Synthesis and Radical Ring-Opening Polymerization of a Vinylcyclopropane Bearing a Cyclic Carbonate Moiety, 1-Vinyl-5,7-dioxaspiro[2.5]octan-6-one

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ABSTRACT: Synthesis and radical polymerization of a vinylcyclopropane bearing a cyclic carbonate moiety, 1-vinyl-5,7-dioxaspiro[2.5]octan-6-one (1), examination of volume change on the polymerization, and thermal analysis of the polymer formed were carried out. 1 was prepared by the reaction of 1,1-bis(hydroxymethyl)-2-vinylcyclopropane with ethyl chloroformate. Radical polymerization of 1 was performed in the presence of an appropriate radical initiator (3 mol % vs 1) at 60–120 °C. Polymers with $\bar{M}_n$ = 15500 and 14100 were obtained by the polymerizations in *N,N*-dimethylformamide (DMF) for 48 h at 60 and 80 °C, respectively. The structure of the polymer was determined to consist of two 1,5-ring-opened units 3 and 3′ and an unknown unit bearing no olefinic moiety. Cross-linked polymers were obtained in the polymerization in bulk and in chlorobenzene at any temperature. Selectivity in the direction of the cleavage of the cyclopropane ring of 1 during the polymerization was well explained by the difference in two-center energies between the two C–C bonds. Volume change during the polymerization of 1 was determined by the density gradient tube method to range from −0.9 to −6.1%, depending on the polymerization conditions. Minimum volume shrinkage was 0.9%, which was attained in the polymerization in DMF at 60 °C where the obtained polymer contained no cross-linked part. The degree of volume shrinkage on the polymerization of 1 increased with increasing polymerization temperature. The glass transition temperature (T_g) of the polymers was in the range 93–110 °C. Some cross-linked polymers did not show their T_gs. The 10% weight loss temperature under nitrogen of the polymers was in the range 276–356 °C, and that of the cross-linked polymers was higher than that of the non-cross-linked polymers.

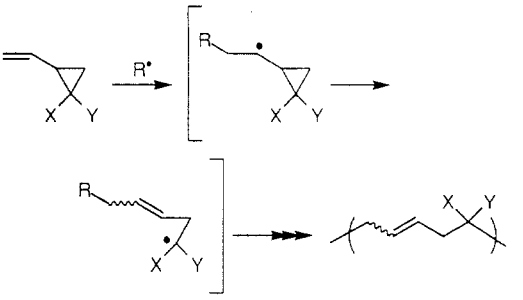
Introduction

Cyclic monomers which undergo ring-opening polymerization are important in the fields of precision materials, adhesives, and so on because they show low shrinkage or sometimes expansion in volume on polymerization.[1] Meanwhile, many monomers and materials polymerize and cure via a radical process. Since generally vinyl polymerization suffers from larger volume shrinkage than ring-opening polymerization, monomers and materials that show low or no shrinkage through radical polymerization are particularly useful. Radical ring-opening polymerization is strongly expected to be a polymerization method capable of solving such problems. Some cyclic monomers bearing vinyl groups such as vinylcyclopropanes,[2] α-cyclopropylstyrenes,[3] spiroorthocarbonates bearing *exo*-methylene groups,[4] and cyclic ketene acetals[5] have been reported to undergo radical ring-opening polymerization. 1,1-Disubstituted 2-vinylcyclopropanes radically polymerize to afford polymers consisting mainly of a 1,5-ring-opened unit (Scheme 1).[2]

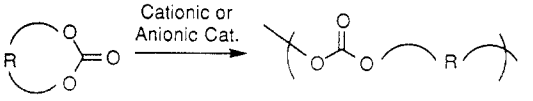
On the other hand, cyclic carbonates have recently been explored and found to be novel expanding monomers that show ca. 10% expansion in volume on ionic ring-opening polymerization (Scheme 2).[6]

The mechanism proposed for volume expansion on polymerization of bicyclic and spirocyclic monomers which have been reported to show volume expansion on polymerization[7] cannot explain this volume change, because cyclic carbonates polymerize only through a single ring-opening process. However, it is suggested that this volume expansion can be accounted for by the difference in strength of the intermolecular interaction between monomers and polymers. That is, strong interaction in monomer and weak interaction in polymer eventually cause volume expansion during polymerization.[8] Recently, we have designed and synthesized a novel cyclic carbonate (1) having a vinylcyclopropane moiety which is bound by a spiro junction to develop a monomer capable of showing volume expansion on radical polymerization. This monomer 1 is expected to cause some volume expansion on polymerization, if 1 polymerizes via anionic ring-opening of the cyclic carbonate moiety to yield a polycarbonate having the vinylcyclopropane moiety, whereas 1 may radically polymerize via ring opening of the vinylcyclopropane moiety to give the corresponding polymer having

