Anionic Ring-Opening Alternating Copolymerization of a Bicyclic Bis(γ-lactone) with an Epoxide: A Novel Ring-Opening Polymerization of a Monomer Containing a γ-Lactone Structure

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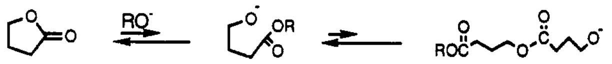
Received January 25, 1993; Revised Manuscript Received May 10, 1993

ABSTRACT: Anionic ring-opening polymerization of a bicyclic bis(γ-lactone) (**1b**) was carried out under anionic conditions. **1b** had no homopolymerizability but copolymerized with epoxide **2** to selectively give the corresponding alternating copolymer. IR, ^{1}H NMR, and ^{13}C NMR spectra and products of the alkaline hydrolysis of the obtained polymer strongly suggested an alternating copolymer structure consisting of two successive units derived from **1b** and **2**. The unit from **1b** was a linear diester, probably formed by a successive double ring-opening polymerization with isomerization. The 1:1 copolymer composition was not changed by varying the monomer feed ratio in the range between 20:80 and 80:20. From the results of the model reaction of an equimolar mixture of **1b** and **2** with 0.6 equiv of sodium methoxide in THF, the initiation of this copolymerization was suggested to involve a nucleophilic attack of the initiator alkoxide at the carbonyl carbon of the γ-lactone ring of **1b** to form a carboxylate via a double ring-opening isomerization. The propagation mechanism was studied by the results of the model reaction as well as the formation of the alternating copolymer. It was found that the propagation consisted only of cross-propagation; that is, the resulting carboxylate end derived from **1b** reacts only with **2**, whereas the alkoxide end derived from **2** undergoes selective nucleophilic attack at **1b**. The carboxylate end attack at **2** was suggested as the rate-determining step from the time–conversion curves. The rate of the copolymerization and the molecular weight and molecular weight distribution of the copolymer were strongly affected by solvent and counterion. The rate and the molecular weight distribution increased in the order of the counterions $Na^+ < K^+ < Cs^+$ and also increased with increasing solvent polarity.

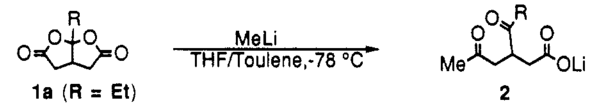
Introduction

Ring-opening polymerization of lactones provides one of the typical entries to polyester synthesis. Although most lactones readily polymerize to afford the corresponding polyesters, five-membered lactones such as γ-butyrolactone and related γ-lactone-containing compounds are known not to polymerize on treatment with any initiator.[1,2] However, a few ring-opening polymerizations of γ-lactones have successfully been accomplished by using strained monomers or under extremely severe conditions.[3-6] Korte[3] reported that polymerization of γ-butyrolactone at 20 000 atm at 160 °C affords poly(γ-butyrolactone) with a degree of polymerization of 14–40. Polymerization of bicyclic γ-lactones was studied by Hall *et al.*,[4,5] who demonstrated that cyclobutane 1,3-lactones (2-oxabicyclo[2.1.1]hexan-3-ones) polymerize readily with anionic and cationic catalysts to yield the corresponding polyesters.[4] Okada and Sumitomo reported a cationic polymerization of a bicyclic γ-lactone giving a mixture of cyclic oligomers.[6] As for the copolymerization of γ-lactones, several attempts[7-10] were made but no efficient copolymerization was attained, except for Kimura's report. Kimura *et al.* recently reported that γ-valerolactone cationically copolymerizes with β-butyrolactone in the presence of BF_3OEt_2 as initiator at 25 °C for 7 days to give the corresponding copolyester containing ca. 34% of the γ-valerolactone unit.[8] Thus, achievement of efficient ring-opening polymerization of five-membered lactones is very difficult, and therefore design of polymerizable five-membered lactones and novel polymerization systems are important subjects in the field of polymer synthesis. The lack of polymerizability of γ-lactones can be explained by presuming that ring-closing is much more favorable than ring-opening (Scheme I). Accordingly, to attain ring-opening polymerization of γ-lactones, it is necessary to suppress ring-closing, possibly by some molecular design of monomers.

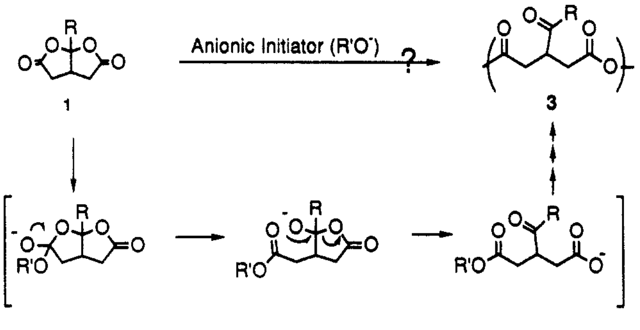
Scheme I



Scheme II



Scheme III



We have considered the introduction of an isomerization process into the polymerization scheme to retard the ring-closing, and designed a bis(γ-lactone) (**1**) as a candidate monomer capable of anionically polymerizing. The anionic ring-opening isomerization reaction of **1a** (R = Et) has actually been reported (Scheme II). In the proposed ring-opening polymerization, initial nucleophilic attack of the anionic initiator at the carbonyl carbon of **1** is followed by successive ring-opening and isomerization to afford poly(acid anhydride), as shown in Scheme III.

Recently, we found that the anionic copolymerization of **1b** (R = Me) with an epoxide proceeds in excellent efficiency to afford the corresponding alternating copolymer, although anionic homopolymerization of **1b** does

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not proceed at all.[11] This paper describes the anionic polymerization of **1b** in detail.

