Anionic Ring-Opening Alternating Copolymerizations of Bicyclic and Spirocyclic Bis(γ-lactone)s with Epoxides via a Tandem Double Ring-Opening Isomerization of the Bislactones

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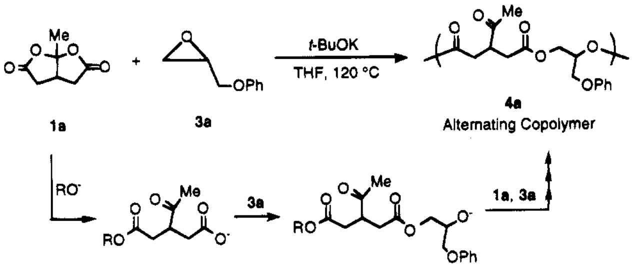
ABSTRACT: Anionic copolymerizations of several bicyclic and spirocyclic bis(γ-lactone)s (**1** and **2**) with various epoxides (**3**) were carried out at 120 °C in tetrahydrofuran in the presence of potassium *tert*-butoxide (4 mol %) as the anionic initiator. The copolymerizations of bicyclic bis(γ-lactone)s **1** (7-substituted 1,6-dioxabicyclo[3.3.0]octa-2,5-diones) with glycidyl phenyl ether (**3a**) smoothly proceeded regardless of the structure of the substituent at the 7-position of **1** to give corresponding copolymers (**4**) in 44−78% yield. The structures of **4** were determined as the alternating copolymers by their IR and ^{1}H and ^{13}C NMR spectra. The copolymerization of spirocyclic bis(γ-lactone) **2a** (1,6-dioxaspiro[3.3]octa-2,7-dione) with **3a** was sluggish but was accelerated by addition of a crown ether (8 mol %) to the polymerization system to yield the alternating copolymer **5aa** in 80% yield. The copolymerization of **2b** (dibenzo derivative of **2a**) with **3a** gave 81% yield of the alternating copolymer **5ba** in the absence of the crown ether. The copolymerizations of **1** or **2** with a variety of epoxides **3** were carried out, and the effect of the structure of **3** was examined. As a result, both the steric hindrance and polarity of **3** were suggested to influence the rate of the copolymerization. Thermal properties such as glass transition and 10% weight loss temperatures of the alternating copolymers **4** and **5** were evaluated by DSC and TGA.

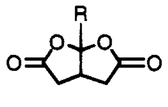
Introduction

Most lactones except for γ-lactones such as γ-butyrolactone polymerize via an efficient ring opening to give corresponding polyesters independent of the mode of polymerization.[1,2] To accomplish the polymerization of γ-lactones as ring-opening monomers, Korte,[3] Hall,[4,5] and Okada[6] have examined the polymerizations under special high-pressure and high-temperature conditions or by using highly strained bicyclic monomers, although their results are mostly unsatisfactory. Meanwhile, several attempts to introduce the γ-lactone moieties into polymers by copolymerization with other monomers such as propylene oxide, β-propiolactone, β-butyrolactone, and tetrahydrofuran (THF) have been reported.[7−10] Yield of the copolymers or the incorporation ratio of the γ-lactone unit in the copolymers is generally low, but a relatively high content of γ-valerolactone (less than 34% of incorporation; chemical yield of copolymer, 57%) is achieved in BF_3OEt_2-catalyzed cationic copolymerization with β-butyrolactone.[10] We have examined ring-opening polymerization of γ-lactone derivatives from a different point of view and recently devised a bicyclic bis(γ-lactone) (**1a**) which is capable of undergoing anionic ring-opening copolymerization with an epoxide (glycidyl phenyl ether, **3a**) to give the corresponding copolymer having an *alternating* structure (**4a**) in a high yield (Scheme 1).[11] The alternating copolymerization proceeded via a typical cross-propagation step where the tandem double ring opening of **1a** in addition to the simple ring opening of **3a** took place by an attack of a nucleophile initiator or propagating end (RO$^-$) at the lactone carbonyl of **1a**.[12]

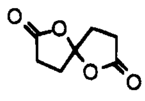
Scheme 1



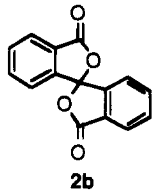
This paper describes the anionic copolymerizations of *spirocyclic* bis(γ-lactone)s (**2a** and **2b**) as well as a few bicyclic bis(γ-lactone)s (**1a−c**) with various epoxides to establish the generality of the novel type of anionic ring-opening alternating copolymerization between bis(γ-lactone)s and epoxides.



R = Me (**1a**)
Et (**1b**)
Pr (**1c**)



2a



2b

Experimental Section

FT-IR spectra were obtained with a Jasco FT/IR-3 and FT/IR-5300. ^{1}H and ^{13}C NMR spectra were recorded on JEOL JMN PMX-60si, FX-100, and GX500 spectrometers using tetramethylsilane (TMS) as the internal standard. UV spectra were measured with a Hitachi 200-10 spectrophotometer. Determination of 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 THF as an eluent and refractive index (IR) and ultraviolet (UV) detectors. Thermal

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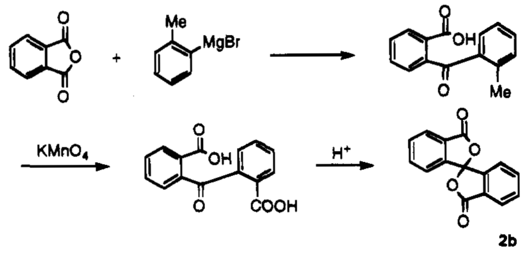
Scheme 2



properties of polymers were measured with a SII DSC 220C for differential scanning calorimetry (DSC) and a SII TG/DTA 220 for thermogravimetric analysis (TGA).

