Vinylcyclopropanone Cyclic Acetal—Synthesis, Polymerization, Structure of the Polymer and Mechanism of the Polymerization

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Received November 15, 1993®

ABSTRACT: Synthesis and radical polymerization of a few hybrid monomers between vinylcyclopropane and cyclic ketene acetal (vinylcyclopropanone cyclic acetals, 1-vinyl-4,7-dioxaspiro[2,4]heptane (**1a**), 1-vinyl-4,9-dioxaspiro[2.6]nonane (**1b**), 1-vinyl-5-phenyl-4,7-dioxaspiro[2.4]heptane (**1c**), and 1-vinyl-6,7-benzo-4,9-dioxaspiro[2.6]nonane (**1d**)) were carried out. **1a–d** were prepared by the reaction of 1,1-dichloro-2-vinylcyclopropane with corresponding diols in the presence of a base. Radical polymerization of **1** was carried out in the presence of an appropriate initiator (3 mol % vs monomer) at 60–120 °C. Polymers which were soluble in *n*-hexane, methanol, chloroform, ether, and tetrahydrofuran (THF) were obtained as pale yellow transparent viscous oils, except for the polymerizations of **1a** and **1b** with DTBP at 120 °C, in which they were obtained as gelled polymers insoluble in common organic solvents. Structures of the polymers obtained were determined by ^{1}H NMR and IR spectra referring to those of model compounds of double ring-opened units. Poly(**1a**) was determined to consist mainly of a single ring-opened unit. On the other hand, poly(**1b**) was determined to consist mainly of a double ring-opened unit. **1c**, which has the structure of phenyl-substituted **1a**, afforded a double ring-opened unit in addition to a single ring-opened unit. **1d**, which has a structure of benzo-substituted **1b**, afforded mainly a double ring-opened unit. Calculation of two-center energies with the semiempirical molecular orbital method (PM3) was carried out to examine the mechanism of the radical ring-opening polymerization of **1**. Results of the examination of two-center energies agreed well with the selectivity in the bond cleavage of the cyclopropane ring of **1**. Moreover, it was confirmed that the higher the polymerization temperature becomes, the more thermodynamically superior path proceeds, from the comparison of the formation energies of the various radical intermediates. The volume shrinkages of **1c** and **1d** were 8.86 and 3.15% in the polymerization with DTBP at 120 °C, respectively, which were regarded as the smallest ones for a radically polymerizable monomer.

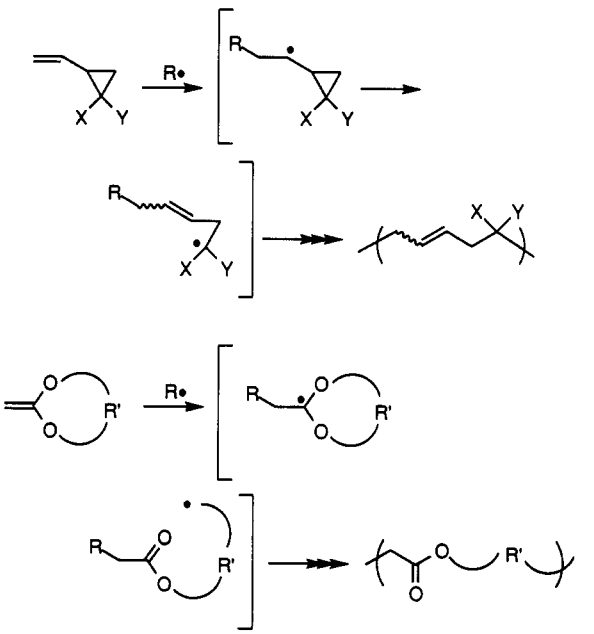
Introduction

Cyclic monomers which undergo ring-opening polymerization are important in the field of materials such as precision materials, adhesives, and so on, since they show low shrinkage or sometimes expansion in volume on polymerization.[1] Many monomers and materials undergo polymerization and curing through the radical process. Since, generally, vinyl polymerization is accompanied by volume shrinkage larger than ring-opening polymerization, monomers and materials that show low shrinkage or volume expansion through radical polymerization are especially useful. A few cyclic monomers bearing vinyl groups such as vinylcyclopropanes and cyclic ketene acetals have been reported to undergo radical ring-opening polymerization.[2] For instance, 1,1-disubstituted 2-vinylcyclopropanes undergo radical ring-opening polymerization to give polymers bearing mainly a 1,5-ring-opened unit.[3] Furthermore, cyclic ketene acetals undergo radical polymerization to give mainly poly(ester)s via a ring-opening isomerization process (Scheme 1).[4]

