Anionic Cross-Linking of Polymers Having an Epoxy Group in the Side Chain with Bicyclic and Spirocyclic Bis(γ-lactone)s

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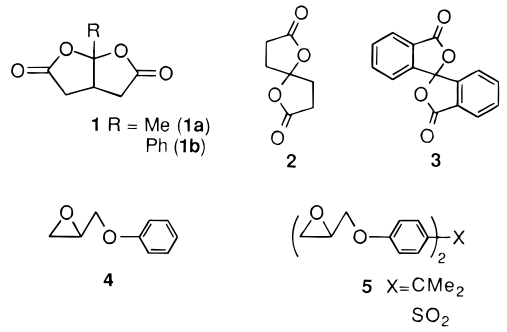
ABSTRACT: Anionic cross-linkings of epoxy group containing polymers such as poly(glycidyl methacrylate) (**6**) and poly(4-(glycidylmethyl)styrene) (**7**) with bicyclic and spirocyclic bis(γ-lactone)s (**1**−**3**) are described. A model study using glycidyl pivalate (**8**) as the polymer model compound was carried out at 120 °C in THF ([C] = 4.0 M) in the presence of potassium *tert*-butoxide (2 mol %) to obtain the corresponding alternating copolymers (**9**−**11**) in 62−69% yields. The anionic cross-linkings of **6** and **7** with **1**−**3** and homopolymerizations of **6** and **7** under similar conditions afforded dichloromethane-insoluble cross-linked (co)polymers (**12**−**19**) quantitatively. The IR spectral change might suggest strongly that the cross-linked copolymers formed had polyester group consisting of an almost completely alternating copolymer unit. Recovery of a small amount of **1**−**3** would suggest that the polyester side chain contained a small amount of a polyether unit in some cases. The degree of ring-opening of epoxy group of **6** and **7** was 100% in most cases. Homopolymerizations of **6** and **7** were accompanied by 5.4% and 6.3% volume shrinkage, respectively, although the degree of ring-opening of the epoxy group was very low (27% and 38%). Volume shrinkage (2.5−5.4%) observed in the cross-linkings of **6** and **7** with **1**−**3** was relatively lower in spite that the degree of ring-opening of epoxy group was 100%. It was concluded that volume shrinkage during cross-linking of epoxy group containing polymers can be considerably suppressed by addition of **1**−**3** as an additive. Thermal properties such as glass transition and 10% weight loss temperatures of the cross-linked polymers **12**−**19** obtained were evaluated by DSC and TGA.

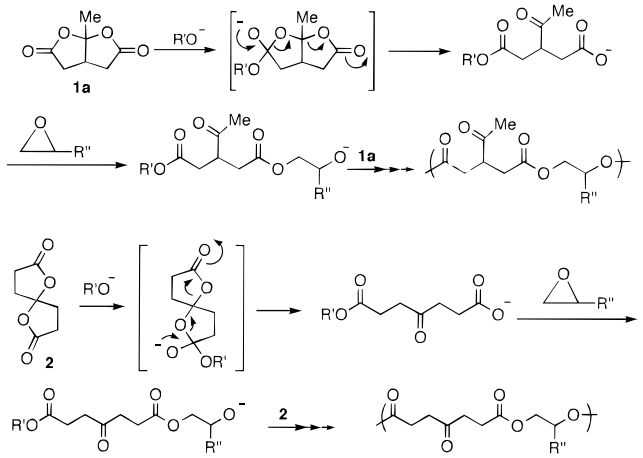
Introduction

Volume shrinkage on polymerization and curing is one of the continuing problems to be settled in industrial applications of polymeric materials and in the field of materials science.[1] To solve it, monomers and materials are required that undergo polymerization and curing without a volume change or with volume expansion. We have developed many shrinkage-free and sometimes expanding monomers and materials where the fundamental skeletons consist of bicyclic orthoesters (BOEs), spirocyclic orthoesters (SOEs), and spirocyclic orthocarbonates (SOCs).[2] However, they all are only cationically polymerizable. Many cases need expanding monomers and materials that polymerize and cure radically and anionically. We have reported on monomers and materials showing volume expansion on radical polymerization.[3,4] Recently, we have found bicyclic and spirocyclic bis(γ-lactone)s (**1**−**3**) with epoxy monomers (**4** and **5**) anionically copolymerize via a tandem double ring-



opening isomerization of bis(γ-lactone)s and ring-opening of the epoxy monomers to give the corresponding copolymers[5, 6] (Scheme 1).

Scheme 1



In the case of the monomeric epoxide (**4**), the copolymerization with **1** selectively gave a corresponding alternating copolymer to reduce the volume shrinkage of the epoxide.[7] Similarly, volume shrinkage of bifunctional epoxides such as epoxy resins (**5**) decreased by adding these monomers which copolymerized alternatively with the epoxides.[7] These monomers, therefore, can be regarded as the expanding monomers capable of polymerizing anionically. Then we selected polyfunctional epoxides as epoxy monomers to examine the capability of such expanding monomers for reduction of volume shrinkage on anionic cross-linking of epoxy-functionalized polymers by adding it as the cross-linker. The problem encountered with this method is how many epoxy group take part in the cross-linking reaction in addition to alternating copolymerizability, because it would directly affect the degree of volume change. In

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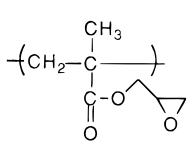
the cationic copolymerization of epoxides with SOCs, the amount of SOC added is clearly proportional to the volume change on the copolymerization.[8]

This paper discloses anionic cross-linking of epoxy group containing polymers (**6** and **7**) with bicyclic and spirocyclic bis(γ-lactone)s (**1**−**3**) and the volume change on the cross-linking.



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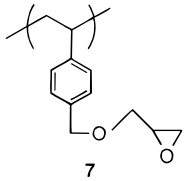

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Experimental Section

Materials. Glycidyl methacrylate and 4-(chloromethyl)-styrene were purified by distillation before use. DMF and benzene were distilled and dried according to the conventional methods. THF was purified by distillation from sodium benzophenone ketyl. Azobis(isobutyronitrile) was used as received. 1,6-Dioxaspiro[4.4]nonane-2,7-dione (**2**) (Aldrich Chemical Co.) was purified by recrystallization from methanol.