Scheme 1



Scheme 2



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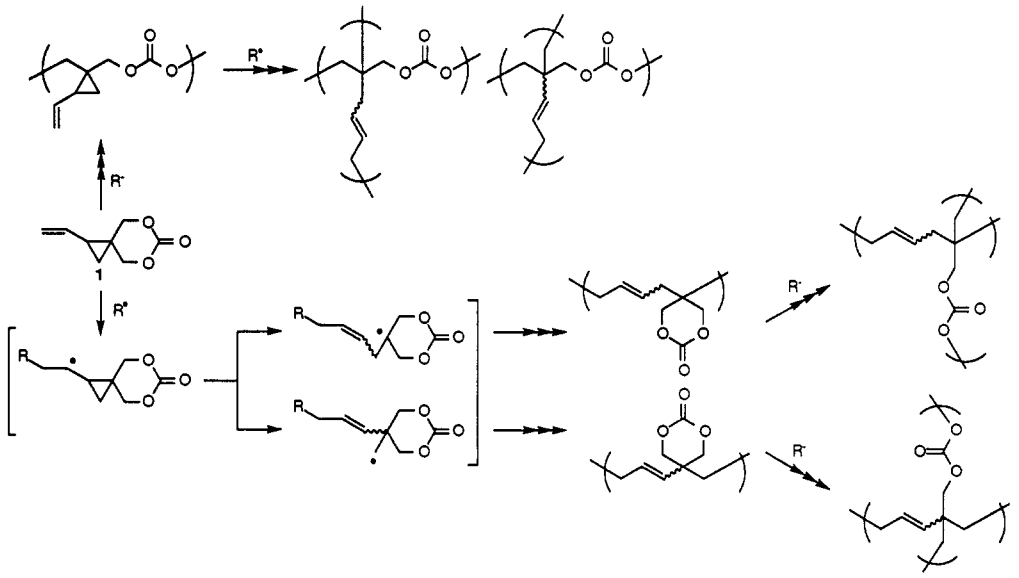
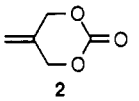
Scheme 3



a cyclic carbonate moiety which can be regarded as an expanding polymer (Scheme 3).

These polymers thus expected to be formed are able to cross-link by further treatment with radical and anionic initiators. Polymerization of 1 with 2,2′-azobis(isobutyronitrile) (AIBN) is also interesting, because the polymerization of 5-methylene-1,3-dioxan-2-one (2) has been reported to give a linear polycarbonate, probably via anionic ring opening of the cyclic carbonate moiety[9] initiated by a keteneimine generated by decomposition of AIBN.[10] In this paper, the synthesis and radical polymerization of 1 are disclosed.



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Experimental Section

Measurements. ^{1}H and ^{13}C NMR spectra of monomers and polymers were recorded on a JEOL JNM EX-90 spectrometer operating in the pulsed FT modes, using tetramethylsilane (TMS) as an internal standard in deuteriochloroform ($CDCl_3$) or hexadeuteriodimethyl sulfoxide (CD_3SOCD_3) at 27 °C. FT-IR spectra were obtained with a JEOL JIR-5300 at 25 °C. Molecular weight ($\bar{M}_w$ and $\bar{M}_n$) and its distribution (MWD; $\bar{M}_w/\bar{M}_n$) were estimated by gel permeation chromatography (GPC) on a Tosoh HPLC HLC-8020 system with a data processor, equipped with three polystyrene gel columns (TSK gel, G2000H, G2500H, and G3000H), using DMF (10 mM lithium bromide solution) as eluent, a flow rate of 1.0 mL/min, polystyrene calibration, and refractive index (RI) and ultraviolet (UV) detectors. Densities of 1 and poly(1) were measured by the density gradient tube method at 25 °C with a Shibayama Scientific Co., Ltd., Model A. Thermal analyses were performed on Seiko Instruments TG/DTA220 and DSC220C. A 10% weight loss temperature was determined by thermogravimetric analysis (TGA) at a heating rate of 10 °C/min under a nitrogen atmosphere. The glass transition temperature (T_g) by differential scanning calorimetry (DSC) was taken as an inflection point on a trace.

Molecular Orbital Calculations. All computations were done on an Apple Macintosh IIci equipped with a 21 MIPS coprocessor board with use of the SONY Tektronix CAChe system version 2.7. Geometries were optimized first with molecular mechanics using the CAChe MM2 program, second with molecular dynamics using CAChe MM2 force field parameters, and finally with MOPAC version 6.00 (QCPE No. 455[11]) revised as version 6.10 for the CAChe system, using the PM3 Hamiltonian. The calculations were carried out by the restricted Hartree–Fock (RHF) method on nonradical compounds and by the unrestricted Hartree–Fock (UHF) method on radical compounds. All calculations were done with full optimization of all geometrical variables (bond lengths, bond angles, and dihedral angles).

