Anionic Alternating Ring-Opening Copolymerization of Spirocyclic Bis(γ-lactone)s with Bisepoxides and Volume Change during the Copolymerization

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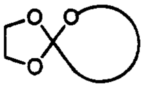
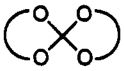
Introduction

Spirocyclic orthoesters, spirocyclic orthocarbonates (SOCs), and bicyclic orthoesters have been studied as monomers showing expansion in volume on cationic ring-opening polymerization.[1-3] The volume expansion is believed to come from their successive double ring-opening polymerization mode.

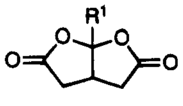




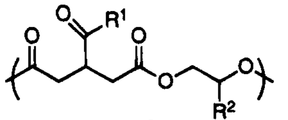
There have been some attempts to reduce volume shrinkage during polymerization of epoxides. The polymerization shrinkage of epoxides is actually controlled by addition of SOCs into the polymerization system.[4] The expanding monomers which have been reported so far polymerize only cationically but neither anionically nor radically. Expanding monomers which can polymerize with anionic[2,5] and radical[6] initiators have been reported. Brady et al. have reported that bicyclic and tricyclic monomers undergo copolymerization with epoxy and polyamide resins via an anionic mechanism to control the polymerization shrinkage of such resins.[7] Further, they have succeeded in the reduction of volume shrinkage which is achieved by addition of small amounts of spirocyclic γ-lactones to the anionic copolymerization system with epoxy resins.[8] However, in these copolymerizations suppression of volume shrinkage is attained only in the initial stage of the copolymerization and the final volume change is shrinkage, probably because the amount of bicyclic and spirocyclic comonomers is too small to suppress the whole volume shrinkage.

Recently we have found that bicyclic (**1**) and spirocyclic bis(γ-lactone)s (**4**) have no homopolymerizability but good copolymerizability with epoxides to selectively afford corresponding alternating copolymers (**3** and **5**) via the double ring-opening isomerization of **1**[9] and **4**.

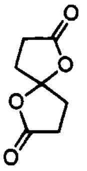
From these results we have concluded that the partial suppression of volume shrinkage in the initial stage of the copolymerizations reported by Brady et al. is rationally explained by our result, i.e., the alternating copolymerization.[9,10] Since no volume shrinkage has been confirmed in the copolymerization of **1** with epoxides,[11] we have proposed that **1** should be regarded as an expanding monomer. We have extended our study to the copolymerization with epoxy resins, i.e., bifunctional epoxides, to demonstrate the characteristic property of **1** and **4** as novel monomers exhibiting volume expansion via anionic polymerization processes. In this paper the results of the anionic alternating copolymerizations of **4** with a few epoxy resins (**6**) and volume change on these copolymerizations are disclosed.



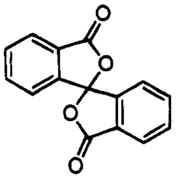
1 R^1= Me, Et, Pr



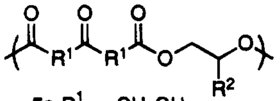
3 R^2 = -CH_2OPh



4a

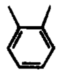


4b



5a R^1 = -CH_2CH_2-

5b R^1 =



Experimental Section

Measurements. ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL EX-90 spectrometer, using tetramethylsilane (TMS) as the internal standard in deuteriochloroform. FT-IR spectra were obtained with a Jasco FT/IR-3. Thermal analyses of polymers were carried out using a Seiko differential scanning calorimeter (DSC220C) and a Seiko thermogravimetric analyzer (TG/DTA220) operated at a heating rate of 10 °C/min under a nitrogen atmosphere. Densities of monomer mixtures and polymers were measured by the density gradient tube method at 25 °C with a Shibayama Kagaku Seisakusho Model A.

Materials. Diglycidyl 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. 1,6-Dioxaspiro[4.4]nonane-2,7-dione (**4a**) (Aldrich Chemical Co.) was purified by recrystallization from methanol.

Synthesis of Monomer 4b. Preparation of **4b** was carried out by Brady's method: yield 3.0 g (49%); mp 211–213 °C (lit.[8] mp 212 °C); IR (KBr) 3105, 2956, 2858, 1787, 1606, 1464, 1343, 1285, 1088, 1009, 912, 794, 759 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.22–8.07 (m, 8H, aromatic); ^{13}C NMR ($CDCl_3$) δ 166.6, 144.3, 135.5, 131.9, 126.3, 126.0, 123.0, 107.0.

Anionic Copolymerization: A Typical Procedure. A mixture of spirocyclic bis(γ-lactone) (**4a**; 0.156 g, 1 mmol), diglycidyl ether of Bisphenol A (**6a**; 0.171 g, 0.5 mmol), and potassium *tert*-butoxide (6.8 mg, 4 mol %) was heated at 140 °C for 24 h in an evacuated sealed tube. To the cooled polymerization mixture was added a dichloromethane solution of acetic acid (2 vol %, 1 mL), and the resulting mixture was washed with dichloromethane with a Soxhlet extractor for 6 h. Dichloromethane-insoluble polymer was collected and dried in vacuo at 60 °C for 24 h: yield 0.317 g (97%); IR (KBr) 3422, 3040, 2964, 1739, 1711, 1649, 1608, 1581, 1510, 1462, 1363, 1246, 1182, 1099, 1043, 933, 831 cm^{-1}.