Measurements. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL EX-90 (^{1}H, 90 MHz; ^{13}C, 22.5 MHz) spectrometer, using tetramethylsilane (TMS) as internal standard in deuteriochloroform. FT-IR spectra were obtained with a JASCO FT/IR-3 spectrometer. Molecular weights ($\bar{M}_n$ and $\bar{M}_w$, number- and weight-average molecular weights) and their distribution ($\bar{M}_w/\bar{M}_n$) were estimated by gel permeation chromatography (GPC) on a Tosho HPLC CCP & 8000 system with a data processor, equipped with three consecutive linear polystyrene gel columns (G2500H, G4000H, and G5000H), using tetrahydrofuran as solvent (flow rate 1.0 mL/min, polystyrene calibration, and refractive index (RI) and ultraviolet (UV, 254 nm) detectors). Recycling preparative high-pressure liquid chromatography (HPLC) was performed with a Japan Analytical Industry LC-908 equipped with both ultraviolet (254 nm) and refractive index detectors and two consecutive gel columns, JAIGELs 1H and 2H (eluting solvent, commercial grade inhibitor-free tetrahydrofuran; flow rate, 3.8 mL/min). The epoxy equivalent weight of polymers having epoxy group was determined by HCl/dioxane method.[9] Densities of the monomers and polymers were measured by the density gradient tube method at 25 °C with a Shibayama Kagaku Seisakusho Model A.

Synthesis of Bicyclic Bis(γ-lactone)s (1). Preparations of **1a** and **1b** were carried out by Tadokoro[7] and Lawson's methods.[10] **1a.** Yield: 6.1 g (45%). Mp: 102−103 °C (lit.[7] mp 98−99 °C). IR (KBr): 2965, 2937, 2878, 1816, 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 172.4, 113.1, 38.9, 35.4, 28.3. **1b**. Yield: 4.9 g (24%). Mp: 138−139 °C (lit.[10] mp 122 °C). IR (KBr): 3065, 3036, 3003, 2934, 1797, 1452, 1340, 1255, 1199, 1001, 866, 763 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.43 (s, 5H, aromatic), 2.50−3.53 (m, 5H, CH_2 + CH). ^{13}C NMR ($CDCl_3$): δ 172.5, 136.3, 130.2, 129.0, 124.9, 111.7, 41.4, 35.2.

Synthesis of 3,3-Spirobiphthalide (**3**). Preparation of **3** was carried out by Brady's method.[11] Yield: 3.0 g (49%). Mp: 211−213 °C (lit.[11] mp 212 °C). IR (KBr): 3105, 2956, 2858, 1787, 1606, 1464, 1343, 1285, 1088, 1009, 912, 794, 759 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.22−8.07 (m, 8H, aromatic). ^{13}C NMR ($CDCl_3$): δ 166.6, 144.3, 135.5, 131.9, 126.3, 126.0, 123.0, 107.0.

Synthesis of Poly(glycidyl methacrylate) (**6**). A mixture of glycidyl methacrylate (5.0 g, 0.035 mol), azobis(isobutyronitrile) (AIBN; 0.17 g, 3 mol %) and dry DMF (17 mL, 2 M) was heated at 60 °C for 4 h. The mixture was cooled to room temperature and poured into 500 mL of methanol to precipitate a polymeric product, which was filtered off. The methanol-insoluble white solid was dried at 60 °C for 24 h in vacuo. Yield: 2.97 g (60%). $\bar{M}_n$ = 25 300 ($\bar{M}_w/\bar{M}_n$ = 2.02). Epoxy equivalent weight = 142.2 g/equiv[9] IR (KBr): 3435, 3001, 2947, 1732, 1485, 1450, 1390, 1342, 1259, 1149, 993, 906, 846, 760 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.38−3.72 (m, 2H, CH_2O(C=O)), 3.21−3.24 (1H, CH of epoxy ring), 2.62−2.89 (m, 2H, CH_2 of epoxy ring), 1.91 (br, 2H, CH_2), 0.95−1.10 (br, 3H, CH_3).

Synthesis of Poly(4-(glycidylmethyl)styrene) (**7**). To a mixture of 4-(chloromethyl)styrene (96.5%, 40 g, 0.26 mol) and glycidol (9.6 g, 0.13 mol) in DMF (50 mL) was added dropwise a solution of potassium *tert*-butoxide (11.2 g, 0.10 mol) in DMF (50 mL) at 0 °C for 2 h. The mixture was stirred at room temperature for 6 h, washed with water (100 mL × 3), and extracted with ethyl acetate (50 mL × 3). The combined extract was dried over anhydrous magnesium sulfate. After removal of DMF in vacuo, the residual mixture was subjected to silica gel column chromatography (eluted with *n*-hexane−ethyl acetate 9:1). The collected product was purified by distillation in the presence of 1,1-diphenyl-2 picrylhydrazyl (DPPH) as radical inhibitor. Bp: 105−107 °C (0.15 mmHg) [lit.[12] bp 100−104 °C (0.11 mmHg)]. Yield: 5.5 g (49%, based on *t*-BuOK). IR (neat): 3086, 3053, 3001, 2860, 1630, 1512, 1406, 1253, 1095, 991, 906, 829, 763 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.18−7.41 (m, 4H, aromatic), 6.67 (dd, J = 17.6 Hz, 10.8 Hz, 1H, =CH), 5.69 (dd, J = 17.6 Hz, 1.1 Hz, 1H, $=CH_2$), 5.19 (dd, J = 10.8 Hz, 1.1 Hz, 1H, $=CH_2$), 4.49 (s, 2H, CH_2O), 3.69 (dd, J = 11.1 Hz, 2.7 Hz, 1H, OCH_2−epoxy ring), 3.33 (dd, J = 11.1 Hz, 5.6 Hz, 1H, OCH_2−epoxy ring), 3.03−3.18 (m, 1H, CH of epoxy ring), 2.69 (dd, J = 5.0 Hz, 4.0 Hz, 1H, CH_2 of epoxy ring), 2.51 (dd, J = 5.0 Hz, 2.4 Hz, 1H, CH_2 of epoxy ring). ^{13}C NMR ($CDCl_3$): δ 137.6, 136.7, 136.5, 127.8, 126.1, 113.7, 72.8, 70.7, 50.7, 43.9.