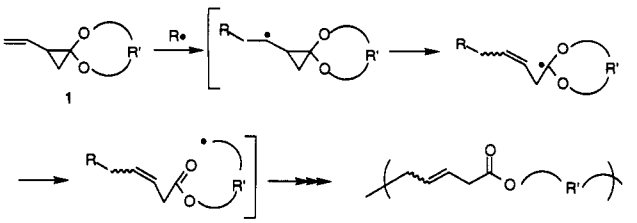
Meanwhile, bicyclic and spirocyclic oxygen-containing monomers such as spiro orthocarbonates cationically polymerize via the double ring-opening process to cause volume expansion.[1] We have devised a candidate monomer **1** capable of radically polymerizing via the double ring-opening process, since the double ring-opening polymerization is suggested to actually contribute to volume expansion.[5]

A new monomer **1** can be regarded as a hybrid monomer consisting of vinylcyclopropane and cyclic ketene acetal, because **1** can polymerize through a similar radical intermediate, as shown in the ideal polymerization scheme (Scheme 2). Therefore, **1** will be expected to exhibit a good ring-opening polymerizability, and show some volume expansion on polymerization. Methylene spiro orthoesters[6] and methylene spiro orthocarbonates[7] have been

Scheme 1



Scheme 2



® Abstract published in *Advance ACS Abstracts,* February 1, 1994.

0024-9297/94/2227-1099$04.50/0

reported to undergo radical double ring-opening polymerization besides vinyl polymerization. In this paper, synthesis and radical polymerization of vinylcyclopropanone cyclic acetal (1) are disclosed.

Experimental Section

Measurements. ^1H and ^{13}C NMR spectra of monomers, model compounds, 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 at 27 °C. FT-IR spectra were obtained with a JEOL JIR-5300 at 25 °C. Molecular weight 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 tetrahydrofuran as an eluent, a flow rate of 1.0 mL/min, polystyrene calibration, and refractive index (RI) and ultraviolet (UV) detectors.

Materials. 2,2′-Azobis(isobutyronitrile) (Tokyo Kasei Kogyo Co.), benzoyl peroxide (Kosoh Chemical Co.), and di-*tert*-butyl peroxide (Nacalai Tesque, Inc.) as initiators were used as received.

Synthesis of 1,1-Dichloro-2-vinylcyclopropane. To a solution of butadiene (162 g, 3.00 mol), chloroform (179 g, 1.50 mol), and benzyltriethylammonium chloride (6.84 g, 30.0 mmol) in dichloromethane (400 mL) was added dropwise a solution of sodium hydroxide (66.0 g, 1.65 mol) in water (132 mL) at room temperature. The addition was followed by vigorous stirring at room temperature for 12 h. The mixture was washed with water, 1 M hydrochloric acid, and again water. The organic layer was separated, dried over anhydrous sodium sulfate, and evaporated. The residue was distilled under reduced pressure to yield a colorless oil: bp 70 °C/120 mmHg (lit.[8] 48 °C/40 mmHg); yield 47.0 g (23%); ^1H NMR δ ($CDCl_3$) 1.26–1.90 (m, 2 H), 2.08–2.50 (m, 1 H), 5.03–5.58 (m, 3 H) ppm; IR (neat) 3060, 2980, 2810, 1630, 1418, 1218, 915, 759, 665 cm^{-1}.