Results and Discussion

According to the conditions previously reported in the copolymerizations of **1** with glycidyl phenyl ether (**2**),[9,10] the anionic copolymerization of spirocyclic bis(γ-lactone) (**4a**) with **2** in THF ([C] = 4.0 M) was performed at 120 °C for 48 h (Table 1, run 1). The product obtained in 80% yield was the expected alternating copolymer, of which the structure was determined by referring to the previously reported data. Meanwhile, the anionic copolymerization of **4a** with **6a** (feed ratio = 1.0:0.5) was carried out in the presence of potassium *tert*-butoxide (4 mol %) as the initiator for 24 h under the same

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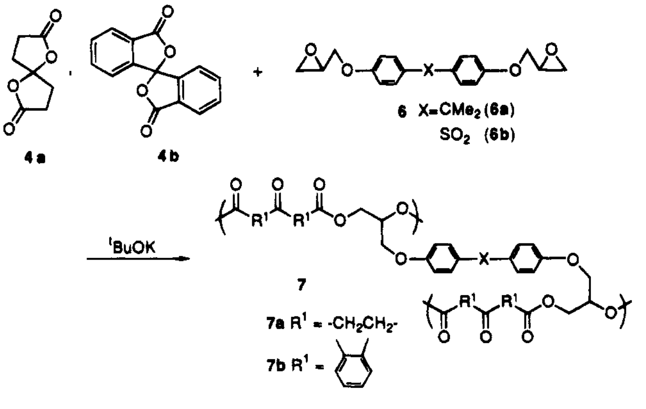
Table 1. Anionic Copolymerization of Spirocyclic Bis(γ-lactone) with Epoxide[a]

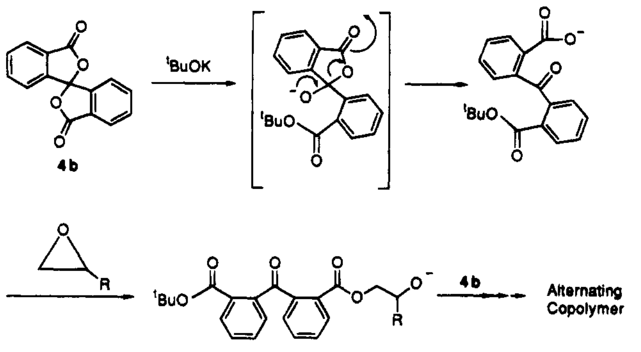
run	temp (°C)	time (h)	solvent (M)	monomer		copolymer	yield[c] (wt %)	copolymer composition[d]	
				spirolactone	epoxide[b]			spirolactone	epoxide
1[e]	120	48	THF (4)	**4a**	**2** (1.0)	**3a**	80[f]	1	1[g]
2	140	24	none	**4a**	**6a** (0.21)	**7aa**	73	1	0.36
3	140	24	none	**4a**	**6a** (0.33)	**7aa**	95	1	0.34
4	140	24	none	**4a**	**6a** (0.50)	**7aa**	97	1	0.50
5	140	24	none	**4a**	**6a** (0.75)	**7aa**	92	1	0.66
6	140	24	none	**4a**	**6b** (0.50)	**7ab**	98	1	0.50
7	120	48	THF (4)	**4b**	**2** (1.0)	**3b**	81[h]	1	1[g]
8	150	24	none	**4b**	**6a** (0.21)	**7ba**	53	1	0.48
9	150	24	none	**4b**	**6a** (0.33)	**7ba**	75	1	0.55
10	150	24	none	**4b**	**6a** (0.50)	**7ba**	93	1	0.59
11	150	24	none	**4b**	**6a** (0.75)	**7ba**	95	1	0.73
12	150	24	none	**4b**	**6b** (0.50)	**7bb**	90	1	0.50

[a] Initiator; potassium *tert*-butoxide (4 mol %). [b] Feed ratio (mol/mol). [c] Dichloromethane-insoluble part. [d] Determined by ^{1}H NMR integration of the dichloromethane-soluble part. [e] Cocatalyst (*cis*-dicyclohexane-18-crown-6; 8 mol %). [f] Separated by preparative HPLC. [g] Determined by ^{1}H NMR. [h] Methanol-insoluble part.

Scheme 1



Scheme 2



conditions to afford the corresponding solvent-insoluble copolymer (Table 1, run 4; Scheme 1).

