Anionic Ring-Opening Copolymerization of Bicyclic Bis(γ-lactone)s with Mono- and Bifunctional Epoxides via Double Ring-Opening Isomerization of the Bis(γ-lactone)s and Volume Change during Copolymerization

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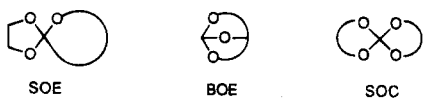
Received October 12, 1994; Revised Manuscript Received January 23, 1995®

ABSTRACT: The first anionic polymerization with small volume shrinkage is described. Volume change in anionic copolymerization of bicyclic bis(γ-lactone) **1c** and glycidyl phenyl ether (**2**) with potassium *tert*-butoxide (4 mol %) at 120 °C was nearly zero (small expansion, +0.25 ± 0.15%). The anionic copolymerization of aromatic substituent-containing bicyclic bis(γ-lactone)s (**1e−g**) with **2** was carried out at 120 °C in THF and in bulk for 72 h in the presence of potassium *tert*-butoxide (4 mol %). The ^{1}H NMR, ^{13}C NMR, and IR spectra of the methanol-insoluble parts clearly suggested the proposed alternating copolymer structures consisting of two successive units derived from **1e−g** and **2**. The anionic copolymerizations of bicyclic bis(γ-lactone)s (**1a−g**) with equimolar amounts of bifunctional epoxides (**5a,b**) in bulk were carried out at 120−160 °C in the presence of potassium *tert*-butoxide (4 mol %) to afford the corresponding dichloromethane-insoluble copolymers (**6aa−gb**) in quantitative yields. The copolymer composition was ca. 1:0.5 in any case, as estimated from the ^{1}H NMR spectra of the dichloromethane-soluble parts. Yield of the copolymers decreased when the monomer feed ratio was deviated from 1:0.5. The IR spectral analysis of **6aa−gb** strongly suggested the occurrence of the efficient alternating copolymerization. Small shrinkages or expansions in volume (−2.5 ± 0.15% to +2.4 ● 0.15%) were observed during the copolymerizations of **1** and **5**, definitely indicating the possibility of **1** as expanding monomers. Thermal properties such as glass transition and 10% weight loss temperatures of the obtained copolymers were evaluated by DSC and TGA.

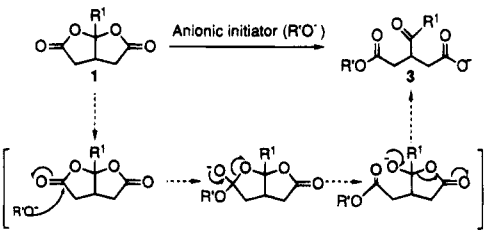
Introduction

Common vinyl monomers and cyclic monomers show volume shrinkage on polymerization. When thermosetting resins such as epoxy resin and phenol resin are cured, volume shrinkage is also observed. This volume shrinkage produces big problems such as internal strain in the polymer, loss of adhesion in adhesives, formation of cracks and voids, etc. As a result, the volume shrinkage often diminishes the mechanical properties of the polymers. Suppression or control of the volume shrinkage is of great importance in material science. In the last 20 years polymerization and copolymerization that proceed with expansion or without shrinkage in volume have been intensively studied. Bailey has proposed structures of oxabicyclic and oxaspirocyclic monomers such as spiroorthoesters (SOE), bicyclic orthoesters (BOE), and spiroorthocarbonates (SOC) which can be expected to show no shrinkage or some expansion in volume on cationic polymerization.[1] Their unique property is believed to come from the polymerization mode: successive double ring-opening polymerization.[2]



Bailey, Endo, and Takata have proved the capability of these monomers as expanding monomers by a great deal of experimental results. These monomers polymerize cationically without shrinkage or with small expansion in volume[3−5] but do not undergo polymerization by anionic or radical initiator. Some attempts to develop monomers capable of showing volume expansion on polymerization with anionic[3] and radical initiators[6−8] have been done, but no volume expansion system has been constructed so far. Recent studies on anionic polymerization reported by Brady *et al.* have suggested the possibility of volume expansion on anionic polymerization.[9−11] The copolymerization of a small amount of spiro-fused bicyclic and tricyclic compounds with epoxy and polyamide resins resulted in an initial volume expansion but finally showed volume shrinkage. Recently, we have found that anionic copolymerization of bicyclic bis(γ-lactone)s (**1**) with epoxide **2** efficiently proceeds to afford the corresponding completely alternating copolymers via both double ring-opening isomerization of **1** and ring opening of **2**, although anionic homopolymerization of **1** does not proceed at all.[12,13] We have proposed the mechanism of their alternating copolymerization as shown in Scheme 1. In this mechanism, initial nucleophilic attack of an anionic initiator at the carbonyl carbon of **1** is followed by successive double ring-opening and isomerization to afford the carboxylate anion (**3**). This carboxylate anion attacks the oxirane ring of **2** to produce an alkoxide anion

Scheme 1



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® Abstract published in *Advance ACS Abstracts,* April 1, 1995.

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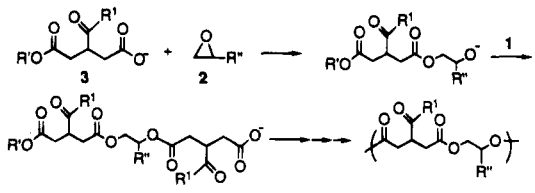
Scheme 2



(Scheme 2). Subsequently, the alkoxide end attacks monomer **1** like the initiator. These processes are involved in the propagation, and, as a result, the copolymer becomes an alternating copolymer. This copolymerization behavior explains Brady's results mentioned above by an idea that the volume shrinkage is suppressed only in the initial stage by occurrence of this type of alternating copolymerization with a limited amount of such monomers.