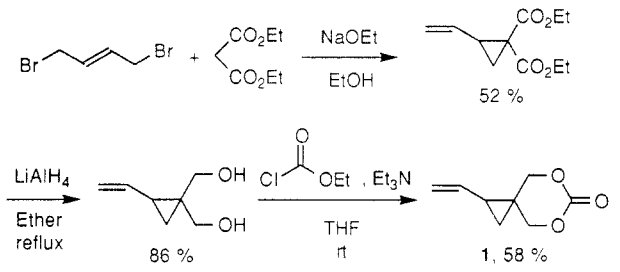
Materials. Radical initiators, 2,2′-azobis(isobutyronitrile) (Tokyo Kasei Kogyo Co.), benzoyl peroxide (Kosoh Chemical Co.), and di-*tert*-butyl peroxide (Nacalai Tesque, Inc.), were used as received. Chlorobenzene and DMF were used after purification by the usual methods.

Synthesis of 1. 1,1-Bis(ethoxycarbonyl)-2-vinylcyclopropane. To a mixture of 1,4-dibromo-2-butene (200 g, 935 mmol) and diethyl malonate (145 g, 935 mmol) in ethanol (500 mL) was added dropwise an ethanol solution of sodium ethoxide at 70 °C, which was prepared from sodium (45.1 g, 1.96 mol) and ethanol (1 L). The reaction mixture was refluxed for 4 h. The resulting mass was filtered off and washed with ethanol. The combined filtrate was evaporated and the residue was distilled under reduced pressure: yield 102 g (52%), bp 94 °C/2 mmHg (lit.[12] bp 69–72 °C/0.5 mmHg). ^{1}H NMR ($CDCl_3$): δ 1.27 (t, J = 7.2 Hz, 6 H), 1.46–1.76 (m, 2 H), 2.39–2.70 (m, 1 H), 4.20 (q, J = 7.2 Hz, 4 H), 5.05–5.19 (m, 1 H), 5.31–5.49 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ 14.10, 14.23, 20.33, 31.07, 35.97, 61.42, 61.60, 118.42, 133.24, 167.41, 169.64. IR (neat): 3075, 2960, 1722, 1638, 1365, 1315, 1264, 1200, 1130 cm^{-1}.

1,1-Bis(hydroxymethyl)-2-vinylcyclopropane. To a suspension of lithium aluminum hydride (5.82 g, 153 mmol) in ether (500 mL) was added dropwise 1,1-bis(ethoxycarbonyl)-2-vinylcyclopropane (25.0 g, 118 mmol). The reaction mixture was refluxed for 4 h. Saturated aqueous sodium sulfate (33 mL) was carefully introduced. The resulting white mass was filtered off and washed with ether. The combined filtrate was evaporated and distilled; yield 13.07 g (86%), bp 97 °C/0.5 mmHg. ^{1}H NMR ($CDCl_3$): δ 0.60–0.93 (m, 2 H), 1.47–1.71 (m, 1 H), 3.42 (s, 2 H), 3.53–3.92 (m, 4 H), 4.99–5.27 (m, 2 H), 5.52–5.91 (m, 1 H). ^{13}C NMR ($CDCl_3$): δ 15.56, 25.30, 30.59, 64.61, 69.30, 115.90, 136.25. IR (neat): 3356, 3077, 2998, 2924, 2878, 1636, 1422, 1190, 1020, 903, 681 cm^{-1}. Anal. Calcd for $C_7H_{12}O_2$: C, 65.60; H, 9.44. Found: C, 65.50; H, 9.51.

1-Vinyl-5,7-dioxaspiro[2.5]octan-6-one (1). To a solution of 1,1-bis(hydroxymethyl)-2-vinylcyclopropane (6.50 g, 50.7 mmol) and ethyl chloroformate (11.01 g, 101 mmol) in THF (254 mmol) was added triethylamine (10.74 g, 106 mmol) dropwise at 0 °C. The reaction mixture was stirred at room temperature for 20 h. Triethylamine hydrochloride generated was filtered off and the filtrate was evaporated. The residual product was purified by column chromatography [solid support, silica gel (300 mesh); eluent, *n*-hexane/ethyl acetate = 1/1 (volume ratio)]. The solid (6.20 g) obtained was recrystallized from ether: yield 4.53 g (58%), mp 50 °C. ^{1}H NMR ($CDCl_3$): δ 0.92–1.22 (m, 2 H), 1.75–1.98 (m, 1 H), 4.06–4.43 (m, 4 H), 5.08–5.31 (m, 2 H), 5.49–5.86 (m, 1 H). ^{13}C NMR ($CDCl_3$): δ 14.21, 20.87, 25.17, 70.82,

Scheme 4



74.76, 118.18, 133.13, 148.97. IR (KBr) 3086, 3017, 2906, 1730, 1638, 1464, 1412, 1178, 1096 cm^{-1}. Anal. Calcd for $C_8H_{10}O_3$: C, 62.33; H, 6.54. Found: C, 62.09; H, 6.62.