7 was prepared according to the reported method.[12] A mixture of 4-(glycidylmethyl)styrene (5 g, 0.026 mol) and AIBN (0.023 g, 0.5 mol %) in dry benzene (13 mL, 2 M) was heated at 60 °C for 48 h. The mixture was cooled to room temperature and poured into methanol (400 mL). The methanol-insoluble product was collected by filtration and dried at 60 °C in vacuo to give a solid material. Yield: 2.0 g (40%). $\bar{M}_n$ = 18600. ($\bar{M}_w/\bar{M}_n$ = 3.17). Epoxy equivalent weight = 190.2 g/equiv IR (KBr): 3400, 3051, 3005, 2924, 2856, 1716, 1610, 1512, 1421, 1346, 1253, 1093, 902, 844, 758 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.41−6.98 (br, 4H, aromatic), 4.46 (s, 2H, CH_2O), 3.16−3.66 (br, 3H, OCH_2 + CH of epoxy ring), 2.61−2.76 (br, 2H, CH_2 of epoxy ring), 1.36−1.63 (br, 3H, CH_2 + CH of styrene). ^{13}C NMR ($CDCl_3$): δ 135.2, 128.4, 127.5, 73.2, 70.9, 50.8, 44.3, 40.3, 40.1.

Synthesis of Glycidyl Pivalate as a Model Compound (**8**). To a mixture of glycidol (20.9 g, 0.28 mol), triethylamine (28.3 g, 0.28 mol), and 4,4-(dimethylamino)pyridine (2.69 g, 5 mol %) in dichloromethane (50 mL) was added dropwise a solution of pivaloyl chloride (24.1 g, 0.2 mol) in dichloromethane (25 mL) at 0 °C for 2 h. The mixture was stirred at room temperature for 6 h, washed with a dilute aqueous HCl solution (150 mL × 3) and subsequently 5% aqueous $NaHSO_3$ solution (150 mL × 3). The organic layer was dried over anhydrous magnesium sulfate, and dichloromethane was removed by evaporation. The resulting residue was distilled in vacuo to give a colorless oily product (**8**). Yield: 16 g (66% based on pivaloyl chloride). Bp: 61−62 °C (6 mmHg) [lit.[13] bp 61−62 °C (6 mmHg)]. IR (neat): 2976, 2876, 1732, 1481, 1460, 1398, 1367, 1284, 1155, 1035, 991, 912, 858, 758 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.40 (dd, J = 12.4 Hz, 3.0 Hz, 1H, CH_2O(C=O)), 3.92 (dd, J = 12.4 Hz, 6.0 Hz, 1H, CH_2O(C=O)), 3.11−3.28 (m, 1H, CH of epoxy ring), 2.84 (dd, J = 4.9 Hz, 4.1 Hz, 1H, CH_2 of epoxy ring), 2.64 (dd, J = 4.9 Hz, 2.7 Hz, 1H, CH_2 of epoxy ring), 1.16 (s, 9H, *t*-Bu). ^{13}C NMR ($CDCl_3$): δ 178.2, 64.6, 49.4, 44.4, 38.3, 27.1.

Anionic Copolymerization of 8 with 1a. A mixture of **1a** (0.078 g, 0.5 mmol), **8** (0.082 g, 0.5 mmol), potassium *tert*-butoxide (2.3 mg, 2 mol %), and 0.5 mL of THF ([C] = 2.0 M) was charged in a polymerization tube. The tube was cooled then evacuated, sealed off, and heated at 120 °C for 96 h. The mixture was cooled to room temperature, and a dichloromethane solution of acetic acid (2 vol %, 1 mL) was added to it. The higher molecular weight polymer (**9**) was separated by preparative HPLC. Yield: 0.098 g (62%). $\bar{M}_n$ = 2300 ($\bar{M}_w/\bar{M}_n$ = 1.05). IR (neat): 2974, 1738, 1481, 1363, 1282, 1155,

Table 1. Anionic Copolymerization of 8 with 1a−3[a]

run	feed ratio (mol %) lactone:epoxide	copolymer	copolymer yield[b] (%)	$\bar{M}$n ($\bar{M}$w/$\bar{M}$n)[c]	copolymer composition[d] lactone:epoxide
1	**1a** (20):**8** (80)	**9a**	16	2200 (1.06)	48:52
2	**1a** (40):**8** (60)	**9b**	40	2600 (1.08)	46:54
3	**1a** (50):**8** (50)	**9c**	62	2300 (1.05)	47:53
4	**1a** (60):**8** (40)	**9d**	60	2000 (1.13)	50:50
5	**1a** (80):**8** (20)	**9e**	15	1600 (1.15)	50:50
6[e]	**2** (50):**8** (50)	**10**	69	6100 (1.69)	48:52
7[e]	**3** (50):**8** (50)	**11**	63	3300 (1.32)	51:49

[a] Polymerization conditions: THF (2 M), *t*-BuOK (2 mol %), 120 °C, 96 h. [b] Separated by preparative HPLC (eluent; THF). [c] Estimated by GPC (based on PSt standards). [d] Determined by ^{1}H NMR. [e] Polymerization conditions: *cis*-dicyclohexano-18-crown-6 (8 mol %) as cocatalyst, THF (4 M), *t*-BuOK (2 mol %), 120 °C, 96 h.

1095, 1037, 949, 769 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.25 (br, 1H, C(=O)OCH), 4.13−4.61 (m, 4H, $CH_2OC(=O) + CH_2OC(=O)O$-*t*-Bu), 3.26−3.56 (m, 1H, CH), 2.55−3.07 (br, 4H, 2 × $CH_2C(=O)O$), 2.28 (s, 3H, CH_3), 1.19 (s, 9H, *t*-Bu). ^{13}C NMR ($CDCl_3$): δ 207.7, 177.4, 170.6, 69.3, 68.2, 61.4, 43.4, 38.4, 34.4, 28.5, 26.7.

Anionic Copolymerization of 8 with 2. A mixture of **2** (0.156 g, 1.0 mmol), **8** (0.158 g, 1.0 mmol), potassium *tert*-butoxide (4.5 mg, 2 mol %) as initiator, *cis*-dicyclohexano-18-crown-6 (42 mg, 8 mol %) as cocatalyst, and 0.5 mL of THF ([C] = 4.0 M) was allowed to react as above. Yield: 0.219 g (69%). $\bar{M}_n$ = 6100. $\bar{M}_w/\bar{M}_n$ = 1.69. IR (neat): 3512, 2972, 2876, 1732, 1481, 1406, 1367, 1284, 1159, 1099, 1037, 939, 769, 733 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.20−5.30 (br, 1H, C(=O)OCH), 4.06−4.39 (m, 4H, $CH_2OC(=O) + CH_2OC(=O)$-*t*-Bu), 2.55−2.78 (m, 8H, 2 × $CH_2CH_2C(=O)O$), 1.19 (s, 9H, *t*-Bu). ^{13}C NMR ($CDCl_3$): δ 206.6, 177.9, 172.4, 69.3, 62.3, 61.9, 43.4, 38.8, 36.8, 27.8, 27.1.