Experimental Section

FT-IR spectra were obtained with a JASCO FT/IR-3. ^{1}H NMR and ^{13}C NMR spectra were recorded on JEOL PMX-60si and JEOL EX-90 spectrometers, using tetramethylsilane (TMS) as internal standard. Estimation of the number- and weight-average molecular weights ($\overline{M}_n$ and $\overline{M}_w$) by gel permeation chromatography (GPC) was carried out with a Toyo Soda HPLC CCP & 8000 system equipped with three polystyrene gel columns (TSK gel G2000H, G2500H, and G3000H), using tetrahydrofuran as an eluent and refractive index (RI) and ultraviolet (UV) detectors. Purification of low molecular weight polymer was carried out with a preparative HPLC (Nihon Bunseki Kogyo LC-908) equipped with two polystyrene gel columns (JAIGEL-H1 and JAIGEL-H2), using chloroform as an eluent and RI and UV detectors.

Solvents used in the polymerization and glycidyl phenyl ether were distilled and stored over drying agents according to the conventional methods.

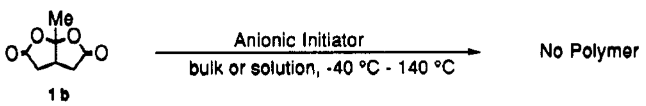
Synthesis of 2,8-Dioxa-1-methylbicyclo[3.3.0]octane-3,7-dione (1b, R = Me). A mixture of tricarballylic acid (6.0 g, 34.2 mmol, from Tokyo Kasei Kogyo), acetic anhydride (49 mL), and pyridine (0.6 mL) was refluxed for 6 h. After removal of acetic acid and acetic anhydride by distillation, the residue was dissolved in acetone (300 mL) and treated with active charcoal. Removal of charcoal by filtration and evaporation of the solvent in vacuo yielded a pale yellow material. Recrystallization from toluene (three times) afforded almost colorless crystals: yield 3.15 g, (66%); mp 98–99 °C; IR (KBr) 2477, 2359, 1813, 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 172.5, 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.

Reaction of 1b with Sodium Methoxide. A mixture of **1b** (0.239 g, 1.5 mmol) and sodium methoxide (0.092 g, 1.7 mmol) was refluxed in tetrahydrofuran (3.0 mL) for 4 h. HCl (0.5 M) was added to the mixture until the solution attained a pH of ca. 3, and the resulting mixture was extracted three times with ether (50 mL × 3). The combined extracts were dried over anhydrous magnesium sulfate. After removal of ether by evaporation, the residue was recrystallized from *n*-hexane–ethyl acetate mixed solvent to give a white solid: yield 0.197 g (70%); mp 95–97 °C; IR (KBr) 3200–3000, 1740, 1700, 1291, 1213, 1003 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.25 (s, 3H, COMe), 3.78 (s, 3H, MeOCO), 2.46–2.80 (m, 4H, CH$_2$), 3.10–3.51 (q, 1H, CH); ^{13}C NMR (CDCl$_3$) δ 209.1, 177.3, 172.1, 52.2, 43.9, 35.2, 35.1, 29.1.

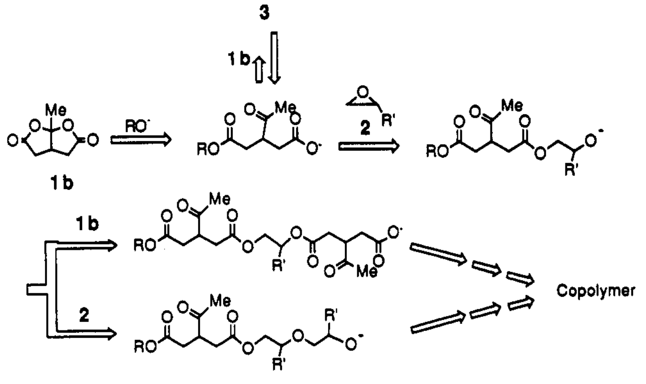
Anionic Homopolymerization: A Typical Procedure. **1** (R = Me, 0.165 g, 1.0 mmol) and potassium *tert*-butoxide (6 mg, 5 mol %) were placed in a polymerization tube. The tube was evacuated, sealed off, and heated at 140 °C for 48 h. After the mixture cooled, a methylene dichloride solution of acetic acid (1 vol %, 2.0 mL) was added, and the resulting mixture was washed three times with 0.5 M HCl (10 mL). The reaction mixture was dried over anhydrous magnesium sulfate and evaporated to give **1b**: yield 0.156 g (95%).

Anionic Copolymerization: A Typical Procedure. **1b** (0.478 g, 3.0 mmol), potassium *tert*-butoxide (27 mg, 4 mol %), glycidyl phenyl ether (**2**) (0.41 mL, 3.0 mmol), and 1.5 mL of tetrahydrofuran (THF) were placed in a polymerization tube. The tube was cooled, evacuated, sealed off, and heated at 120 °C for 72 h. The heterogeneous mixture became almost homogeneous as the polymerization proceeded. After the mixture cooled to room temperature, a methylene dichloride solution of acetic acid (1 vol %, 4.0 mL) was added, and the resulting mixture was precipitated into 70 mL of methanol. Centrifugal separation of the insoluble material afforded 0.70 g (75%) of viscous oil (methanol-insoluble polymer **4**). Evaporation of the supernatant gave mixtures of low molecular weight polymer (methanol-soluble polymer) and monomer. Spectral data of the methanol-insoluble polymer: IR (neat) 1740, 1720, 1602, 1592, 1253, 1162, 758, 753 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.36–6.02 (m, 5H, arom), 5.58–5.21 (m, 1H, C(=O)OCH), 4.62–4.20 (m, 2H, CH$_2$OC(=O)), 4.08–4.03 (d, 2H, CH$_2$OPh), 3.57–3.16 (m, 1H, CH), 2.91–2.31 (br, 4H, 2 × CH$_2$C(=O)O), 2.23 (s, 3H, CH$_3$); ^{13}C NMR (CDCl$_3$) δ 208.2, 171.1, 170.7, 158.1, 129.6, 121.5, 114.6, 70.1, 65.8, 62.7, 43.9, 35.8, 34.8, 28.9.

