Synthesis and Radical Polymerization of Spiroorthocarbonates Bearing *exo*-Methylene Groups

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ABSTRACT: Synthesis and radical polymerization of unsymmetrical spiroorthocarbonates bearing *exo*-methylene groups at the β-position have been studied. Monomers **7a–c** were prepared by the two-step reactions of dichlorodiphenoxymethane with two different diols. Radical polymerization was carried out in the presence of appropriate initiators (3 mol % vs monomer). Conversion of monomers increased as polymerization temperature rose. The GPC of these polymers showed single modal curves. Ring opening and vinyl polymerizations occurred together in any case. Degree of ring opening in the polymerization depended upon the ring size: The order of ease of ring opening was spiroorthocarbonate consisting of two six-membered rings < spiroorthocarbonate consisting of six- and seven-membered rings < spiroorthocarbonate consisting of two seven-membered rings. This result appeared to correspond to the order of ring strain. The degree of ring opening increased as polymerization temperature rose.

Introduction

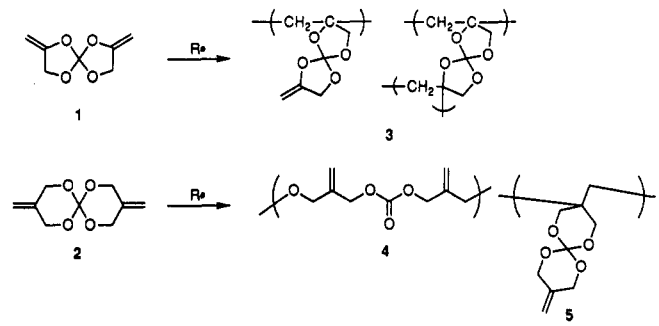
Spiroorthocarbonates (SOCs) are useful monomers which show expansion in volume on cationic polymerization via ring-opening isomerization process.[1-5] SOCs generally polymerize with Lewis acids such as BF_3·OEt_2. In some cases SOCs that can polymerize with radical initiators are quite useful. SOCs bearing *exo*-methylene groups are candidate monomers capable of undergoing ring-opening polymerization not only with cationic initiators but also with radical initiators. Syntheses and radical polymerization of two symmetrical SOCs (**1**[6] and **2**[7]) bearing *exo*-methylene groups have been already reported (Scheme I).

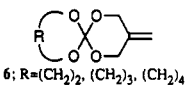
When the polymerization of **1** was carried out in the presence of di-*tert*-butyl peroxide at 130 °C, the obtained polymer **3** was insoluble in any organic solvent.[6] On the contrary, in the polymerization of **2** in the presence of di-*tert*-butyl peroxide in chlorobenzene at 130 °C, a soluble polymer was obtained, the structure of which was a polyether–carbonate with *exo*-methylene groups.[7] In the case of bulk polymerization of **2**, the obtained polymer was not soluble in any organic solvent. Recently, we investigated the radical polymerization of **2** in detail and found that the main structure of the polymer was not **4** but vinyl polymer **5**.[8]

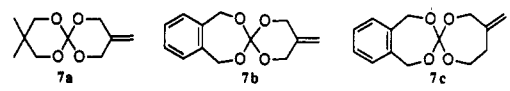
Introduction of an *exo*-methylene group is a useful method for radical ring-opening polymerization of a cyclic monomer. **1** and **2** have two *exo*-methylene groups in their structures, so it is inevitable that they undergo cross-linking reaction. With the aim of designing a monomer which shows expansion in volume on radical polymerization, cross-linking taking place via vinyl polymerization is not desirable because it should cause a substantial shrinkage in volume. Since radical polymerization requires one *exo*-methylene group, unsymmetrical SOCs bearing one *exo*-methylene group have been selected as candidate SOC monomers capable of clean radical ring-opening polymerization.

It has been reported that a few unsymmetrical SOCs **6** bearing *exo*-methylene groups undergo radical ring-opening polymerizations to give polyether–carbonates,[9,10]

Scheme I







but the precise structures of the polymers were not determined. In this paper, radical polymerizations behavior and polymerizability of SOCs **7a–c**, which have an *exo*-methylene group at the β-position of the ether oxygen, as described.

Experimental Section

Measurements. ^1H and ^{13}C NMR spectra of monomers and polymers were recorded on JEOL JNM-PMX-60SI and JNM-GX-500 spectrometers, using tetramethylsilane (TMS) as internal standard in deuteriochloroform or dimethyl sulfoxide at 27 °C. FT-IR spectra were obtained with a JASCO FT/IR-3 at 25 °C. Molecular weight and its distribution (MWD; $\bar{M}_w/\bar{M}_n$) were determined by gel permeation chromatography (GPC) on a Tosoh HPLC CCP & 8000 system with a data processor, equipped with three polystyrene gel columns (TSK gel, G2000H, G2500H, and G3000H), using tetrahydrofuran as an eluent, flow rate 1.0 mL/min, polystyrene calibration, and refractive index (RI) and ultraviolet (UV) detectors.

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Materials. Chlorobenzene was distilled after the removal of water by the usual method and stored over molecular sieves (4A). Initiators benzoyl peroxide (Koso Chemical Co.), di-*tert*-butyl peroxide (Nacalai Tesque, Inc.), and *tert*-butyl hydroperoxide (Nacalai Tesque) were used as received.