We have extended aliphatic group (R^1)-containing bicyclic bis(γ-lactone)s and epoxide **2** in their copolymerization to aromatic group (R^1)-containing bicyclic bis(γ-lactone)s and bifunctional epoxides to study the copolymerization behavior and volume change on the copolymerization, which are described in this paper.

Results and Discussion

Synthesis of Bicyclic Bis(γ-lactones)s (1). Preparation of **1a–d** having alkyl substituents (R^1) was carried out by the reaction of tricarballylic acid with corresponding acid anhydrides according to the Strunz method.[14] Similarly, monomers **1e–g** bearing aryl substituents (R^1) were prepared according to the Lawson method.[15] The structure of **1** was determined by IR, ^{1}H NMR, and ^{13}C NMR spectra and elemental analysis.

Volume Change on Anionic Copolymerization of 1c with 2. In the anionic copolymerization of bicyclic bis(γ-lactone)s (**1**) with epoxides **2**, **1** undergoes the double ring-opening polymerization with isomerization (Schemes 1 and 2). Therefore, it is expected to show volume expansion during the copolymerization, because volume expansion is often observed in cationic polymerizations which involve successive double ring-opening of SOE, BOE, and SOC as described previously.[2]

To evaluate the volume change on the anionic copolymerization of **1** with **2**, the copolymerization of **1c** (R^1 = Pr) and glycidly phenyl ether (**2**) (R′ = CH_2OPh) was selected because of their high mutual solubility. An equimolar mixture of **1c** (d^{25} = 1.288 g/cm^3) and **2** (d^{25} = 1.111 g/cm^3) was heated at 120 °C in the presence of potassium *tert*-butoxide (4 mol % vs mixture of **1c** and **2**) in THF ([C] = 4.0 M) for 93 h. The methanol-insoluble polymer was obtained in 92% yield and its density was measured as d^{25} = 1.215 g/cm^3. The structure of the obtained polymer was determined as the corresponding alternating copolymer **4c** by its ^{1}H NMR, ^{13}C NMR, and IR spectra, of which characteristics were in complete accordance with those reported in our previous study.[12,18] From the density change (density of monomer mixture: d^{25} = 1.218 g/cm^3), it was concluded that nearly zero shrinkage (volume change: 0.25 ± 0.15%) took place in this copolymerization. Under similar reaction conditions, the anionic homopolymerization of **2** to poly(**2**) (d^{25} = 1.194 g/cm^3) showed 7.5% volume shrinkage. From these results, **1c** can be regarded as one of expanding monomers, and the copolymerization of **1** with **2** is the first polymerization without volume shrinkage under anionic conditions.

Anionic Copolymerization of 1e–g with 2. Previously we have reported that the copolymerization of alkyl-substituted (R^1) bicyclic bis(γ-lactone) **1a** with glycidyl phenyl ether (**2**) affords the corresponding alternating copolymer with ca. 50:50 unit ratio, independent of the feed ratio.[13] To develop this copolymerization and enhance the thermal properties of the copolymers obtained, we decided to prepare bicyclic bis(γ-lactone)s **1e–g** having aryl substituents (R^1), which were obtained by the reaction of tricarballylic acid with the corresponding aromatic acid anhydrides. The copolymerizations of **1e–g** with **2** were carried out in the presence of potassium *tert*-butoxide (4 mol %) at 120 °C in THF ([C] = 4.0 M) or in bulk to afford methanol-insoluble polymers in 21–86% yields (Scheme 3). The results are shown in Table 1. Number-average molecular weights ($\bar{M}_n$) of the methanol-insoluble polymers were ca. 2300–4400 as estimated by gel permeation chromatography (GPC). The copolymer compositions of the polymers were ca. 50:50 in any case in accordance with the feed ratios (50:50). The structure of the copolymer was determined by the IR, ^{1}H NMR, and ^{13}C NMR spectra. Typical spectra are shown in Figures 1 and 2. The ^{1}H NMR spectrum involves the very characteristic signal at 5.3 ppm of the methine proton adjacent to the ester oxygen in the main chain which is originated from **2**, in any copolymer. The corresponding methine carbon signal at 70.1 ppm and two kinds of carbonyl carbon signals of the ketone (200.3 ppm) and ester groups (170.5 and 170.9 ppm) are observed in the ^{13}C NMR spectra. In addition, the carbonyl absorptions at 1740 cm^{-1} (Figure 2, band a) and 1685 cm^{-1} (Figure 2, band b) due to the ester and aromatic ketone groups, respectively, are also confirmed in the IR spectrum. Therefore, the methanol-insoluble polymers were decided as the alternating copolymers (**4**), which were formed via the successive double ring opening of **1e–g** with isomerization and ring opening of **2**. These results were in good accordance with our previously reported alternating copolymerization of **1a** with **2**, and it was concluded that the copolymerization behavior is independent of the substituent (R^1).[12,13]

Scheme 3

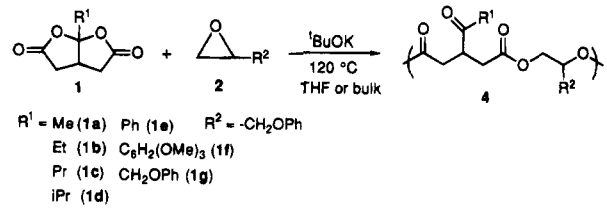


Table 1. Anionic Copolymerization of Bicyclic Bis(γ-lactone) (1) with Glycidyl Phenyl Ether (2)[a]

run	monomer	solvent (M)	yield[b] (%)	$\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$)[c]	composition[d] (lactone:epoxide)
1	**1e**	THF (2)	86	3300 (1.16)	53:47
2	**1e**	bulk	71	3040 (1.44)	49:51
3	**1f**	THF (2)	71	3700 (1.19)	50:50
4	**1f**	bulk	76	4400 (1.32)	53:47
5	**1g**	THF (2)	21	2300 (1.56)	48:52
6	**1g**	bulk	34	2920 (1.57)	50:50

[a] Polymerization conditions: monomer feed mole ratio; bis(γ-lactone):epoxide = 50:50, *t*-BuOK (4 mol %), 120 °C, 72 h. [b] Methanol-insoluble polymer. [c] Estimated by GPC (based on PSt standards). [d] Determined by ^{1}H NMR.