Scheme IV



Scheme V



Hydrolysis of Polymer 4. A mixture of **4** (1.56 g, 5.1 mmol of unit, $\overline{M}_n$ = 4200), dioxane (10 mL), and 2 M KOH (18 mL) was refluxed for 24 h. The resulting mixture was cooled and extracted three times with ether (50 mL). The combined organic layers were dried over anhydrous magnesium sulfate and evaporated to afford 1,2-dihydroxy-3-phenoxypropane (**7**) in 97% (0.89 g) yield. The aqueous phase was adjusted to pH 3 with 1 M HCl. The solution was evaporated to remove water, and the residue was extracted with ethanol (500 mL). The extract was evaporated to give β-acetylglutaric acid (**6**) in 87% (0.77 g) yield. **6**: IR (KBr) 3600–3200, 2960, 2920, 1700, 1418, 1369 cm^{-1}; ^{1}H NMR (D$_2$O) δ 2.25 (s, 3H, COMe), 2.47–2.72 (dd, 4H, J = 7.0 Hz, J = 7.0 Hz, 2 × CH$_2$), 3.02–3.43 (q, 1H, J = 7.0 Hz, CH). **7**: IR (KBr) 3400–3100, 2920, 2870, 1600, 1498, 1250, 1178, 1118 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.86 (br, 2H, OH), 3.73–3.85 (d, 2H, J = 3.0 Hz, CH$_2$OH), 3.95–4.22 (m, 3H, CH + CH$_2$OPh), 6.73–7.40 (m, 5H, arom).

Results and Discussion

Anionic Homopolymerization. Bicyclic bis(γ-lactone) (**1b**, R = Me) was prepared according to the method for the corresponding ethyl derivative (**1a**, R = Et).[12] The structure of **1b** was determined by its IR and NMR spectra and elemental analysis. Anionic homopolymerization of **1b** was carried out with a few initiators under various conditions (bulk and solution; MeONa, *t*-BuOK, and *n*-BuLi; −40 to +120 °C) (Scheme IV). However, no polymer was obtained; instead **1b** was recovered in 90–95% yield in all cases.

This result seems to depend on the structure of the desired polymer (**3**), which bears an acid anhydride function in the main chain, rather than on ring-closing being faster than ring-opening. That is, the acid anhydride function is much more reactive than the lactone moiety of **1b**, and thus no polymerization took place. Thus we designed a copolymerization in which epoxide was allowed to react with an alkoxide instead of a carboxylate propagating group to avoid the formation of the reactive acid anhydride function in the polymer main chain structure, because the linear ester structure, which would be formed in the polymer main chain by this change, is generally less reactive than the cyclic ester lactone. Therefore, the corresponding copolymer is expected to be formed by the copolymerization with epoxide if this hypothesis is correct. Since epoxide is able to homopolymerize, the proposed alkoxide end may attack at not only **1b** but also **2** in the propagation process (Scheme V).

Table I. Anionic Copolymerization of 1b with 2

run	feed ratio (mol %) 1b:2	solvent	temp (°C)	time (h)	yield (%)	$\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$)^e	copolymer comp^f (mol %) 1b:2
1	33:67	none	100	20	50^c	1200 (1.26)	20:80
2	33:67	none	120	18	65^c	1300 (1.26)	25:75
3	33:67	THF^a	120	72	47^d	5100 (1.38)	50:50
4	50:50	THF^b	120	72	75^d	6500 (1.27)	50:50

[a] Initial total monomer concentration: 3.4 mol/L, *t*-BuOK (4.0 mol %). [b] Initial total monomer concentration: 4.0 mol/L, *t*-BuOK (4.0 mol %). [c] Yield of polymer separated by preparative HPLC. [d] MeOH-insoluble polymer. [e] Estimated by GPC (based on PSt standards). [f] Estimated by ^{1}H-NMR.

Anionic Copolymerization. The anionic polymerization of **1b** was carried out in the presence of more than an equimolar amount of glycidyl phenyl ether (**2**), which serves to scavenge the carboxylate propagating end and convert it to an alkoxide propagating end. Results are summarized in Table I. When a mixture of **1b** and **2** (twofold molar excess) was heated at 100 °C for 20 h in the presence of *t*-BuOK (4 mol % vs **1b**) without solvent, low molecular weight polymer ($\bar{M}_n$ = 1200) was isolated in 50% yield by preparative HPLC (run 1). The unit ratio of **1b** to **2** was estimated as 20:80 from the ^{1}H NMR spectrum of the obtained polymer. In the polymerization at 120 °C for 18 h, a similar polymer was obtained in 65% yield (unit ratio **1b**:**2** = 25:75) (run 2). However, the microstructure of the polymer could not be determined from the NMR spectrum due to the broad signals, although the IR spectrum indicated the disappearance of lactone carbonyl (1810 and 1790 cm^{-1}) and the appearance of linear ester and ketone carbonyls (1740 and 1720 cm^{-1}).