Synthesis of Monomer 7a. (a) Dichlorodiphenoxymethane. A mixture of diphenyl carbonate (214 g, 1.00 mol) and phosphorus pentachloride (208 g, 1.00 mol) was stirred at 200 °C for 20 h during which time the phosphorus oxychloride formed was removed by distillation. The resultant reaction mixture was distilled in vacuo. Bp: 178–184 °C (13 mmHg) [lit.[11] bp 183–185 °C (12 mmHg)]. Yield: 215 g (80%). ^{1}H NMR ($CDCl_3$): δ 7.33 (s).

(b) 3-Acetoxy-2-(acetoxymethyl)-1-propene. A mixture of 3-chloro-2-(chloromethyl)-1-propene (516 g, 4.13 mol), sodium acetic (745 g, 9.08 mol), methyltri-*n*-octylammonium chloride, (18.3 g, 45.4 mmol), and toluene (90 mL) was stirred at 130 °C for 6 h. Water (1.5 L) was added and the organic layer separated. The organic layer was washed with water (400 mL) and dried over anhydrous sodium sulfate. The residual material was distilled. Bp: 97–101 °C (13 mmHg) [lit.[12] bp 109–112 °C (20 mmHg)]. Yield: 619 g (87%). ^{1}H NMR ($CDCl_3$): δ 2.10 (s, 6 H), 4.60 (s, 4 H), 5.20 (s, 2 H). IR (neat): 2920, 1740, 1658, 1435, 1362, 1220, 1025, 911, 837, 599 cm^{-1}.

(c) 2-Methyl-1,3-propanediol. To a solution of 3-acetoxy-2-(acetoxymethyl)-1-propene (172 g, 1.00 mol) in methanol (500 mL) was added dropwise a solution of sodium hydroxide (96.0 g, 2.40 mol) in water (1 L) at room temperature. The addition was followed by stirring the mixture at 80 °C for 2 h. After evaporation, a white mass that solidified was washed with 2-propanol (1.5 L), and the mixture was filtered off. The filtrate was evaporated and distilled. Bp: 87–91 °C (0.35 mmHg) [lit.[3] bp 75–76 °C (0.18 mmHg)]. Yield: 51.9 g (59%). ^{1}H NMR (CD_3SOCD_3): δ 3.89 (d, J = 5.6 Hz, 4 H), 4.65 (t, J = 5.6 Hz, 2 H), 4.97 (s, 2 H). IR (neat): 3395, 2873, 1660, 1460, 1209, 1018, 910 cm^{-1}.

(d) Diphenoxy-5-methylene-1,3-dioxane. To a solution of 2-methylene-1,3-propanediol (9.69 g, 110 mmol) and triethylamine (20.2 g, 200 mmol) in dichloromethane (50 mL) was added dropwise a solution of dichlorodiphenoxymethane (26.9 g, 100 mmol) in dichloromethane (50 mL) at room temperature. After the mixture was stirred for 20 h at room temperature, the mixture was washed with water (50 mL × 2). The organic layer was dried over anhydrous sodium sulfate, and the residual material was distilled. Bp: 162–168 °C (0.25 mmHg). Yield: 18.3 g (64%). ^{1}H NMR ($CDCl_3$): δ 4.50–4.65 (m, 4 H), 4.96–5.08 (m, 2 H), 6.90–7.40 (m, 10 H). IR (neat): 3074, 3066, 2986, 2926, 2914, 2872, 1942, 1860, 1782, 1591, 1491, 1162, 1080, 755, 692 cm^{-1}.

(e) 3,3-Dimethyl-9-methylene-1,5,7,11-tetraoxaspiro[5.5]undecane (7a). To a solution of 2,2-diphenoxy-5-methylene-1,3-dioxane (11.4 g, 40.0 mmol) and *p*-toluenesulfonic acid monohydrate (342 mg, 1.80 mmol) in dichloromethane (40 mL was added 2,2-dimethyl-1,3-propanediol (4.17 g, 40.0 mmol) dropwise at room temperature. After stirring for 6 h at room temperature, the mixture was washed with 1 M sodium hydroxide (60 mL × 2). The organic layer was separated and dried over anhydrous sodium sulfate. Evaporation of the organic layer afforded a pale yellow solid. The solid was purified by preparative HPLC (Nihon Bunseki Kogyo), equipped with two polystyrene gel columns (JAIGEL-H1 and JAIGEL-H2), using chloroform as an eluent, flow rate 3.8 mL/min, RI and UV detectors: Yield 1.24 g (40%); purity 88% (estimated by ^{1}H NMR spectrum; impurity was 3,3,9,9-tetramethyl-1,5,7,11-tetraoxaspiro[5.5]-undecane; **7a** was used as the mixture of the product in the radical polymerization). ^{1}H NMR ($CDCl_3$): δ 1.02 (s, 6 H), 3.65 (s, 4 H), 4.37–4.50 (m, 4 H), 4.88–5.03 (m, 2 H); [lit.[10] ^{1}H NMR δ 0.99 (s, 6 H), 3.62 (s, 4 H), 4.36 (br s, 4 H), 4.87 (br s, 2 H)].

Synthesis of Monomer 7b. (a) 1,2-Benzenedimethanol. To a suspension of lithium aluminum hydride (51.8 g, 1.36 mol) in dry ether (1 L) was added dropwise a solution of dimethyl phthalate (194 g, 1.00 mol) in dry ether (200 mL) at room temperature with keeping ether-refluxing. After the addition, the mixture was refluxed for 30 h. Saturated aqueous sodium sulfate (100 mL) was carefully introduced from a dropping funnel until a white mixture was solidified. The resulting white mass was filtered off and washed with THF and ethanol. The combined filtrate was dried over anhydrous sodium sulfate, evaporated, and recrystallized from water. Yield: 60.5 g (44%). Mp: 65–66 °C (lit.[13] mp 65–66.5 °C). ^{1}H NMR ($CDCl_3$): δ 3.93 (s, 2 H), 4.60 (s, 4 H), 7.28 (s, 4 H). IR (KBr): 3250, 2920, 2892, 1038, 1003, 760 cm^{-1}. The title compound is commercially available (from, e.g., Aldrich) too.