Polymerization of 1. General Procedure. To the monomer (1, 2 mmol) in a polymerization tube were introduced a radical initiator and, subsequently, a dry solvent, if required. The tube was cooled, degassed, sealed off, and heated at a set temperature for 48 h. The resulting mixture was diluted with DMF (2 mL) and poured into ether (50 mL) to precipitate a polymer. Centrifugal separation followed by removal of a solvent by decantation afforded the solvent-insoluble polymer. The solvent-soluble part was concentrated under reduced pressure to afford a mixture of monomer 1 and lower molecular weight polymer. The ^1H NMR, ^{13}C NMR, and IR spectra of the solvent-insoluble polymer were measured.

Results and Discussion

1. Synthesis of a Monomer. The monomer (1) was prepared by the reaction of 1,1-bis(hydroxymethyl)-2-vinylcyclopropane, obtained by the reduction of 1,1-bis-(ethoxycarbonyl)-2-vinylcyclopropane by lithium aluminum hydride, with ethyl chloroformate according to the recently developed method.[13] Thus, the reaction of the diol with 2 equiv each of ethyl chloroformate and triethylamine afforded 1 (mp 50 °C) in 58% yield. 1,1-Bis-(ethoxycarbonyl)-2-vinylcyclopropane was prepared by treating a mixture of 1,4-dibromo-2-butene and diethyl malonate with sodium ethoxide in 52% yield (Scheme 4).[12] The structure of 1 was determined by ^1H NMR, ^{13}C NMR, and IR spectra besides elemental analysis. The ^1H NMR, ^{13}C NMR, and IR spectra are shown in Figure 1.

2. Radical Polymerization of 1. Radical polymerization of 1 with typical radical initiators was carried out under several different conditions. The conditions and results are summarized in Table 1.

The conversion of 1 was nearly the same (83–90%) for all conditions except for those with DTBP in bulk at 120 °C (run 3), in which 100% conversion was attained. The molecular weight of the white powdery polymers obtained as the ether-insoluble part in runs 7 and 8 was ca. 15 000. The polymers which were insoluble in any organic solvent were obtained in the polymerizations in bulk and in chlorobenzene in addition to the polymerization in DMF at 120 °C. Precipitation of the polymers was observed in several minutes after the heating started during the polymerization in chlorobenzene. On the other hand, the polymerization mixture was homogeneous even after 48 h in bulk and in DMF. ^1H NMR, ^{13}C NMR, and IR spectra of poly(1) obtained in the polymerization with AIBN in DMF at 60 °C are shown in Figure 2. It was confirmed that no cyclopropane ring structure was incorporated into the polymer by the absence of a signal based on the cyclopropane ring protons which would appear around 1.1 ppm in the ^1H NMR spectrum (Figure 2A). It is clear that unit structure 3′ is contained in addition to 3, which is another polymer unit formed via the 1,5-ring-opening polymerization (Scheme 3) because of the existence of the

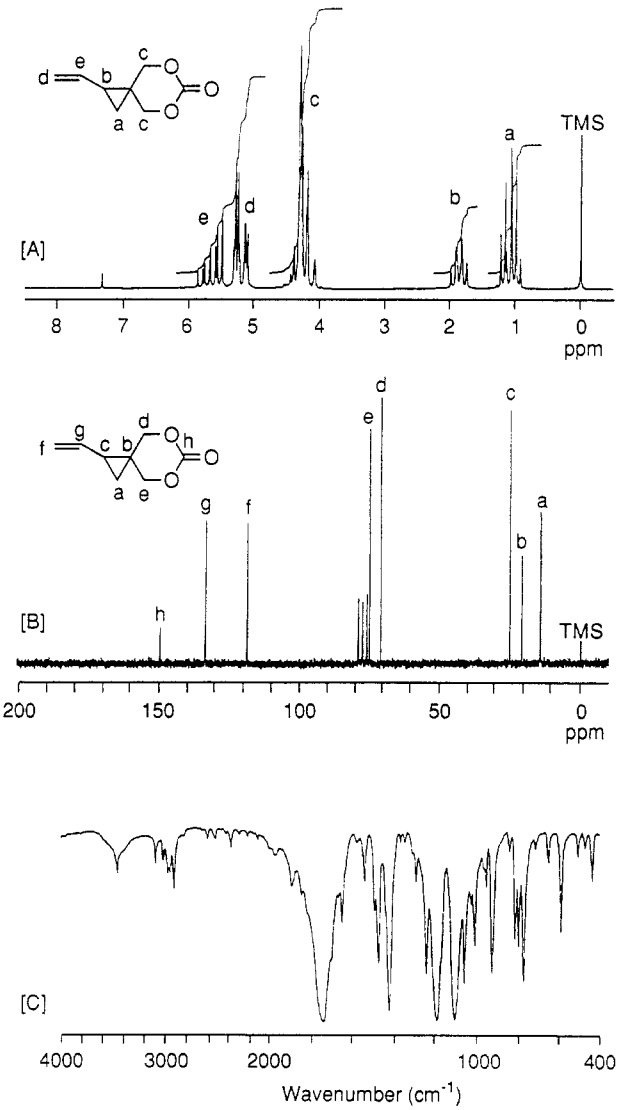
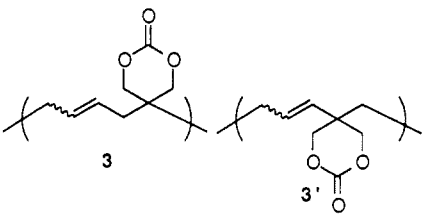