Solution copolymerization was carried out to reduce the influence of the homopolymerization of **2** (Table I), since **2** was anionically homopolymerizable. In the solution polymerization the polymerization system was heterogeneous because of the low solubility of *t*-BuOK. A relatively high molecular weight polymer ($\bar{M}_n$ = 5100) was obtained as a methanol-insoluble viscous material in the copolymerization of a 1:2 mixture of **1b** and **2** at 120 °C (run 3). In this case, the copolymer composition was estimated to be 50:50 (**1b**:**2**), in spite of the 1:2 feed ratio. Furthermore, the 50:50 copolymer composition was also confirmed in the polymer ($\bar{M}_n$ = 6500) which was obtained in 75% yield in the copolymerization with the 1:1 feed ratio of **1b** and **2** (run 4). Meanwhile, the $\bar{M}_n$ of the methanol-soluble polymer was less than 3000, and the unit ratio of this polymer was also 50:50. Consequently, the polymer containing more unit of **2** was formed in the bulk polymerization, whereas the higher molecular weight polymer with ca. 50:50 unit ratio was produced independent of the feed ratio in the solution polymerization. The formation of **2**-unit rich polymer in the bulk polymerizations seems to be due to the relatively fast homopolymerization of **2** under the conditions. In the solution polymerizations, the homopolymerization of **2** was much more slower than that in the bulk polymerizations. This rate retardation was larger than that of the copolymerization, presumably because of the reduced polarity of the polymerization system in the solution polymerizations.

Since the IR, ^{1}H NMR, and ^{13}C NMR spectra of the polymer with the 50:50 unit ratio obtained in the solution polymerization were very clean, the structure of the polymer (**4**) was decided to be *alternating*. Copolymer **4** included both the ring-opening isomerization unit of **1** and the ring-opening unit of **2** in the same ratio, as shown in Scheme VI.

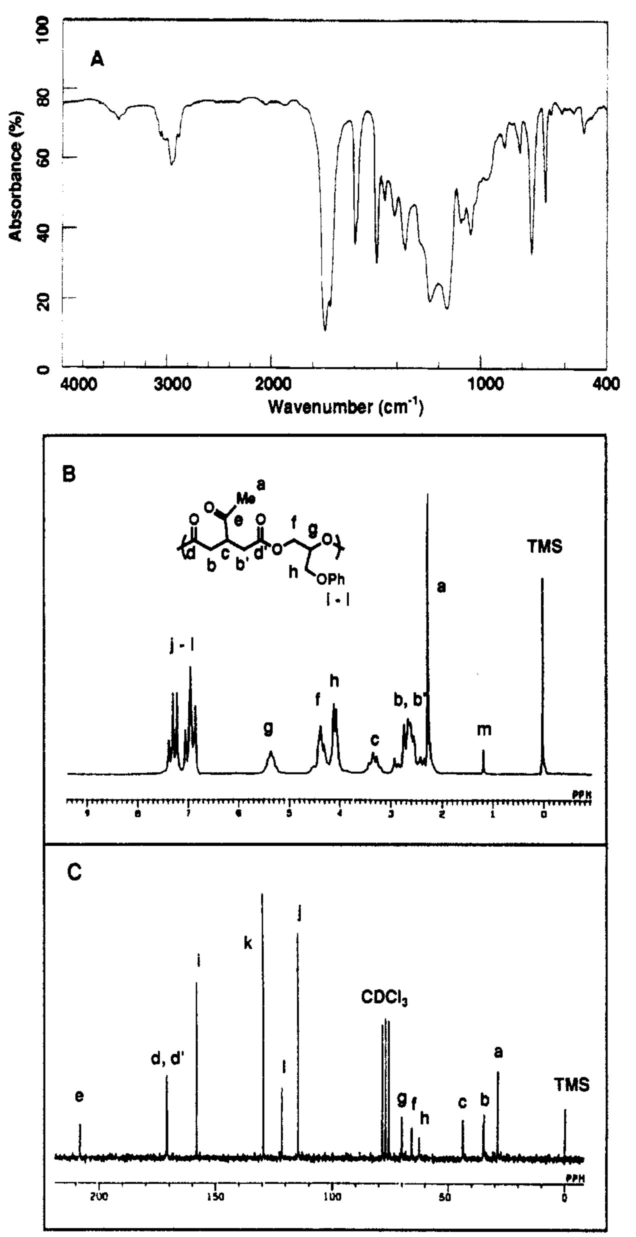
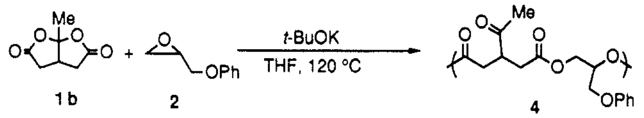


Figure 1. Structural analysis of **4**. (A) IR spectrum of **4** ($\bar{M}_n$ = 4200). (B) ^{1}H NMR and (C) ^{13}C NMR spectra of **4** ($\bar{M}_n$ = 4200) in CDCl$_3$ at 27 °C. Signal m is assigned to the *tert*-butyl group derived from the initiator *t*-BuOK.

Scheme VI



In addition to the IR spectrum showing two carbonyl absorptions similar to those of the polymer obtained in the bulk polymerization (Figure 1A), the ^{1}H NMR and ^{13}C NMR spectra (Figure 1B,C) were well consistent with the proposed alternating structure **4**, as assigned in Figure 1. That is, the carbonyl absorptions at 1720 and 1740 cm^{-1} are attributed to those of the ketone and ester groups of **4**, respectively, while the proton and carbon signals of a–e come from the unit of **1b** and those of f–l are assigned to the unit of **2** (Figure 1). The ^{13}C NMR spectrum showed two kinds of carbonyl signals those from the ester groups of **4** (208.2 ppm) and those from the ketone groups of **4** (171.1 and 170.7 ppm). The most characteristic signal for the alternating structure was a new triplet appearing at 5.3 ppm in the ^{1}H NMR spectrum, which was assigned to methine proton g adjacent to the ether oxygen of the main