Commercially available solvents, reagents, and epoxides were purified by distillation according to the common methods. 1,6-Dioxaspiro[4.4]nonane-2,7-dione (**2a**) (Aldrich Chemical Co.) was purified by recrystallization from methanol.

Synthesis of Bicyclobis(γ-lactone)s (1). Typical Procedure for 1c. A mixture of tricarballylic acid (6.0 g, 34.2 mmol), *n*-butyric anhydride (49 mL), and pyridine (0.6 mL) was refluxed for 6 h. Removal of *n*-butyric acid and excess *n*-butyric anhydride was followed by dissolution of the residue with acetone, and the solution was treated with active charcoal. Removal of charcoal by filtration and successive evaporation of the filtrate yielded a pale yellow solid. Recrystallization of the solid material from ethanol three times afforded light yellow crystals of **1c** (30% yield): mp 56–58 °C; IR (KBr) 2967, 2938, 2878, 1788, 1462, 1234, 1123, 1109, 1024, 951 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.20–3.29 (m, 5H, 2 × CH$_2$ + CH), 1.82–2.08 (m, 2H, CH$_2$Et), 1.29–1.76 (m, 2H, –CH$_2$), 0.90–1.80 (t, 3H, –CH$_3$); ^{13}C NMR (CDCl$_3$) δ 172.8, 114.9, 39.2, 37.3, 35.6, 13.8. Anal. Calcd for $C_9H_{12}O_4$: C, 58.69; H, 6.57. Found: C, 58.55; H, 6.62.

Bis(γ-lactone)s **1a** and **1b** were similarly synthesized using acetic anhydride and propionic anhydride, respectively, instead of *n*-butyric anhydride. **1a**: yield 66%; mp 98–99 °C from toluene (lit.[12] mp 98–99 °C); IR (KBr) 2477, 2359, 1813, 1790, 1291, 1269, 1085, 1062 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.40–3.23 (m, 5H, 2 × CH$_2$ + CH), 1.82 (s, 3H, Me); ^{13}C NMR (CDCl$_3$) δ 172.5, 113.1, 39.0, 35.4, 23.8. **1b**: yield 20%; mp 66–67.5 °C from ethanol (lit.[13] mp 65–66 °C); IR (KBr) 2992, 2949, 2888, 1729, 1236, 1117, 1061, 1026, 960 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.98–1.17 (t, 3H, –CH$_3$), 1.93–2.18 (q, 2H, –CH$_2$–), 2.44–3.24 (m, 5H, 2 × CH$_2$ + CH); ^{13}C NMR (CDCl$_3$) δ 173.2, 115.6, 36.8, 35.9, 30.3, 7.4.

Synthesis of 3,3-Spirobiphthalide (2b).[14] *o*-Tolylmagnesium bromide was prepared from *o*-bromotoluene (17.3 g, 0.1 mol) and magnesium (2.7 g, 0.11 mol) in ether. The Grignard reagent was added from a dropping funnel to a vigorously stirred solution of phthalic anhydride (22.1 g, 0.15 mol) in 500 mL of a benzene–diethyl ether mixed solvent (3:1, v/v) under an argon atmosphere. The mixture was refluxed for 12 h, and ice–water (250 mL) was added to the reaction mixture. The organic layer was separated and extracted with a 6% sodium bicarbonate solution (100 mL × 3). Concentrated sulfuric acid was slowly added to the combined aqueous extract with cooling with an ice-bath until the pH of the solution reached less than 3. Product keto acid precipitated from the solution was collected by filtration (5.0 g, 18% yield).

A solution of the keto acid (9.0 g, 0.32 mol) in 150 mL of a 10% sodium hydroxide solution was heated to reflux. To the refluxing solution was added dropwise a solution of potassium permanganate (12g in 280 mL of water) over a period of 6 h, and the resulting mixture was refluxed for an additional 6 h. The mixture was cooled and filtered twice to remove precipitated manganese dioxide. The filtrate was carefully acidified with concentrated hydrochloric acid to pH 1 and refluxed for 2 h. The mixture was cooled to room temperature, and a white crystalline material precipitated was collected by filtration. The product was washed with a cold 5% sodium bicarbonate solution until the filtrate became neutral. Recrystallization from ethanol afforded white crystals of **2b** (Scheme 2; 5.0 g, 63% yield): mp 208–212 °C (lit.[14] mp 208–212 °C); IR (KBr) 1788, 1606, 1088, 1009 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.07–7.22 (m, aromatic); ^{13}C NMR (CDCl$_3$) δ 166.7, 144.3, 135.6, 132.0, 126.3, 126.0, 123.0.

Anionic Copolymerization. Typical Procedure for 1a and 3a. To **1a** (0.478 g, 3.0 mmol) placed in a polymerization tube were added potassium *tert*-butoxide (27 mg, 4 mol %), **3a** (0.41 mL, 3.0 mmol), and 1.5 mL of THF, in this order. The tube was cooled, evacuated, sealed off, and heated at 120 °C for 72 h. The initial heterogeneous mixture turned to the homogeneous one as the polymerization proceeded. A methylene dichloride solution of acetic acid (1 vol %, 2.0 mL) was added to the cooled mixture. The resulting mixture was slowly poured into 70 mL of methanol to precipitate polymeric material insoluble in methanol. By the centrifugal separation, 0.70 g of viscous oil was obtained as the insoluble material (75% yield). The evaporation of the supernatant gave a mixture of low molecular weight polymer and the monomers.