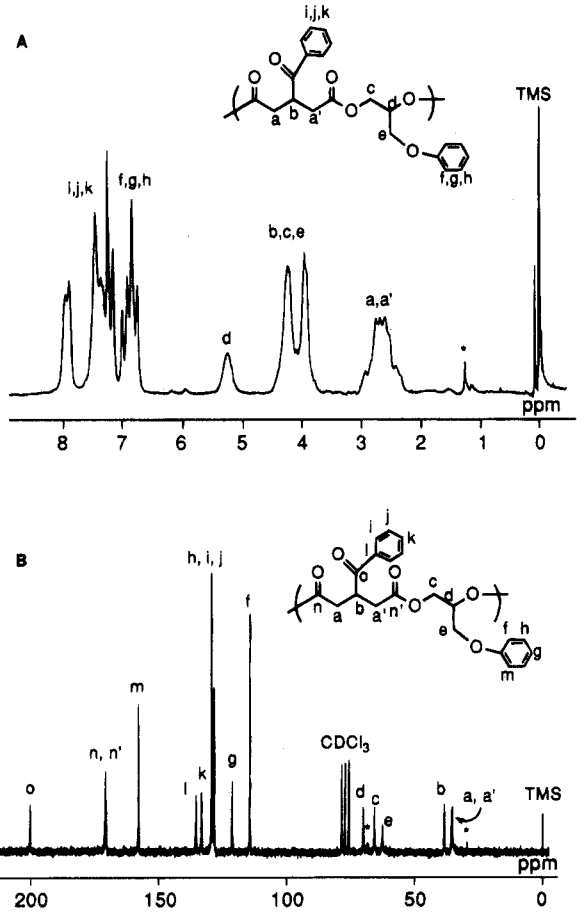


Figure 1. ^{1}H NMR (90 MHz) (A) and ^{13}C NMR (22.5 MHz) (B) spectra of **4e** ($\bar{M}_n$ = 3300) in $CDCl_3$ at 27 °C. Asterisks are assigned to the *tert*-butyl group derived from the initiator.

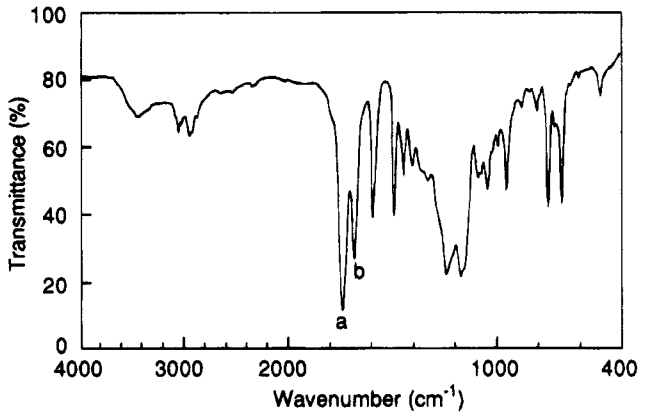


Figure 2. IR spectrum (neat) of **4e** ($\bar{M}_n$ = 3300).

erization of **1a** (R^1 = Me) with **5a** in the presence of potassium *tert*-butoxide was carried out at 120 °C for 6−72 h in bulk. The solvent-insoluble polymer (**6aa**) was quantitatively obtained, when the reaction time was over 24 h. The unit ratio[16] of **1a** to **5a** of the obtained polymer was 1:0.51 (**1a**:**5a**), which was determined from the yield of the solvent-soluble fraction and its composition estimated by ^{1}H NMR (Table 2, run 4). In addition to this result, the IR spectral analysis of **6aa** indicated the disappearance of the five-membered lactone carbonyl (1790 cm^{-1}; Figure 3B, band a) of **1a** and the oxirane C−O bond (912 cm^{-1}; Figure 3B, band b) of **5a** but instead the appearance of the ester (1739 cm^{-1}; Figure 3A, band c) and ketone (1720 cm^{-1}; Figure 3A, band d) carbonyl absorptions (Figure 3).

Scheme 4

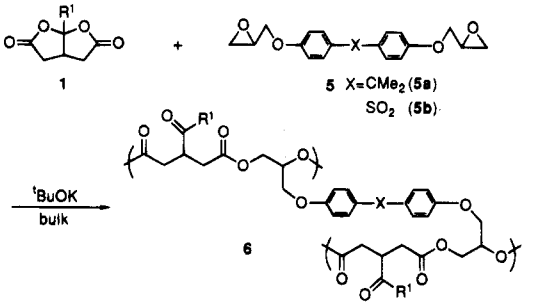


Table 2. Anionic Copolymerization of Bicyclic Bis(γ-lactone) 1a with Epoxide 5a[a]

	feed ratio (molar ratio)		copolymer	copolymer composition[c]	
run	**1a**	**5a**	yield[b] (wt %)	**1a**	**5a**
1	1	0.12	48	1	0.35
2	1	0.21	69	1	0.39
3	1	0.33	89	1	0.39
4	1	0.50	98	1	0.51
5	1	0.75	94	1	0.71
6	1	1.17	55	1	0.80

[a] Polymerization conditions: *t*-BuOK (4 mol %), 120 °C, 24 h. [b] Dichloromethane-insoluble part. [c] Determined from the yields of the dichloromethane-soluble part and its compositions estimated by the ^{1}H NMR integration ratio of unreacted monomers and/or low molecular weight polymer.