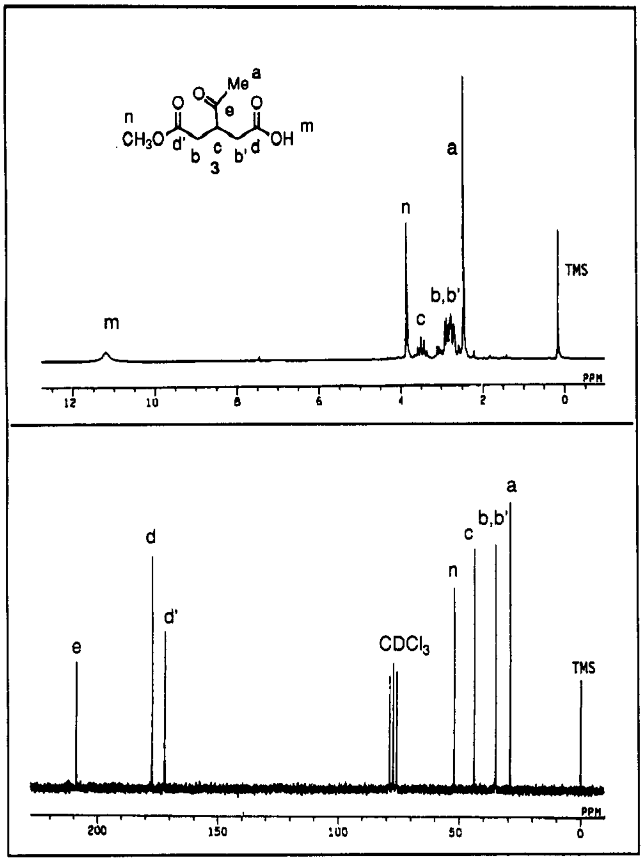
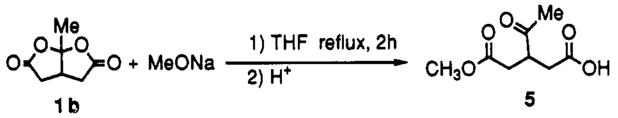
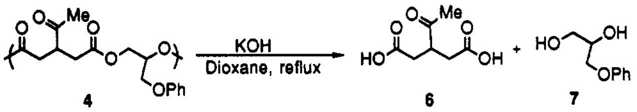


Figure 2. ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra of 5 in $CDCl_3$ at 27 °C.

Scheme VII



Scheme VIII



chain ester group. The ^{1}H NMR integration was well consistent with the structure of 4 and demonstrated that both ring-opening units of **1b** and **2** were contained in the polymer in exactly 50:50 ratio. These clean NMR spectra seem to suggest a clean polymer structure without any other unit.

The partial unit structure formed by the double ring-opening isomerization of **1b** was further confirmed by the reaction of **1b** with MeONa as a model propagating alkoxide end (Scheme VII). The corresponding 1:1 adduct (**5**) was isolated in 70% yield as a colorless oil whose NMR spectrum (Figure 2) clearly supported the partial unit structure of **4**, as indicated in Scheme VII. In particular, characteristic signals are a, b, b′, and c in the ^{1}H NMR spectrum and a, b, b′, c, d′, and e in the ^{13}C NMR spectrum which appear in regions very similar to those of **4**.

Further evidence for the alternating structure was obtained by analysis of the products of the alkaline hydrolysis of **4**. Polymer **4** ($\bar{M}_n$ = 4200) was hydrolyzed with 2 M KOH in refluxing dioxane to afford dicarboxylic acid **6** in 87% yield and diol **7** in 97% yield (Scheme VIII). Products **6** and **7** are produced by the hydrolysis of the units derived from **1b** and **2**, respectively. Thus, the alternating copolymer structure of **4** was strongly suggested by the results mentioned above. Meanwhile, the mode of ring-opening of the epoxy ring of **2** was considered to involve exclusive cleavage of the methylene carbon–oxygen bond, according to the general scheme of anionic ring-opening polymerization of epoxides. If a different mode is involved, it is impossible to distinguish them, because both modes afford structurally identical polymers. The probability that both modes are involved together in the polymer is a very low, since the NMR spectra of the polymer formed are clean enough to support its structural simplicity.

Table II. Anionic Copolymerization of 1b with 2[a]

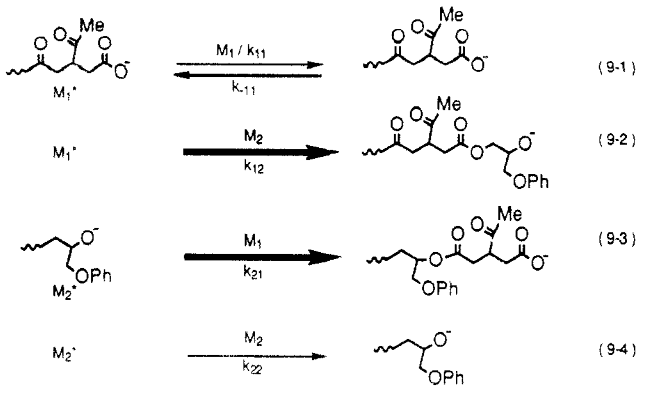
run	feed ratio (mol %) 1b:2	polymer yield[b] (%)	$\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$)[c]	copolymer compd[d] (mol %) 1b:2
1	20:80	16	4600 (1.22)	50:50
2	40:60	49	8200 (1.24)	50:50
3	50:50	39	7400 (1.20)	50:50
4	60:40	21	6600 (1.30)	50:50
5	80:20	6	3000 (1.28)[e]	50:50

[a] Solvent: THF (initial total monomer concentration: 4.0 mol/L, initiator 4 mol % (vs **1b** + **2**), 120 °C, 24 h). [b] Methanol-insoluble polymer. [c] Estimated by GPC (based on PSt standards). [d] For the methanol-insoluble polymer, determined by ^{1}H NMR. [e] Separated by preparative HPLC.