Anionic Copolymerization of 8 with 3. A mixture of **3** (0.126 g, 0.5 mmol), **8** (0.079 g, 0.5 mmol), potassium *tert*-butoxide (2.2 mg, 2 mol %) as initiator, *cis*-dicyclohexano-18-crown-6 (21 mg, 8 mol %) as cocatalyst, and 1.0 mL of THF ([C] = 4.0 M) was allowed to react a in the case of the copolymerization of **8** with **1a**. Yield: 0.127 g (63%). $\bar{M}_n$ = 3300. $\bar{M}_w/\bar{M}_n$ = 1.32. IR (neat): 3449, 3069, 2972, 2874, 1730, 1680, 1575, 1481, 1446, 1367, 1280, 1130, 1093, 935, 769, 733 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.26−7.76 (m, 4H, aromatic), 5.45 (br, 1H, C(=O)OCH), 4.07−4.36 (m, 4H, $CH_2OC(=O) + CH_2OC(=O)$-*t*-Bu), 1.06−1.17 (s, 9H, *t*-Bu). ^{13}C NMR ($CDCl_3$): δ 195.4, 177.7, 166.5, 138.9, 131.0, 129.5, 70.5, 63.4, 61.8, 38.8, 27.0.

Anionic Cross-Linking of Epoxy Group Containing Polymers with Bis(γ-lactone)s. A Typical Procedure for 1a and 6. A mixture of **1a** (0.156 g, 1.0 mmol), **6** (0.142 g, 1.0 mmol (monomer unit)), potassium *tert*-butoxide (4.5 mg, 2 mol %), and THF (0.5 mL, 4.0 M) was placed in a polymerization tube. The tube was frozen and then evacuated, sealed off, and heated at 120 °C for 72 h. A dichloromethane solution of acetic acid (2 vol %, 1.0 mL) was added to the cooled reaction mixture, and the resulting solid material was washed with dichloromethane in a Soxhlet extractor for 12 h. Solvent-insoluble polymer was collected and dried at 60 °C for 24 h in vacuo. **12a.** Yield: 0.271 g (91%). IR (KBr): 3452, 2962, 1736, 1714, 1581, 1394, 1363, 1261, 1165, 997, 842, 733 cm^{-1}.

12b. IR (KBr): 3468, 3063, 2955, 1736, 1684, 1597, 1581, 1448, 1390, 1257, 1153, 956, 848, 696 cm^{-1}.

13. IR (KBr): 3449, 2961, 1736, 1577, 1483, 1450, 1408, 1261, 1170, 1099, 993, 848, 758, 605 cm^{-1}.

14. IR (KBr): 3526, 3067, 2957, 2860, 1732, 1680, 1575, 1446, 1388, 1259, 1130, 1078, 935, 769, 731, 636 cm^{-1}.

15. IR (KBr): 3501, 3061, 3001, 2947, 1732, 1485, 1452, 1390, 1265, 1149, 993, 906, 846, 758 cm^{-1}.

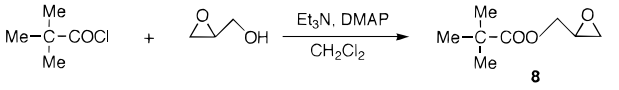
16a. IR (KBr): 3464, 2924, 1739, 1716, 1608, 1577, 1512, 1417, 1363, 1271, 1161, 1095, 1018, 846, 819, 733 cm^{-1}.

17. IR (KBr): 3439, 2920, 2864, 1738, 1610, 1575, 1512, 1410, 1369, 1176, 1097, 846, 814, 733, 605 cm^{-1}.

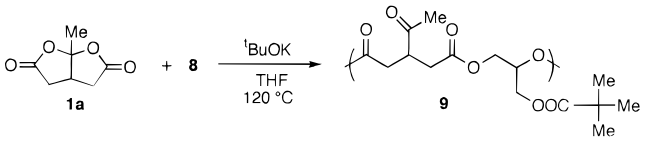
18. IR (KBr): 3524, 3059, 2922, 2860, 1728, 1676, 1575, 1446, 1385, 1261, 1126, 1080, 933, 769, 731, 636 cm^{-1}.

19. IR (KBr): 3447, 3051, 2997, 2992, 2856, 1716, 1608, 1512, 1419, 1253, 1091, 1018, 900, 819, 760 cm^{-1}.

Scheme 2



Scheme 3



Results and Discussion

Model Study. Two epoxy group containing polymers, poly(glycidyl methacrylate) (**6**) and poly(4-(glycidylmethyl)styrene) (**7**), were chosen for the cross-linking with **1**−**3**. Prior to investigation of the copolymerization, a model study was carried out using glycidylpivalate (**8**). This model reaction is to evaluate the polymerizability of the glycidyl ester group of **6** and stability of the ester function of **6**, because a glycidyl ester type epoxide has never been used as a comonomer. **8** was prepared in 66% yield by the reaction of pivaloyl chloride with glycidol in the presence of triethylamine (Scheme 2).

The anionic copolymerization of **8** with **1a** was carried out at 120 °C for 96 h in the presence of potassium *tert*-butoxide (2 mol %) in THF ([C] = 2.0 M) (Scheme 3). The product polymer (**9**) was purified by preparative HPLC. The effect of monomer feed ratio on the yield, molecular weight, and copolymer composition was examined (Table 1).

All polymers obtained (**9a**−**e**) had a monomer composition of ca. 50:50 independent of feed ratio ranging from 20:80 to 80:20 (**1a**:**8**), suggesting the formation of an alternating copolymer. The number-average molecular weight (M_n) of the copolymers was low (from 2600 to 1600), indicating slow polymerization, which was confirmed by the fact that the copolymer was too low in molecular weight to be obtained by the precipitation method. In addition to the highest yield (62%) obtained in the feed ratio of 50:50 (**9c**, Table 1, run 3) and the yield decrease by deviation of the feed ratio from 50:50, the IR, ^{1}H NMR, and ^{13}C NMR spectra of **9** clearly supported the proposed alternating copolymer structure (e.g. for **9c**, Figure 1A−C). Disappearance of five-membered ring lactone carbonyl (1780 cm^{-1}) and oxirane C−O bond absorptions (912 cm^{-1}) and appearance of a new ester carbonyl absorption (1738 cm^{-1}) were observed in the IR spectrum (Figure 1A). The ^{1}H and ^{13}C NMR spectra of **9c** were well consistent with the proposed structure, as assigned in parts B and C of Figure 1. The most characteristic signal for the alternating structure appeared at 5.25 ppm in the ^{1}H NMR spectrum, which was assigned to the methine proton

