6686 *Macromolecules* **1993,** *26,* 6686-6687

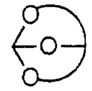
Anionic Copolymerization of Bicyclic Bis(γ-lactone)s with Epoxides and Volume Change during the Copolymerization

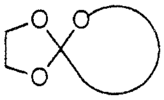
Toshikazu Takata, Keunwo Chung, Atsuhito Tadokoro, and Takeshi Endo*

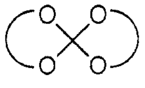
Research Laboratory of Resources Utilization,
Tokyo Institute of Technology, Nagatsuta-cho,
Midori-ku, Yokohama 227, Japan

Received July 13, 1993
Revised Manuscript Received October 12, 1993

Introduction. Bicyclo orthoester (BOE), spiro orthoesters (SOEs), and spiro orthocarbonates (SOCs) are the only monomers which have been reported so far to expand in volume during polymerization, and this unique property is believed to come from their polymerization mode: successive double ring-opening polymerization.[1]


BOE


SOE

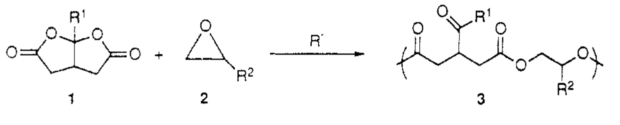

SOC

These monomers can polymerize with cationic initiators but not with anionic or radical initiators. Attempts to develop monomers capable of polymerizing with anionic[2,3] and radical[4,5] initiators have been done, but no volume expansion system has been constructed so far. Brady *et al.* reported the occurrence of some reduction of volume shrinkage in anionic polymerization of epoxy resins by addition of a small amount of bicyclic[6] and spirocyclic[7] lactones (final volume shrinkage was 3.0–3.5%). The possibility of these lactone derivatives being expanding monomers under anionic conditions was first suggested from the results that the reduction of volume shrinkage and the formation of copolymer took place in the initial stage of the polymerization.

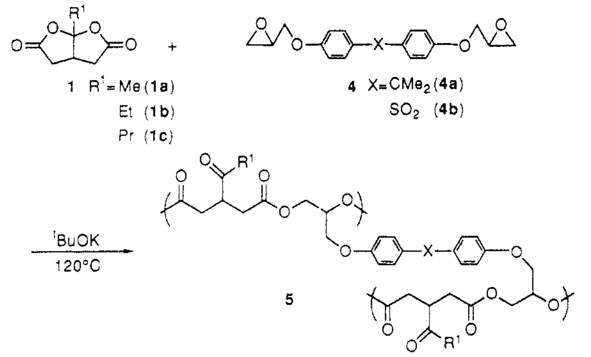
Recently, we have found that bicyclic bis(γ-lactone)s (1) undergo efficient anionic copolymerization with epoxides (2) to give the corresponding completely alternating copolymers via both double ring-opening isomerization of 1 and ring-opening of 2 (Scheme I).[8,9] It might be expected that the observed volume shrinkage in the homopolymerization of 2 will be largely annihilated by the double ring-opening reaction of 1. That is, 1 could possibly be an expanding monomer. In this paper, the volume change in the copolymerization is investigated. Moreover, the anionic copolymerization of 1 with bifunctional epoxides is studied.

Results and Discussion. Volume change in the anionic polymerization of 1 with 2 as a typical example was evaluated by use of a bicyclic bis(γ-lactone) (**1c**; R^1 = nPr)[10] and glycidyl phenyl ether (**2a**; R^2 = CH$_2$OPh) because of their high mutual solubility. An equimolar mixture of **1c** (d^{25} = 1.288 g/cm^3) and **2a** (d^{25} = 1.111 g/cm^3) was heated at 120 °C in the presence of 4 mol % of potassium *tert*-butoxide (*t*-BuOK) in THF ([C] = 4.0 M) for 93 h. Methanol-insoluble polymer (72%) was obtained, and its density was measured to be d^{25} = 1.215 g/cm^3. The structure of the obtained copolymer was determined to be the corresponding completely alternating copolymer (**3ca**) by its ^{1}H NMR, ^{13}C NMR, and IR spectra, the characteristics of which were completely in accordance with our previous results.[8] It was demonstrated that nearly zero shrinkage (0.25 ± 0.15% expansion in volume) could be observed in this copolymerization on the basis of the density of the monomer mixture (d^{25} = 1.218 g/cm^3). Since the anionic homopolymerization of **2a** to poly(**2a**) (d^{25} = 1.194 g/cm^3) was accompanied by 7.5% volume shrinkage under similar conditions, this result seems to indicate that **1c** polymerizes with a considerable volume expansion. Thus, the authors herewith demonstrate the first anionic polymerization without volume shrinkage.

