Radical Polymerization of 3,9-Dimethylene-1,5,7,11-tetraoxaspiro[5.5]undecane. Study of the Structure of the Polymer and Mechanism of Polymerization

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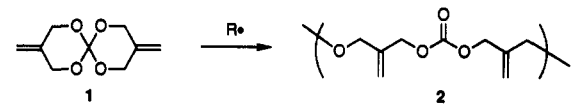
ABSTRACT: Radical polymerization of 3,9-dimethylene-1,5,7,11-tetraoxaspiro[5.5]undecane (1) was investigated. No polymer was obtained by polymerization with AIBN at 60 °C or BPO at 80 °C in chlorobenzene for 20 h. A white powdery polymer which was insoluble in *n*-hexane but soluble in chloroform and THF was obtained by polymerization with DTBP at 130 °C in chlorobenzene. From the detailed ^{1}H NMR, ^{13}C NMR, and IR spectral analyses of the model compounds (3 and 4) of the polymer unit and three fractions obtained by HPLC separation of the polymer as well as the polymer itself, the ratio of the ring-opening polymerization unit in the obtained polymer was about 5% and the main unit was the vinyl polymerization unit (65%). Molecular orbital calculation was carried out to examine the mechanism of the radical ring-opening polymerization of 1. It was suggested that if first single ring opening occurs, successive second ring opening takes place more smoothly. Densities of the obtained polymers were measured, and the volume change on polymerization was evaluated. The volume shrinkage of 1 was 5.9% in solution polymerization and 12.5% in bulk.

Introduction

Monomers that show no shrinkage in volume on polymerization are important in the field of materials such as precision materials, adhesives, and so on. We have reported various monomers and materials based on spiroorthoester (SOE), bicyclo orthoester (BOE), and spiroorthocarbonate (SOC) skeletons, that undergo expansion in volume.[1,2] However, they can polymerize only by cationic catalysts, while many monomers and materials polymerize and cure via a radical process. Since generally vinyl polymerization is accompanied by larger volume shrinkage than ring-opening polymerization, monomers and materials that expand through radical polymerization as the major mode of vinyl polymerization would be especially useful. We have reported several monomers bearing SOE and BOE skeletons which are capable of undergoing radical ring-opening polymerization. However, SOC-based radically polymerizable monomers should be more favorable, because SOC is the monomer showing the biggest volume expansion of all.[2] Synthesis and radical polymerization of SOC having two *exo*-methylene groups (1)[3] (Scheme I) have been communicated, but details of the polymerization such as yield of the polymer, structure of the polymer, and volume change on polymerization are not reported yet. In this paper the detailed study of the radical polymerization of 1 is disclosed.

Scheme I



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Experimental Section

Measurements. ^{1}H and ^{13}C NMR spectra of monomer, model compounds, and soluble polymers were recorded on JEOL JNM-EX-90 and JNM-GX-500 spectrometers operating in the pulsed FT modes, using tetramethylsilane (TMS) as internal standard in deuteriochloroform at 27 °C. The ^{13}C NMR spectrum of cross-linked polymer was recorded on a JEOL JNM-GX-270 spectrometer operating in the CP/MAS mode. FT-IR spectra were obtained with a JASCO FT/IR-3 at 25 °C. The 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, a flow rate 1.0 mL/min, polystyrene calibration, and refractive index (RI) and ultraviolet (UV) detectors. Thermal analyses were performed on Seiko Instruments TG/DTA220 and DSC220C. A 10% weight loss temperature by thermogravimetric analysis (TGA) was determined at a heating rate of 10 °C/min in nitrogen. The glass transition temperature (T_g) by differential scanning calorimetry (DSC) was taken as the inflection point on the trace.

Purification of Poly(1). Purification of poly(1) was carried out with a preparative HPLC (Nihon Bunseki Kogyo LC-908), equipped with two polystyrene gel columns (JAIGEL-H1 and JAIGEL-H2), using chloroform as an eluent, a flow rate 3.8 mL/min, and RI and UV detectors.

Measurement of the Density of Poly(1). The density of poly(1) was measured by the density gradient tubes at 25 °C with a Shibayama Kagaku Seisakusho Model A.

Molecular Orbital Calculations. All computations were done on an Apple Macintosh IIfx with use of MOPAC version 6.00 (QCPE No. 455) revised as version 6.02 for Apple Macintosh.[4] The calculations were carried out by the PM3 program. Geometries were optimized in internal coordinates, and the calculations were terminated when the change in energy on successive iteration was less than 0.000 01 kcal/mol. The energies of 1 and radical intermediates in the ring-opening reaction were calculated by an unrestricted Hartree–Fock (UHF) method. All calculations were done with full optimization of all geometrical variables (bond length, bond angles, and dihedral angles).

Materials. Chlorobenzene was distilled after the removal of water by the usual method and stored over molecular sieves (4A). Initiators 2,2′-azobis(isobutyronitrile) (Tokyo Kasei Kogyo Co.), benzoyl peroxide (Koso Chemical, Co.), and di-*tert*-butyl peroxide (Nacalai Tesque, Inc.) were used as received.

Synthesis of Monomer 1. A mixture of 3-chloro-2-(chloromethyl)-1-propene (516 g, 4.13 mol), sodium acetate (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 phase was separated. The organic layer was washed with water (400 mL) and dried over anhydrous sodium sulfate. After the organic layer was evaporated, the residue was distilled. Yield of 3-acetoxy-2-(acetoxymethyl)-1-propene: 619 g (87%), Bp: 97–101 °C (13 mmHg)

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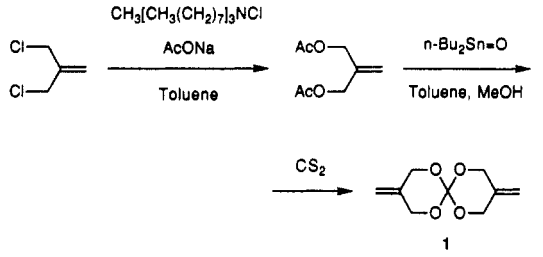
Table I
Radical Polymerization of 1[a]