(b) Spiro[2,4-benzodioxepine-5′-methylene-3,2′-[1.3]dioxane] (7b). To a solution of 2,2-diphenoxy-5-methylene-1,3-dioxane (14.2 g, 50.0 mmol) and *p*-toluenesulfonic acid monohydrate (572 mg, 3.00 mmol) in dichloromethane (60 mL) was added solid 1,2-benzenedimethanol (6.91 g, 50.0 mmol) in several portions at room temperature. The addition was folloed by stirring for 30 h at room temperature. After that time, the mixture was washed with 1 M sodium hydroxide (60 mL × 2). The organic layer was dried over anhydrous sodium sulfate. Evaporation of the organic layer afforded a pale yellow solid. The solid was recrystallized from *n*-hexane/ethyl acetate/triethylamine (volume ratio 50/50/1) and distilled using a Kugelrohr apparatus. Bp: 140–160 °C (0.15 mmHg). Mp: 114–115 °C. Yield: 6.08 g (52%). ^{1}H NMR ($CDCl_3$): δ 4.36–4.50 (m, 4 H), 4.83–5.05 (m, 6 H), 6.85–7.27 (m, 4 H). IR (KBr): 3061, 3029, 2982, 2936, 2879, 1462, 1376, 1270, 1187, 1101, 1084, 1049, 988, 926, 752, 646 cm^{-1}. High-resolution MS. Calcium for $C_{13}H_{14}O_4$: m/e 234.0892. Found: m/e 234.0891.

Synthesis of Monomer 7c. (a) 11-(Methoxycarbonylmethyl)-11-(methoxycarbonyl)-9,10-dihydro-9,10-ethanoanthracene. A mixture of dimethy itaconate (158 g, 1.00 mol), anthracene (178 g, 1.00 mol), and xylene (1.1 L) was stirred at 150 °C for 60 h. Evaporation of the mixture afforded a pale yellow solid. The solid was recrystallized from chloroform (500 mL), and the mother liquor was precipitated into *n*-hexane (3 L). Precipitated solid was washed with *n*-hexane. Yield: 171 g (53%). Mp: 148–149 °C (lit.[14] mp 151 °C). ^{1}H NMR ($CDCl_3$): δ 1.42 (dd, J = 3.0, 13.8 Hz, 1 H), 1.88 (d, J = 16.0 Hz, 1 H), 2.75 (dd, J = 3.0, 13.8 Hz, 1 H), 2.87 (d, J = 16.0 Hz, 1 H), 3.37 (s, 3 H), 3.48 (s, 3 H), 4.20 (dd, J = 3.0, 3.0 Hz, 1 H), 4.29 (s, 1 H), 6.83–7.30 (m, 8 H). IR (KBr): 3000, 2950, 1735, 1715, 1460, 1435, 1360, 1305, 1190, 1170, 770 cm^{-1}.

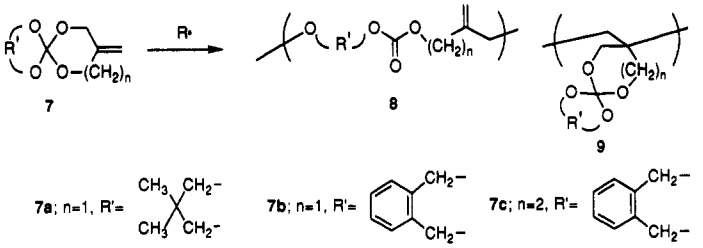
(b) 11-(2-Hydroxyethyl)-11-(hydroxymethyl)-9,10-dihydro-9,10-ethanoanthracene. A solution of 11-(methoxycarbonylmethyl)-11-(methoxycarbonyl)-9,10-dihydro-9,10-ethanoanthracene (154 g, 460 mmol) in dry THF (700 mL) was added dropwise to a suspension of lithium aluminum hydride (30.0 g, 750 mmol) in dry THF (600 mL) at room temperature. After the addition, the mixture was refluxed for 3 h. Saturated aqueous sodium sulfate (150 mL) was carefully introduced from a dropping funnel until a white mixture was solidified. The resulting white mass was filtered off and washed with THF. The combined filtrate was dried over anhydrous sodium sulfate and evaporated. Crude product yield: 125 g (97%). Mp: 132–133 °C. ^{1}H NMR ($CDCl_3$): δ 1.10–1.50 (m, 4 H), 2.80 (d, J = 12.0 Hz, 1 H), 3.17 (d, J = 12.0 Hz, 1 H), 3.40–3.90 (m, 4 H), 4.18 (dd, J = 3.0, 3.0 Hz, 1 H), 4.27 (s, 1 H), 6.90–7.50 (m, 8 H). IR (KBr): 3250, 3005, 2910, 1460, 1050, 740 cm^{-1}.

