Anionic Ring-Opening Alternating Copolymerization of a Bicyclobis(γ-butyrolactone) with Epoxide

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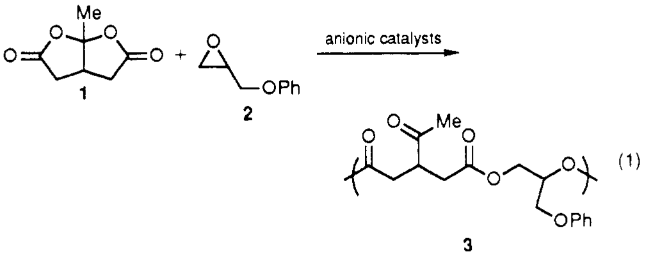
Introduction. In spite of the fact that various lactones efficiently polymerize to polyesters via a ring-opening process, γ-butyrolactones afford no corresponding polyesters.[1-3] There are only two successful polymerizations of γ-butyrolactones by Hall[4] and Okada et al.[5] Meanwhile, an inefficient copolymerization of γ-butyrolactone with β-propiolactone has been reported by Furukawa et al.[6] Therefore, it is quite significant to accomplish ring-opening polymerization of γ-butyrolactone and related monomers containing γ-butyrolactone skeletons by some molecular design, since few reports are presented on the polymerization of γ-butyrolactones. Recently, we have succeeded in converting a γ-butyrolactone moiety-containing monomer to a polymer through ring-opening copolymerization with an epoxide. This paper describes preliminary results of the *anionic ring-opening alternating copolymerization* of bicyclobis(γ-butyrolactone) (1) with glycidyl phenyl ether (2).



(1)

Results and Discussion. The bis(γ-butyrolactone) (1)[7] did not polymerize with anionic catalysts such as potassium *tert*-butoxide (*t*-BuOK) and sodium methoxide at all but copolymerized with epoxide. An equimolar mixture of 1 and 2 was heated at 120 °C in the presence of *t*-BuOK (4 mol %) in tetrahydrofuran (THF) for 74 h in a sealed tube.[8] The gel permeation chromatogram (GPC) of the reaction mixture indicated formation of a polymer having a unimodal peak and $\bar{M}_n$ 6600 ($\bar{M}_w/\bar{M}_n$ 1.6). Methanol-insoluble polymer isolated (3, 78% yield) was subjected to structural analysis with their spectroscopic data. In the IR spectrum no lactone carbonyl absorption was observed, but two carbonyl absorptions assigned to ester and ketone carbonyls appeared at 1740 and 1720 cm^{-1}, respectively. The ^{1}H NMR spectrum of 3 was rather simple, and all the signals were clearly observed: signals a–c at higher field corresponded to the protons of the unit derived from 1, and signals e–g were assigned to those from 2. NMR integration showed that 1 and 2 were incorporated into the polymer in exactly a 1:1 ratio. The most characteristic was the appearance of a triplet signal at a new region (5.3 ppm) which was assigned to methine proton e adjacent to ester oxygen (Figure 1a). The ^{13}C NMR spectrum strongly supported the presented copolymer structure 3. These clear NMR spectra suggest the clean and highly symmetrical polymer structure of 3.

