27	21	23	22	

[a] Measured by TG/DTA (rate, 10°C/min; in N_2 gas).
[b] Measured by DSC (rate, 10°C/min; in N_2 gas).

higher temperature (220–250°C) the crosslinked poly-(BOE-OH-*co*-GPE). This copolymerization may afford soluble polymers even at higher temperature than the case of the homopolymerization of BOE-OH by suppressing the crosslinking originated from the dehydration of the methylol group in the side chain of BOE-OH component. The evaluation on the volume change during the cationic copolymerization revealed that the double-ring-opening polymerization of BOE-OH reduced the volume shrinkage attributed to the polymerization of GPE proportionally with the BOE-OH feed ratio in the copolymerizations giving soluble polymers (80–150°C). On the other hand, the volume shrinkage in the crosslinking copolymerization of BOE-OH and GPE was independent on the BOE-OH feed ratio. Thermal analysis demonstrated that the BOE-OH units in the copolymer have both softening and hardening roles by its flexible structure and crosslinking ability, respectively. BOE-OH that can reduce volume shrinkage and give crosslinking units in cationic copolymerization may be expected to be useful for curing and modification of epoxy resins.

References

1. Bailey, W. J.; Sun, R. L.; Katsuki, H.; Endo, T.; Iwama, H.; Tsushima, R.; Saigo, K.; Bitritto, M. M. In Ring-Opening Polymerization; Saegusa, T., Goethals, E., Eds.; ACS Symposium Series; American Chemical Society: Washington, DC, 1977; p 38.
2. Tagoshi, H.; Endo, T. J Polym Sci Part C: Polym Lett 1987, 26, 77.
3. Endo, T.; Bailey, W. J. J Polym Sci Polym Lett Ed 1980, 18, 25.
4. Takata, T.; Endo, T. Macromolecules 1988, 21, 900.
5. Endo, T.; Maruoka, S.; Yokozawa, T. J Polym Sci Part A: Polym Chem 1987, 25, 2925.
6. Endo, T.; Maruoka, S.; Yokozawa, T. Macromolecules 1987, 20, 2690.
7. Sanda, F.; Takata, T.; Endo, T. Macromolecules 1993, 26, 729.
8. Bailey, W. J.; Endo, T. J Polym Sci Polym Chem Ed 1976, 14, 1735.
9. Endo, T.; Bailey, W. J. J Polym Sci Polym Chem Ed 1975, 13, 2525.
10. Endo, T.; Bailey, W. J. Makromol Chem 1975, 176, 2897.
11. Endo, T.; Saigo, K.; Bailey, W. J. J Polym Sci Polym Lett Ed 1980, 18, 457.
12. Endo, T.; Okawara, M.; Bailey, W. J. Polym J 1980, 13, 715.
13. Endo, T.; Song, M. C.; Okawara, M.; Bailey, W. J. Polym J 1982, 14, 485.
14. Saigo, K.; Bailey, W. J.; Endo, T.; Okawara, M. J Polym Sci Polym Chem Ed 1983, 21, 1435.
15. Uno, H.; Takata, T.; Endo, T. Macromolecules 1989, 22, 2502.
16. Padis, A. B.; Hall, H. K., Jr.; Tomalia, D. A.; McConnell, J. R. J Org Chem 1987, 52, 5303.
17. Gitsov, I.; Wu, Sh.; Ivanova, P. T. Polym Mater Sci Eng 1997, 77, 214.
18. Kume, M.; Endo, T. J Network Polym Jpn 2004, 25, 74.
19. Takata, T.; Endo, T. Polym Prepr Jpn 1988, 37, 241.