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Anionic Copolymerization of Bicyclic Bis(γ-lactone)s with Poly(glycidyl methacrylate) and Volume Change during the Copolymerization

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Introduction. Some bicyclic and spirocyclic compounds such as bicyclic orthoesters (BOEs), spirocyclic orthoesters (SOEs), and spirocyclic orthocarbonates (SOCs) have been reported as expanding monomers on cationic ring-opening polymerization.[1−3] There have been some attempts to reduce volume shrinkage during polymerization of epoxides under cationic conditions. Actually, the shrinkage of epoxides in volume during polymerization can be controlled by addition of SOCs to the polymerization system.[4] Although the expanding monomers which undergo the cationic polymerization have been reported, recently some attempts to develop expanding monomers which can polymerize with anionic[5−7] and radical initiators[8,9] have been reported. Brady *et al.* have reported the possibility of suppression of volume shrinkage in the copolymerization of epoxides with spirocyclic bis(lactone) as expandable comonomers under anionic conditions.[6,7] The volume expansion capability of these monomers under anionic conditions can be suggested at the initial stage during polymerization and the final volume change is shrinkage, because the amount of spirocyclic comonomer added may be too small to suppress the volume change.

Meanwhile, we have recently found that bicyclic bis(γ-lactone)s (**1**) can undergo clean alternating copolymerization with various mono-[10−12] and bifunctional epoxides[13,14] to give corresponding alternating copolymers with no observed volume shrinkage during the copolymerization. Thus, **1** can be regarded as the first expanding monomers capable of undergoing anionic polymerization, although they cannot homopolymerize at all. Therefore, we have extended this reaction to polyfunctional epoxides such as poly(glycidyl methacrylate) (**2**) having an epoxy functional group in the side chain to examine the capability of **1** to reduce volume shrinkage during copolymerization. It is interesting how many epoxide groups of **2** take part in the copolymerization because the degree of volume change is proportional to the degree of epoxide ring-opening. The polymerization shrinkage of epoxides was directly proportional to the amount of SOCs added to the polymerization system.[4]

This paper describes preliminary results of the copolymerization behavior and volume change on the copolymerization of bicyclic bis(γ-lactone)s (**1**) with polyfunctional epoxide poly(glycidyl methacrylate) (**2**).

Results and Discussion. Before we examined the copolymerization of **1** with **2**, a model study was carried out using glycidyl pivalate (**3**). This model reaction was attempted to evaluate the copolymerizability of **3** and the effect of its ester function. **3** was prepared by the reaction of pivaloyl chloride with glycidol in the presence of triethylamine in 66% yield (Scheme 1). The anionic copolymerization of **1a** with **3** was carried out at 120 °C for 96 h in the presence of potassium *tert*-butoxide (2 mol %) in THF ([M] = 4.0 M) (Scheme 2). The obtained polymer (**4**) was purified by preparative HPLC, since **4** was soluble in any solvent. The effect of monomer feed ratio on yield, molecular weight, and copolymer composition was examined (Table 1). The obtained polymers (**4a−e**) had a composition of ca. 50:50 independent of feed ratio ranging from 20:80 to 80:20 (**1a:3**), suggesting the formation of an alternating copolymer. The copolymerization mechanism involves a typical cross propagation, as reported previously.[11]

Scheme 1

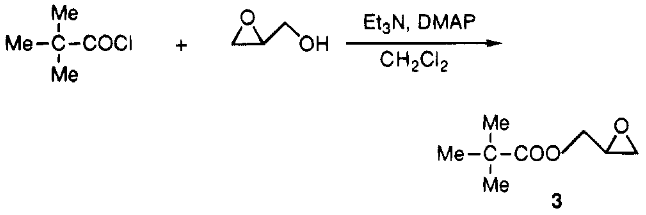

Table 1. Anionic Copolymerization of 1a with 3[a]

run	feed ratio (mol %) **1a:3**	copolymer	copolymer yield[b] (%)	$\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$)[c]	copolymer composition[d] **1a:3**
1	20:80	**4a**	16	2200 (1.06)	48:52
2	40:60	**4b**	40	2600 (1.08)	46:54
3	50:50	**4c**	62	2300 (1.05)	47:53
4	60:40	**4d**	60	2000 (1.13)	50:50
5	80:20	**4e**	15	1600 (1.15)	50:50

[a] Polymerization conditions: THF (4.0 M), *t*-BuOK (2 mol %), 120 °C, 96 h. [b] Separated by preparative HPLC (eluent; THF). [c] Estimated by GPC of polymer without purification by precipitation (eluent, THF; based on PSt standards). [d] Determined by ^{1}H NMR.