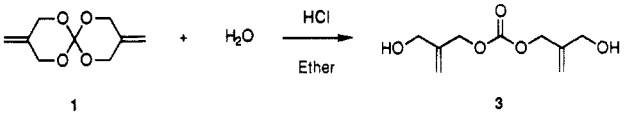
run	init[b]	solv[c]	temp (°C)	conv[d] (%)	yield[e] (%)	T_g[f] (°C)	10% wt loss temp[g] (°C)
1	AIBN	CB	60	0			
2	BPO	CB	80	0			
3	DTBP	CB	130	30	28	71	297
4	DTBP		130	100	*h*	70	

[a] Conditions: monomer, 3 mmol; 20 h. [b] 3 mol % AIBN, 2,2′-azobis(isobutyronitrile); BPO, benzoyl peroxide; DTBP, di-*tert*-butyl peroxide. [c] CB, chlorobenzene, 2.4 mL (1.25 M). [d] Estimated by GC. [e] *n*-Hexane-insoluble polymer. [f] Measured by DSC. [g] Measured by TGA, under N_2. [h] Cross-linked polymer was obtained.

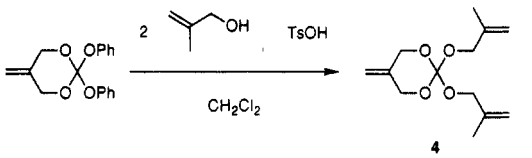
Scheme II



Scheme III



Scheme IV



[lit.[5] bp 109–112 °C (20 mmHg)]. ^{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}.

A mixture of 3-acetoxy-2-(acetoxymethyl)-1-propene (258 g, 1.50 mol), dibutyltin oxide (400 g, 1.61 mol), toluene (500 mL), and methanol (300 mL) was stirred at 65 °C for 0.5 h. After stirring, a mixture of methyl acetate, methanol, water, and toluene was distilled off. Carbon disulfide (130 g, 1.71 mol) was gradually added to the reaction mixture at room temperature. After the addition, the mixture was stirred at 80 °C for 5 h and distilled to yield a colorless liquid [135 g, bp 65–94 °C (2 mmHg)]. Ether (300 mL) and a 1 M sodium hydroxide solution (300 mL) were added to the obtained product, and the resulting mixture was stirred at room temperature for 1 h. The organic layer was separated and dried over anhydrous sodium sulfate. Evaporation of the mixture afforded a white solid (89 g). A portion of the solid (10 g) was recrystallized from *n*-hexane/ethyl acetate/triethylamine (volume ratio 100/10/1). The recrystallized solid was distilled from calcium hydride. Yield: 4.8 g (31%). Mp: 81–82 °C (lit.[6] mp 82 °C). ^{1}H NMR ($CDCl_3$): δ 4.44–4.47 (m, 8 H), 4.92–4.98 (m, 4 H). ^{13}C NMR ($CDCl_3$): δ 65.63, 109.18, 116.18, 138.31. IR (KBr): 2960, 1460, 1362, 1218, 1197, 1003 cm^{-1}.

Synthesis of Bis[2-(hydroxymethyl)-2-propenyl] Carbonate (3). To a solution of 1 (580 mg, 3.15 mmol) and water (0.30 g, 17 mmol) in ether (30 mL) was added dropwise at room temperature 1 M hydrochloric acid (0.32 mL, 0.315 mmol). The addition was followed by stirring for 24 h at room temperature. The mixture was evaporated, and the residue was purified with a preparative HPLC. Yield of 3: 172 mg (54%). ^{1}H NMR ($CDCl_3$): δ 2.72 (s, 2 H), 4.10 (s, 4 H), 4.65 (s, 4 H), 5.17–5.21 (m, 4 H). ^{13}C NMR ($CDCl_3$): δ 63.37, 68.32, 114.99, 142.78, 155.15. IR (neat): 3350, 2920, 2850, 1743, 1655, 1256 cm^{-1}. Anal. Calcd for $C_9H_{14}O_5$: C, 53.46; H, 6.98. Found: C, 53.19; H, 7.11.

Synthesis of 2,2-Bis[(2-methyl-2-propenyl)oxy]-5-methylene-1,3-dioxane (4). To a solution of 2,2-diphenoxy-5-methylene-1,3-dioxane[7] (4.00 g, 14.0 mmol) were added dropwise at 0 °C *p*-toluenesulfonic acid monohydrate (160 mg, 0.84 mmol) dissolved in dichloromethane (40 mL) and 2-methyl-2-propenol (2.03 g, 28.0 mmol). The addition was followed by stirring for 8 h at room temperature. The mixture was washed with a 2 M sodium hydroxide solution (100 mL × 3). The organic layer was separated and dried over anhydrous sodium sulfate. Evaporation of the organic layer afforded a pale yellow liquid (1.59 g). A portion of this liquid (497 mg) was predistilled with a Kugelrohr apparatus [bp 150 °C (3 mmHg)]. The distillate was purified with a preparative HPLC using THF as an eluent (flow rate 3.8 mL/min) and further distilled again with a Kugelrohr apparatus. Yield of 4: 273 mg (26%). ^{1}H NMR ($CDCl_3$): δ 1.77 (s, 6 H), 4.09 (s, 4 H), 4.44 (s, 4 H), 4.87–5.02 (m, 6 H). ^{13}C NMR ($CDCl_3$): δ 19.70, 66.33, 67.11, 109.80, 111.56, 117.59, 137.88, 141.39. IR (neat): 2950, 2850, 1652, 1441, 1260, 1190, 1110, 896 cm^{-1}. Anal. Calcd for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 64.72; H, 8.66.