Scheme I



Scheme II



In light of application to epoxy resins, the epoxides for the copolymerizations were extended to bifunctional epoxides such as **4a**. The bulk copolymerization of a mixture of **1a** and **4a** (molar ratio = 2:1) in the presence of *t*-BuOK (4 mol % vs the mixture) was carried out at 120 °C for 24 h to give the solvent-insoluble polymer in 98% yield (Scheme II).[11]

The composition of the polymer (**1a**:**4a** = 2.0:1.02), which was estimated from the ^{1}H NMR spectrum of the dichloromethane-soluble fraction, suggested the occurrence of alternating copolymerization. Furthermore, IR spectral analysis indicated the appearance of ester (1739 cm^{-1}) and ketone (1720 cm^{-1}) carbonyl absorptions and the nearly complete disappearance of lactone carbonyl (1780 cm^{-1}) and oxirane C–O bond absorptions (912 cm^{-1}) by the conversion of the monomer mixture to the polymer (Figure 1), clearly revealing the efficient alternating copolymerization and the proposed polymer structure (**5aa**). A lowering in yield of the polymer and deviation of the composition from the ideal value 2:1 were observed in the copolymerizations with monomer feed ratios of 3:1 and 3:2 (Table I, runs 2 and 4). In these cases, the solvent-soluble fractions consisted of the unreacted excess of monomer and low molecular weight polymer. These changes are consistent with the mode of the alternating copolymerization.

The change in copolymer composition would be attributed to both the contamination of each homopolymer unit and the low degree of polymerization, especially in the case of the 1-rich system (run 2), because neither 1 nor **4a** homopolymerize under these conditions. In the copolymerizations of **1b** and **1c** with **4a**, similar copolymers were obtained as solvent-insoluble polymers in 93% (**5ba**) and 95% (**5ca**) yields, respectively.

A low shrinkage in volume (1–2%) could also be observed in these copolymerizations of **1a** with bifunctional epoxide **4a** (Table I, run 3). Generally, **4a** is known to polymerize with 4.2% volume shrinkage.[1] Therefore, similarly to the case of **2a**, it is concluded that volume shrinkage during

0024-9297/93/2226-6686$04.00/0

Table I. Anionic Copolymerization of Bis(γ-lactone) (1 and 6) with Epoxides (2 and 4)[a]

run no.	feed ratio bis(lactone):epoxide (mol ratio)	copolymer	yield[d] (wt %)	copolym[g] composition		$T_d{}^{10}$,[i] (°C)	T_g[j] (°C)	vol[k] change (%)
				bis(lactone)	epoxide			
1[b]	**1c**:**2a** (1.0)	**3ca**	72[e]	1	1[h]			+0.25
2	**1a**:**4a** (0.33)	**5aa**	89	1	0.39	253	42	
3	**1a**:**4a** (0.50)	**5aa**	98	1	0.51	282	51	−1.4
4	**1a**:**4a** (0.75)	**5aa**	94	1	0.71	318	52	
5	**1b**:**4a** (0.50)	**5ba**	93	1	0.54	287	75	−0.9
6	**1c**:**4a** (0.50)	**5ca**	95	1	0.54	267	66	−2.5
7	**1a**:**4b** (0.50)	**5ab**	98	1	0.50	296	60	+1.4
8[c]	**6a**:**2a** (1.0)	**7aa**	80[f]	1	1[h]	299	60	

[a] Polymerization conditions: *t*-BuOH (4 mol %), 120 °C, 24 h, bulk. [b] Polymerization conditions: *t*-BuOK (4 mol %), 120 °C, 93 h, THF (4.0 M). [c] Polymerization conditions: *t*-BuOK (4 mol %), 120 °C, 48 h, THF (4.0 M), cocatalyst (*cis*-dicyclohexano-18-crown-6; 8 mol %). [d] Dichloromethane-insoluble part. [e] Methanol-insoluble part. [f] Separated by preparative HPLC. [g] Estimated by ^{1}H NMR integration of dichloromethane-soluble part. [h] Determined by ^{1}H NMR. [i] Determined by thermogravimetric analysis under N_2 atmosphere. [j] Determined by differential scanning calorimetry. [k] Determined by a density gradient tube at 25 °C (standard error of the measurement = ±0.15%).