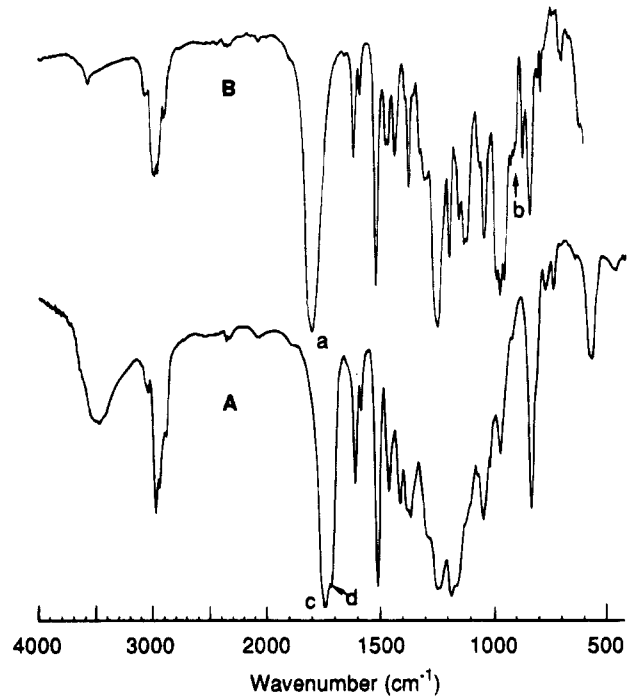


Figure 3. IR spectra (KBr) of **6aa** (A) and a monomer mixture of **1a** and **5a** (B).

Yield and composition of the copolymers obtained in varying monomer feed ratios of **1a** to **5a** from 1:0.12 to 1:1.17 are summarized in Table 2. The yields of the copolymers decreased, while the composition was deviated from the expected value 1:0.5, as the feed ratio was deviated from 1:0.5. In these cases, the solvent-soluble fraction consisted of unreacted excess monomers and low molecular weight polymer. This deviation of the composition from 1:0.5 appears to be consistent with the alternating copolymerization and can be well explained by assuming that the composition is strongly affected by the end group when the degree of polymerization is

Table 3. Anionic Copolymerization of Bicyclic Bis(γ-lactone)s (1) with Bifunctional Epoxides (5)[a]

run	bis(lactone)	epoxide	temp (°C)	time (h)	copolymer	yield[b] (wt %)	copolymer composition[c] bis(lactone):epoxide
1	**1a**	**5a**	120	24	**6aa**	98	1:0.51
2	**1a**	**5b**	120	24	**6ab**	98	1:0.53
3	**1b**	**5a**	120	24	**6ba**	93	1:0.54
4	**1b**	**5b**	120	24	**6bb**	93	1:0.54
5	**1c**	**5a**	120	24	**6ca**	95	1:0.54
6	**1c**	**5b**	120	24	**6cb**	95	1:0.54
7	**1d**	**5a**	120	24	**6da**	97	1:0.5
8	**1d**	**5b**	120	24	**6db**	98	1:0.55
9	**1e**	**5a**	120	24	**6ea**	98	1:0.5
10	**1e**	**5b**	120	24	**6eb**	89	1:0.56
11	**1f**	**5a**	150	72	**6fa**	89	1:0.49
12	**1f**	**5b**	160	24	**6fb**	84	1:0.52
13	**1g**	**5a**	120	96	**6ga**	94	1:0.49
14	**1g**	**5b**	150	72	**6gb**	91	1:0.53

[a] Polymerization conditions: monomer feed mole ratio; bis(γ-lactone):epoxide = 1:0.5, *t*-BuOK (4.0 mol %), bulk. [b] Dichloromethane-insoluble part. [c] Determined from the yields of the dichloromethane-soluble part and its compositions estimated by the ^{1}H NMR integration ratio of unreacted monomers and/or molecular weight polymer.

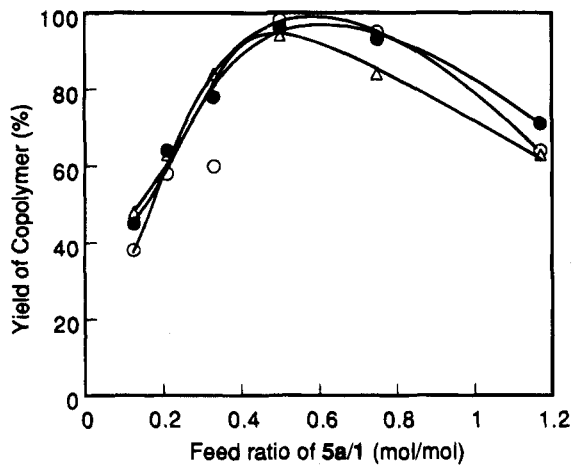


Figure 4. Relationship between the yield of copolymers and the feed ratios of **5a** to **1b**, **1c**, and **1e** (△, **6ba**; ●, **6ca**; ○, **6ea**).

low. In fact, the composition is changed according to the feed ratio, and, therefore, the copolymers should have an end group derived from excess monomer. The following facts clearly support the above explanation. That is, **1a** has no homopolymerizability[13] and **5a** did not polymerize under the same conditions without **1a**.