The number-average molecular weight ($\bar{M}_n$) of the copolymers was lower (from 2600 to 1600), indicating slow polymerization which was confirmed by the fact the copolymer molecular weight was too low to obtain the solvent-insoluble copolymer by the precipitation method. In addition to the highest yield (62%) obtained with the feed ratio of 50:50 (**4c**, Table 1, run 3) and the yield decrease by deviation of the feed ratio from 50:50, the IR, ^{1}H NMR, and ^{13}C NMR spectra of **4c** clearly supported the proposed alternating copolymer structure. There were the disappearance of five-membered ring lactone carbonyl (1780 cm^{-1}) and oxirane C−O bond absorptions (912 cm^{-1}) and the appearance of new ester (1738 cm^{-1}) and ketone (1714 cm^{-1}) carbonyl absorptions in the IR spectrum. The ^{1}H and ^{13}C NMR spectra of **4c** (Figure 1) were very consistent with the proposed structure. The most characteristic signal for the alternating structure appeared at 5.25 ppm in the ^{1}H NMR spectrum, which was assigned to the methine proton (g) adjacent to the ester oxygen of the polymer main chain (Figure 1A). The ^{13}C NMR spectrum of **4c** is characterized by four carbonyl signals due to the ketone (207.7 ppm, k) and three ester groups (177.4 ppm, j, and 170.6, 170.2 ppm, i, i′). Two signals of methyl and the tertiary carbon of the *tert*-butyl group of **4c** were observed at 26.7 (a) and 38.4 (d) ppm, respectively (Figure 1B). Thus, the alternating copolymer structure

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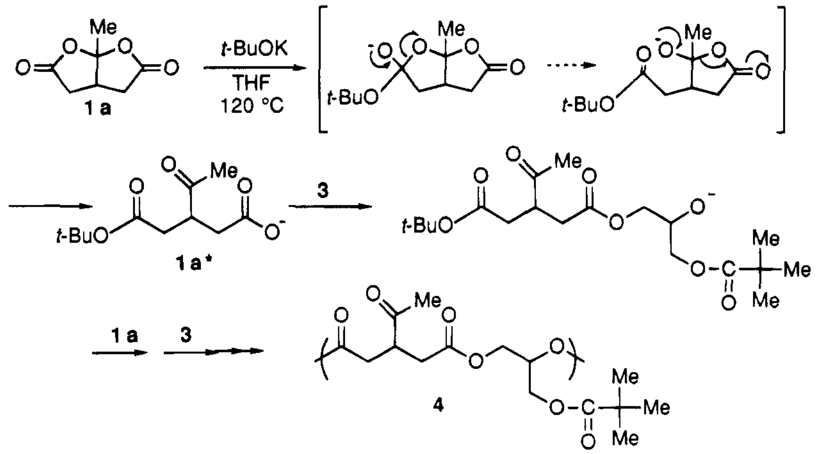
Scheme 2



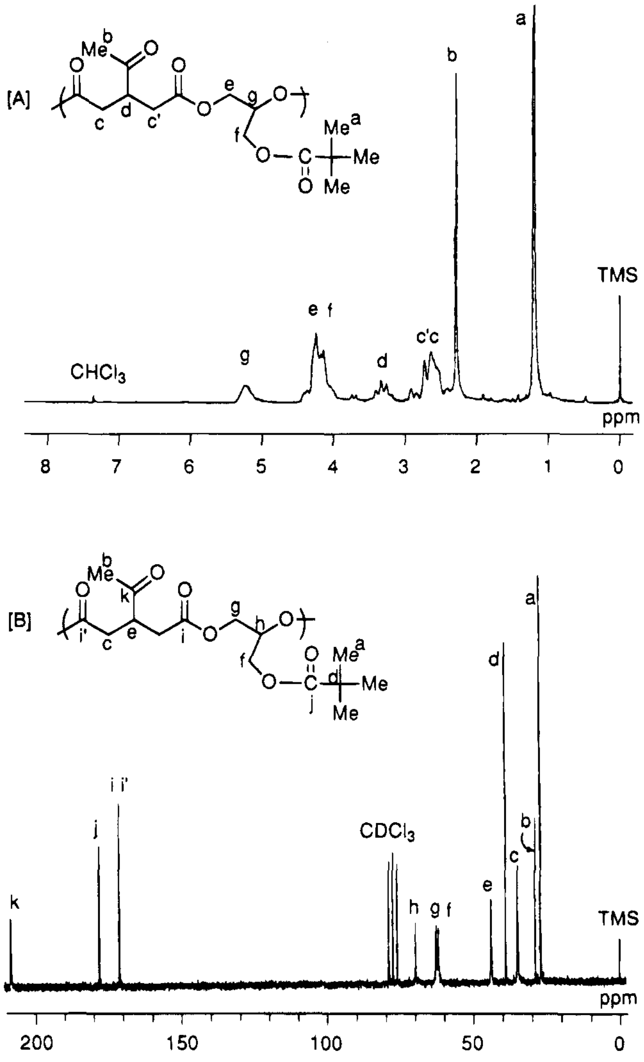


Figure 1. ^{1}H NMR (solvent, CDCl$_3$; 90 MHz) spectrum (A) and ^{13}C NMR (solvent, CDCl$_3$; 22.5 MHz) spectrum (B) of **4c** ($\overline{M}_n$ 2300).