Since the yield was nearly quantitative, the composition of the obtained copolymer (**7aa**) should be equal to the feed ratio. In fact this ratio was consistent with that determined from the ^{1}H NMR spectrum of the solvent-soluble fraction, although the amount of this fraction was quite small. From the IR spectral analyses of the copolymer and the corresponding monomer mixture, it was confirmed that the absorptions of the spirolactone carbonyl of **4a** (1788 cm^{-1}) and the oxygen ring of **6a** (912 cm^{-1}) completely disappeared and instead those of the ester (1739 cm^{-1}) and ketone (1711 cm^{-1}) carbonyls appeared after the copolymerization. In the copolymerization of **4b** and **6a** giving **7ba**, a characteristic aromatic ketone absorption derived by the double ring-opening isomerization of **4b** (Scheme 2) was confirmed at 1678 cm^{-1} in **7ba** (Figure 1).

In addition to the results of the IR analyses, the following results of the experiments with variable feed ratios suggested the alternating copolymerization of **4a** and **6a**. Namely, when the monomer feed ratio was varied from 1.0:0.21 to 1.0:0.75 (=**4a**:**6a**), yield of the copolymers decreased and deviation of the copolymer composition (determined from solvent-soluble fraction) from the ideal value (1.0:0.5) for alternating copolymerization was observed (Table 1, runs 2–5). This deviation, however, can be reasonably accounted for by assuming that in the copolymerizations under unbalanced monomer feed ratios the molecular weight of copolymer obtained is low enough to generate a somewhat large unbalance in the copolymer composition as well as a considerable reduction of the yield of copolymer. The highest yield of the copolymer **7aa** was attained when the feed ratio was 1.0:0.5, as shown in Table 1, undoubtedly indicating the occurrence of the alternating copolymerization. In the copolymerizations using different monomers such as **4b** and **6b** besides **4a** and **6a** under the same conditions, similar results were obtained (Table 1, runs 6–12). These results clearly suggest the general feature of the copolymerization between these types of monomers.[12] The mechanism of the alternating copolymerization is illustrated in Scheme 2.

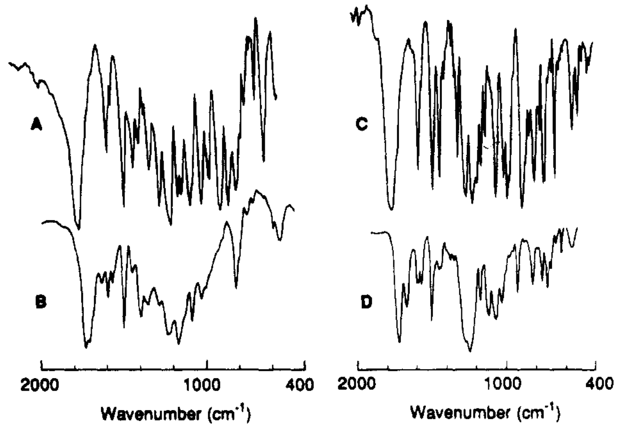


Figure 1. IR spectra (KBr) of copolymers and monomer mixtures: (A) monomer mixture of **4a** and **6a**; (B) copolymer **7aa**; (C) monomer mixture of **4b** and **6a**; (D) copolymer **7ba**.

Since bicyclic bislactone (**1**) had been recognized as an expanding monomer which controls volume shrinkage on polymerization of epoxides,[11] volume change on the copolymerization of **4** with **6** was evaluated. The results are listed in Table 2.

A 0.8–1.9% volume shrinkage was observed in the copolymerization of 1.0:0.5 molar ratio mixtures of **4** and

Table 2. Volume Change during Copolymerization and Thermal Properties of Copolymers

conditions[a]	density[b]		volume[e] change (%)	copolymer	thermal properties	
	D_m[c]	D_p[d]			T_{d10}[f] (°C)	T_g[g] (°C)
run 4	1.233	1.255	−1.8	**7aa**	304	54
run 6	1.349	1.375	−1.9	**7ab**	295	74
run 10	1.255	1.266	−0.9	**7ba**	354	139
run 12	1.334	1.345	−0.8	**7bb**	341	104

[a] Run no. of Table 1. [b] Determined by the density gradient tube method at 25 °C. [c] Density of the monomer mixture. [d] Density of the copolymer. [e] $[(D_m - D_p)/D_m] \times 100$, standard error of the measurement = ±0.15%. [f] Determined by thermogravimetric analysis under a N_2 atmosphere. [g] Determined by differential scanning calorimetry under a N_2 atmosphere.

6. The degree of volume shrinkage on the copolymerization using **4b** was nearly half of that using **4a**, independent of the structure of bisepoxides (**6**). Generally, **6a** is known to show 4.2% volume shrinkage during polymerization,[4] and therefore the spirocyclic bis(γ-lactone)s (**4**) can be expected as second expanding monomers which undergo anionic polymerization accompanying volume expansion, although **4** does not homopolymerize but copolymerizes with epoxy compounds.

As for the thermal properties of the copolymers **7**, glass transition temperatures (T_g) ranged from 50 to 140 °C and 10% weight decrease temperatures (T_{d10}) ranged from 295 to 354 °C. These properties depended on their structure: 30−80 °C temperature enhancement in T_g and T_{d10} was observed when aromatic group-containing bislactone **4b** was used instead of **4a**. This tendency is little affected by the structure of **6**, being consistent with that of the above volume change. This thermal property difference would be explained simply by the content of the aromatic group or the presence of a bulky aromatic group.

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