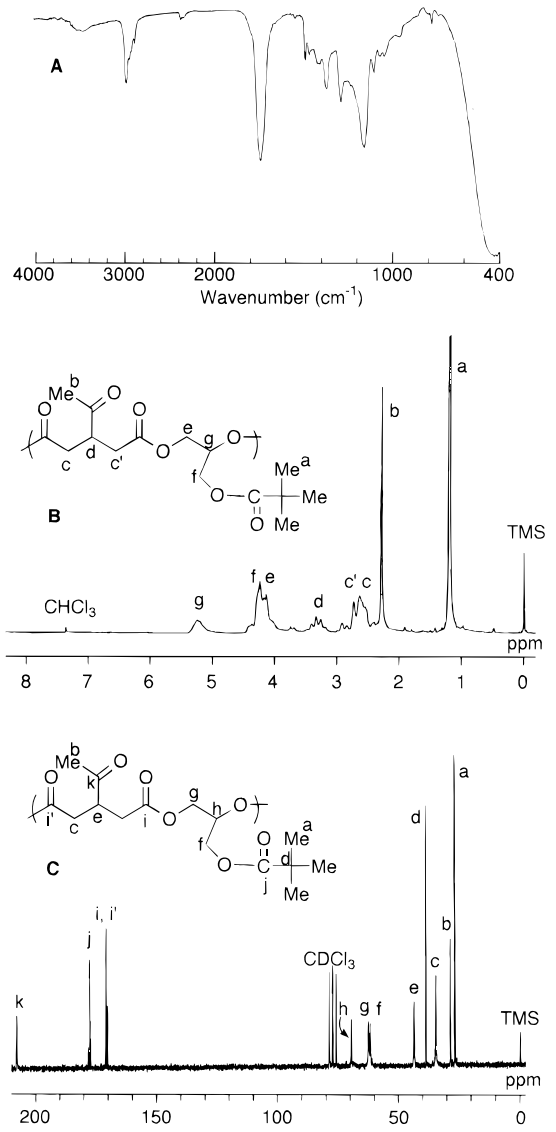


Figure 1. IR (neat) spectrum (A), ^{1}H NMR ($CDCl_3$) spectrum (B), and ^{13}C NMR ($CDCl_3$) spectrum (C) of **9c** ($\bar{M}_n$ 2300).

adjacent to the ester oxygen of the polymer main chain (Figure 1B, signal g). The ^{13}C NMR spectrum of **9c** is characterized by four carbonyl signals due to the one ketone (207.7 ppm) and three ester groups (177.4, 170.6, 170.2 ppm) (Figure 1C). Two signals, for methyl and tertiary carbons of the *tert*-butyl group of **9c**, were observed at 26.7 and 38.4 ppm, respectively. Thus, the alternating copolymer structure of **9** was established by the above results. The model reactions of **8** with spirocyclic bis(γ-lactone)s (**2** and **3**) were also carried out under similar conditions to afford the corresponding copolymers in 69% yield (**10**) and 63% (**11**), respectively, and the number-average molecular weights ($\bar{M}_n$) of the copolymers were 6100 (**10**) and 3300 (**11**), respectively (Table 1, runs 6, 7). The copolymer compositions were ca. 50:50 (**2** or **3**:**8**) in both cases as determined by the ^{1}H NMR spectra. The structures of the copolymers were similarly determined by ^{1}H NMR, ^{13}C NMR, and IR spectra. Figure 2 depicts typical ^{1}H NMR spectra of **10** and **11** in which all signals attributable to the unit structures could be assigned. Consequently, glycidyl ester in addition to the glycidyl ether also copolymerizes with the bicyclic and spirocyclic bis(γ-lactone)s (**1**−**3**) to give the corresponding alternating copolymers (Scheme 4).

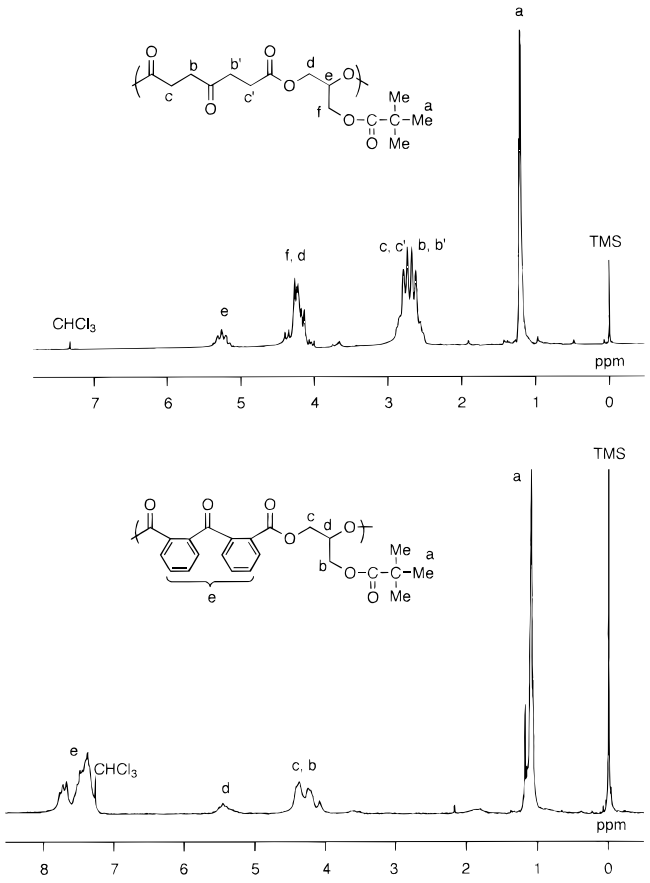
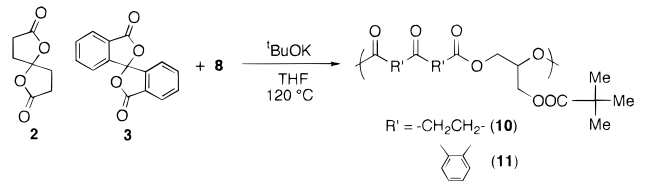
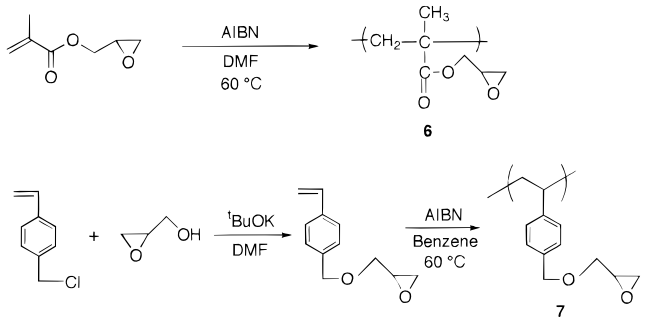


Figure 2. ^{1}H NMR spectra ($CDCl_3$) of the copolymers **10** (top, $\bar{M}_n$ 6100) and **11** (bottom, $\bar{M}_n$ 3300).