4aa: IR (neat) 1740, 1720, 1602, 1592, 1253, 1162, 758, 753 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.36–6.02 (m, 5H, aromatic) 5.58–5.21 (m, 1H, COOCH), 4.62–4.20 (m, 2H, CH$_2$OCO), 4.08–4.03 (d, 2H, CH$_2$OPh), 3.57–3.16 (m, 1H, CH), 2.91–2.31 (br, 4H, 2 × CH$_2$COO), 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.

4ba: IR (neat) 3468, 3065, 3040, 2976, 2940, 1740, 1719, 1599, 1497, 1242, 1173, 758, 693 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 6.82–7.36 (m, 5H, Ph), 5.19–5.49 (br, 1H, CHOCO), 3.94–4.51 (m, 4H, CH$_2$OPh + CH$_2$OCO), 3.19–3.53 (m, 1H, CH), 2.31–2.90 (m, 6H, COCH_2Me + 2 × CH$_2$COO), 1.04–1.11 (t, 3H, CH$_3$); ^{13}C NMR (CDCl$_3$) δ 211.0, 171.1, 170.8, 158.1, 129.6, 121.5, 121.3, 114.5, 70.1, 65.9, 62.8, 43.0, 35.3, 34.9, 7.6.

4ca: IR (neat) 2964, 2930, 2878, 1742, 1714, 1599, 1497, 1173, 756, 693 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 6.82–7.34 (m, 5H, Ph), 5.26–5.48 (br, 1H, CHOCO), 4.03–4.52 (br, 4H, CH$_2$OPh + CH$_2$OCO), 3.18–3.47 (m, 1H, CH), 2.30–2.89 (m, 6H, 2 × CH$_2$COO + CH$_2$CO), 1.40–1.78 (m, 2H, CH$_2$), 0.80–0.98 (t, 3H, CH$_3$); ^{13}C NMR (CDCl$_3$) δ 210.2, 171.3, 170.9, 158.3, 129.8, 121.7, 114.6, 72.3, 66.0, 62.9, 43.6, 35.2, 35.0, 17.1, 13.8.

4ab: IR (neat) 3466, 2932, 2890, 2798, 1740, 1712, 1159, 1113 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ 4.93–5.30 (br, 1H, CHOCO), 3.50–3.90 (m, 2H, CH$_2$OCO), 2.90–3.70 (br, 3H, CH + CH$_2$O), 2.53–2.70 (m, 4H, 2 × CH$_2$), 3.23 (s, 3H, OCH$_3$), 2.28 (s, 3H, CH$_3$).

4ac: IR (neat) 3466, 2975, 2930, 2878, 1740, 1715, 1163, 1090, 1022 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 4.90–5.30 (br, 1H, CHOCO), 4.10–4.40 (br, 2H, CH$_2$), 2.90–3.61 (br, 3H, CH + CH$_2$O), 2.55–2.76 (m, 4H, 2 × CH$_2$), 1.20 (s, 9H, *t*-Bu).

4ad: IR (neat) 3450, 2983, 2942, 2883, 1735, 1715, 1160, 1080 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 4.83–5.20 (m, 1H, CHOCO), 3.98–4.2 (m, 2H, CH$_2$OCO), 2.90–3.50 (m, 1H, CH), 2.46–2.56 (m, 4H, 2 × CH$_2$), 2.22 (s, 3H, CH$_3$CO), 1.18 (d, 3H, CH$_3$); ^{13}C NMR (CDCl$_3$) δ 208.7, 171.2, 171.0, 170.8, 68.7, 66.2, 43.9, 35.3, 34.9, 29.0, 16.4.

4ae: IR (neat) 3450, 3105, 3064, 3036, 2956, 2927, 1737, 1717, 1587, 1158, 733, 701 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.20 (s, 5H, Ph), 5.76–5.95 (t, 1H, CHOCO), 4.15–4.26 (d, 2H, CH$_2$-OCO), 2.32–3.50 (br, 5H, 2 × CH$_2$ + CH), 2.18 (s, 3H, CH$_3$); ^{13}C NMR (CDCl$_3$) δ 208.3, 171.1, 170.5, 135.9, 128.7, 128.5, 126.7, 126.6, 126.1, 73.6, 66.1, 43.8, 35.1, 34.8, 28.9.

5aa: IR (neat) 2926, 1740, 1719, 1599, 1497, 1244, 1175, 756, 693 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 6.88–7.28 (m, 5H, Ph), 5.34–5.35 (br, 1H, CHOCO), 4.20–4.47 (br, 2H, CH$_2$CO), 4.20–4.47 (m, 2H, CH$_2$O), 2.75–2.78 (m, 4H, 2 × CH$_2$COO), 2.60–2.62 (m, 4H, 2 × CH$_2$CO); ^{13}C NMR (CDCl$_3$) δ 206.63, 206.55, 172.6, 172.2, 171.9, 158.3, 129.5, 121.3, 114.6, 69.9, 65.9, 62.5, 36.8, 27.9, 27.7.