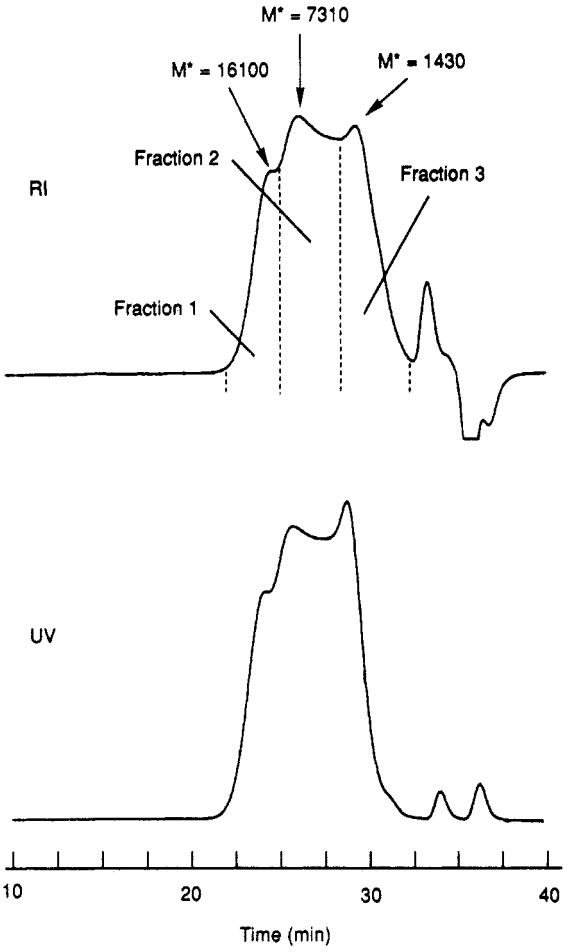


Figure 1. GPC eluent curves of poly(1) by RI and UV detections (run 3 in Table I).

Polymerization of 1. General Procedure. To a solid monomer (1, 3 mmol) in a polymerization tube was introduced an initiator and subsequently a dry solvent, if required. The tube was cooled, degassed, sealed off, and heated at a set temperature for 20 h. The resulting mixture was diluted with dichloromethane (2 mL) and precipitated into *n*-hexane (50 mL). After centrifuging, the solvent was decanted, leaving the insoluble part. ^{1}H NMR, ^{13}C NMR, and IR spectra of the insoluble part were measured. The soluble part as a *n*-hexane solution was concentrated under reduced pressure to afford monomer 1.

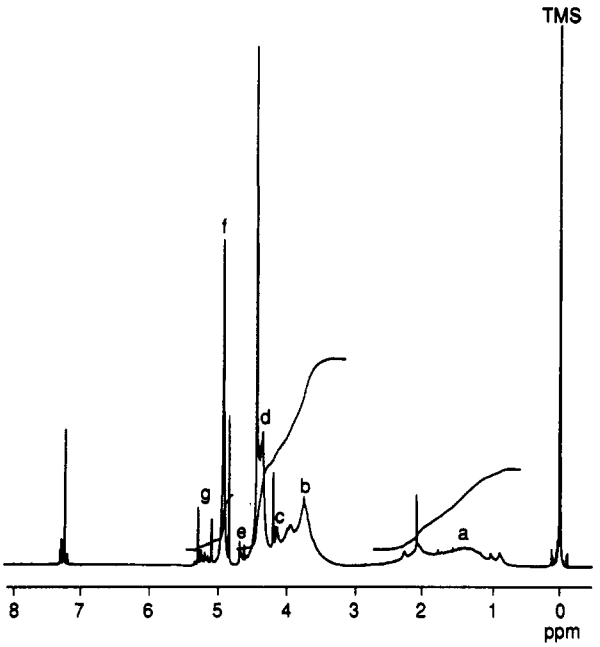


Figure 2. ^{1}H NMR spectrum of poly(1) (run 3 in Table I; solvent, $CDCl_3$; 500 MHz).

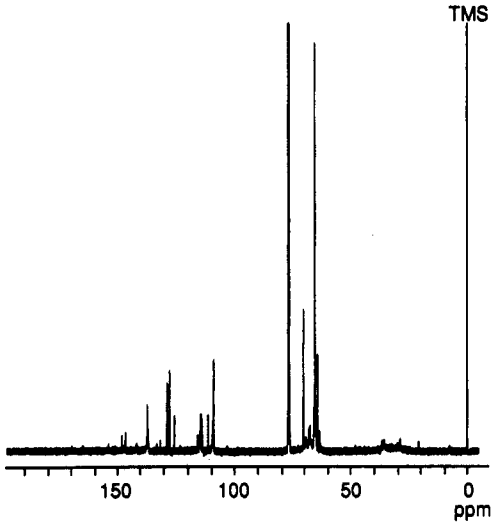


Figure 3. ^{13}C NMR spectrum of poly(1) (run 3 in Table I; solvent, $CDCl_3$; 125 MHz).

Results and Discussion

1. Synthesis of Monomer 1. Monomer 1 was prepared by the combination of sodium acetate and 3-chloro-2-(chloromethyl)-1-propene in the presence of methyltri-*n*-octylammonium chloride followed by reactions with methanol, dibutyltin oxide, and carbon disulfide according to the previously reported method (Scheme II).[5]

2. Syntheses of Model Compounds 3 and 4. Model compound 3 for an analysis of the polymer structure was prepared by the acid-catalyzed hydrolysis of 1 with hydrochloric acid in ether (Scheme III).

Model compound 4 was prepared in a satisfactory yield by the reaction of 2,2-diphenoxy-5-methylene-1,3-dioxane with 2-methyl-2-propenol (Scheme IV). Preparation of 2,2-diphenoxy-5-methylene-1,3-dioxane will be reported in the following paper.

3. Radical Polymerization of 1. Polymerization of 1 was carried out under a variety of different radical conditions. Results and the conditions are summarized in Table I. No polymer was obtained with AIBN at 60 °C and BPO at 80 °C in chlorobenzene for 20 h. A white powdery polymer which was insoluble in *n*-hexane but soluble in chloroform and THF was obtained by polymerization with DTBP at 130 °C in chlorobenzene. The GPC analysis of this polymer showed a multimodal curve with local molecular weight maximas (M^*) corresponding to 16 100, 7310, and 1430 (Figure 1). These results suggest that the radical polymerization of 1 proceeds in multimodes. The possible processes are discussed later with the estimation of the polymer structure.