Scheme 4



Scheme 5



Anionic Cross-Linking of Epoxy Group Containing Polymers with 1. Poly(glycidyl methacrylate) (**6**) and poly(4-(glycidylmethyl)styrene) (**7**) were selected as polyfunctional epoxides. **6** was prepared by the radical polymerization of glycidyl methacrylate ($\bar{M}_n$ = 25300, $\bar{M}_w/\bar{M}_n$ = 2.02) in 60% yield. **7** was obtained in 40% yield ($\bar{M}_n$ = 18600, $\bar{M}_w/\bar{M}_n$ = 3.17) by the radical polymerization of 4-(glycidylmethyl)styrene, which was prepared in 49% yield by the reaction of 4-(chloromethyl)styrene with glycidol (Scheme 5).

The anionic cross-linking of **6** with **1**−**3** was carried out by heating an equimolar mixtures of the polymers and monomers in the presence of potassium *tert*-

Table 2. Anionic Cross-Linking of Epoxy Group Containing Polymers (6, 7) with Bis(γ-lactone) is 1−3[a]

run	lactone	epoxide	solvent	time (h)	cross-linked polymer	convn of[b] lactone (%)	yield[c] (%)	DROE[d] (%)
1	**1a**	6	THF	72	**12a**	84	91	100
2	**1a**	6	none	72	**12a**		82	71
3	**1b**	6	THF	72	**12b**	84	92	100
4[e]	**2**	6	none	72	**13**	99	99	100
5[f]	**3**	6	THF	72	**14**	76	88	100
6	none	6	THF	72	**15**		98	27
7	**1a**	7	THF	72	**16a**	95	98	100
8	**1a**	7	none	72	**16a**	90	98	100
9[e]	**2**	7	none	72	**17**	97	99	100
10[f]	**3**	7	THF	72	**18**	72	84	100
11	none	7	THF	48	**19**		66	38

[a] Polymerization conditions: *t*-BuOK (2 mol %), THF (4.0 M). [b] Determined by ^{1}H NMR spectra of dichloromethane-soluble part. [c] Dichloromethane-insoluble part. [d] Degree of ring-opening of epoxy group, determined by IR analysis. [e] Reaction temperature 150 °C. [f] Reaction temperature 150 °C, THF (1.0 M).

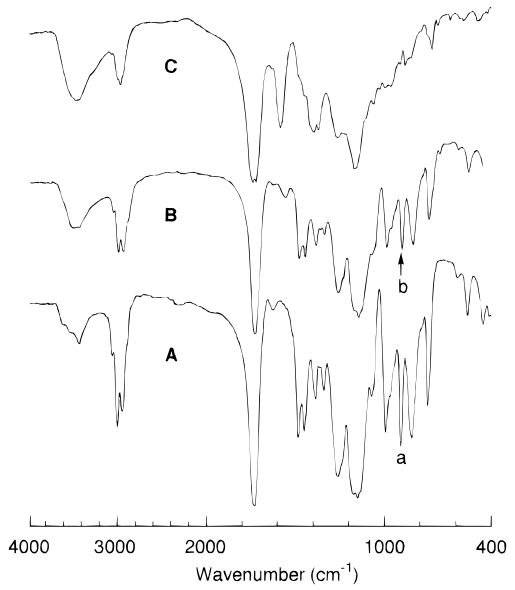
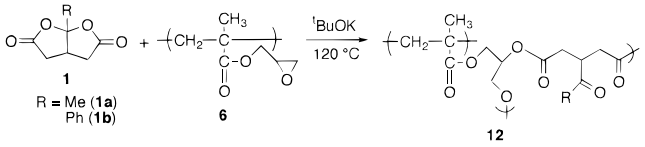


Figure 3. IR (KBr) spectra of **6** (A), homopolymer (**15**) of **6** (run 6 in Table 2) (B), and cross-linked copolymer (**12a**) of **1a** and **6** (run 1 in Table 2) (C).

Scheme 6

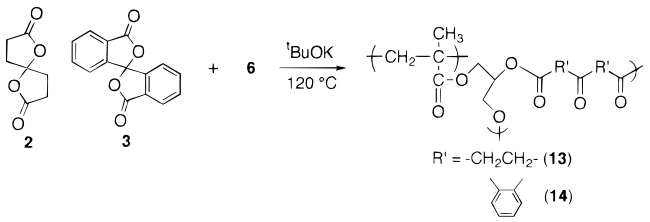


butoxide (2 mol %) at 120 °C for 72 h in THF ([C] = 4.0 M) or in bulk. Results are summarized in Table 2. In the case of **6** and **1a**, the yield of copolymer (91%) and degree of ring-opening of the epoxy group (100%) in solution polymerization (Table 2, run 1) was higher than those in bulk (82%, 71%) (Table 2, run 2). This seems to come from the miscibility of the reaction mixture, because the mixture of **6** and **1a** was not completely homogeneous under bulk conditions.

Disappearance of the lactone carbonyl (1780 cm^{-1}) of **1a** and the epoxy absorption (906 cm^{-1}) of **6** and appearance of new ester (1736 cm^{-1}) and ketone (1714 cm^{-1}) carbonyl absorptions were observed in the IR spectrum of **12a** (Figure 3C). These changes suggest the formation of cross-linked copolymer with the side chain polyester structure, as illustrated in Scheme 6.

Furthermore, the structure of the polyester side chain is considered to be alternating judging from the above model copolymerizations of **8** with **1a**. However, a small amount of **1a** (ca. 8.3%) was recovered in the dichloromethane-soluble fraction, which was confirmed by the

Scheme 7



^{1}H NMR spectrum, although the degree of opening of the epoxy ring of **6** was 100% (Table 2, run 1). So, the cross-linked polymer was suggested to contain a small amount of the polyether unit due to the homopolymerization of the epoxy group besides the polyester unit. In the reaction of **6** with phenyl-substituted bicyclic bis(γ-lactone) **1b**, the cross-linked copolymer was similarly obtained as a solvent-insoluble polymer in 92% yield (**12b**) and the degree of opening of the epoxy ring in **6** was 100%, although the conversion of **1b** was 84% (Table 2, run 3).