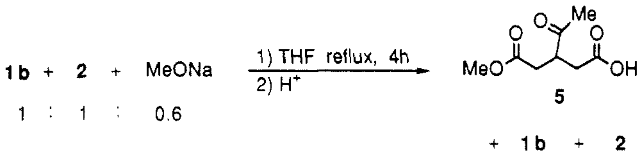
Since the solution copolymerization was found to yield the alternating copolymer in a high efficiency, the effects of monomer feed ratio on the yield, molecular weight, and copolymer composition were examined under similar conditions (Table II). By any copolymerization, the corresponding alternating copolymer with the composition of 50:50 was obtained as a methanol-insoluble fraction, and the composition was independent of the feed ratio in the range from 20:80 to 80:20. The methanol-soluble fraction contained a lower molecular weight polymer ($\bar{M}_n$ < 3000) as well as unreacted monomers. Conversion of **1b** was nearly complete in the feed ratio of 20:80 (**1b**:**2**) but decreased as the feed ratio of **1b** increased, whereas conversion of **2** was always less than 100%, even at the feed ratio of 80:20 (**1b**:**2**), although the conversion increased as the feed ratio of **2** decreased. The NMR spectra of the methanol-soluble polymers were entirely the same as those of the methanol-insoluble ones, suggesting exclusive formation of the alternating copolymer. The highest yield (49%) and molecular weight ($\bar{M}_n$ = 8400) of the methanol-insoluble polymer were obtained in the feed ratio of 40:60 (**1b**:**2**), which not only supported the alternating copolymerization but also suggested some characteristics of the mechanism of the copolymerization as described later.

Mechanism of the Copolymerization. As mentioned above, the addition of epoxide **2** as a trapping agent of the carboxylate propagation end group formed by ring-opening of **1b** successfully resulted in the achievement of the proposed copolymerization of a monomer containing a γ-lactone structure. In principle, propagation reactions of the copolymerization are schematically given by eqs 9-1 to 9-4 in Scheme IX. The equations show that the carboxylate end derived from **1b** (M_1^*) and the alkoxide end derived from **2** (M_2^*) can react with either M_1 or M_2. Reaction of M_1^* with M_1 should be negligible because no homopolymerization of **1b** occurred. In this case $k_{11} \ll k_{-11}$. On the other hand, k_{22} (rate constant of reaction of M_2^* with M_2) should be small, since no homopolymer of **2** was detected in the solution copolymerization, but k_{22} is in fact not negligible because some homopolymerization of **2** was confirmed in the bulk polymerization. Important propagating processes therefore consist of cross-propagation, which certainly leads to alternating copolymeri-

Scheme IX



Scheme X



zation as shown in eqs 9-2 and 9-3 of Scheme IX. Thus the following experiments were carried out to clarify the mechanism of the copolymerization.

First, the initiation reaction and reactivity of the alkoxide end (M_2*) were experimentally examined using MeONa as a model of M_2*. When an equimolar mixture of **1b** and **2** in THF was refluxed in the presence of 0.6 equiv (vs **1b** or **2**) of MeONa, β-acetylglutaric acid monomethyl ester (**5**) (56%) was obtained in addition to the recovery of **1b** (44%) and **2** (>99%) (Scheme X). The yield of **5**, the 1:1 adduct of **1b** and MeONa, was 93% on the basis of the amount of NaOMe used. These results undoubtedly demonstrate the selective attack of MeONa at the bicyclic lactone **1b** but not the epoxide **2**, consistent with the proposed relation between the two reaction rate constants of the alkoxide end (M_2*): $k_{21} \gg k_{22}$. Furthermore, the initiation of this copolymerization consists only of reaction of the initiator alkoxide with **1b**, because **2** was quantitatively recovered. This is in good agreement with the reactivity of the bicyclic lactone **1b** toward the nucleophile, which is presumably much higher than that of the epoxide **2**.

Time–conversion curves of the monomers (Figure 3) were obtained by directly monitoring the copolymerization (t-BuOK, THF-d_8, 120 °C) by ^{1}H NMR. In the curves prepared from the change of the intensity of the two methyl signals of the monomer **1b** (1.8 ppm) and the copolymer **4** (2.2 ppm) during the copolymerization, decreasing amounts of the two monomers were nearly equal independent of both feed ratio and reaction time, as shown in Figure 3. This shows a characteristic feature of the alternating copolymerization.

In this copolymerization, the most efficient copolymerization could be observed at a feed ratio of 40:60 of 1:2 or with an epoxide-rich feed (Table II, run 2). Furthermore, in comparison of the feed ratio of 20:80 with that of 80:20, a higher yield and molecular weight are obtained in the former (Table II, runs 1 and 5). Since such higher yield and molecular weight of the methanol-insoluble polymer should come from the faster reaction, these results show that the rate-determining step of this copolymerization involves the reaction of epoxide **2** in the propagation. Consequently, the rate-determining step is the reaction of the carboxylate end M_1* with the epoxide M_2 (k_{12}). This is in good accordance with the relation $k_{12} < k_{21}$ mentioned above (Scheme IX). As seen in Figure 3, the rate of decrease of the monomers decreases in parallel with the decreasing ratio of the epoxide in the feed. Thus, the conclusion can be rationalized by the pronounced difference in nucleophilic reactivity between the carboxylate and alkoxide ends. Thus, by the above-mentioned experimental results, the initiation and propagation of the copolymerization could be well elucidated.