Figure 1. (A) ^1H NMR spectrum of 1 (solvent, $CDCl_3$; 90 MHz). (B) ^{13}C NMR spectrum of 1 (solvent, $CDCl_3$; 22.5 MHz). (C) IR spectrum of 1 (KBr disk).

broad signal a around 1.6 ppm as assigned in Figure 2A.



Since the integration ratio of the signal d based on the olefinic protons of this polymer is smaller than that expected for a polymer that consists only of 3 and 3′, another polymer unit must be present. The single-modal GPC curve of the polymer suggests that the reduction of the ratio of the olefinic structures is not caused by an intermolecular reaction such as grafting or cross-linking as reported in the radical polymerization of spiro-orthocarbonate[4e] but by an intramolecular reaction as reported in the case of 1,1-disubstituted 2-vinylcyclopropanes.[2a,n] The most probable structure seems to be cyclobutane-containing units 4 and/or 4′ formed through ring formation via intramolecular radical addition to double bond, which is similar to that reported in the radical polymerization of vinylcyclopropanes.[2a,n]

Table 1. Radical Polymerization of 1[a]

run	init[b]	solvent[c]	temp (°C)	conv[d] (%)	yield[e] (%)	$\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$)[f]	polymer content[d] 3	3'	other[j]	vol change[g]	T_g[h] (°C)	10% weight loss temp[i]
1	AIBN	none	60	88		*k*				−3.0	*l*	329
2	BPO	none	80	90		*k*				−4.6	*l*	356
3	DTBP	none	120	100		*k*				−6.1	*l*	349
4	AIBN	CB	60	87	79	*k*				−2.1	110	337
5	BPO	CB	80	85	80	*k*				−3.5	*l*	329
6	DTBP	CB	120	87	76	*k*				−5.9	*l*	316
7	AIBN	DMF	60	85	64	15500 (1.32)	42	33	25	−0.9	93	301
8	BPO	DMF	80	83	58	14100 (1.25)	35	31	34	−1.4	110	285
9	DTBP	DMF	120	88	80	*k*				−3.1	*l*	276

[a] Monomer, 2 mmol; polymerization time, 48 h. [b] Initiator, 3 mol %. AIBN = 2,2'-azobis(isobutyronitrile), BPO = benzoyl peroxide, DTBP = di-*tert*-butyl peroxide. [c] CB = chlorobenzene, DMF = *N,N'*-dimethylformamide. [C] = 1 M. [d] Determined by ^{1}H NMR. [e] Either-insoluble part. [f] Estimated by GPC (based on PSt.). [g] [Density(monomer) − density(polymer)]/density(monomer) × 100. Density(monomer) = 1.256. Density of monomer and polymer was measured in density gradient tubes at 25 °C. [h] Determined by DSC. [i] Determined by TGA, under nitrogen. [j] Supposed to be a cyclobutane-containing unit as described in the text. [k] Cross-linked polymer was obtained. [l] T_g was not observed.