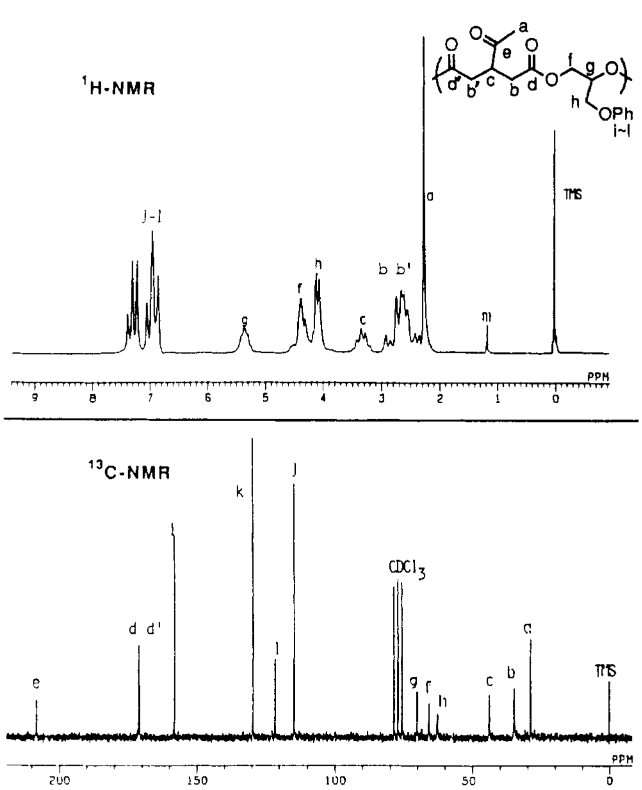


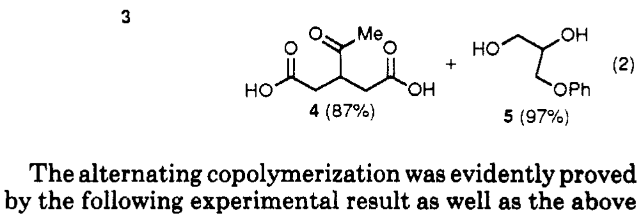
Figure 1. ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra of copolymer 3 ($\bar{M}_n$ 4200) in CDCl$_3$ at 27 °C. Signal m is assigned to the *tert*-butyl group derived from the initiator *t*-BuOK.

Table I
Anionic Copolymerization of 1 with 2[a]

run	feed ratio for 1–2, mol %	polymer yield, % soluble[b]	polymer yield, % insoluble[b]	$\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$)[c]	copolym composition for 1–2,[d] mol %
1	20:80	83	16	4600 (1.22)	50:50
2	40:60	39	49	8200 (1.24)	50:50
3	50:50	55	39	7400 (1.20)	50:50
4	60:40	73	21	6600 (1.30)	50:50
5	80:20	94	6	3000 (1.28)[e]	50:50

[a] Solvent: THF (total monomer concentration: 3.0 mol/L). Catalyst: *t*-BuOK (4 mol %), 120 °C, 24 h. [b] Solvent:methanol. [c] Molecular weight of the methanol-insoluble fraction, estimated by GPC (based on PSt standards). [d] For the methanol-insoluble fraction, determined by ^{1}H NMR. [e] Separated by HPLC.

The structure of 3 was further confirmed by products of the alkaline hydrolysis. A copolymer ($\bar{M}_n$ 4200) was heated to reflux for 24 h in dioxane–2 M KOH (10/18, v/v). From the reaction mixture corresponding products presumably formed by the hydrolysis of 3, dicarboxylic acid (4) and diol (5), were isolated in high yields (eq 2).

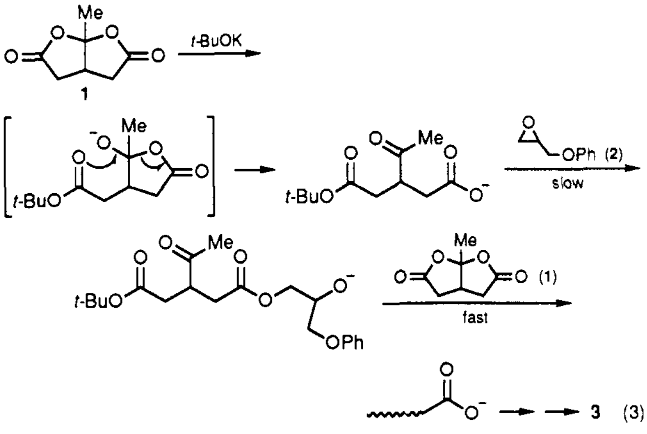


(2)

The alternating copolymerization was evidently proved by the following experimental result as well as the above results: when the monomer feed ratio was varied from

20:80 to 80:20 (**1**–**2**), the copolymer composition of the methanol-insoluble fraction was not changed at all, as shown in Table I.[9,10]

These results certainly demonstrate the occurrence of the alternating copolymerization of **1** with **2** in which the ring-opening *isomerization* of **1** is accompanied. The mechanism of the copolymerization (eq 3), therefore, would



involve the initial nucleophilic attack of the catalyst *tert*-butoxide at the carbonyl carbon of the γ-butyrolactone ring of **1** to form a carboxylate via ring-opening isomerization. The resulting carboxylate attacks both **1** and **2**, but only the attack at **2** is effective for the polymerization, because **1** does not homopolymerize. The alkoxide resulting from ring opening of the epoxide similarly attacks at the lactone ring of **1**. In this case, the alkoxide should selectively undergo nucleophilic attack at **1** but not **2**, since **1** is much more electrophilic than **2**.