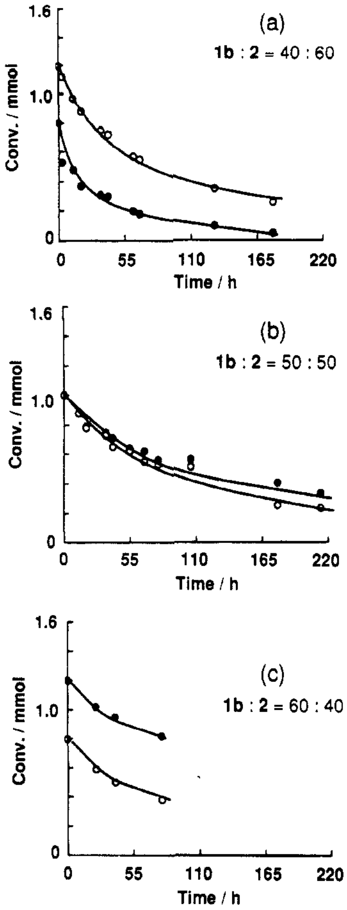


Figure 3. Time–conversion curves of the copolymerization of **1b** with **2** in the presence of t-BuOK in THF-d_8 (4.4 M): (a) **1b** (0.8 mmol), **2** (1.2 mmol); (b) **1b** (1.0 mmol), **2** (1.0 mmol); (c) **1b** (1.2 mmol), **2** (0.8 mmol).

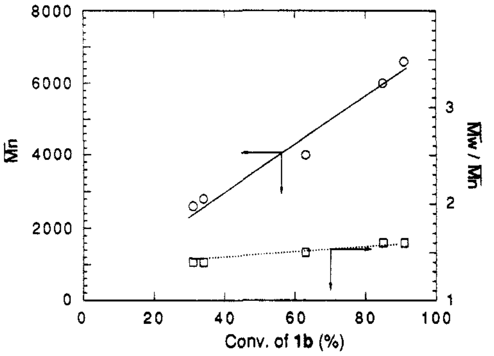
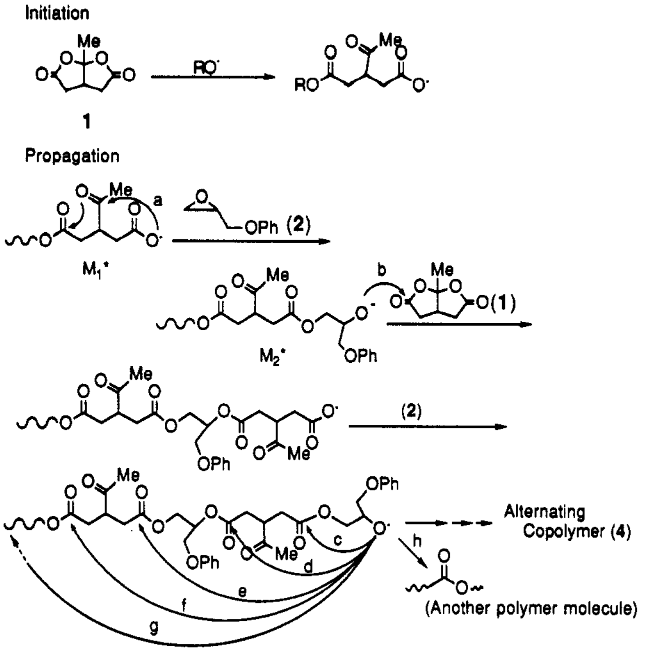


Figure 4. Relationship between $\bar{M}_n$ or $\bar{M}_w/\bar{M}_n$ of the copolymer and conversion of the monomer in the polymerization of **1b** (1.0 mmol) with **2** (1.0 mmol) in the presence of t-BuOK (4.0 mol %) in THF (4.0 M) at 120 °C.

On the other hand, the change of the polymer molecular weight during the copolymerization was examined under similar conditions. As shown in Figure 4, the molecular weight of the alternating copolymer before precipitation increased with increasing conversion of the monomers, whereas the molecular weight distribution (MWD) increased a little as the polymerization proceeded. The somewhat wide MWD (1.4–1.6) may come from the slow initiation due to the low solubility of t-BuOK in THF.

Scheme XI



This copolymerization behavior seems to suggest that the propagation end is stabilized enough to exclude chances for chain transfer reaction. Because the reactivity of the alkoxide end toward ester functions like that of the polymer main chain is not low, such stability of the propagation end is probably due to the contribution of the low reactivity of the carboxylate end, which is more long-lived than the alkoxide end. The lifetime of the alkoxide end should be much shorter than that of the carboxylate end in this copolymerization, because the reaction of the strong nucleophilic alkoxide M_2^* with the excellent electrophilic lactone **1b** would be very fast in comparison with that of M_1^* with **2**. Thus, the living polymerization-like behavior of the copolymerization can be rationalized by the structure and reactivity of the long-lived carboxylate propagation end.

As predicted at first in the addition of epoxide as comonomer, the change of carboxylate end to alkoxide end effectively promoted the occurrence of the copolymerization. The most important factor for the successful copolymerization is to efficiently control chain transfer reactions such as back-biting by the copolymerization and the introduction of the isomerization process into the polymerization scheme. This would depend on both reactivity of the unique bis(γ-lactone) structure of the monomer **1b**, which is much higher than that of the linear ester function of the main chain of the polymer formed, and the lifetime of the carboxylate end, which is much longer than that of the alkoxide end due to the low reactivity of the carboxylate. This copolymerization is schematically illustrated in Scheme XI. In the propagation after the initiation reaction of **1b** with initiator RO^-, the nucleophilic attacks of the carboxylate end at the ester carbonyl carbons of the polymer are in vain, since the attacks always form acid anhydride structures with higher reactivity. The generation of the alternating nature in the copolymerization was previously elucidated.

Among the possible nucleophilic attacks of the alkoxide end (b–h, Scheme XI), path c essentially causes a change of the structure of the constitutional unit arising from **2**, and path d may be unfavorable due to the nine-membered ring transition state. Paths e–g are possible but seem not to be very frequent, because the change in MWD during the copolymerization is small and $\bar{M}_n$ increases with an increase of the conversion, as mentioned above (Figure 4). Carbonyl attacks such as those in paths c and e do not cause a significant change in polydispersity. The probability of these paths is small, because the ^1H and ^{13}C NMR spectra are very clean, indicating little structural disorder in the copolymers. Furthermore, the amount of low molecular weight polymer is small in the product obtained, as indicated in the GPC curves (Figure 5).