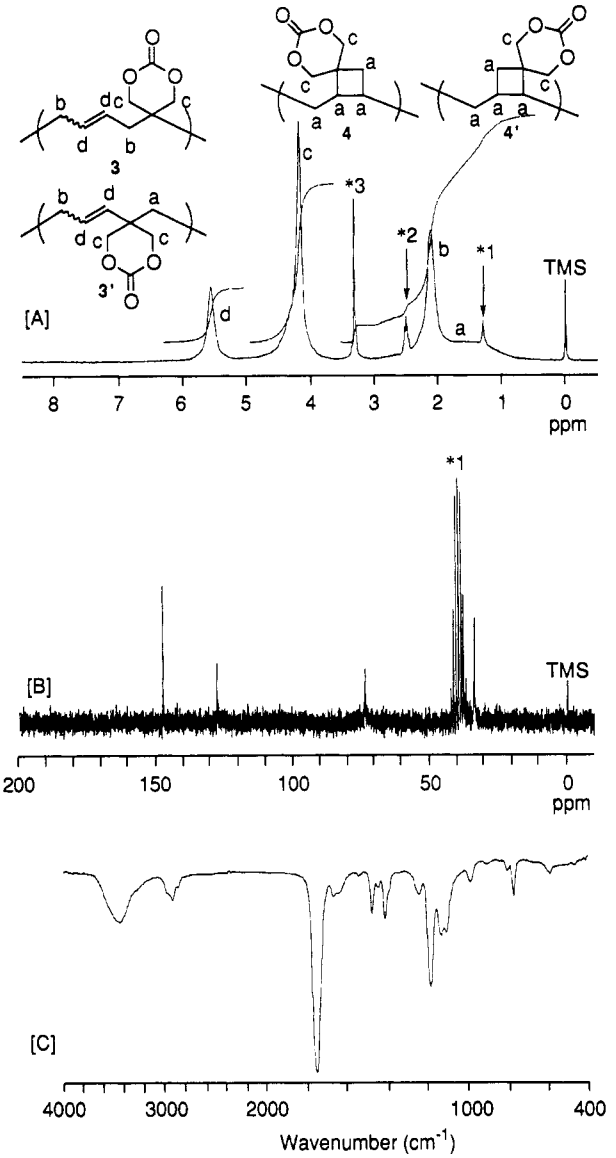
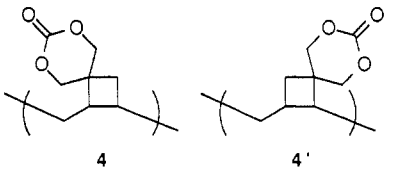
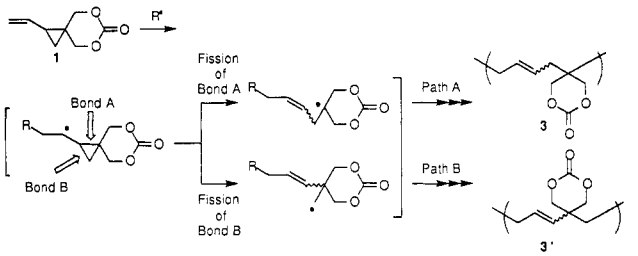


Figure 2. (A) ^{1}H NMR spectrum of poly(1) (solvent, CD_3SOCD_3; 90 MHz). *1, signal derived from AIBN fragment attached to the polymer end; *2, signal derived from incompletely deuterated CD_3SOCD_3; *3, signal derived from water. (B) ^{13}C NMR spectrum of poly(1) (solvent, CD_3SOCD_3; 22.5 MHz). *1, signal derived from CD_3SOCD_3. (C) IR spectrum of poly(1) (KBr disk). The broad absorption around 3450 cm^{-1} was derived from water contained in the IR sample disk.

However, the detailed structure is not clear yet because of difficult identification of the cyclobutane structure by NMR spectra.



Scheme 5



In the ^{13}C NMR spectrum (Figure 2B), a signal assigned to the carbonate carbon was observed at 148 ppm, nearly the same region as that of the monomer 1, but no signal around 155 ppm expected for a linear carbonate carbon[14] was observed. Furthermore, no remarkable increase in intensity of absorption at 1200–1300 cm^{-1} which could be attributed to C–O stretching of the linear carbonate moiety was observed in the IR spectrum. The IR spectrum of the polymer (Figure 2C; Table 1, run 7) was nearly the same as that of the solvent-insoluble polymers, which showed slightly broader absorptions. From these results, the formation of the solvent-insoluble polymer probably by cross-linking would not be caused by ring opening of the cyclic carbonate moiety but by some radical reactions such as hydrogen abstraction from the polymer. At 120 °C, the cross-linking reaction proceeded even in the polymerization in DMF, in which non-cross-linked polymers were formed at 60 and 80 °C. The tendency to afford cross-linked polymers of 1 larger than those of other functionalized vinylcyclopropanes should be caused by the high polarity and large intermolecular interaction of the cyclic carbonate moiety.[6,8]

There is some possibility of ring opening of the cyclic carbonate moiety and cross-linking by it during the polymerizations of 1 with AIBN, as mentioned in the Introduction. However, the cross-linked polymer was formed in the polymerization in bulk and in chlorobenzene but not in DMF. In addition, the above spectral data rule out the possibility of the ring opening of the cyclic carbonate moiety.