(c) 2-Methylene-1,4-butanediol. Into a heated (330 °C) round-bottom flask equipped with a distillation apparatus was added dropwise melted (180 °C) 11-(2-hydroxyethyl)-11-(hydroxymethyl)-9,10-dihydro-9,10-ethanoanthracene (76.1 g, 272 mmol) under a nitrogen stream. Distilled mixture was collected, washed with methanol (400 mL), and filtered off. The filtrate was evaporated and distilled. Bp: 103–124 °C (2.0 mmHg) [lit.[15] 62–63 °C (0.01 mmHg)]. Yield: 19.6 g (71%). ^{1}H NMR ($CDCl_3$): δ 2.33 (t, J = 6.0 Hz, 2 H), 3.50 (s, 2 H), 3.72 (t, J = 6.0 Hz, 2 H), 4.05 (s, 2 H), 4.95 (s, 1 H), 5.12 (s, 1 H). IR (neat): 3300, 2860, 1655, 1430, 1040, 900, 862 cm^{-1}.

(d) 2,2-Diphenoxy-5-methylene-1,3-dioxepane. 2,2-Diphenoxy-5-methylene-1,3-dioxepane was prepared from 2-methylene-1,4-butanediol (10.2 g, 100 mmol) and dichlorodiphenoxymethane (26.9 g, 100 mmol), similarly to 2,2-diphenoxy-5-methylene-1,3-dioxane. Bp: 158–161 °C (0.3 mmHg). Yield: 20.4 g (68%). ^{1}H NMR ($CDCl_3$): δ 2.53 (t, J = 5.0 Hz, 2 H), 4.03 (t, J = 5.0 Hz, 2 H), 4.38 (s, 2 H), 5.00 (s, 2 H), 6.87–7.22 (m, 10 H). IR (neat): 3070, 2950, 2900, 1940, 1855, 1780, 1725, 1650, 1590, 1492, 1150, 910, 690 cm^{-1}.

(e) Spiro[1,5-dihydro-5′-methylene-2,4-benzodioxepine-3,2′-[1.3]dioxepane] (7c). **7c** was prepared from 2,2-diphenoxy-

Table I
Radical Polymerization of 7a–c



run	monomer	init[a]	temp (°C)	solv[b] (mL)	time (h)	conv[c] (%)	yield[d] (%) insol	yield[d] (%) sol	$\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$)[e] insol	$\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$)[e] sol	degree of ring opening[f]
1	7a	BPO	80		20	21	1	20	3100 (1.3)	1700 (1.3)	0
2	7a	DTBP	130		20	64	16	36	2800 (1.4)	1300 (1.4)	4
3	7a	DTBP	130	CB (0.8)	20	20	0	17		1400 (1.5)	4[g]
4	7a	TBHP	180		20	86	41	16	2000 (2.2)	600 (1.3)	24
5	7b	BPO	80	CB (1.7)	20	0	0	0			
6	7b	DTBP	130		20	71	48		1400 (1.4)		8
7	7b	DTBP	130	CB (1.7)	20	14	5		1300 (1.3)		9
8	7b	TBHP	180		20	98	90		1500 (1.8)		55
9	7c	DTBP	130		20	69	52		1100 (2.0)	400 (1.3)	34
10	7c	DTBP	130	CB (2.6)	20	13	9	2	900 (1.4)	600 (1.2)	21
11	7c	TBHP	160		20	100	71[h]	0			
12	7c	TBHP	180		20	100	63[h]	0			
13	7c	TBHP	180		4	25	20	5	1400 (2.0)	40 (1.6)	86

[a] BPO, benzoyl peroxide; DTBP, di-*tert*-butyl peroxide; TBHP, *tert*-butyl hydroperoxide. [b] CB, chlorobenzene. [c] Estimated by GC. [d] *n*-Hexane-insoluble and soluble part. [e] Estimated by GPC (based on polystyrene). [f] Estimated by ^{1}H NMR and IR for *n*-hexane-insoluble part. [g] *n*-Hexane-soluble part. [h] Cross-linked polymer was obtained.

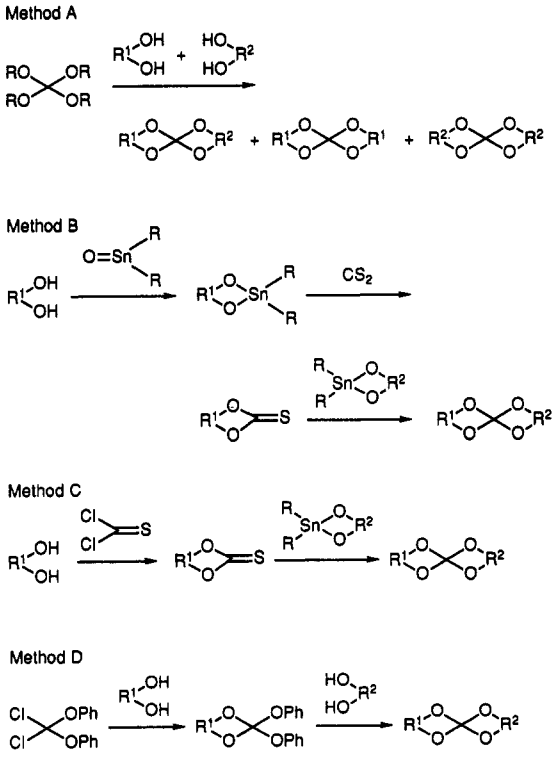
5-methylene-1,3-dioxepane (10.4 g, 35.0 mmol) and 1,2-benzenedimethanol (4.84 g, 35.0 mmol), similarly to **7b**. Mp: 114–115 °C. Yield: 4.73 g (55%). ^{1}H NMR ($CDCl_3$): δ 2.48 (t, J = 4.8 Hz, 2 H), 3.90 (t, J = 4.8 Hz, 2 H), 4.25 (s, 2 H), 4.95 (s, 6 H), 6.83–7.40 (m, 4 H). IR (KBr): 3050, 2950, 2875, 1652, 1145, 1130, 1096, 742 cm^{-1}. Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.53; H, 6.45. MS: *m/e* (relative intensity) 248 (M, 10.0%).