The glass transition temperature of this polymer was 71 °C, and 10% weight loss temperature under nitrogen was 297 °C. A pale yellow transparent polymer was obtained by bulk polymerization with DTBP at 130 °C, which, however, was insoluble in chloroform, THF, DMSO, DMF, *n*-hexane, and methanol. This polymer was assumed to

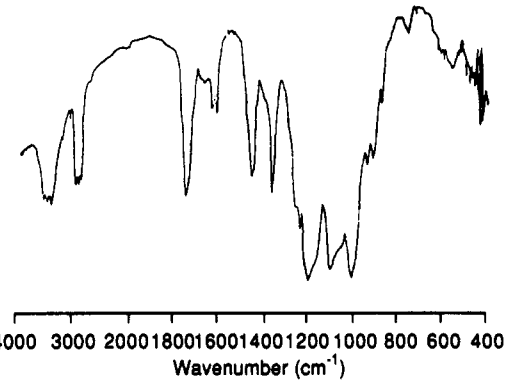


Figure 4. IR spectrum of poly(1) (run 3 in Table I).

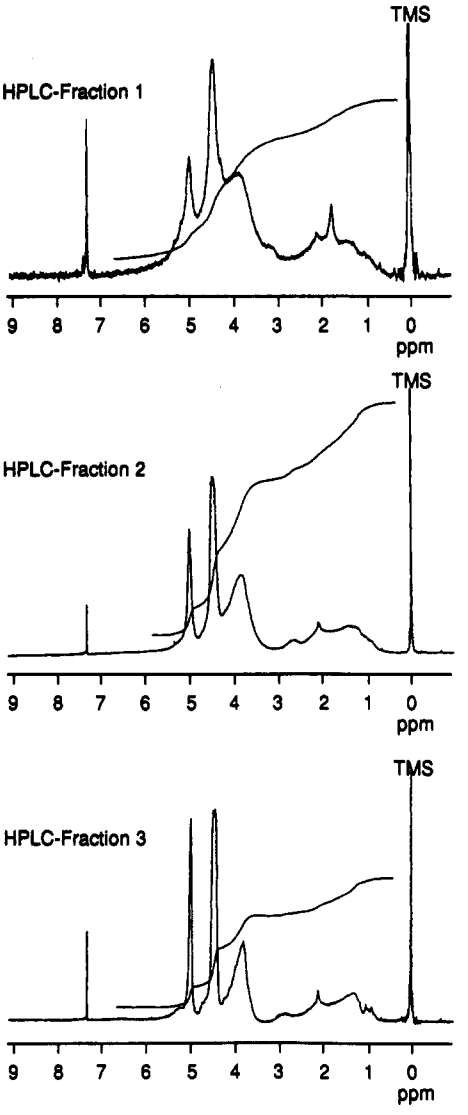


Figure 5. ^{1}H NMR spectrum of HPLC-separated fractions of poly(1) (solvent, $CDCl_3$; 90 MHz).

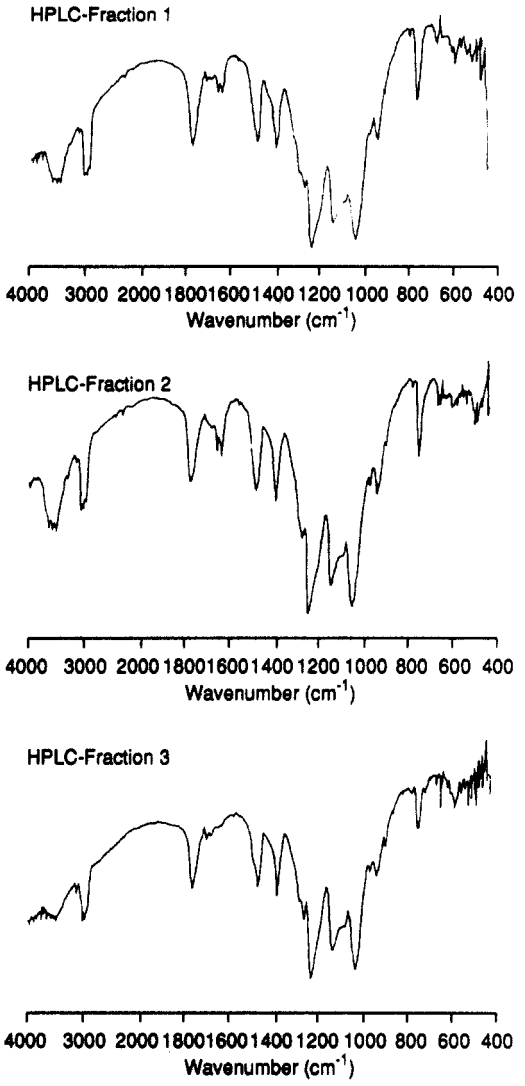


Figure 6. IR spectra of HPLC-separated fractions of poly(1).

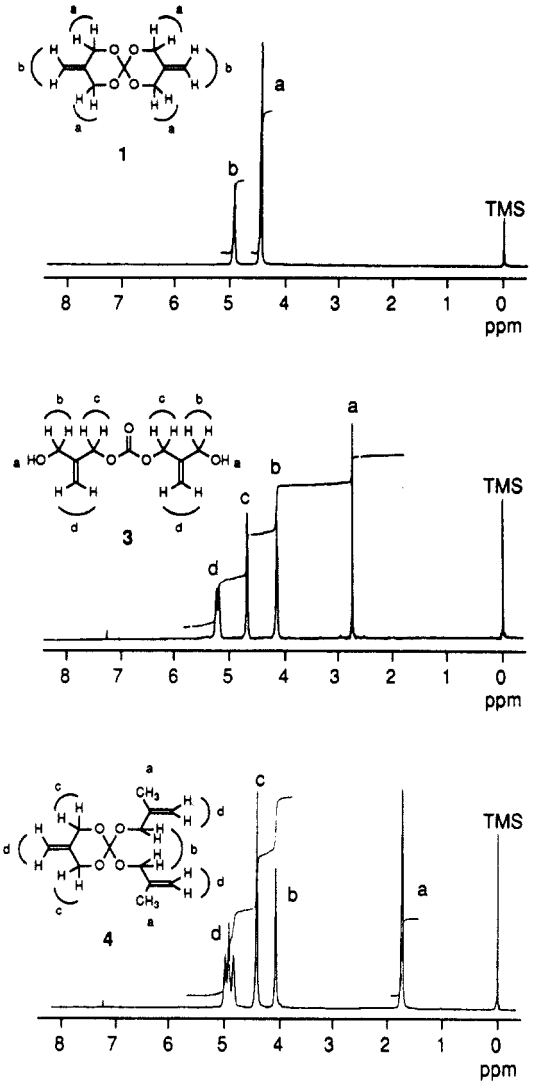


Figure 7. ^{1}H NMR spectra of 1, 3, and 4 (solvent, $CDCl_3$; 90 MHz).

be cross-linked. The glass transition temperature of this polymer was 70 °C.