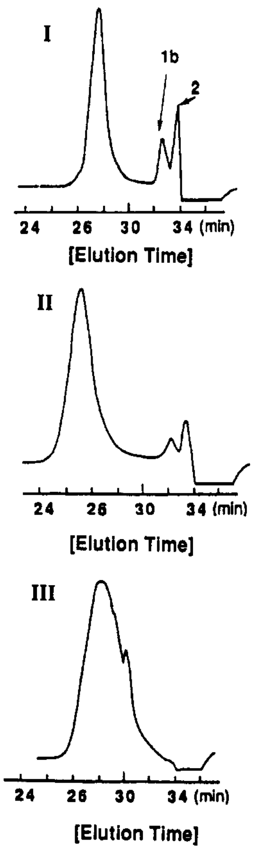


Figure 5. GPC profiles of the polymers **4** obtained (detected by refractive index (RI)): I, Table III, run 1; II, Table III, run 2; III, Table III, run 3.

Effects of Solvent and Counterion. The mechanistic feature of the copolymerization was considerably clarified by the above discussion. This copolymerization can be regarded as an anionic copolymerization involving both alkoxide and carboxylate propagation ends. Thus, the effects of countercation and solvent were examined, particularly in terms of the molecular weight distribution (MWD) of the copolymers or reactivity of the propagation ends. Results are summarized in Table III. GPC profile types are illustrated in Figure 5.

In the copolymerization of an equimolar mixture of **1b** and **2** in THF at 120 °C, six anionic initiators including *t*-BuOK were tested. The copolymer (**4**) obtained was classified into three groups according to the type of their GPC profiles (Figure 5). First, the MeONa system yielded a copolymer with a farily narrow MWD (1.21). The GPC profile of this system was categorized as type I. Second, although the $\bar{M}_n$s of the copolymers were different, similar MWDs were obtained in the cases of *t*-BuOK, PhOK, and AcOK. The GPC profiles of them were classified as type II. Third, in the cases of PhOCs and Et_3N, the $\bar{M}_n$ was lower than those of the other initiators, and the GPC showed a type III profile with a large MWD. However, the rate of the copolymerization with these initiators was considerably faster than those with the others. Although the structures of the alkoxy (and carboxyl) groups are different in these five initiators except for Et_3N, the effect of the countercation on the copolymerization can be

Table III. Effects of Solvent and Counterion on the Anionic Alternating Copolymerization of 1b with 2[a]

run	initiator	solvent	time (h)	conv[b] (%)	$\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$)[c]	type of GPC profile[d]
1	MeONa	THF	70	73	3300 (1.21)	I
2	*t*-BuOK		74	91	6600 (1.62)	II
3	PhOK		93	94	3200 (1.64)	II
4	CH_3COOK		93	94	4100 (1.50)	II
5	PhOCs		18	100	1900 (—)	III
6	Et_3N		28	94	2400 (1.64)	III
7	MeONa	CH_3CN	46	83	3600 (1.26)	I
8	*t*-BuOK		24	100	1700 (—)	III
9	PhOCs		18	100	1000 (—)	III
10	MeONa	toluene	93	31	2300 (1.57)[e]	
11	*t*-BuOK		93	97	4200 (1.38)	II
12	PhOCs		45	94	1600 (1.45)	III

[a] Solvent: THF (initial total monomer concentration: 4.0 M), initiator (4.0 mol % (vs **1b** + **2**), 120 °C. [b] Estimated by GPC area % and ^{1}H-NMR. [c] Estimated by GPC (based on PSt standards). [d] See Figure 5. [e] Heterogeneous system.

discussed from the GPC profile because both the MWD and the GPC profile are nearly equal in the systems with initiators having a common countercation K, *t*-BuOK, PhOK, and AcOK. Thus, the GPC profile might be determined mainly by the propagation but not the initiation. The difference in $\bar{M}_n$ among the three systems (Table III), therefore, may be explained probably by the difference in initiation efficiency of these initiators. As a result, the type of GPC profile results from the reactivity of the propagating end, if the MWD is controlled by the frequency of the chain transfer reaction taking place during the copolymerization. That is, in the MeONa system few chain transfers occur due to the low reactivity of the propagating end, which corresponds to the low conversion of the monomers (Table III, run 1). On the contrary, the most reactive PhOCs system gives the copolymer with a low $\bar{M}_n$ and a large MWD owing to fast chain transfer, although the reaction rate is also very fast (run 5). The effect of counterion could be compared with that of the anionic polymerization of ethylene oxide (EO) with Na–, K–, and Cs–naphthalene complexes as initiators in THF.[13] It has been reported that the polymerization rate of EO increases in the order $Na^+ < K^+ < Cs^+$, similar to the results obtained above.

To evaluate the effect of solvent, the results obtained in THF can be compared with those in CH_3CN and toluene. In the more polar solvent CH_3CN (runs 7–9), the reaction was accelerated as expected, and therefore, lowering of $\bar{M}_n$ and a type III GPC profile were observed in the case of *t*-BuOK as well as PhOCs. On the other hand, the MWD became smaller (1.38, 1.45) in the case of *t*-BuOK and PhOCs in the less polar solvent toluene (runs 10–12) in which the reaction rate was generally lowered. This solvent effect may be accounted for probably by the difference in relative rate between the propagation and chain transfer which will be controlled by solvent polarity. This tendency of solvent-dependent rate is consistent with the general profiles of the anionic polymerization involving the alkoxide propagating end.[14]

Summary. This paper described that the γ-lactone derivative **1b** can be converted to polymer via the double ring-opening isomerization process by anionic copolymerization with epoxide **2**, although **1b** gives no homopolymer. The alternating copolymer **4** was cleanly formed in the solution polymerization, and the anionic ring-opening copolymerization behavior and its mechanistic feature were discussed.

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