Consequently, the formation of the alternating copolymer in the copolymerization of **1a** with bifunctional epoxide **5a** was undoubtedly from the above-mentioned discussions, like in the copolymerization of **1a** and monofunctional epoxide **2**.[13]

The copolymerizations of various bicyclic bis(γ-lactone)s (**1a**–**g**) with **5a** and **5b** were carried out under similar conditions. The results are summarized in Table 3. Effects of the monomer feed ratio on the yield and composition of the copolymers formed were examined. The yields of the solvent-insoluble copolymers in the copolymerizations of **1a**–**d** having alkyl substituents were slightly higher (Table 3, runs 1–8, 93–98%) than those of **1e**–**g** having aryl ones (Table 3, runs 9–14, 84–98%). This can be due to the steric hinderance of bulky aromatic substituents (**1f** and **1g**) and/or high melting point (mp 203–204 °C (**1f**) and 162–164 °C (**1g**)). The compositions of the copolymers were ca. 1:0.5 in any case. In addition to similar IR characteristics of the copolymers of **1b**–**g** and **5** to those of **1a** and **5a**, the highest yield obtained at the feed ratio of 1:0.5 (**1**:**5**) (Figure 4) strongly suggested that the copolymerizations of **1a**–**g** with **5** occur independent of not only the substituent (R^1) of **1** but also the structure of the epoxide, giving the corresponding alternating copolymers.

Volume Change during the Copolymerization. As mentioned in the introductory part, SOE, BOE, and SOC show expansion in volume during cationic polymerization which can be attributed to their polymerization mode, i.e., the double ring-opening isomerization polymerization.[1,2] There has been no polymerization resulting in volume expansion under anionic conditions. The above-mentioned anionic copolymerization of **1c** with **2** showed nearly zero shrinkage (small expansion, 0.25 ± 0.15%), suggesting **1c** as expanding monomer. Densities of the copolymers of **1a** with **5a** obtained in the feed ratios from 1:0.12 to 1:1.17 and those of the corresponding monomer mixtures were measured by the density gradient tube method at 25 °C (Table 4, runs 2–7). The degree of volume change ranged from −1.4 ± 0.15% to −3.8 ± 0.15%, as shown in Table 4. The volume shrinkage decreased as the feed ratio came close to 1:0.5, but further reduction of the volume shrinkage could not be observed at any feed ratio (Figure 5). These results probably correspond to the copolymerization behavior of **1a** with **5a**.

The densities of the monomer mixtures of **1a**–**g** and **5a** and **5b**, and the corresponding copolymers obtained at the feed ratio of 1:0.5 were measured (Table 4). A small volume change (−2.5 ± 0.15% to +2.4 ± 0.15%) in the copolymerizations of **1** with **5** was observed: a little volume shrinkage took place in the copolymerization of **1** with **5a**, whereas slight volume expansion occurred in the case of **5b**. **5a** is known to polymerize with 4.2% volume shrinkage under cationic conditions.[2] As a result, it would be concluded that volume shrinkage during polymerization of **5** is somewhat suppressed by addition of **1** as comonomer. These results are in accordance with our previous results that volume shrinkage of **2** or **5a** is released by addition of SOCs under catioinic polymerization conditions.[17]

Therefore, to achieve effective and successful suppression of volume shrinkage during anionic copolymerization of epoxy resins with bicyclic bis(γ-lactone)s, it is necessary to use an equimolar amount of the bis(γ-lactone)s vs the epoxy moiety, although this substantially changes the polymer structure.

Thermal Properties of Copolymers. Glass transition temperature (T_g) and 10% weight loss temperature ($T_{d_{10}}$) of the copolymers obtained from **1** and **5** were evaluated by DSC and TGA, respectively, under a nitrogen atmosphere. The results are summarized in Table 4. As the feed ratio of **1a**:**5a** was varied from

Table 4. Volume Change during Copolymerization of Bicyclic Bis(γ-lactone)s (1) with Bifunctional Epoxides (5) and Thermal Properties of the Copolymers

run	feed ratio bis(lactone):epoxide (molar ratio)	copolymer	density (g/cm³)[a] D_m[b]	density (g/cm³)[a] D_p[c]	volume[d] charge (%)	T_g[e] (°C)	$T_{d_{10}}$[f] (°C)
1	**1c 2**	**4c**	1.218	1.215	+0.25		
2	**1a 5a** (0.12)	**6aa**	1.227	1.274	−3.8	31	252
3	**1a 5a** (0.21)	**6aa**	1.232	1.265	−2.7	30	251
4	**1a 5a** (0.33)	**6aa**	1.232	1.262	−2.4	42	253
5	**1a 5a** (0.5)	**6aa**	1.242	1.259	−1.4	51	282
6	**1a 5a** (0.75)	**6aa**	1.233	1.255	−1.8	52	318
7	**1a 5a** (1.17)	**6aa**	1.214	1.235	−1.7	51	311
8	**1a 5b** (0.5)	**6ab**	1.385	1.365	+1.4	60	296
9	**1b 5a** (0.5)	**6ba**	1.221	1.232	−0.9	75	287
10	**1b 5b** (0.5)	**6bb**	1.359	1.340	+1.4	68	293
11	**1c 5a** (0.5)	**6ca**	1.195	1.225	−2.5	66	267
12	**1c 5b** (0.5)	**6cb**	1.317	1.301	+1.2	66	281
13	**1d 5a** (0.5)	**6da**	1.211	1.214	−0.2	79	266
14	**1d 5b** (0.5)	**6db**	1.341	1.313	+2.1	70	265
15	**1e 5a** (0.5)	**6ea**	1.286	1.259	+2.1	60	303
16	**1e 5b** (0.5)	**6eb**	1.369	1.350	+1.4	76	290
17	**1f 5a** (0.5)	**6fa**	1.255	1.257	−0.2	103	319
18	**1f 5b** (0.5)	**6fb**	1.336	1.360	−1.8	120	314
19	**1g 5a** (0.5)	**6ga**	1.260	1.288	−2.2	76	316
20	**1g 5b** (0.5)	**6gb**	1.386	1.352	+2.4	76	309

[a] Determined by a density gradient tube method at 25 °C. [b] D_m = density of monomer mixture. [c] D_p = density of copolymer. [d] Volume change = $(D_m - D_p/D_m) \times 100$ (standard error of the measurement = ±0.15%). [e] Determined by DSC under a nitrogen atmosphere. [f] Determined by TGA under a nitrogen atmosphere.