Polymerization of 7a–c. All polymerizations were carried out in sealed tubes. Amounts of initiators and solvent are shown in Table I as well as polymerization conditions. To a solid monomer (1.0 mmol) in a tube were introduced an initiator and, if necessary, subsequently a dry solvent. The tube was degassed, sealed off, and heated at a set temperature. The resulting mixture was diluted with dichloromethane (2 mL) and precipitated into *n*-hexane (50 mL). After centrifuging, the solvent was decanted, to isolate the insoluble part. The soluble part was isolated by evaporation of the solvent to afford the monomer and low molecular weight polymer.

Results and Discussion

Synthesis of Monomer 7a–c. A few methods are conceivable for synthses of unsymmetrical SOCs (Scheme II). The first method involves transesterification using orthocarbonate which reacts with two different diols in the presence of an acid catalyst such as *p*-toluenesulfonic acid (method A).[16,17] The main disadvantage of this method comes from inevitable formation of symmetrical SOCs and difficult separation of unsymmetrical SOC. The second method consists of reactions of organotin compounds (method B). In this method, preparation of a cyclic tin compound from diol and an alkyltin compound is followed by preparation of thionocarbonate by reaction with carbon disulfide. Reaction of the thionocarbonate with another cyclic tin compound affords unsymmetrical SOC.[18,19] Since this procedure requires many steps, cyclic tin compounds are very unstable, and organotin compounds are highly toxic, this method is not recommended. In method C, thionocarbonate is prepared from diol and thiophosgene in one step.[20] However, thiophosgene is highly toxic and prohibited to transport. Thus, none of the above three methods seems to be suitable.

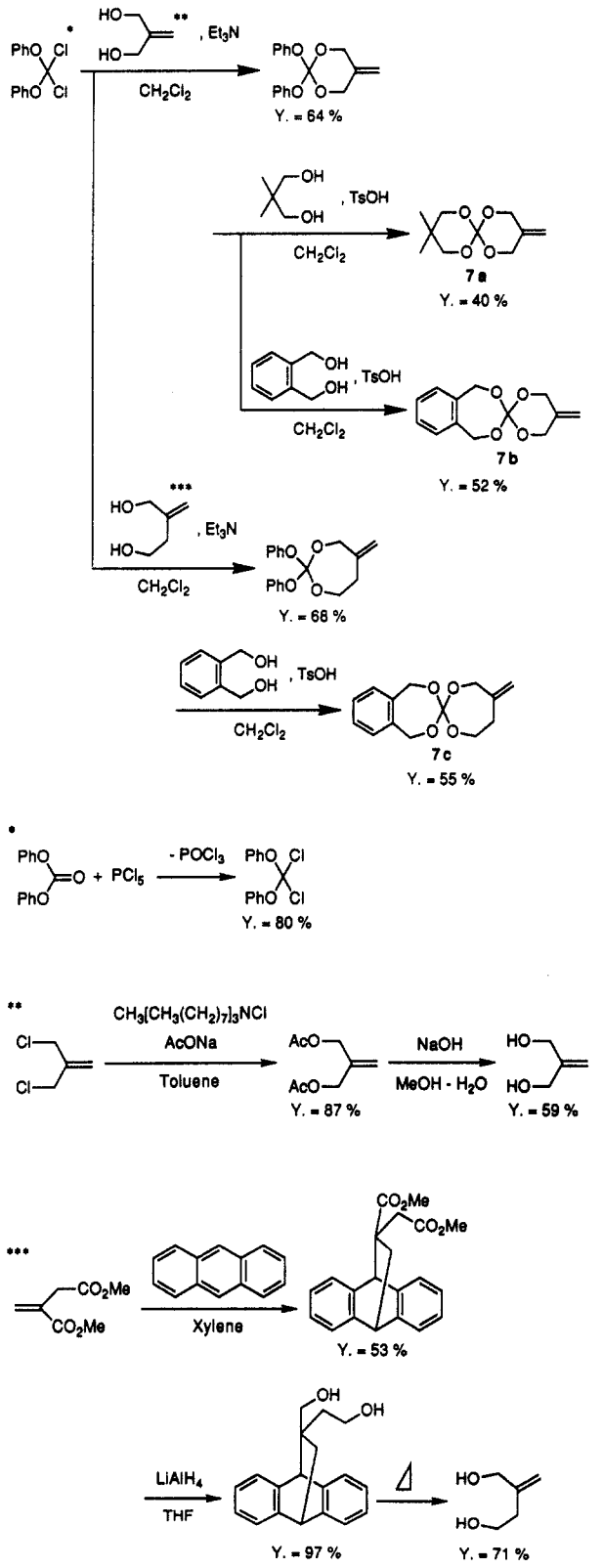
Scheme II



In this work, we adopted a recently reported method (method D) using reaction of dichlorodiphenoxymethane[21] with two different diols as a suitable route for the preparation of unsymmetrical SOCs (Scheme III).