In the previous paper,[3] the radical polymerization of 1 was reported to afford double-ring-opened polymer 2. In this work, we have found that the radical polymerization of 1 is more complicated and proceeds to afford polymer units other than 2.

The structure of the polymer (run 3 in Table I) was examined by its ^{1}H NMR, ^{13}C NMR, and IR spectra (Figures 2–4). A total of 3 mol % (vs polymer unit) of dihydroxy carbonate 3 was detected in the precipitated polymer, which is thought to be formed by hydrolysis of 1 during the polymerization or work-up process. The polymer was separated to three fractions by preparative HPLC. ^{1}H NMR and IR spectra of these fractions are shown in Figures 5 and 6.

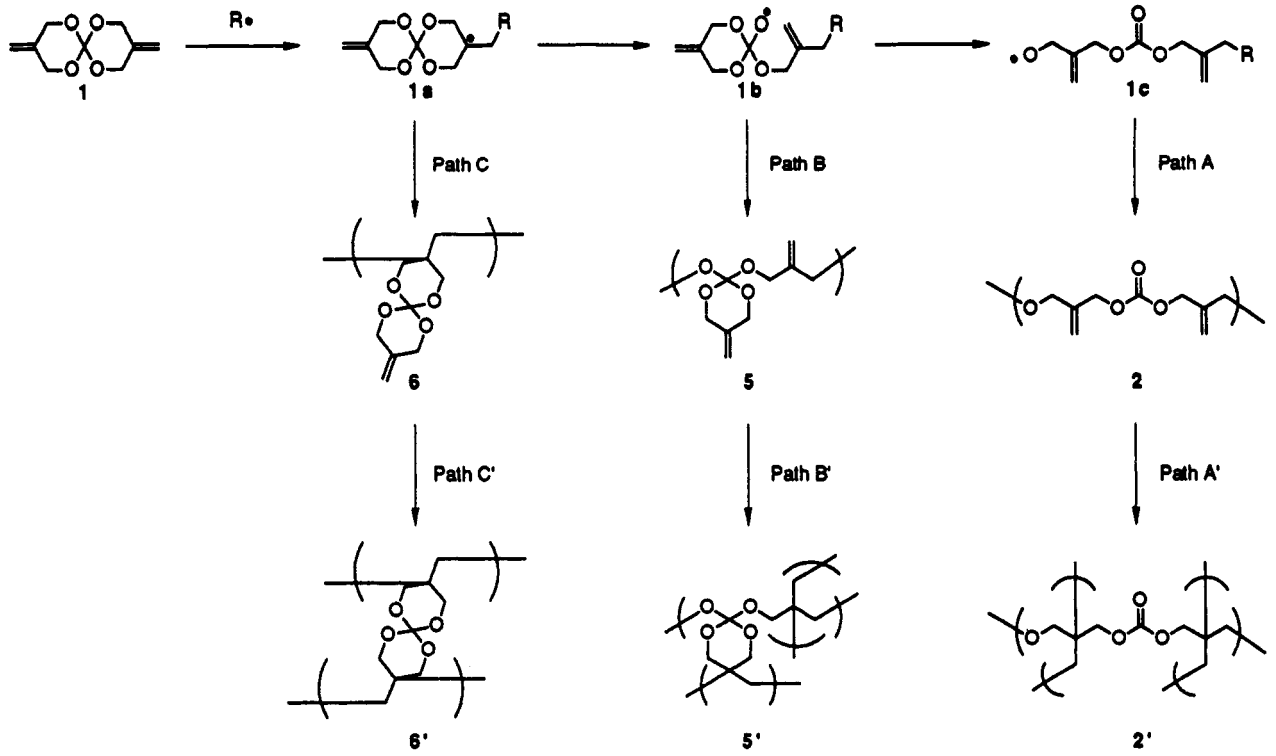
In the ^{1}H NMR spectrum (Figure 2), signals at 4.1–4.2 (4 H, $-CH_2O$), 4.6–4.8 (4 H, $-CH_2OC{=}O$), and 5.1–5.4 ($=CH_2$) ppm expected for doubly-ring-opened polymer 2 were very weak. In addition, both the signal at 155 ppm (linear carbonate group) in the ^{13}C NMR spectrum (Figure 3) and the carbonyl absorption around 1750 cm^{-1} in the IR spectrum (Figure 4) of the obtained polymer were weak. From these spectra, it is obvious that the polymer consists of not only the structure 2 but also some other structures. Possible structures for the polymer would be a set of uncross-linked polymers 2, 5, and 6 formed through paths A, B, and C and a set of cross-linked polymers 2′, 5′, and 6′ formed through paths A′, B′, and C′, as shown in Scheme V.

Path A is the double-ring-opening process to afford the poly(ether carbonate) 2, path B is the single-ring-opening process to give the poly(monocyclic orthocarbonate) 5, and path C is the non-ring-opening (vinyl polymerization) process to yield the poly(SOC) 6. Paths A′, B′, and C′ are the cross-linking processes for the each polymer unit.

The model compounds 3 and 4 correspond to the polymer units 2 or 2′ and 5 or 5′, respectively. A model compound for 6 is thought to be monomer 1. ^{1}H NMR, ^{13}C NMR, and IR spectra of 1, 3, and 4 are shown in Figures 7–9. From these spectra, ^{1}H NMR chemical shifts of the proposed structures 2, 5, 6, 2′, 5′, and 6′ were estimated and are listed in Table II.