Thus, this work demonstrated the anionic ring-opening copolymerization of γ-butyrolactone moiety-containing monomer (**1**) with epoxide (**2**),[11] which selectively yielded the alternating copolymer. Since γ-butyrolactone and **2** did not copolymerize at all,[1,2,12] the present attainment of the copolymerization arises from the unique structure of **1** which is capable of isomerizing during the ring-opening reaction.[13]

References and Notes

(1) Johns, D. B.; Lenz, R. W.; Luick, A. *Ring-Opening Polymerization*; Ivin, K. J., Saegusa, T., Eds.; Elsevier Applied Science Publishers: Essex, U.K. **1984**; Vol. 1, Chapter 7, p 461.

(2) Jerome, R.; Teyssie, Ph. *Comprehensive Polymer Science*; Eastmond, G. C., Ledwith, A., Russo, S., Sigwalt, P., Eds.; Pergamon Press: Oxford, U. K., **1989**; Vol. 3, Part 1, Chapter 34, p 501.

(3) However, γ-butyrolactone polymerizes under rather extreme conditions (20 000 atm, 160 °C) to afford polymers with degrees of polymerization of 14–40: Korte, F.; Glet, W. *J. Polym. Sci.* **1966**, *4*, 685.

(4) Hall, H. K., Jr. *J. Am. Chem. Soc.* **1958**, *80*, 6412.

(5) Okada, M., Sumitomo, H. *Makromol. Chem., Suppl.* **1985**, *14*, 29.

(6) Tada, K.; Numata, Y.; Saegusa, T.; Furukawa, J. *Makromol. Chem.* **1964**, *77*, 220.

(7) Preparation of **1** was carried out by reference to Strunz's method: Strunz, G. M.; Lal, G. S. *Can. J. Chem.* **1982**, *60*, 2528. **1**: Mp 98–99 °C; IR (KBr) 1816, 1790 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.40–3.23 (m, 5 H, 2 × CH_2 + CH), 1.82 (s, 3, H, Me); ^{13}C NMR ($CDCl_3$) δ 172.5, 113.1, 39.0, 35.4, 23.8. Anal. Calcd for $C_7H_8O_4$: C, 53.84; H, 5.10. Found: C, 53.93; H, 5.20.

(8) The polymerization was carried out with 3.0 mmol of **1** (0.468 mg), 3.0 mmol of **2** (0.41 mL), and *t*-BuOK (27 mg, 4 mol %). The polymerization mixture obtained was quenched by addition of acetic acid diluted with methylene dichloride and precipitated with methanol (70 mL).

(9) In the presence of excess **2**, a prolonged reaction time for achievement of the high monomer conversion brought about the formation of the homopolymer of **2**, although the homopolymerization of **2** was rather slow under the conditions.

(10) In this experiment, the methanol-soluble fraction contained a considerable amount of low molecular weight polymer (ca. $\bar{M}_n$ 3000) with the same composition and structure besides both monomers. For example, in the case of **1**:**2** = 20:80 (run 1) the yield of the methanol-soluble polymer was 7% ($\bar{M}_n$ 1500) and the rest consisted of a mixture of **1** (trace %) and **2** (76%).

(11) Other epoxides such as propylene oxide and other nucleophiles such as triethylamine could be used analogously as comonomers and anionic catalysts, respectively.

(12) An equimolar mixture of γ-butyrolactone and epoxides such as **2** was heated at various temperatures in the presence of alkoxides such as *t*-BuOK, but no polymer was obtained other than homopolymers of the epoxides.

(13) This report presents the first example of alternating copolymerization accompanied by ring-opening isomerization, whereas ring-opening alternating copolymerization is known between, e.g., maleic anhydride and propylene oxide.[14]

(14) Tanaka, Y.; Kakiuchi, H. *J. Polym. Sci.* **1963**, *A2*, 3405. Fisher, R. F. *J. Polym. Sci.* **1960**, *44*, 155.

Registry No. 1, 98546-44-2; **2**, 122-60-1; **1**/**2** (copolymer), 139943-21-8; **3** (SRU), 140201-37-2.