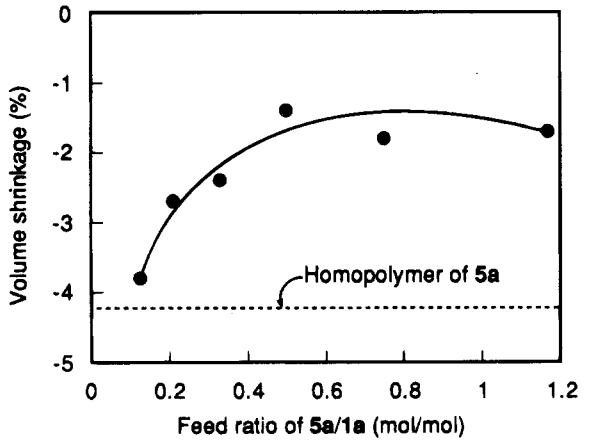


Figure 5. Relationship between the volume shrinkage of **6aa** and the feed ratio of **5a** to **1a**.

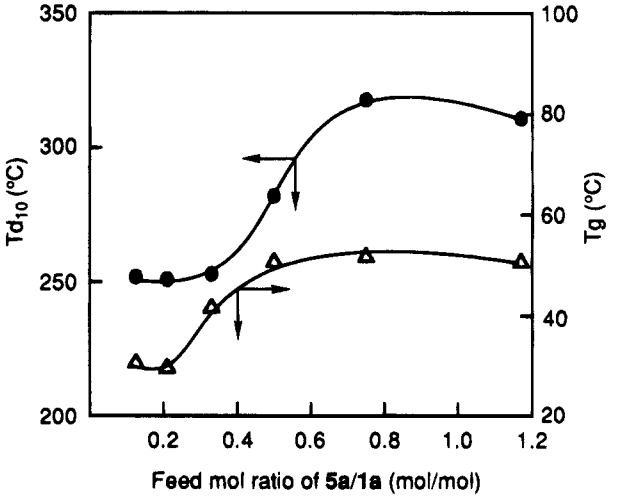


Figure 6. Relationship between T_g and $T_{d_{10}}$ of **6aa** and the feed ratio of **5a** to **1a**.

1:0.12 to 1:0.5, the T_g and $T_{d_{10}}$ increased from 30 to 52 °C and from 252 to 318 °C, respectively. However, T_g did not change with use of excess epoxy resin, although $T_{d_{10}}$ slightly increased (Table 4, runs 2–7; Figure 6). These T_g data seem to suggest that the degree of cross-linking of **6aa** is almost the same in the feed ratio range from 1:0.5 to 1:1.17. This is consistent with the alternating copolymerization behavior of **1a** with **5a**. Namely, since **1a** has no homopolymerizability, the alternating copolymer structure does not change basically by use of excess epoxide, although the end group of the copolymer can be changed.

T_gs of the copolymers **6aa**–**db** having alkyl substituents in the side chain ranged from 50 to 70 °C, and $T_{d_{10}}$s ranged from 250 to 300 °C. T_gs and $T_{d_{10}}$s of **6ea**–**gb** having aryl groups ranged from 60 to 120 °C and 290 to 319 °C, respectively. These data suggest the enhancement of the thermal stability of the copolymers by the introduction of the aromatic substituents (R^1) in the polymer side chain as expected previously.

Summary

The anionic copolymerizations of the bicyclic bis(γ-lactone)s (**1**) having alkyl and aryl substituents (R^1) with the bifunctional epoxides (**5**) proceeded via successive double ring-opening isomerization of **1** and ring opening of the epoxy group to afford the corresponding solvent-insoluble copolymers quantitatively. The structure of the copolymers was alternating and independent of the substituent of **1**. In the evaluation of volume change during copolymerization of **1** and **5**, volume shrinkage on polymerization of **5** was largely reduced by the addition of **1** as comonomer.

Experimental Section

Measurements. ^1H NMR and ^{13}C NMR spectra were recorded on JEOL EX-90 spectrometers, using tetramethylsilane (TMS) as the internal standard in deuteriochloroform. FT-IR spectra were obtained with a JASCO FT/IR-3. Molecular weights ($\bar{M}_n$ and $\bar{M}_w$, number- and weight-average molecular weights) and its distribution ($\bar{M}_w/\bar{M}_n$) were estimated by gel permeation chromatography (GPC) on a Toyo Soda HPLC CCP & 8000 system with a data processor, equipped with three consecutive linear polystyrene gel columns (G2500H, G4000H, and G5000H), using tetrahydrofuran as solvent (flow rate 1.0 mL/min, polystyrene calibration, and refractive index

(RI) and ultraviolet (UV, 254 nm) detectors). The density of the monomer mixtures and copolymers was measured by the density gradient tube method at 25 °C with a Shibayama Kagaku Seisakusho Model A. Determination of the glass transition temperature (T_g) was determined with a Seiko differential scanning calorimeter (DSC220C) at a heating rate of 10 °C/min under a nitrogen atmosphere, and determination of the 10% weight loss temperature (T_{d10}) was carried out with a Seiko thermogravimetric analyzer (TG/DTA220) operated at a heating rate of 10 °C/min under a nitrogen atmosphere.