of **4** was established by the above results. Consequently, formation of **4** suggests that not only glycidyl ether[10,11] but also glycidyl ester can copolymerize alternatingly via successive double ring-opening isomerization of bicyclic bis(γ-lactone) (**1**) and ring-opening of the epoxide of glycidyl ester, although the copolymerization is somewhat slow judging from the molecular weight (e.g. **4c**, $\overline{M}_n$ 2300) of the copolymer.

Poly(glycidyl methacrylate) (**2**) ($\overline{M}_n$ = 25 300, $\overline{M}_w/\overline{M}_n$ = 2.02) as a polyfunctional epoxide was prepared in 60% yield by the radical polymerization of glycidyl methacrylate. The anionic copolymerization of **1a** and **2** was carried out with potassium *tert*-butoxide (2 mol %) at 120 °C for 24–72 h in THF ([M] = 4.0 M) to afford dichloromethane-insoluble copolymer (**5a**).[15] The yield of the copolymer in solution polymerization (91%) (Table 2, run 2) was slightly higher than that in bulk (82%) (Table 2, run 3) under the same reaction conditions. Results are summarized in Table 2.

In the IR spectrum of **5a** (Table 2, run 2), new ester (1736 cm^{-1}) and ketone (1714 cm^{-1}) carbonyl absorptions were observed instead of the lactone carbonyl (1780 cm^{-1}) of **1a**, whereas the epoxy absorption (906 cm^{-1}) completely disappeared (Figure 2C). These IR changes suggest the formation of cross-linked copolymer (**5a**), as illustrated in Scheme 3. Furthermore, the structure of the polyester side chain was considered to be an alternating copolymer in accordance with the above alternating copolymerization of **1a** with **3**. However, the side chain was suggested to contain a small amount of polyether unit besides the polyester unit, judging from the complete opening of the epoxy ring of **2** and recovery of a small amount of **1a** (ca. ~8.3%), which was confirmed by the ^{1}H NMR spectrum of the dichloromethane-soluble fraction and its weight (Table 2, run 2). Table 2 demonstrates the results of the copolymerization of phenyl-substituted bicyclic bis(γ-lactone) (**1b**). In the copolymerization of **1b** with **2**, the cross-linked copolymer was similarly obtained as solvent-insoluble polymer in 92% yield (**5b**) and the degree of opening of the epoxy ring of **2** was quantitative (Table 2, run 4).

To evaluate the reactivity of the epoxy group of **2**, i.e. ease of opening of the epoxy ring under the anionic conditions, homopolymerization of **2** in solution was carried out under the same conditions as the copolymerization. The corresponding solvent-insoluble homopolymer (**6**) was obtained quantitatively. From the IR C–O absorption change of the epoxy (906 cm^{-1}, Figure 2A,B, absorption bands a and b), the degree of ring-opening of the epoxide of **2** was very low (27%) (Table 2, run 6). This result can be compared with the highly efficient epoxy ring-opening in the anionic copolymerization of **1** with **2** as described above. So, it should be worthy of special mention that the opening of the epoxy ring in the copolymerization is complete in spite of the polymer reaction. Thus, the copolymerizations of **1** with the epoxy group-containing polymer **2**

Table 2. Anionic Copolymerization of 1 with Poly(glycidyl methacrylate) (2)[a]

run	bis(lactone)	epoxide	solvent	time (h)	cross-linked polymer	yield[b] (%)	DROE[c] (%)	vol[d] change (%)
1	**1a**	**2**	THF	24	**5a**	81	82	
2	**1a**	**2**	THF	72	**5a**	91	100	−4.6
3	**1a**	**2**	none	72	**5a**	82	71	
4	**1b**	**2**	THF	72	**5b**	92	100	−2.5
5	none	**2**	THF	24	**6**	96	22	
6	none	**2**	THF	72	**6**	98	27	−6.3

[a] Polymerization conditions: *t*-BuOK (2 mol %), THF (4.0 M). [b] Dichloromethane-insoluble part. [c] Degree of ring-opening of epoxide, determined from IR area ratio of absorption bands of ester carbonyl (1732 cm^{-1}) and oxirane ring (906 cm^{-1}) of **2** before and after polymerization. [d] Measured by the density gradient tube method at 25 °C, [density (monomer mixture) − density (polymer)]/density (monomer mixture) × 100.