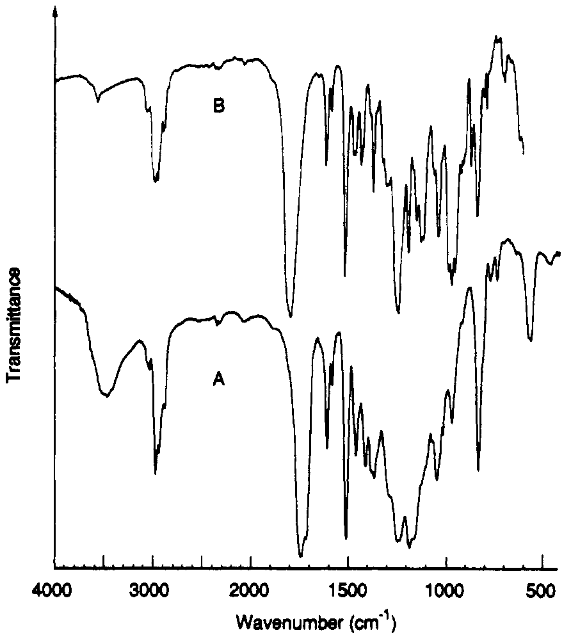
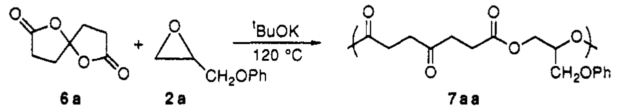


Figure 1. IR spectra of **5aa** (A) and the monomer mixture of **1a** and **4a** (B).

Scheme III



polymerization of **4a** is somewhat suppressed by the addition of **1**, and hence **1** can be regarded as expanding monomers. These results are in accordance with our previous results that the volume shrinkage decreases by the addition of spirocyclic orthocarbonates in the cationic polymerization system of **2a** or **4a**.[12]

As for thermal properties of the copolymers, as summarized in Table I, the glass transition temperatures ranged from 50 to 70 °C, and the 10% weight loss decomposition temperatures were from 250 to 300 °C.

The results of this study in addition to the following new results on the anionic alternating copolymerization of a *spirocyclic* bis(γ-lactone) (**6a**) with **2a** (Scheme III) can help elucidate Brady's results[7] which are described at the beginning of this paper.

That is, copolymerization of **6a** with **2a** also proceeded smoothly to afford similar alternating copolymer **7aa** ($\bar{M}_n$ = 7300) in 80% yield under the same conditions (Table I, run 8). Meanwhile, in Brady's case,[7] the amount of **6a** and its derivatives added was less than 10% to the epoxy resins, and, therefore, the volume change during the copolymerization would be suppressed only at the initial stage of the copolymerization, since the copolymerization of **6a** with epoxy resins is faster than the homopolymerization of epoxy resins, as suggested by the above results. As a result, for effective and successive suppression of the volume shrinkage during the copolymerization of epoxy resins with such bis(lactones) it is necessary to use nearly equimolar amounts of the bis(lactones) vs an epoxy moiety, but this would substantially change the polymer structure.

References and Notes

(1) Takata, T.; Endo, T. *Expanding Monomers*; *Synthesis, Characterization, and Application*; Sadhir, K., Ed.; CRC Press: Boca Raton, FL, 1992; Chapter 3.

(2) Bailey, W. J.; Sun, R. K.; Katsuki, H.; Endo, T.; Iwama, H.; Tsushima, R.; Saigo, K.; Bitritto, M. M. *Ring-Opening Polymerization with Expansion in Volume*; ACS Symposium Series 59; Saegusa, T.; Goethals, E., Eds.; American Chemical Society: Washington, DC, 1977; p 38.

(3) Brady, R. F., Jr.; Sikes, A. M. *Macromolecules* **1991**, *24*, 688.

(4) Sanda, F.; Takata, T.; Endo, T. *Macromolecules* **1993**, *26*, 737.

(5) Sanda, F.; Takata, T.; Endo, T. *Macromolecules* **1993**, *26*, 1818.

(6) Brady, R. F., Jr.; Simon, F. E. *J. Polym. Sci., Part A: Polym. Chem.* **1987**, *25*, 231.

(7) Sikes, A. M.; Brady, R. F., Jr. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 2533.

(8) Takata, T.; Tadokoro, A.; Endo, T. *Macromolecules* **1992**, *25*, 2782.

(9) Tadokoro, A.; Takata, T.; Endo, T. *Macromolecules*, in press.

(10) Preparation of **1c** was carried out by Strunz's method: Strunz, G. M.; Sankar Lal, G. *Can. J. Chem.* **1982**, *60*, 2528. Mp (**1c**): 56–57 °C. Anal. Calcd for $C_9H_{12}O_4$: C, 58.70; H, 6.52. Found: C, 58.46; H, 6.78.

(11) Experimental procedure: A mixture of **1a** (156 mg, 1.0 mmol), **4a** (177 mg, 0.5 mmol), and *t*-BuOK (6.8 mg, 4 mol %) was heated at 120 °C for 24 h in an evacuated sealed tube. The polymerization mixture was treated with dichloromethane–acetic acid (2 vol %) and 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 to yield 327 mg of a yellowish brown solid (98%).

(12) Takata, T.; Endo, T. *Polym. Prepr. Jpn.* **1989**, *37*, 1559.