7a and **7b** were prepared by the reaction of 2,2-diphenoxy-5-methylene-1,3-dioxane with 2,2-dimethyl-1,3-propanediol and 1,2-benzenedimethanol, respectively. 2,2-Diphenoxy-5-methylene-1,3-dioxane was prepared by the reaction of dichlorodiphenoxymethane and 2-methylene-1,3-propanediol. Dichlorodiphenoxymethane was prepared from diphenyl carbonate and phosphorus pentachloride, and the diol was prepared from 3-chloro-2-

Scheme III

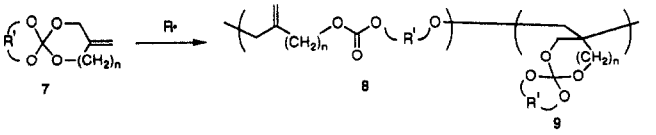


(chloromethyl)-1-propene in two steps. **7c** was prepared from dichlorodiphenoxymethane by successive reactions with 1,2-benzenedimethanol and 2-methylene-1,4-butanediol, which was prepared by the lithium aluminum hydride reduction of the Diels–Alder adduct of dimethyl itaconate and anthracene, followed by retro-Diels–Alder reaction. Direct reduction of dimethyl itaconate was reported to give the desired diol in very low yield (20%) because of polymerization of dimethyl itaconate.[15] **SOCs 7b and 7c** were prepared in satisfactory yields; however, the yield of **7a** was slightly lower than those of **7b and 7c**, because of unusual formation of symmetrical SOCs. This probably comes from low nucleophlicity of 2,2-dimethyl-1,3-propanediol due to steric hindrance of the alkyl group.

Radical Polymerization of SOCs. Polymerization of the SOCs was carried out with benzoyl peroxide, di-*tert*-butyl peroxide, or *tert*-butyl hydroperoxide as radical initiator. Results obtained are summarized in Table I.

Conversion of the monomers increased as the polymerization temperature rose in bulk polymerization. The conversion in solution polymerization was lower than in bulk polymerization. The monomers **7a–c** showed nearly the same conversion under the same conditions (runs 2, 6, and 9 and runs 4, 8, and 12 in Table I). White powdery polymers were obtained by the polymerization at 80 and 130 °C. Pale yellow sticky polymers were obtained at 160 and 180 °C. Yields of the polymers are determined for both *n*-hexane-insoluble and soluble parts. The GPC of these polymers showed single modal curves except for the polymers obtained in the experiments of runs 11 and 12, for which the obtained polymers were insoluble in any organic solvent.

^{1}H NMR, ^{13}C NMR, and IR spectra of the polymers obtained at 180 °C for **7a**, **7b**, and **7c** are shown in Figures 1–3, respectively. These polymers showed similar characteristics in these spectra. Carbonyl absorptions around 1750 cm^{-1} in the IR spectra and signals at 152–155 ppm in the ^{13}C NMR spectra suggest the presence of a linear carbonate structure such as **8** in the polymer. Relatively low intensity of carbonate carbonyl absorption in the IR spectra and the presence of both a broad peak at 1–2 ppm in the ^{1}H NMR spectra and a broad peak at 30–40 ppm in the ^{13}C NMR spectra probably indicate contamination of the vinyl polymerization unit. The percentage of the double ring-opening polymerization unit **8** in the polymer (degree of ring-opening) was estimated by the ^{1}H NMR spectra. In the case of poly(**7a**), ratios of peak b for the vinyl polymerization unit **9a** and peak f for ring-opening polymerization unit **8a** were used for this estimation (Figure 1). In the case of poly(**7b**), the ratio of peak a for the vinyl polymerization unit and peak g for the sum of the two units was used. In the case of poly(**7c**), the ratio of peak a for the vinyl polymerization unit and peak b for the ring-opened unit was used. In some cases, degree of ring opening was estimated from IR absorption ratio at 2870 cm^{-1} for ν_{sCH2} and 1750 cm^{-1} at $\nu_{C=O}$ unit for comparison with that estimated by ^{1}H NMR. [One of the referees commented on the propriety of the estimation method of the degree of ring opening. In this paper, the unit ratio is estimated from the ^{1}H NMR spectrum of each polymer by supposing that the polymer consists only of a mixture of the homopolymers of the two units (**8** and **9**). However, the referee pointed out that the following combination of the two units (below) is possible and might



cause overestimation of the degree of ring opening, according to the estimation method described in this paper. His comment is acceptable, but taking the sequenc of the two units into consideration, it should be impossible to estimate the ratio, because the ratio of head–head, head–tail, and tail–tail structures of the segments cannot be determined. We have tried to estimate using another ^{1}H NMR signal. In the case of poly(**7a**), the degree of ring opening estimated by the ratio of peak a for the sum of the two units to peak f for the ring-opening unit (Figure