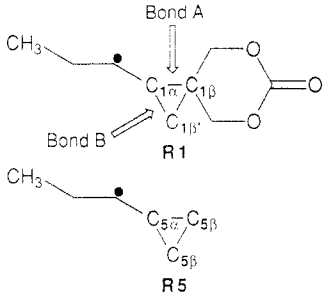
3. Selectivity of the Ring Cleavage of the Cyclopropane Ring. The mechanism of the radical polymerization of 1 is considered as shown in Scheme 5.

Table 2. Two-Center Energy, Bond Order, and Interatomic Distance of $C_{1\alpha}$–$C_{1\beta}$ and $C_{1\alpha}$–$C_{1\beta'}$ of R1 and $C_{5\alpha}$–$C_{5\beta}$ of R5

	two-center energy term[a] (eV)								
atom pair	J	K	E-E	E-N	N-N	C	EE	bond order	interatomic distance (Å)
$C_{1\alpha}$–$C_{1\beta}$	−11.03	−4.77	119.96	−235.87	120.41	4.50	−11.30	0.924	1.523
$C_{1\alpha}$–$C_{1\beta'}$	−11.66	−5.10	118.22	−235.06	121.55	4.71	−12.04	0.977	1.503
$C_{5\alpha}$–$C_{5\beta}$	−11.33	−4.96	119.66	−236.11	121.10	4.65	−11.64	0.957	1.510

[a] J = resonance energy, K = exchange energy, E-E = electron–electron repulsion, E-N = electron–nuclear attraction, N-N = nuclear repulsion, C = Coulombic interaction = E-E + E-N + N-N, EE = total of electronic and nuclear energies.

1,5-Type ring-opened units 3 and 3′ are formed through paths A and B, respectively. As described above, path A slightly predominates over path B (Table 1, runs 7 and 8). To examine this point, two-center energies, bond order, and interatomic distance of the radical intermediate **R1**, which was formed from 1 by addition of methyl radical, were calculated by a semiempirical molecular orbital method (PM3). The results are summarized in Table 2. The same terms for radical intermediate **R5**, which was formed from simple vinylcyclopropane by addition of methyl radical, are also listed for comparison.



Atom–atom pair energy (two-center energy, EE) was obtained as a sum of resonance energy (J), exchange energy (K), and Coulombic interaction (C). The two-center energy between two atoms which are bound to each other is an energy term which corresponds to the bond energy of that bond.[15] Therefore, the more negative EE is, the more stable the bond is. Since bond B ($C_{1\alpha}$–$C_{1\beta'}$) of **R1** has a more negative EE by 0.74 eV than bond A ($C_{1\alpha}$–$C_{1\beta}$), bond A can be regarded to be more easily broken than bond B. This result agrees well with the experimental results (Table 1, runs 7 and 8).

The resonance energy (J) and exchange energy (K) of $C_{1\alpha}$–$C_{1\beta'}$ are more negative than those of $C_{1\alpha}$–$C_{1\beta}$ by 0.63 and 0.33 eV, respectively. On the other hand, the Coulombic interaction (C) of $C_{1\alpha}$–$C_{1\beta'}$ is less negative than that of $C_{1\alpha}$–$C_{1\beta}$ by 0.21 eV. Therefore, the more negative two-center energy of $C_{1\alpha}$–$C_{1\beta'}$ relative to $C_{1\alpha}$–$C_{1\beta}$ results because there is a larger contribution from the resonance and exchange energies than there is from the Coulombic term. That is to say, the cleavage of the cyclopropane ring proceeds at $C_{1\alpha}$–$C_{1\beta'}$ electrostatically more easily than at $C_{1\alpha}$–$C_{1\beta}$ but in reverse by the overlap of orbitals. The interatomic distance (bond length) of $C_{1\alpha}$–$C_{1\beta}$ is larger than that of $C_{1\alpha}$–$C_{1\beta'}$ by 0.02 Å, and the bond order of $C_{1\alpha}$–$C_{1\beta}$ is smaller than that of $C_{1\alpha}$–$C_{1\beta'}$ by 0.053. These results agree well with the conclusion obtained by the analysis of the two-center energy. All parameters listed for $C_{5\alpha}$–$C_{5\beta}$ of **R5** show values intermediate between those of $C_{1\alpha}$–$C_{1\beta}$ and $C_{1\alpha}$–$C_{1\beta'}$ of **R1**. Thus, it is concluded that the changes of bonding parameters of $C_{1\alpha}$–$C_{1\beta}$ caused by the cyclic carbonate moiety correspond reversely to those of $C_{1\alpha}$–$C_{1\beta'}$.