5ac: IR (neat) 2973, 2934, 2876, 1740, 1686, 1366, 1192 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.01–5.12 (br, 1H, COOCH), 4.12–4.31 (br, 2H, COOCH$_2$), 3.36–3.49 (br, 2H, –OCH$_2$), 2.76–2.81 (br, 4H, 2 × CH$_2$CO–), 2.50–2.70 (br, 4H, 2 × CH$_2$COO–), 1.15 (s, 9H, *t*-Bu), ^{13}C NMR (CDCl$_3$) δ 206.9, 172.7, 172.4, 172.1, 73.5, 72.3, 69.0, 37.1, 27.5, 27.3.

5ae: IR (neat) 1740, 1706, 1371, 1173, 760, 702 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.33 (s, 5H, Ph), 5.98 (br, 2H, COOCH), 4.30 (br, 2H, COOCH$_2$), 2.69 (br, 4H, 2 × CH$_2$CO–), 2.17 (br, 4H, 2 × CH$_2$COO–); ^{13}C NMR (CDCl$_3$) δ 206.6, 172.6, 172.2, 158.3, 156.2, 121.5, 121.2, 114.6, 69.9, 65.8, 62.3, 36.9, 36.8, 27.9, 27.8.

Table 1. Anionic Copolymerization of Bis(γ-lactone)s 1 and 2 with Glycidyl Phenyl Ether 3a[a]

					copolymer			
run	lactone	additive	time (h)	conv[b] (%)	no.	yield[c] (%)	$\overline{M}_n$ ($\overline{M}_w/\overline{M}_n$)[b]	composition[d] (mol %) lactone:**3a**
1	**1a**	none	74	91	**4aa**	78[e]	6600 (1.60)	50:50
2	**1b**	none	91	100	**4ba**	44	6600 (1.17)	49:51
3	**1c**	none	93	100	**4ca**	72	7600 (1.30)	45:55
4	**2a**	none	74	ND[g]	**5aa**	13[f]	2600 (1.88)	53:47
5	**2a**	crown[h]	12	ND	**5aa**	24[f]	2600 (1.61)	49:51
6	**2a**	crown	26	ND	**5aa**	46[f]	6200 (1.70)	49:51
7	**2a**	crown	48	ND	**5aa**	80[f]	7300 (1.63)	47:53
8	**2b**	crown	24	ca. 100	**5ba**	77	2600 (1.63)	53:47
9	**2b**	none	48	ca. 100	**5ba**	81	3300 (1.64)	54:46

[a] Conditions: feed ratio, lactone:**3a** = 50:50; solvent, THF (initial monomer concentration: 4.0 M); catalyst, *t*-BuOK (4.0 mol %), 120 °C. [b] Conversion of **1** or **2** estimated by GPC based on polystyrene standards. [c] Yield of the methanol-insoluble part. [d] Determined by the ^{1}H NMR spectrum. [e] Polymer obtained by centrifugal separation. [f] Yield obtained by separation with preparative HPLC. [g] Not determined. [h] *cis*-Dicyclohexano-18-crown-6 (8.0 mol %).

Table 2. Anionic Copolymerization of Bis(γ-lactone)s 1a, 2a, and 2b with Various Epoxides 3[a]

					copolymer			
run	lactone	epoxide	time (h)	conv[c] (%)	no.	yield (%)	$\overline{M}_n$ ($\overline{M}_w/\overline{M}_n$)[d]	composition (mol %)[c] lactone:epoxide
1[e]	**1a**	**3a**	74	91	**4aa**	78[f]	6600 (1.60)	50:50
2	**1a**	**3b**	82	100	**4ab**	86[g]	4100 (1.62)	47:53
3	**1a**	**3c**	82	100	**4ac**	70[g]	3700 (1.39)	50:50
4	**1a**	**3d**	72	100	**4ad**	65[h]	3400 (1.57)	50:50
5	**1a**	**3e**	72	100	**4ae**	42[h]	3000 (1.57)	49:51
6	**1a**	**3f**[b]	82	15		6[g]	2300 (1.73)	49:51
7	**1a**	**3g**[b]	72	15		7[h]	1300 (1.24)	47:53
8	**1a**	**3h**[b]	72	trace		~0		
9[e]	**2a**	**3a**	74	ND[i]	**5aa**	24[f]	2600 (1.61)	49:51
10	**2a**	**3e**	72	ND	**5ae**	13[h]	1900 (1.94)	54:46
11	**2a**	**3c**	72	ND	**5ac**	6.4[h]	2400 (1.91)	58:42
12[e]	**2b**	**3a**	48	ca. 100	**5ba**	81[f]	3300 (1.64)	54:46
13	**2b**	**3d**	72	ND	**5bd**	trace		54:46

[a] Conditions: feed ratio, lactone:**3** = 50:50; solvent, THF (initial monomer concentration: 4.0 M); catalyst, *t*-BuOK (4.0 mol %), 120 °C. [b] Epoxide: **3f**, 1,2-epoxyhexane; **3g**, cyclohexene oxide; **3h**, isobutylene oxide. [c] Determined by the ^{1}H NMR spectrum. [d] Estimated by GPC (based on polystyrene standards). [e] Data of Table 1. [f] Methanol-insoluble. [g] Separated by silica gel column chromatography. [h] Separated by preparative HPLC. [i] Not determined.