Materials. Diglycidly ether of Bisphenol A (Asahi Kasei Co.), diglycidyl ether of Bisphenol S (YBS-564, Nikka Chemical Co.), and potassium *tert*-butoxide (Aldrich Chemical Co.) were used as received.

Synthesis of 2,8-Dioxa-1-methylbicyclo[3.3.0]octane-3,7-dione (1a; R = Me). Tricarballylic acid (13.6 g, 77.4 mmol, from Aldrich Chemical Co.) was added to refluxing acetic anhydride (110 mL, distilled before use) containing pyridine (1.0 mL). The solution was refluxed for 6 h. After removal of acetic acid and unreacted acetic anhydride by distillation, the residue was dissolved in acetone (300 mL) and treated with active charcoal. Removal of charcoal by filtration and evaporation of the filtrate yielded a pale yellow solid. It was purified by recrystallization from ethanol to give a colorless crystal. Yield: 6.1 g (45%). Mp: 102–103 °C (lit.[13] mp 98–99 °C). IR (KBr): 2965, 2937, 2878, 1816, 1790, 1291, 1269, 1085, 1069 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.40–3.23 (m, 5H, CH_2 + CH), 1.82 (s, 3H, Me). ^{13}C NMR ($CDCl_3$): δ 172.4, 113.1, 38.9, 35.4, 28.3.

Synthesis of 2,8-Dioxa-1-ethylbicyclo[3.3.0]octane-3,7-dione (1b; R = Et). A solution of tricarballylic acid (17.8 g, 100 mmol), propionic anhydride (180 mL, distilled before use), and pyridine (1.5 mL) was allowed to react similarly to the case of the synthesis of **1a**. By recrystallization from ethanol, a colorless crystal was obtained. Yield: 3.2 g (18%). Mp: 63–65 °C (lit.[14] mp 65–66 °C). IR (KBr): 2990, 1788, 1237, 1211, 1145, 1111, 976, 944 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.44–3.24 (m, 5H, $2CH_2$ + CH), 1.93–2.18 (q, 2H, CH_2), 0.98–1.17 (t, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 173.2, 115.6, 36.7, 35.8, 30.3, 7.4.

Synthesis of 2,8-Dioxa-1-propylbicyclo[3.3.0]octane-3,7-dione (1c; R = Pr). A solution of tricarballylic acid (8 g, 45 mmol), *n*-butyric anhydride (114 mL, distilled before use), and pyridine (0.5 mL) was allowed to react according to the method of the synthesis of **1a**. Yield: 1.2 g (18%). Mp: 56–57 °C (lit.[18] mp 56–58 °C). IR (KBr): 2964, 2937, 2878, 1786, 1290, 1149, 983 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.44–3.38 (m, 5H, $2CH_2$ + CH), 1.83–2.08 (m, 2H, CH_2), 1.29–1.70 (m, 2H, CH_2), 0.91–1.07 (t, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 173.3, 115.0, 39.0, 37.1, 35.4, 16.2, 13.7.

Synthesis of 2,8-Dioxa-1-isopropylbicyclo[3.3.0]octane-3,7-dione (1d; R = iPr). A solution of tricarballylic acid (8 g, 45 mmol), isobutyric anhydride (105 mL, distilled before use), and pyridine (0.5 mL) was allowed to react by the same method as the synthesis of **1a**. Yield: 2.4 g (30%). Mp: 90–92 °C. IR (KBr): 2995, 2943, 2885, 1786, 1415, 1244, 1184, 1080, 983, cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.09–3.38 (m, 6H, $CH(CH_3)_2$, $2CH_2$ + CH), 1.02–1.09 (t, 6H, $C(CH_3)_2$). ^{13}C NMR ($CDCl_3$): δ 172.9, 116.9, 35.4, 34.6, 15.5. Anal. Calcd for $C_9H_{12}O_4$: C, 58.70; H, 6.52. Found: C, 58.76; H, 6.56.

Synthesis of 2,8-Dioxa-1-phenylbicyclo[3.3.0]octane-3,7-dione (1e; R = Ph). A mixture of tricarballylic acid (20 g, 114 mmol) and benzoic anhydride (51.4 g, 340 mmol) was added to refluxing xylene (30 mL) containing pyridine (1.0 mL). The solution was refluxed for 9 h. After removal of xylene by evaporation, the residue was dissolved in acetone (300 mL) and treated with active charcoal. Removal of charcoal by filtration and evaporation of the filtrate yielded a pale yellow solid. Recrystallization from benzene afforded a colorless crystal. Yield: 4.9 g (24%). Mp: 138–139 °C (lit.[15] mp 122 °C). IR (KBr): 3065, 3036, 3003, 2934, 1797, 1452, 1340, 1255, 1199, 1001, 866, 763 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.43 (s, 5H, Ph), 2.50–3.53 (m, 5H, CH_2 + CH). ^{13}C NMR ($CDCl_3$): δ 172.5, 136.3, 130.2, 129.0, 124.9, 111.7, 41.4, 35.2. Anal. Calcd for $C_{12}H_{10}O_4$: C, 66.05; H, 4.59. Found: C, 66.11; H, 4.23. Although the melting point of the product was considerably higher than that of the literature,[15] the above spectral data as well as the elemental analysis clearly supported the proposed structure.