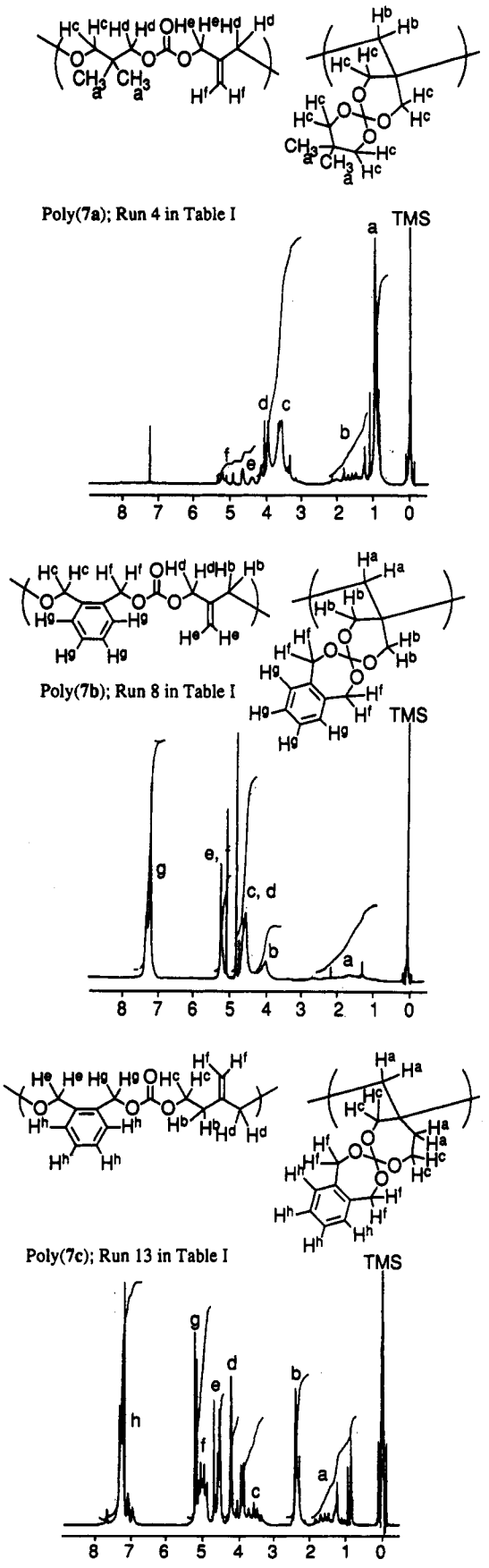


Figure 1. ^{1}H NMR spectra of poly(7a) (run 4 in Table I), poly(7b) (run 8 in Table I), and poly(7c) (run 13 in Table I) (solvent, $CDCl_3$; 500 MHz).

1) was nearly the same (22%) as that estimated by the method described in the text of this paper (24%). This was also the case for poly(7b) or poly(7c). Therefore, the error caused by the estimation method of the unit ratio of the poly(7) used in this paper is concluded to be considerably small.] IR absorption at 3500 cm^{-1} was considered to be attributable to hydroxy group. The hydroxy group would be involved in a unit structure like 8′, which can be formed by hydrogen abstraction at the propagating end, although details are not clear from the NMR spectra.

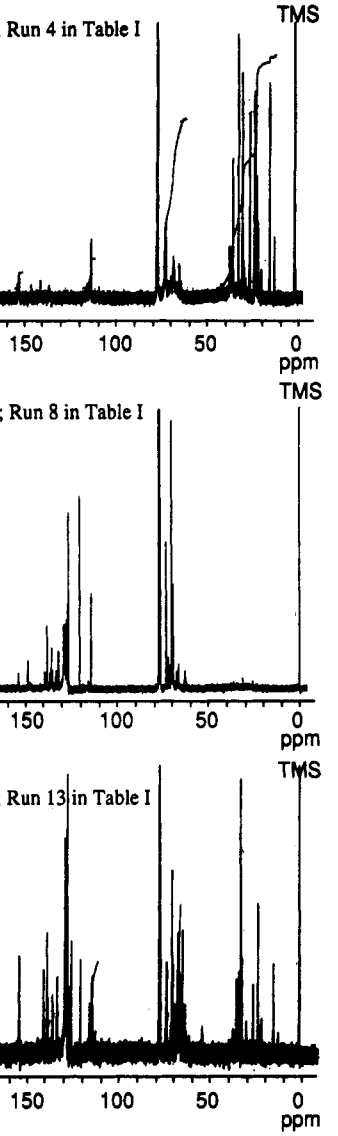
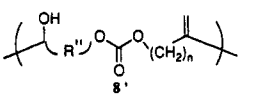


Figure 2. ^{13}C NMR spectra of poly(7a) (run 4 in Table I), poly(7b) (run 8 in Table I), and poly(7c) (run 13 in Table I) (solvent, $CDCl_3$; 125 MHz).



8′

No elimination product could be observed by gas chromatographic analysis of the reaction mixtures after the polymerization in any case. The single modal GPC curve of the polymer shows that the polymer is not a mixture of different polymers but the "copolymer" or the polymer having more than two units. The soluble part consisted of a mixture of monomer and low molecular weight polymer. In some cases, soluble polymer was separated from monomer by preparative HPLC using chloroform as an eluent. Since ^{1}H NMR and IR spectra of the soluble polymer were very similar to those of the insoluble polymer, these polymers were concluded to have similar structures.

In the polymerization of 7c, cross-linked polymer was obtained under the conditions of runs 11 and 12 in Table

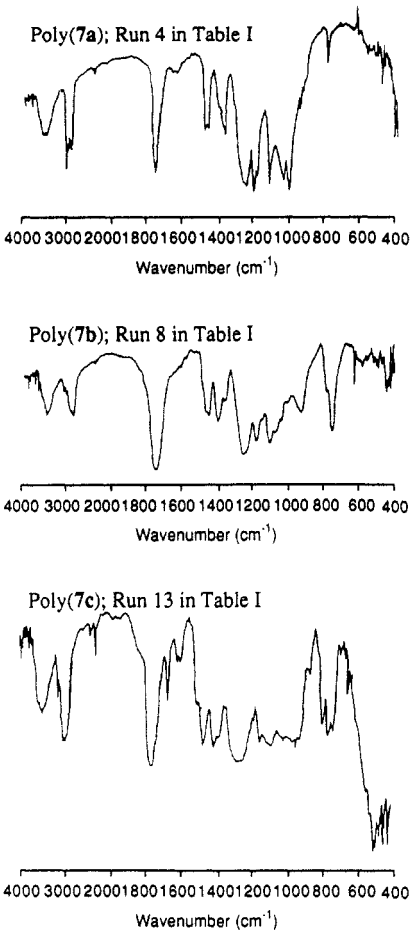


Figure 3. IR spoectra of poly(**7a**) (run 4 in Table I), poly(**7b**) (run 8 in Table I), and poly(**7c**) (run 13 in Table I), and of poly (1) (run 3 in Table I).