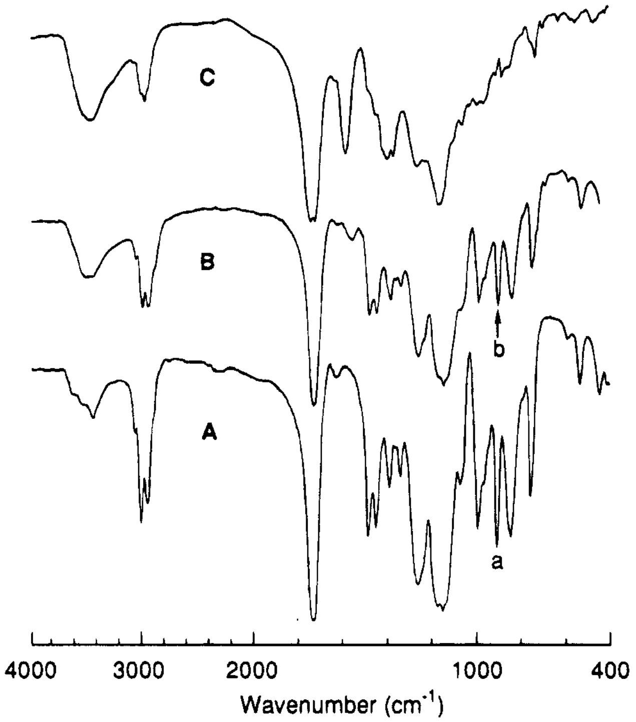
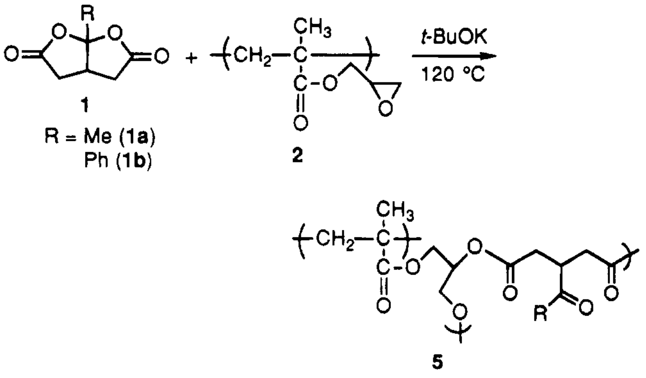


Figure 2. IR (KBr) spectra of **2** (A), the homopolymer (**6**) of **2** (run 6 in Table 2) (B), and the copolymer (**5a**) of **1a** and **2** (run 2 in Table 2) (C).

Scheme 3



proceeded to afford quantitatively the corresponding cross-linked copolymers **5** bearing the alternating copolymer structure in the side chain, although the reaction was a polymer reaction.

Volume change during the homopolymerization of **2** and copolymerization with **1** was evaluated from a change in density of **2** (or mixture with **1**) and (co)polymers of **1** and **2**. The results are summarized in Table 2. The homopolymerization of **2** showed a 6.3% volume shrinkage, even though the degree of ring-opening of epoxy groups was very low (27%). Small volume shrinkage (2.5–4.6%) was observed in the copolymerizations of **1** with **2**. The degree of volume shrinkage seems fairly small compared with those of the homopolymerization of **2**, because the degree of ring-opening of **2** is 100% in the copolymerization with **1**. Therefore, it can be concluded that volume shrinkage during polymerization of the epoxy group-containing polymer **2** is considerably suppressed by addition of **1** as comonomer, giving the corresponding cross-linked copolymer by the alternating copolymerization of the side chain epoxy group and bicyclic bis(γ-lactone)s (**1**).

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(15) Experimental procedure: A mixture of **1a** (0.156 g, 1.0 mmol), **2** (0.142 g, 1.0 mmol (monomeric mol unit)), potassium *tert*-butoxide (4.5 mg, 2 mol %), and THF (0.5 mL, 4.0 M) was placed in a polymerization tube. The tube was cooled, evacuated, sealed off, and heated at 120 °C. A dichloromethane solution of acetic acid (2 vol %, 1.0 mL) was added to the cooled reaction mixture, and the resulting mixture was washed with dichloromethane in a Soxhlet extractor for 12 h. Solvent-insoluble polymer was collected and dried at 60 °C for 24 h in vacuo to yield 0.271 g (91%).

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