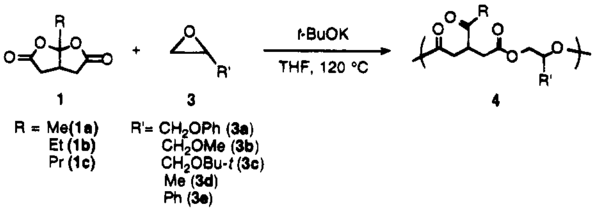
5ba: IR (neat) 1730, 1678, 1597, 1495, 1286, 1250, 756, 731, 709 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.86–7.85 (m, 8H, Ph), 5.40–5.84 (br, 1H, COOCH), 4.45–4.85 (br, 2H, $COOCH_2$), 4.00–4.32 (br, 2H, $PhOCH_2$); ^{13}C NMR ($CDCl_3$) δ 195.3, 167.2, 166.7, 158.2, 139.0, 131.2, 129.6, 71.0, 65.6, 61.1; UV (THF, [C] 4.7 × 10^{-3} mol unit/L) λ_{max} 332.5 nm (ϵ = 51 M^{-1} cm^{-1}).

Results and Discussion

Bicyclic bis(γ-lactone)s (**1a**–**c**) were prepared in 20–66% yield by the reaction of tricarballylic acid with the corresponding acid anhydrides according to the method reported by Strunz *et al.*[13,15] The structures of **1** were determined by the spectral characteristics, especially by their IR carbonyl absorptions at 1790, 1788, and 1788 cm^{-1} (for **1a**, **1b**, and **1c**, respectively). The ^{1}H and ^{13}C NMR spectra were also consistent with their structures, as well as the elemental analysis data (see the Experimental Section).

Anionic copolymerizations of the bicyclic bis(γ-lactone)s **1** with epoxides **3** were carried out at 120 °C in THF in the presence of 4 mol % of potassium *tert*-butoxide (*t*-BuOK) in a sealed tube (Scheme 3). Results are summarized in Tables 1 and 2. As shown in Table 1, the anionic copolymerizations of **1b** and **1c** with glycidyl phenyl ether (**3a**) (runs 2 and 3) proceeded to give corresponding copolymers **4** having $\overline{M}_n$ 6600–7600. The yield of **4ba** from **1b** being lower than that of **4ca** from **1c** presumably comes from the solubility in methanol of **4ba** being higher than that of **4ca**.

Scheme 3



In our previous reports,[11,12] we have concluded that the copolymerization of **1a** with **3a** proceeds in a complete alternating mode from the following facts: (1) **1a** does not homopolymerize, while **3a** also gives no homopolymer in solution polymerization but affords a small amount of homopolymer in polymerization under the same conditions as employed in the copolymerization; (2) composition of the copolymer of **1a** and **3a** is 50:50, independent of conversion of them or yield of the copolymer; (3) the compositions does not depend upon the feed ratio of **1a** and **3a**; (4) alkaline hydrolysis products of the copolymer consists of two hydrolysis products of each monomer; and (5) IR, ^{1}H NMR, and ^{13}C NMR spectra of the copolymer are consistent with those of the proposed alternating copolymer structure. In this case the cross propagation results in the alternating copolymerization. Since **1b** and **1c** have a structures similar to that of **1a**, the copolymerization of **1b** and **1c** with **3a** should be the alternating one similarly. In fact, it is reasonable from the facts that (1) both **1b** and **1c** did not show any homopolymerizability, (2) copolymer composition was always ca. 50:50

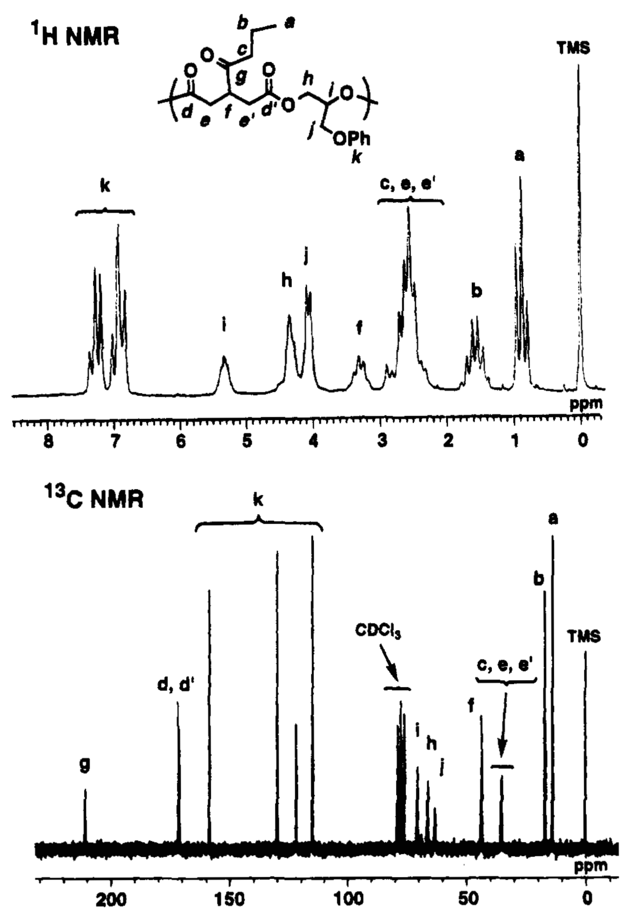
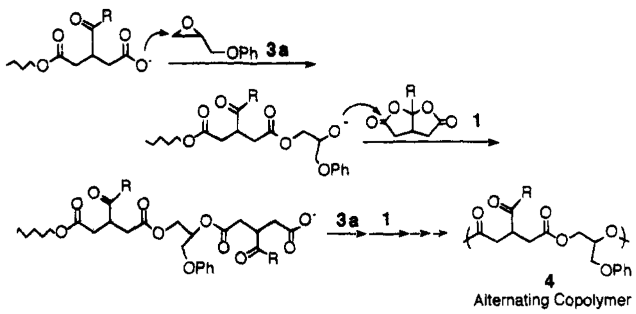


Figure 1. ^{1}H NMR (90 MHz, top) and ^{13}C NMR (22.5 MHz, bottom) spectra of the copolymer **4ca** ($\overline{M}_n$ 7600) (CDCl$_3$, 27 °C).