From these data, the polymer structure obtained in the solution polymerization was speculated. First of all, small signals were observed at an aromatic region of 7.2–7.4 ppm in the ^{1}H NMR spectrum (Figure 2). The GPC curves by both UV (254 nm) and RI detection were similar (Figure 1). Therefore, incorporation of an aromatic group into the polymer was suggested. The aromatic group was thought to be derived from solvent chlorobenzene, the content of which was estimated to be ca. 3% by ^{1}H NMR. Chlorobenzene might be incorporated in the polymer via radical hydrogen abstraction, although there is no evidence. It is obvious that the ring-opened structure 2 is contained in the polymer, from the carbonyl absorption around 1750 cm^{-1} in the IR spectrum and from the weak signal at 155 ppm in the ^{13}C NMR spectrum, both of which are attributed to the linear carbonate group. However, the

Scheme V



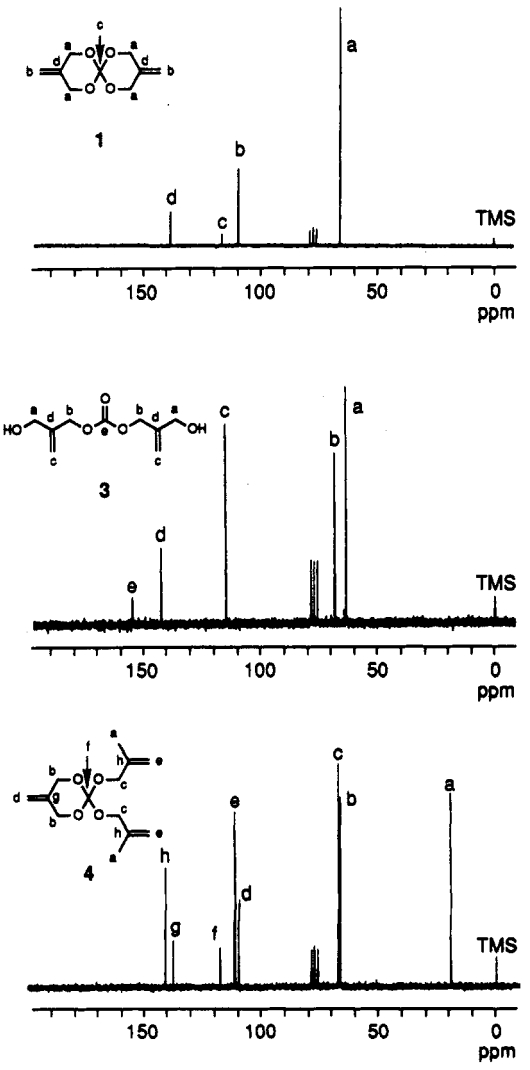


Figure 8. ^{13}C NMR spectra of 1, 3, and 4 (solvent, $CDCl_3$; 22.5 MHz).

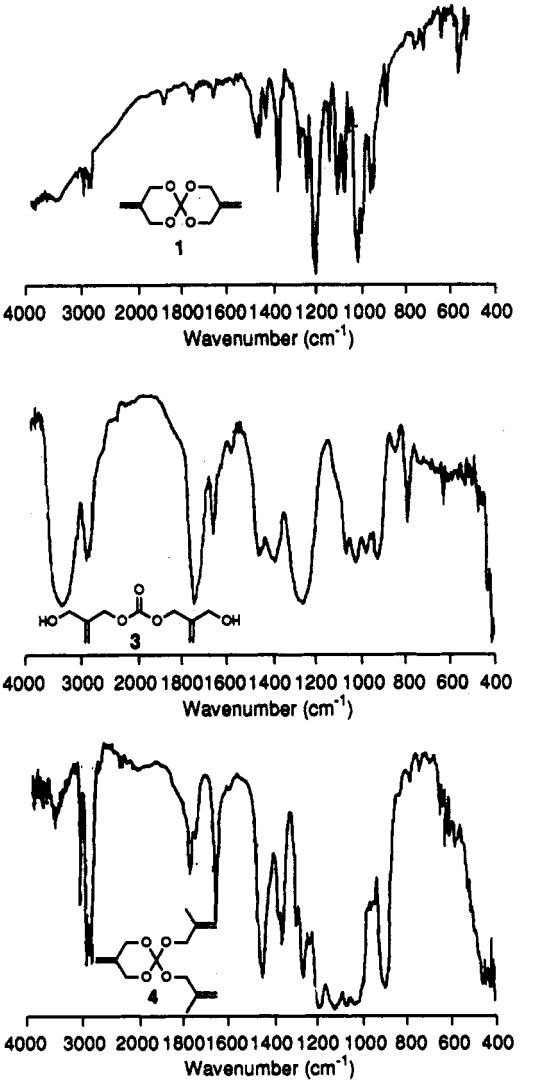
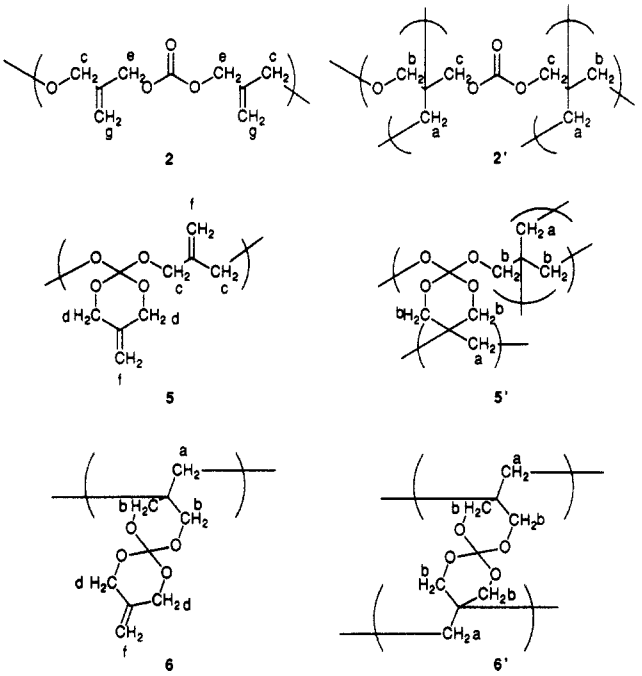


Figure 9. IR spectra of 1, 3, and 4.

main structure of the polymer seems to be 6, because the area ratios of the signals a, b, d, and f in the ^1H NMR spectrum (Figure 2) are larger than others and the ether absorptions at 1200, 1105, and 1005 cm^{-1} in the IR spectrum