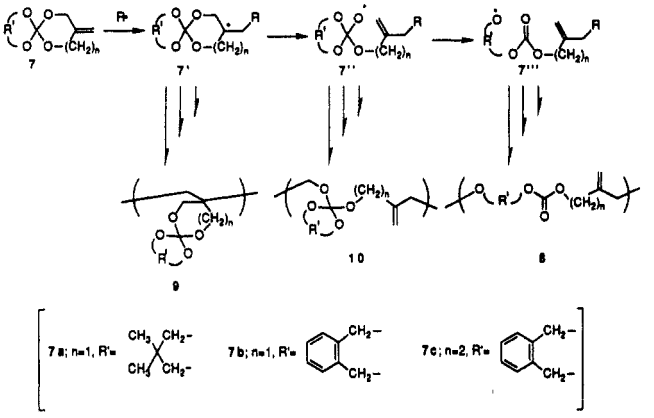
Table II
Enthalpies of Polymerization of Cyclic Acetals[22]

Cyclic Acetal	ΔH (kcal/mol)	Cyclic Acetal	ΔH (kcal/mol)
	-4.0		-3.6
	0		-12.7

I. This cross-linking might occur by the further reaction of the *exo*-methylene group remaining in the initially formed polymer. However, **7c** showed the highest ring-opening polymerizability of all: the order of degree of ring opening was **7a** (consisting of two six-membered rings) < **7b** (consisting of six- and seven-membered rings) < **7c** (consisting of two seven-membered rings). This order of ease of ring opening of **7a–c** appeared to correspond to the order of ring strain.

Enthalpies of polymerization (ΔH) of cyclic acetals are reported in Table II.[22] ΔH values of six- and seven-membered cyclic acetals were 0 and −3.6 kcal/mol, respectively, so the ring strain of the seven-membered ring would be larger than that of the six-membered ing. If a SOC consisting of an eight-membered ring could be synthesized, it must show large ring-opening polymerizability, since eight-membered cyclic acetal shows a larger ΔH (−12.7 kcal/mol) than the seven-membered one. Both conversion of the monomers and degree of ring opening increased as the polymerization temperature rose. Difference of degree of ring opening between bulk and solution

Scheme IV



polymerizations was not observed. This result suggests that the ratio of the alternative pathways of vinyl polymerization and ring-opening polymerization is decided thermodynamically but not kinetically. The reason the kinetic factor was not observed is not clear. If the solution and bulk polymerizations could be carried out at lower temperature, a kinetic factor might be observed. Unfortunately, relatively low radical polymerizability and high melting points (**7b** and **7c**; 114–115 °C) of the SOCs make this examination difficult.

Polymerization Mechanism. The mechanism of the polymerization of **7** is supposed to be as illustrated in Scheme IV. Since a single ring-opening polymerization unit was not observed in the spectra of the polymer, the double ring-opened intermediate 7‴ would be more stable than the single ring-opened intermediate 7″. Therefore, if the first ring opening occurs, the following second ring opening should occur more smoothly. Consequently, the polymer is composed by two units: double ring opening and vinyl polymerization units.

Summary. In this work, we have prepared three unsymmetrical SOCs, two of which are new compounds. In the radical polymerization, ring opening and vinyl polymerizations occurred together. Degree of ring opening in the polymerization depended upon the ring size. The order of ease of ring opening was **7a** < **7b** < **7c**. This order of ease of ring opening appears to correspond to the order of ring strain. Conversion of the monomers and degree of ring opening increased as the polymerization temperature rose.

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Registry Nos. Dichlorodiphenoxymethane, 4885-03-4; diphenyl carbonate, 102-90-0; phosphorus pentachloride, 10026-13-8; phosphorus oxychloride, 10025-87-3; 3-acetoxy-2-(acetoxymethyl)-1-propene, 3775-29-9; 3-chloro-2-(chloromethyl)-1-propene, 1871-57-4; sodium acetate, 127-09-3; methyltri-*n*-octylammonium chloride, 5137-55-3; 2-methylene-1,3-propanediol, 3513-81-3; sodium hydroxide, 1310-73-2; triethylamine, 121-44-8; *p*-toluenesulfonic acid monohydrate, 6192-52-5; 2,2-dimethyl-1,3-propanediol, 126-30-7; **7a**, 96837-21-7; 3,3,9,9-tetramethyl-1,5,7,11-tetraoxaspiro[5.5]undecane, 65849-85-6; 1,2-benzenedimethanol, 612-14-6; lithium aluminum hydride, 16853-85-3; dimethyl phthalate, 131-11-3; 11-(methoxycarbonylmethyl)-11-(methoxycarbonyl)-9,10-dihydro-9,10-ethanoanthracene, 53252-86-1; dimethyl itaconate, 617-52-7; anthracene, 120-12-7; 11-(2-hydroxyethyl)-11-(hydroxymethyl)-9,10-dihydro-9,10-ethanoanthracene, 53252-86-1 [known as 11-(2-α,α-d_2-hydroxyethyl)-11-(d_2-hydroxymethyl)-9,10-dihydro-9,10-ethanoanthracene]; 2-methylene-1,4-butanediol, 53252-91-8. Registry nos. supplied by author.