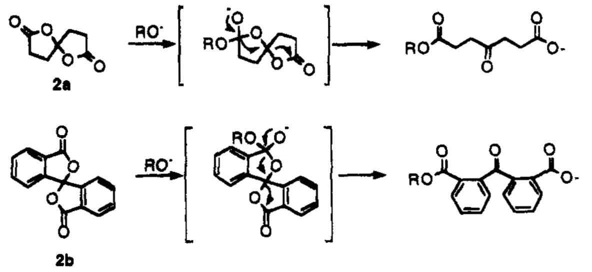
independent of the yield (Tables 1 and 2), and (3) the proposed structure 4 well agreed with the following spectral data as discussed below. In the IR spectra no lactone carbonyl absorption was observed, but instead the ester and ketone carbonyl absorptions appear at 1740−1742 and 1714−1719 cm^{-1}, respectively. This suggests the occurrence of the double ring-opening isomerization of **1** and is in accordance with the proposed linear polyester structure of **4**. Figure 1 indicates the ^{1}H NMR spectrum of **4ca** as a representative in which several clear signals characteristic of the polyester structure of **4** can be observed at the 5.5−2.2 ppm region. Among them, the methine proton signal (i) around 5.3 ppm is particularly characteristic, besides two signals assignable to the methylene protons (h and j) adjacent to the ester and ether oxygens and one methine signal (f). In the ^{13}C NMR spectrum of **4ca**, the carbonyl signals of the side-chain ketone (g, 210.2 ppm) and linear ester (d, and d′, 171.3 and 171.0 ppm) are certainly confirmed as characteristic signals of **4** other than three signals of the methine and methylene carbons adjacent to the ether and ester oxygen atoms at 60−75 ppm.

Thus, the copolymers **4ba** and **4bc** should also be the alternating ones like **4aa**,[11,12] as discussed above. The possibility of random copolymerization can be readily ruled out by the following ^{1}H NMR assignment, besides the above-mentioned things. The homopolymer of **3a** displays their methylene and methine proton signals around 4.4−3.4 ppm as a broad peak. However, as shown in Figure 1 (top), the **3a**-originated methine signal of **4ca** (i) appears around 5.3 ppm in a reasonable integration ratio and therefore is assigned as that adjacent to the ether oxygen of the ester group, in agreement with the structure shown in Figure 1. That is, there is no successive unit of **3a** in the copolymer, strongly indicating the absence of the homopolymer of **3a**. Further, the clean NMR spectra of the copolymers such as those shown in Figure 1 should correspond to the *clean* structure of the copolymer, which includes little different unit structure from **4ca**. Consequently, it is found that the anionic copolymerization of **1** with **3a** smoothly proceeds to produce the corresponding alternating copolymer **4** independent of the structure of **1**. The alternating copolymerization unambiguously involves the following cross propagation (Scheme 4), like the case of **1a** and **3a**.[11,12]

Scheme 4



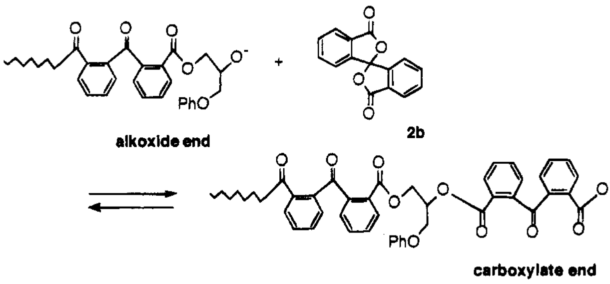
Scheme 5



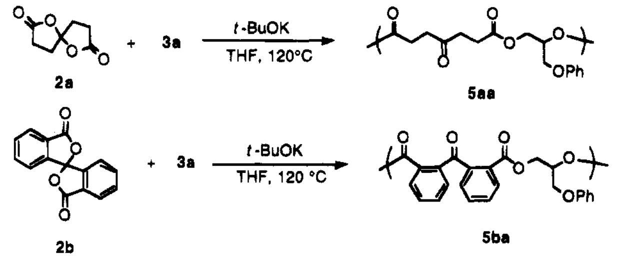
Since spirocyclic bis(γ-lactone)s **2a** and **2b** are able to form the carboxylates by reaction with nucleophile via tandem double ring-opening isomerizations similar to that of **1** (Scheme 5), formation of another type of alternating copolymer is expected in the copolymerizations of **2** with epoxides, like in the case of **1**. In this case the copolymers can possess ketone functions in the main chain as shown in Scheme 5. The synthesis of **2b**[14] was performed by the reaction of phthalic anhydride with *o*-tolylmagnesium bromide followed by oxidation of a methyl group to carboxylic acid and successive acid-catalyzed spirocyclization of keto dicarboxylic acid formed (Scheme 2).