When spirocyclic bis(γ-lactone) (**2** or **3**) was used instead of **1**, the cross-linking of **6** similarly proceeded to afford the corresponding dichloromethane-insoluble copolymer (**13** or **14**) as shown in Scheme 7.

In the reaction of **6** with **2**, the degree of epoxy ring-opening was 100%, while both the yield of copolymer (99%) and the conversion of **2** (99%) were complete. These result indicated that the polymer side chain was exclusively composed of the polyester unit (Table 2, run 4). The lower yield of product (88%) and conversion of **3** (76%) in the reaction of **6** with **3** (Table 2, run 5) may be due to the steric hinderance of the aromatic ring of **3** incorporated in the polymer side chain, since both **2** and **3** showed similar reactivity toward **8** in the model reactions (Table 1, runs 6, 7).

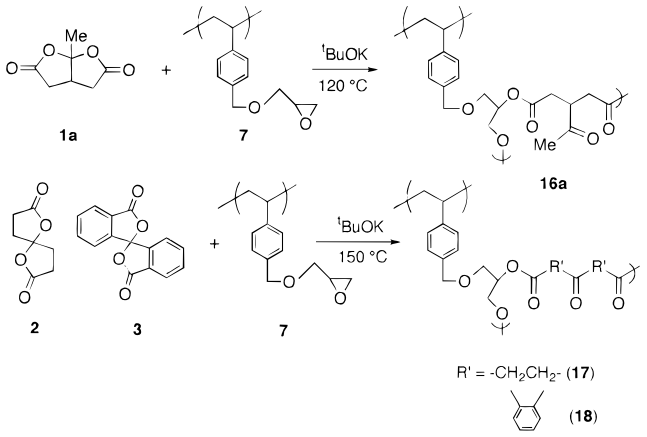
To evaluate the reactivity of the epoxy group of **6**, i.e. ease of opening of the epoxy ring, under the anionic conditions, the homopolymerization of **6** in solution was carried out under the same conditions as those of the cross-linking with **1**. The corresponding solvent-insoluble homopolymer (**15**) was obtained quantitatively. From the IR C−O absorption change of the epoxy group (906 cm^{-1}, Figure 3A,B, absorption band a and b), the degree of ring-opening of the epoxy group was very low (27%) (Table 2, run 6). This result can be compared with the highly efficient epoxy ring-opening in the anionic cross-linking of **6** with **1**−**3** which is described above. The low efficiency is in good accordance with homopolymerization of epoxide like **4** being slower than copolymerization with a bis(γ-lactone) like **1**.[7] So, it should be worthy of special mention that the opening

Table 3. Volume Change during Cross-Linking of 6 or 7 with 1−3 and Thermal Properties of the Obtained Cross-Linked Polymers

conditions[a]	cross-linked polymer	density (g/cm^3)[b] D_m[c]	D_p[d]	vol[e] change (%)	T_g[f] (°C)	$T_{d_{10}}$[g] (°C)
run 1	**12a**	1.270	1.328	−4.6	69	311
run 3	**12b**	1.283	1.315	−2.5	47	310
run 4	**13**	1.276	1.335	−4.7	60	299
run 5	**14**	1.292	1.356	−4.9		313
run 6	**15**[h]	1.213	1.289	−6.3	68	285
run 7	**16a**	1.208	1.261	−4.4	62	318
run 9	**17**	1.188	1.251	−5.2	64	321
run 10	**18**	1.192	1.256	−5.4		328
run 11	**19**[h]	1.174	1.237	−5.4	27	327

[a] Run no. from Table 2. [b] Measured by the density gradient tube method at 25 °C. [c] Density of monomer mixture. [d] Density of cross-linked polymer. [e] [Density(monomer mixture) − density(polymer)]/density(monomer mixture) × 100 (standard error of the measurement = ± 0.15%). [f] Determined by DSC under N_2. Heating rate at 10 °C/min. [g] Determined by TGA under N_2. Heating rate at 10 °C/min. [h] Homopolymer of **6** or **7**.

Scheme 8



of the epoxy ring is complete in spite of a polymer reaction.

Similar anionic cross-linking of an epoxy group containing polystyrene **7** with **1a**−**3** were also carried out under the same conditions as described above. cross-linked products (**16**−**18**) bearing the alternating polyester structure in the side chain (Table 2, runs 7−10) were similarly obtained (Scheme 8).

In any cross-linking, both the yield of the product and the degree of epoxide ring-opening were 100%. The alternating copolymerization in the side chain was similarly confirmed by the IR spectrum (e.g. for **16a**, Table 2, run 7, Figure 4C). When the homopolymerization of **7** was carried out under the same conditions, the yield of the solvent-insoluble polymer (**19**) (66%, Table 2, run 11) was lower than that for **6** (98%). From the epoxy C−O absorption change in the IR spectra (Figure 4A,B, absorption band a and b), the degree of ring-opening of **7** (38%) was higher than that for **6** (27%), but much lower than those for the cross-linking of **7** with **1**−**3** (100%). The reason why the higher degree of ring-opening of **7** compared with that of **6** does not cause a higher yield of the cross-linked polymer is not clear. The degree of ring-opening of **6** being lower than that of **7** would be explained by the glycidyl ester structure of **6**, which does not favorably undergo the epoxy ring-opening compared with the glycidyl ether function of **7**, because of the electron-withdrawing nature of the ester group being stronger than that of the phenoxy group of **7**. Namely,the alkoxy anion formed from **7** seems to be more nucleophilic than that from **6**.

Thus, the anionic cross-linkings of the epoxy group containing polymers **6** and **7** with bis(γ-lactone)s **1**−**3** proceeded to quantitatively afford the corresponding cross-linked copolymers (**12**−**14** and **16**−**18**) bearing the alternating copolymer structures in their side chains.

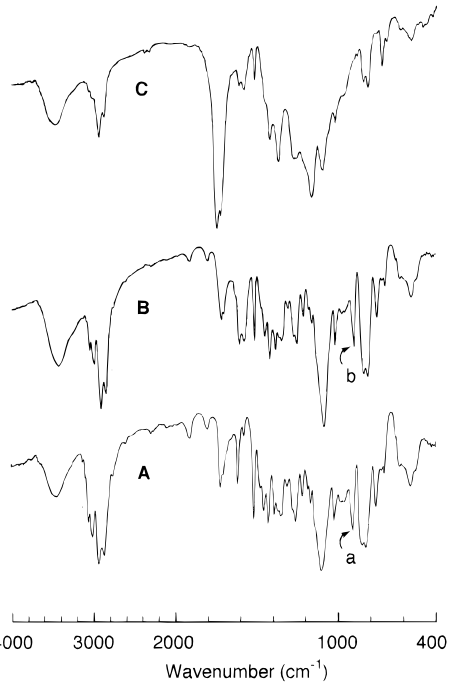


Figure 4. IR (KBr) spectra of **7** (A), homopolymer (**19**) of **7** (run 11 in Table 2) (B), and cross-linked copolymer (**16a**) of **1a** and **7** (run 7 in Table 2) (C).