Table II
Estimated ^{1}H NMR Chemical Shifts for the Structures 2, 5, 6, 2′, 5′, and 6′



peak	^{1}H NMR chemical shift (ppm)	peak	^{1}H NMR chemical shift (ppm)
a	0.86–2.40	e	4.60–4.75
b	3.30–4.10	f	4.85–5.10
c	4.10–4.20	g	5.10–5.40
d	4.30–4.55		

(Figure 4) are stronger than the carbonyl absorption at 1750 cm^{-1}. The broad signal at 25–40 ppm in the ^{13}C NMR spectrum (Figure 3) was assigned to the main-chain carbons of the vinyl polymerization units. The unit ratio of 6 is assumed to be 65% from the ratio of the ^{1}H NMR signals d and f. No incorporation of structure 5, which would be formed through single-ring-opening polymerization, was confirmed by the peak ratio of d:f = 2:1. The reason why 5 is not contained in the polymer can be that the radical intermediate 1c is more stable than the radical intermediate 1b (Scheme IV). Therefore, if first single ring opening occurs, successive second ring opening takes place more smoothly. Molecular orbital calculation was carried out to consider this point. Details of the calculation are discussed later in this paper.

It is possible that *exo*-methylene groups of 2, 5, and 6 further take part in the polymerization to form 2′, 5′, and 6′. The polymer does not include structure 5′, because structure 5 as the precursor of 5′ is not contained in the polymer. 6′ would be one of the units of the polymer, because the peak ratio of peak a in the ^{1}H NMR spectrum (Figure 2) is larger than that of peak f. The ratio of 6′ in the polymer is assumed as 30% from the peak ratio of a and f. On the contrary, formation of 2′ can be ruled out, because the peak ratio of c is the same as that of e or g in the ^{1}H NMR spectrum (Figure 2). The reason why the *exo*-methylene group of 6 reacted to produce 6′ whereas that of 2 did not is because the *exo*-methylene group of 2 is attached directly to the main chain of the polymer while that of 6 is attached apart from the main chain, so steric hindrance around the *exo*-methylene group of 2 should be larger than that of 6.

In the ^{1}H NMR spectra of the three fractions obtained by the preparative HPLC separation of the polymer (Figure 5), the fraction with the higher molecular weight (fraction 1) has larger ratios of the peaks at 0.5–3.1 and

Scheme VI

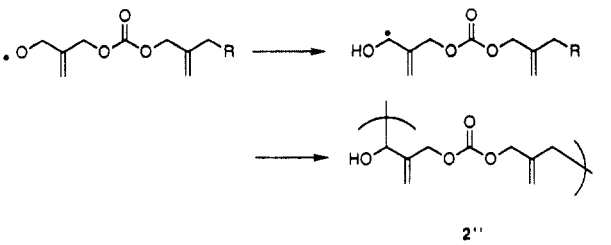


Table III
Structure of Poly(1)[a]

run	polymer	area % in GPC	unit structure (%) 2	6	6′
1	as precipitated[b]		5	65	30
2	fraction 1	19	5	58	37
3	fraction 2	49	3	69	28
4	fraction 3	32	6	79	15

[a] Run 3 in Table I, estimated by ^{1}H NMR. [b] Contained 3% (vs monomer unit) of 3.

3.2–4.6 ppm than those at 4.5 and 5.0 ppm. This means that 6′ is more contained in the polymer with the higher molecular weight than in that with the lower molecular weight. Increase of the molecular weight of the polymer due to further reaction of the *exo*-methylene of 6 can be easily accepted. Since the carbonyl absorption in IR spectra (Figure 6) is observed in any fraction, 2 is contained in all fractions, but the ratio of 2 estimated by the ^{1}H NMR (Figure 5) is still very small (3–6%).

The IR absorption observed at 3500 cm^{-1} would be based on a hydroxy group. A hydroxy group containing unit like 2″ might be formed by abstraction of allylic hydrogen of the polymer, although there is no evidence (Scheme VI).

It is reported that polymer formed in the cationic polymerization of 1 with a boron trifluoride ether complex as an initiator is liquid at room temperature.[6] The polymer formed in the solution polymerization of 1 in this work was solid, of which the glass transition temperature was 71 °C. This can be explained by assuming that the polymer obtained by the radical polymerization has a considerably rigid spirocyclic structure, whereas the polymer obtained by the cationic polymerization does not have such a rigid structure, so the glass transition temperature of the former polymer is higher than that of the latter.

Thus, the structure of the polymer obtained in the polymerization with DTBP at 130 °C in chlorobenzene and those of the three separated fractions can be shown as the sum of the units 2, 6, and 6′ of which ratios are listed in Table III.

In the ^{13}C NMR spectrum of the polymer of 1 collected in the bulk polymerization with DTBP at 130 °C (Figure 10), the ratio of signals at 25–45 ppm to those at 105–120 and 130–140 ppm was larger than that of the polymer obtained by the solution polymerization (Figure 3). This result seems to suggest a higher degree of cross-linking of the former polymer than that of the latter polymer. The IR spectrum of the former polymer (Figure 11) was similar to that of the latter polymer (Figure 4), so the main structure of the polymer obtained in the bulk polymerization should not come from the ring-opening polymerization.

4. Molecular Orbital Calculation of 1 and Radical Intermediates in the Ring-Opening Polymerization of 1. Molecular orbital calculations were carried out to discuss the mechanism of the radical ring-opening polymerization of 1. The calculations were carried out for

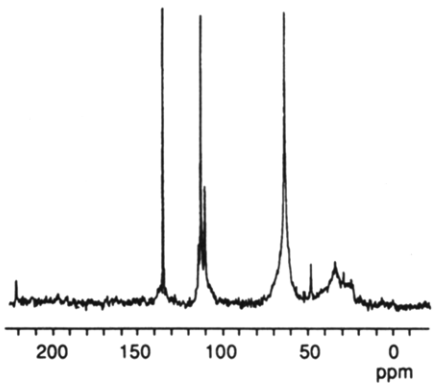


Figure 10. ^{13}C NMR spectrum of poly(1) (run 4 in Table I; CP/MAS, 67.5 MHz).