When spirocyclic bis(γ-lactone) **2** was used instead of the bicyclic one **1** (Table 1, runs 4−7), the copolymerization with **3** similarly proceeded to afford the corresponding alternating copolymer **5**. The progress of the copolymerization of **2a** and **3a** was somewhat sluggish but exceedingly increased by the addition of *cis*-dicyclohexano-18-crown-6 ether (8.0 mol %). Both deviation of the unit ratio of **5aa** from the ideal ratio 50:50 and change in molecular weight of **5aa** were little affected by the addition of the crown ether. The yield and molecular weight of **5aa** increased with an increase of the polymerization time (runs 5−7). In the case of **2b** (the dibenzo derivative of **2a**), the copolymerization was faster than that of **2a** and the copolymer **5ba** was obtained in 81% yield without use of the crown ether, although the $\overline{M}_n$ was fairly lower than that of **5aa**. The enhanced reactivity of **2b** is presumably attributed

Scheme 6



Scheme 7



to the enhanced electrophilicity of the carbonyl group due to the benzo substitution, which is readily attacked by a nucleophilic propagating end. If the polymerization proceeds via a mechanism similar to that of **1** with **3a**,[12] the rate-limiting step is considered to be the step of the nucleophilic attack of a carboxylate anion at the epoxy ring. Therefore, the rate enhancement by the benzo substitution seems to be due to the high concentration of the carboxylate end in the equilibrium with the alkoxide end plus **2b** (Scheme 6).

The structures of **5** were suggested to be the proposed alternating ones (Scheme 7), judging from the copolymerization behaviors similar to those in the cases of **1** and **3a** as mentioned above and their spectral characteristics. Figure 2 shows the ^{1}H NMR spectra of **5aa** and **5ba** in which all signals attributable to the proposed unit structures can be observed in proper intensity ratios. In accordance with the ^{1}H NMR spectra of **4**, three characteristic methylene and methine signals c–d–e (**5aa**) or h–i–j (**5ba**) are clearly observed. Especially, the methine proton signal around 5.4 ppm (d and i) clearly reveals that there is no homopolymer unit of **3a**, because this chemical shift is undoubtedly corresponding to the methine proton adjacent to the ether oxygen of the ester, like in the case of **4**. Meanwhile, disappearance of the spiro carbon signal at 107.0 ppm and appearance of the ketone carbonyl signal at 195.3 ppm confirmed in the ^{13}C NMR spectrum of **5ba** suggested the linear poly(ketone–ester) structure. The IR spectra also supported the structure of **5**. As described above, **5ba** can have the benzophenone moiety in the main chain. The n–π^* absorption in addition to the typical π–π^* absorption was observed as a weak maximum at 332.5 nm (ϵ = 51 M^{-1} cm^{-1}) in the UV spectrum of **5ba** in THF, which is well consistent with the value of benzophenone [332.4 nm (ϵ = 150 M^{-1} cm^{-1})], being consistent with the polymer structure of **5ba**. By the same reason as discussed above in the case of **4**, i.e., lack of homopolymerizability of **5** and the ^{1}H NMR spectra consistent with the alternating structures, there is no possibility of the occurrence of random copolymerization of **5a** and **5b** with **3a**.

The copolymerization was examined with various epoxides under the same conditions as described above (Scheme 3). The results are summarized in Table 2.

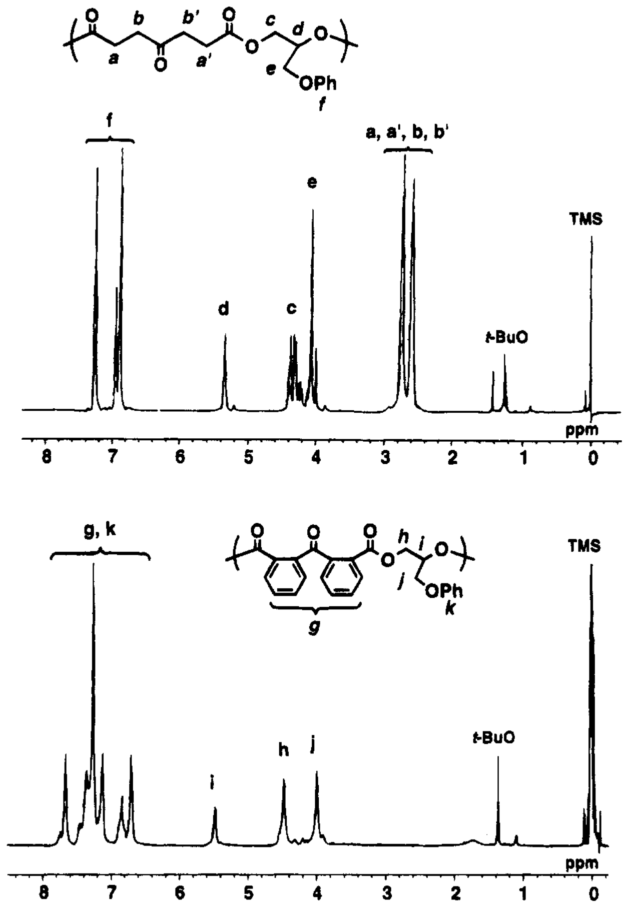


Figure 2. ^{1}H NMR spectra of the copolymers **5aa** (top, $\overline{M}_n$ 7300, 500 MHz) and **5ba** (bottom, $\overline{M}_n$ 3300, 500 MHz) (CDCl$_3$, 27 °C).