4. Volume Change on Polymerization. The volume change during the polymerization of 1 was evaluated from the densities of 1 and poly(1). The results are summarized in Table 1. The density of 1 was 1.256, which is as large as those of other cyclic carbonates as monomers consisting of carbon, hydrogen, and oxygen atoms.[6] The dipole moment of 1 calculated by the PM3 method was 5.49 D, which is as large as those of other cyclic carbonates which show expansion in volume on polymerization.[8] Intermolecular interaction of 1 should be large and the density of 1 is large as a result. The degree of volume shrinkage (0.9%) during the polymerization with AIBN in DMF at 60 °C was smallest of all (Table 1, run 7). In all cases, the volume shrinkage on polymerization became larger as the polymerization temperature increased. This result corresponds to an increase in content of an unknown unit having no olefinic moiety in the polymer and does not contradict that the larger the content of the unknown (cyclobutane-containing) unit is, the larger the volume shrinkage on polymerization becomes. This also agrees with the observation that 1,1-disubstituted 2-vinylcyclopropanes, which afford a cyclobutane-containing unit in addition to a 1,5-ring-opened unit on radical polymerization, show a larger volume shrinkage on polymerization than α-cyclopropylstyrenes, which afford selectively a 1,5-ring-opened unit.[2n,3] In the polymerizations affording the cross-linked polymers, volume shrinkage seems to increase with increasing degree of cross-linking.[4e] The order of the volume shrinkage was in bulk > in chlorobenzene > in DMF at constant temperature. This order probably reflects that of the degree of cross-linking.

5. Thermal Analyses of the Polymer. The glass transition temperatures (T_g) of poly(1) measured by DSC were 93 and 110 °C (Table 1, runs 4, 7, and 8). Some cross-linked polymers did not show a T_g except for the polymers of which the degree of cross-linking would be small (run 4). Rigidness of the polymer chains increased by cross-linking would make their T_gs ambiguous.

The 10% weight loss temperature of the polymers measured by TGA under nitrogen ranged from 276 to 356 °C. The 10% weight loss temperature of the cross-linked polymers obtained in the polymerizations in bulk and in chlorobenzene was higher than that of the polymers obtained in the polymerization in DMF, independent of the polymerization temperature. This tendency would reflect that the rigidness of the polymer chain increased by cross-linking. An inflection point in the TG curve of the polymer obtained in the polymerization in DMF was observed (Figure 3B). However, the corresponding inflection point was not observed in the polymers obtained in the polymerizations in bulk and in chlorobenzene (Figure 3A). Since no carbonyl absorption was observed in the polymeric residue obtained in the distillation of the monomer under reduced pressure at 250 °C and, further, 30% weight loss corresponds to the ratio of the carbon dioxide in the repeating unit of the polymer ($CO_2/C_8H_{10}O_3 \times 100 = 44/154 \times 100 = 29\%$), the first weight loss observed in Figure 3B should be caused by decarboxylation from the polymer. If the decarboxylation is also assumed to proceed in the cross-linked polymers, the reaction should be slow because no inflection point in the TG curve (Figure 3A) is observed. The slow decarboxylation from the cross-

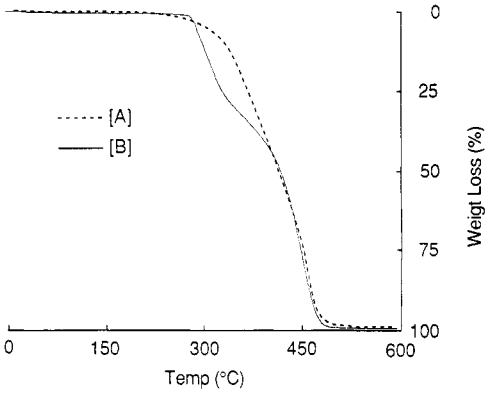


Figure 3. TGA traces of poly(1) under nitrogen at a heating rate of 10 °C/min. (A) Polymerization conditions: bulk, 3 mol % AIBN, 60 °C, 48 h (run 1 in Table 1). (B) Polymerization conditions: 1 M in DMF, 3 mol % AIBN, 60 °C, 48 h (run 7 in Table 1).

linked polymer would come from the small flexibility of the polymer chain as in the case of T_g.

Conclusion

In this work, the synthesis and radical polymerization of a vinylcyclopropane bearing a cyclic carbonate moiety, 1-vinyl-5,7-dioxaspiro[2.5]octan-6-one (1), its volume change on polymerization, and the thermal analysis of the corresponding polymers were examined. The structure of the polymers was determined to consist of two 1,5-ring-opened units and an unknown unit bearing no olefinic moiety. The volume shrinkage on the polymerizations of 1 was rather small (0.9–1.4%) in the cases without cross-linking.

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