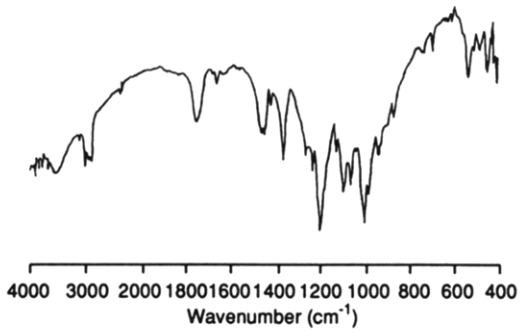


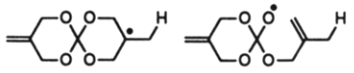
Figure 11. IR spectrum of poly(1) (run 4 in Table I).

Table IV
Calculated Heats of Formation for 1 and Radical Intermediates[a]

compd	heat of formation (kcal/mol)	compd	heat of formation (kcal/mol)
1	−133.30	1c	−104.57
1a	−139.76	1c′	−128.88
1b	−96.61		

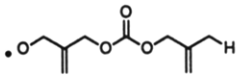
[a] Calculated by the PM3 (UHF) method.

1 and the model compounds of the radical intermediates **1a–c** which can be formed by attack of hydrogen radical at the outside carbon atom of the *exo*-methylene group of 1 followed by ring opening. Intermediate **1c′**, which can be formed from **1c** by 1,2-hydrogen shifts, was also subjected to the calculation.

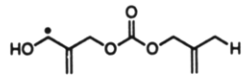


1a

1b



1c



1c′

The heats of formation calculated for 1 and the intermediates are listed in Table IV. From these results, the intermediate **1c** is 7.96 kcal/mol more stable than **1b**. As predicted before, the second-ring-opening process from **1b** to **1c** would occur thermodynamically more smoothly than the first single ring opening from **1a** to **1b**. The optimized geometries of 1 and the intermediates are shown in Figure 12. There is a possibility of transfer of the allylic hydrogen of **1c** to an oxygen radical to form **1c′** for the polymer unit **2″**. The formation energy of **1c′** is lower than that of **1c**, indicating possible formation of **1c′**. However, the amount of ring opening was very small, and

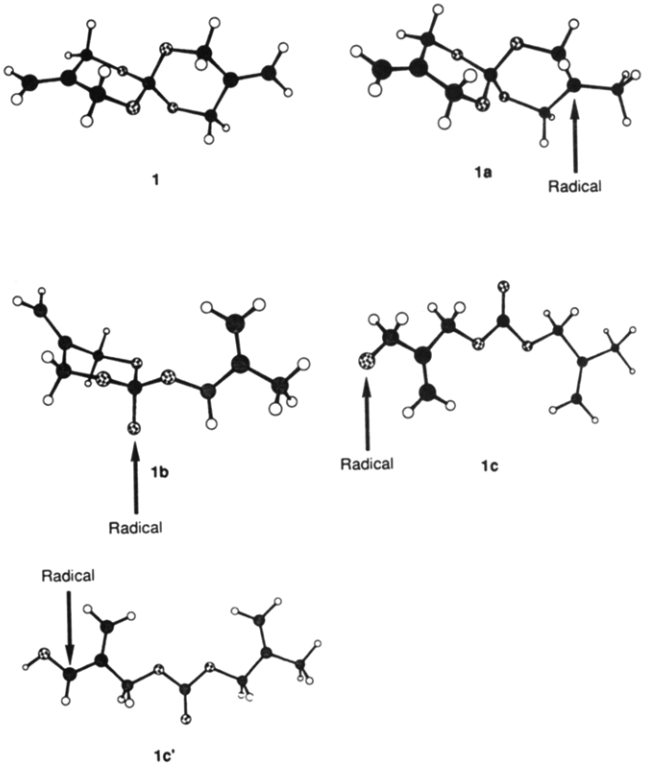


Figure 12. PM3-optimized geometries of 1, **1a–c**, and **1c′**.

Table V
Volume Change on Polymerization of 1[a]

run	polymerization condition: init (mol %)	solv	temp (°C)	time (h)	density of polymer[b] (g/mL)	volume change[c] (%)
1	DTBP (3)	CB	130	20	1.292[d]	−5.90
2	DTBP (3)	none	130	20	1.372[e]	−12.45
3	BF_3OEt_2 (1)	toluene	110	20	1.171[f]	4.02

[a] DTBP, di-*tert*-butyl peroxide; CB, chlorobenzene. [b] Measured by density gradient tubes at 25 °C. [c] [density of 1 (1.220[6]) − density of the polymer]/density of 1 × 100. [d] Run 3 in Table I. [e] Run 4 in Table I. [f] Reported data, measured by dilatometry.[6]

the presence of **2″** could not be observed from the ^1H NMR spectrum.

5. Volume Change on Polymerization of 1. Densities of the polymers obtained by the radical polymerization of 1 were measured by density gradient tubes at 25 °C. The results are summarized in Table V which involves the reported data for those by the cationic polymerization.[6]

Although 1 showed expansion in volume[6] (4.02%) on cationic polymerization, some shrinkage took place on radical polymerization. This behavior is consistent with the polymerization behavior mentioned above. The degree of shrinkage in the bulk polymerization was higher than that in the solution polymerization, because the degree of cross-linking, i.e., degree of vinyl polymerization, of the polymer leading to positive shrinkage was larger in the bulk polymerization than in the solution polymerization of 1. Thus, the volume change also reflects the polymerization behavior.

Summary

In this work, the radical polymerization of 1 was studied in detail. Especially, the structure of the obtained polymer was examined mainly from ^1H NMR, ^{13}C NMR, and IR spectra in comparison with those of the model compounds. The ratio of the ring-opened unit in the obtained polymer by polymerization with DTBP at 130 °C in chlorobenzene

was about 5% and the other unit was the vinyl polymerization unit. Molecular orbital calculations of the radical intermediates as well as the monomer were related with the obtained results. The volume shrinkage on radical polymerization of 1 was 5.9% in solution polymerization and 12.5% in bulk polymerization.

References and Notes

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(7) Preparation of 2,2-diphenoxy-5-methylene-1,3-dioxane will be reported in the following paper.

Registry No. 1, 35143-18-1. Registry no. supplied by author.