Volume Change on Polymerization. Volume change during the cross-linkings was evaluated from change in density change before and after the reaction. The results are summarized in Table 3. The homopolymerizations of **6** and **7** showed 6.3% and 5.4% volume shrinkage, respectively. These values seem large in spite of the fact that the degree of ring-opening of the epoxy groups was very low (27%, 38%). Meanwhile, a small volume shrinkage (2.5−5.4%) was observed in the cross-linking of **6** and **7** with **1**−**3**. These values seem fairly small when compared with those of the homopolymerizations because the degree of ring-opening of **6** and **7** is 100% in the reaction with **1**−**3**. So, it can be concluded that volume shrinkage during cross-linking of the epoxy group containing polymers **6** and **7** is considerably suppressed by the addition of **1**−**3** as a comonomer or cross-linking agent.

Thermal Properties of the Cross-Linked Polymers. Thermal properties of the obtained cross-linked polymers (**12**−**19**) were measured by DSC and TGA. The

results are summarized in Table 3. Glass transition temperatures (T_g) of the cross-linked copolymers (**12a**−**13** and **16a**−**17**) were ranging from 47 to 69 °C and 10% weight loss temperatures ($T_{d_{10}}$) were in the range 299−328 °C, but those of the copolymers of spirocyclic bis(γ-lactone)s (**14** and **18**) could not be observed, possibly because the polymer side chain was a rigid aromatic ketone structure. There was no special difference in thermal properties based on the structural difference between the polymers **6** and **7** and the bis(γ-lactone)s **1**−**3**.

Conclusion. The anionic cross-linkings of epoxy group containing polymer such as poly(glycidylmethacrylate) (**6**) and poly(4-(glycidylmethyl)styrene) (**7**) with bicyclic and spirocyclic bis(γ-lactone)s, (**1**−**3**), and the homopolymerization of **6** and **7** were carried out, which quantitatively resulted in a solvent-insoluble cross-linked (co)polymer. The degree of ring-opening epoxy group containing polymers of with **6** and **7** with **1**−**3** was 100% in most cases, while the of **6** and **7** were 27% and 38%, respectively. It should be noteworthy that the cross-linkings of epoxy group containing polymers with bis(γ-lactone)s proceeded to efficiently afford the cross-linked polymers having the alternating structure in this side chain, in spite of the polymer reaction. In this evaluation of volume change during cross-linkings, volume shrinkages on homopolymerization of **6** and **7** were largely suppressed by addition of **1**−**3** as a comonomer or cross-linking agent.

References and Notes

(1) (a) Bailey, W. J.; Sun, R. L.; Katsuki, H.; Endo, T.; Iwama, H.; Tsushima, R.; Saigo, K.; Bitritto, M. M. *Ring-Opening Polymerization with Expansion in Volume*; Saegusa, T., Goethals, E., Eds.; ACS Symposium Series 59; American Chemical Society: Washington, DC, 1977; p 38. (b) Bailey, W. J. *J. Macromol. Sci.-Chem.* **1975**, *A9*(5), 849. (c) Bailey, W. J.; Endo, T. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 1735.

(2) (a) Takata, T.; Endo, T. *Expanding Monomers*; *Synthesis, Characterization, and Applications*; Sadhir, K., Ed.; CRC Press: Boca Raton, FL, 1992; Chapter 3. (b) Uno, H.; Takata, T.; Endo, T. *Macromolecules* **1989**, *22*, 2502. (c) Tagoshi, H.; Endo, T. *Chem. Lett.* **1987**, 2363. (d) Kitamura, N.; Takata, T.; Endo, T. *J. Polym. Sci., Polym. Chem. Ed.* **1991**, *29*, 1151. (e) Igarashi, M.; Takata, T.; Endo, T. *Macromolecules* **1994**, *27*, 2628. (f) Endo, T.; Bailey, W. J. *J. Polym. Sci., Polym. Lett. Ed.* **1975**, *13*, 193. (g) Endo, T.; Bailey, W. J. *Makromol. Chem.* **1975**, *176*, 2897. (h) Endo, T.; Katsuki, H. *Makromol. Chem.* **1976**, *177*, 3231. (i) Endo, T.; Maruoka, S.; Yokozawa, T. *Macromolecules* **1987**, *20*, 2690. (j) Endo, T.; Sato, H.; Takata, T. *Macromolecules* **1987**, *20*, 1416.

(3) (a) Sanda, F.; Takata, T.; Endo, T. *Macromolecules* **1993**, *26*, 737. (b) Sanda, F.; Takata, T.; Endo, T. *Macromolecules* **1993**, *26*, 1818. (c) Sanda, F.; Takata, T.; Endo, T. *Macromolecules* **1994**, *27*, 1099.

(4) Takata, T.; Endo, T. *Prog. Polym. Sci.* **1993**, 18, 839.

(5) (a) Takata, T.; Tadokoro, A.; Endo, T. *Macromolecules* **1992**, *25*, 2782. (b) Tadokoro, A.; Takata, T.; Endo, T. *Macromolecules* **1993**, *26*, 4400.

(6) Takata, T.; Tadokoro, A.; Chung, K.; Endo, T. *Macromolecules* **1995**, *28*, 1340.

(7) (a) Takata, T.; Chung, K.; Tadokoro, A.; Endo, T. *Macromolecules* **1993**, *26*, 6686. (b) Chung, K.; Takata, T.; Endo, T. *Macromolecules* **1995**, *28*, 3048. (c) Chung, K.; Takata, T.; Endo, T. *Macromolecules* **1995**, *28*, 1711.

(8) Takata, T.; Endo, T. *Polym. Prepr. Jpn.* **1988**, *37*, 1559.

(9) *Encyclopedia of Industrial Chemical Analysis*; Snell, F. D., Ettre, L. S., Eds.; Interscience Publisher, New York, 1971; Vol. 12, p 210.

(10) Lawson, A. *J. Chem. Soc.* **1957**, 144.

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

(12) Tomoi, M.; Oda, H.; Kakiuchi, H. *Makromol. Chem., Rapid Commun.* **1986**, *7*, 143.

(13) Kihara, N. Doctorial Thesis, Tokyo Institute of Technology, Tokyo, 1994, p 148.

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