Among the copolymerizations of **1a** with eight epoxides, satisfactory results were obtained from the copolymerizations with five epoxides (**3a–e**) such as methyl glycidyl ether (**3b**) and styrene oxide (**3e**) (runs 1–5), but the copolymerizations with the other three epoxides such as 1,2-epoxy hexane (**3f**), cyclohexene oxide (**3g**), and isobutylene oxide (**3h**) proceeded very sluggishly to afford a low yield of the corresponding copolymers with low molecular weights (runs 6–8). In the case of **2** the copolymerization was mostly slow to give low yield and low molecular weight copolymers, except for the cases of **2b** and **3a**. Therefore, in general, glycidyl ethers (**3a–c**), even a *tert*-butyl-substituted one (**3c**), copolymerize well with **2** but alkyl-substituted epoxides do not. The reason for the low copolymerizability of **3g** and **3h** would be due to their steric hindrance, while that of **3f** might come from its low polarity, because monomer polarity undoubtedly affects the polymerization rate when the concentration of the monomer is sufficiently high. This assumption on the monomer polarity appears to account for the reactivity and polarity of the glycidyl ethers higher than those of the alkyl-substituted ones. In the case of Table 2, the copolymer composition was ca. 50:50, and the spectral data of the copolymer agreed with the alternating structure, independent of the substituents of **3**.

In the ^{1}H NMR spectra of Figure 2 the initiation end group, a *tert*-butoxy group, can be plainly observed at 1.4 and 1.2 ppm, whereas such a signal is very small in Figure 1 (top). The signals at 1.4 and 1.2 ppm can be assigned as those of the *tert*-butyl ester and *tert*-butyl ether groups, respectively, in comparison with the

Table 3. Thermal Properties of Copolymers 4 and 5

copolymer	lactone	epoxide	$\overline{M}_n$[a]	T_g (°C)[b]	T_d (°C)[b,c]
4aa	**1a**	**3a**	6600	−15.5	287
4ca	**1c**	**3a**	7600	−25.9	
5aa	**2a**	**3a**	7300	60	356
5ba	**2b**	**3a**	3300	66	299

[a] Estimated by GPC (based on PSt standards). [b] Heating rate at 10 °C/min. [c] 10% weight loss temperature under N_2.

chemical shifts of the known compounds. If this is correct, it is expected that the *tert*-butoxy anion attacks at the epoxide ring carbon of **3a**, to form the *tert*-butyl ether function. Since the signal of the *tert*-butyl ether of **5ba** is much smaller than that of **5aa**, the attack of the *tert*-butoxy anion at the epoxide ring of **3a** in the presence of **2a** takes place more rapidly than that in the presence of **2b**. This seems to reasonably correspond to the reactivity of **2b** higher than **2a** as discussed above. Meanwhile, the initiator potassium *tert*-butoxide is known as one of the typical proton-abstracting agents. Therefore, abstraction of carbonyl α-proton of **1** or **2a** yielding enolate during the copolymerizations is conceivable to occur, and thereby copolymer without a *tert*-butyl group can be formed, if the enolate serves as the initiator for the copolymerization. Small *tert*-butyl signals observed in the case of **4** (e.g., Figure 1, top) may be due to that reason. However, it is not clear at the present time, because the *tert*-butyl signal is relatively clearly observed in the case of **2a** (Figure 2, top) which is expected to have possible proton abstraction similar to **1**.

Thermal properties of a few copolymers (**4** and **5**) prepared using **3a** as the comonomer were measured by DSC and TGA. The difference in the thermal properties should be attributed simply to the structural difference of the bis(γ-lactone)s, because the common comonomer **3a** is used. As shown in Table 3, bicyclic bis(γ-lactone)-derived copolymers (**4**) had glass transition temperatures (T_g) lower than 0 °C, which were much lower than those of copolymers of spirocyclic ones (**5**). This can be explained by the main-chain structure of **5** (polyketone structure) more rigid than **4**. T_d was around 300 °C in any case. The decomposition temperature (T_d) of **5ba** which is 57 °C lower than that of **5aa** may depend on the molecular weight of **5ba** ($\overline{M}_n$ 3300) lower than that of **5aa** ($\overline{M}_n$ 7300).

Summary

In this study it has been found that several bicyclic and spirocyclic bis (γ-lactone)s (**1** and **2**) copolymerize anionically with various epoxides (**3**) to afford corresponding alternating copolymers (**4** and **5**), via both the tandem double ring opening of the bis(γ-lactone)s and the ring opening of the epoxides, whereas the rate of the copolymerization is affected probably by the structure and polarity of the epoxides. The results obtained certainly reveal the generality of this novel alternating copolymerization between bis (γ-lactone)s and epoxides, although the bis(γ-lactone)s do not homopolymerize via a ring-opening mode, like γ-lactones such as γ-butyrolactone.[11] Namely, a monomer capable of forming its carboxylate anion by an anionic reaction such as a ring-opening reaction with a nucleophile can be regarded as a monomer which is able to copolymerize with epoxide to yield a corresponding alternating copolymer. From this point of view, the alternating copolymerization mentioned in this study can be quite similar to that of cyclic acid anhydride with epoxide.[16] Meanwhile, it would be noteworthy that the bis(γ-lactone)s serve as expanding monomers[17] in the copolymerizations with epoxides.[14,18–20]

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