Synthesis of 2,8-Dioxa-1-(3,4,5-trimethoxyphenyl)-bicyclo[3.3.0]octane-3,7-dione (1f; R = $C_6H_2(OMe)_3$). 1f was prepared from tricarballylic acid (5 g, 28 mmol), 3,4,5-trimethoxybenzoic anhydride (23 g, 56 mmol), and pyridine (0.5 mL) by the same method as **1e**. Yield: 1.7 g (24%). Mp: 203–204 °C. IR (KBr): 2941, 2843, 1792, 1589, 1413, 1342, 1244, 1118, 999, 893 cm^{-1}. ^{1}H NMR (CD_3COCD_3): δ 6.84 (s, 2H, Ph), 3.75–3.85 (d, 9H, 3 × OCH_3), 2.87–3.16 (m, 5H, $2CH_2$ + CH). ^{13}C NMR (CD_3COCD_3): δ 174.0, 154.6, 133.8, 113.6, 103.9, 60.5, 56.6, 42.1, 35.6. Anal. Calcd for $C_{15}H_{16}O_7$: C, 58.44; H, 5.23. Found: C, 57.95; H, 5.24.

Synthesis of 2,8-Dioxa-1-(phenoxymethyl)bicyclo[3.3.0]-octane-3,7-dione (1g; R = CH_2OPh). 1g was prepared from tricarballylic acid (7.7 g, 43.7 mmol), phenoxyacetic anhydride (25 g, 87.4 mmol), and pyridine (0.5 mL) by the same method as **1e**. Yield: 1.4 g (18%). Mp: 162–164 °C. IR (KBr): 2941, 2843, 1792, 1589, 1413, 1342, 1244, 1118, 999, 893 cm^{-1}. ^{1}H NMR (CD_3COCD_3): δ 6.90–7.4 (m, 5H, Ph), 4.41 (s, 2H, OCH_2), 2.64–3.78 (m, 5H, $2CH_2$ + CH). ^{13}C NMR (CD_3COCD_3): δ 173.9, 158.9, 130.4, 113.6, 122.5, 115.5, 112.1, 69.7, 56.6, 36.7, 35.7. Anal. Calcd for $C_{13}H_{12}O_5$: C, 62.90; H, 4.87. Found: C, 62.62; H, 4.86.

Anionic Copolymerization of 1 with 2. Typical Procedure for 1e. A mixture of **1e** (218 mg, 1.0 mmol), glycidly phenyl ether (**2**) (0.14 mL, 1.0 mmol), potassium *tert*-butoxide (6.8 mg, 4 mol %), and 0.5 mL of tetrahydrofuran (THF) was placed in a polymerization tube. The tube was cooled, evacuated, sealed off, and heated at 120 °C for 72 h. After the mixture was cooled to room temperature, a dichloromethane solution of acetic acid (2 vol %, 1 mL) was added to the reaction mixture. Subsequently, 40 mL of methanol was added to the mixture to precipitate the methanol-insoluble polymer (**4e**). $\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$): 3300 (1.16). Yield: 322 mg (86%).

4e. IR (neat): 3065, 3042, 2959, 1740, 1685, 1599, 1244, 1174, 910, 733 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.75–7.97 (m, 10H, aromatic), 5.26 (s, 1H, C(=O)CH), 3.82–4.25 (m, 5H, CH_2OC(=O), CH_2OPh, CH), 2.31–2.91 (m, 4H, 2 × CH_2C(=O)O). ^{13}C NMR ($CDCl_3$): δ 200.3, 170.9, 170.5, 158.3, 135.5, 133.4, 130.3, 128.7, 128.4, 121.3, 114.5, 70.1, 65.6, 62.6, 38.5, 35.6, 35.4.

4f. IR (neat): 3514, 3067, 2941, 2839, 1739, 1678, 1585, 1502, 1460, 1415, 1236, 1155, 1049, 1001, 912, 756, 733, 692 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.62–7.31 (m, 7H, aromatic), 5.28 (s, 1H, C(=O)CH), 3.83–4.27 (m, 14H, CH_2OC(=O), CH_2OPh, CH, 3 × OCH_3), 2.62–2.72 (m, 4H, 2 × CH_2C(=O)O). ^{13}C NMR ($CDCl_3$): δ 199.1, 171.1, 170.8, 158.0, 153.2, 143.0, 130.3, 121.4, 114.5, 106.1, 70.1, 65.8, 60.8, 56.2, 38.4, 35.9.

4g. IR (neat): 3499, 3065, 3042, 2930, 1738, 1599, 1494, 1458, 1369, 1242, 1174, 1082, 1049, 910, 815, 756, 733 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.83–7.32 (m, 10H, aromatic), 5.28 (s, 1H, C(=O)CH), 4.80 (s, 2H, OCH_2), 3.59–4.33 (m, 5H, CH_2OC(=O), CH_2OPh, CH), 2.66 (m, 4H, 2 × CH_2C(=O)O). ^{13}C NMR ($CDCl_3$): δ 208.0, 170.2, 157.0, 128.6, 120.6, 113.9, 70.0, 69.8, 64.4, 61.8, 38.4, 35.9.

Anionic Copolymerization of 1 with 5. A Typical Procedure for 1a and 5a. A mixture of **1a** (0.156 g, 1 mmol), diglycidyl ether of Bisphenol A (**5a**) (0.117 g, 0.5 mmol), and potassium *tert*-butoxide (6.8 mg, 4 mol %) was heated at 120 °C for 24 h in an evacuated sealed tube. The polymerization mixture was cooled, a dichloromethane solution of acetic acid (2 vol %, 1 mL) was added, and the resulting mixture was washed with dichloromethane with a Soxhlet extractor for 6 h. Dichloromethane-insoluble polymer was collected and dried at 60 °C for 24 h in vacuo to yield 0.327 g (98%) of a yellow–brown solid (**6aa**). IR (KBr): 3466, 3040, 2966, 1739, 1720, 1608, 1510, 1413, 1363, 1246, 1159, 1043, 831 cm^{-1}.

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MA946098H