Synthesis of 1a. To a mixture of sodium hydride (4.32 g, 180 mmol) and DMF (75 mL) were added dropwise a solution of ethylene glycol (4.66 g, 75.0 mmol) in DMF (20 mL) and then a solution of 1,1-dichloro-2-vinylcyclopropane (10.3 g, 75.0 mmol) in DMF (40 mL) at 0 °C. The addition was followed by stirring at room temperature for 12 h. Water (400 mL) was added carefully at room temperature. The mixture was extracted with ether (200 mL), and the organic layer was washed with a saturated solution of sodium hydrogen carbonate (400 mL × 2). The organic layer was dried over anhydrous sodium sulfate and evaporated. The residue was distilled under reduced pressure to yield a colorless oil: bp 100–102 °C/135 mmHg; yield 4.14 g (44 %); ^1H NMR ($CDCl_3$) δ 1.03 (dd, J = 6.8 Hz, 6.8 Hz, 1 H), 1.37 (dd, J = 6.8 Hz, 10.0 Hz, 1 H), 1.68–1.97 (m, 1 H), 3.87–4.12 (m, 4 H), 4.90–5.77 (m, 3 H) ppm; ^{13}C NMR ($CDCl_3$) δ 15.19, 25.99, 64.81, 65.15, 96.72, 114.10, 135.47 ppm; IR (neat) 3083, 2979, 2894, 1637, 1456, 1363, 1267, 1195, 1166, 1064, 1012, 700 cm^{-1}. Anal. Calcd for $C_7H_{10}O_2$: C, 66.65; H, 7.99. Found: C, 66.77; H, 8.07.

Synthesis of 1b. 1b was prepared from 1,4-butanediol (3.17 g, 35.2 mmol) and 1,1-dichloro-2-vinylcyclopropane (4.82 g, 35.2 mmol) similarly to 1a: yield 700 mg (13%); bp 89 °C/55 mmHg; ^1H NMR ($CDCl_3$) δ 0.90 (dd, J = 6.6 Hz, 5.5 Hz, 1 H), 1.23 (dd, J = 5.5 Hz, 10.0 Hz, 1 H), 1.66–2.02 (m, 5 H), 3.76–3.87 (m, 4 H), 4.91–5.78 (m, 3 H) ppm; ^{13}C NMR ($CDCl_3$) δ 20.24, 28.96, 29.07, 29.22, 66.59, 67.15, 92.60, 114.12, 136.23 ppm; IR (neat) 3081, 3004, 2944, 2879, 2844, 1637, 1440, 1338, 1267, 1168, 1085, 1012, 983 cm^{-1}. Anal. Calcd for $C_9H_{14}O_2$: C, 70.10: H, 9.15. Found: C, 69.83; H, 9.31.

Synthesis of 1c. 1c was prepared from 1-phenyl-1,2-ethanediol (10.4 g, 75.0 mmol) and 1,1-dichloro-2-vinylcyclopropane (10.3 g, 75.0 mmol) similarly to 1a: yield 10.3 g (68%); bp 93–94 °C/0.3 mmHg; ^1H NMR ($CDCl_3$) δ 0.99–1.27 (m, 1 H), 1.32–1.63 (m, 1 H), 1.76–2.07 (m, 1 H), 3.67–3.95 (m, 1 H), 4.20–4.48 (m, 1 H), 4.93–5.26 (m, 3 H), 5.44–5.83 (m, 1 H), 7.35 (s, 5 H) ppm; IR (neat) 3083, 3063, 3032, 3005, 2981, 2886, 1636, 1453, 1360, 1263, 1016, 757, 699 cm^{-1}. Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20: H, 6.98. Found: C, 76.78; H, 7.04.

Synthesis of 1d. 1d was prepared from 1,2-benzenedimethanol (10.4 g, 75.0 mmol) and 1,1-dichloro-2-vinylcyclopropane (10.3 g, 75.0 mmol) similarly to 1a: yield 5.83 g (38%); bp 98 °C/0.3 mmHg; mp 61–62 °C; ^1H NMR ($CDCl_3$) δ 1.30–1.44 (m, 1 H), 1.61–1.79 (m, 1 H), 2.20–2.53 (m, 1 H), 5.20 (s, 4 H), 5.21–5.60 (m, 2 H), 5.76–6.16 (m, 1 H), 7.48 (s, 4 H) ppm; IR (KBr) 2928, 2866, 1636, 1338, 1169, 1167, 1042, 1028, 776, 742, 620 cm^{-1}. Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.20; H, 6.98.

Synthesis of *trans*-3-Hexenoyl Chloride. *trans*-3-Hexenoic acid (25.0 g, 219 mmol) was added dropwise to thionyl chloride (31.3 g, 263 mmol) at room temperature and the mixture was stirred at 110 °C for 2 h. The reaction mixture was distilled under reduced pressure to yield a colorless oil: yield 23.2 g (80%); bp 73–77 °C/68 mmHg; ^1H NMR ($CDCl_3$) δ 0.98 (*t*, J = 7.4 Hz, 3 H), 1.89–2.23 (m, 2 H), 3.48–3.57 (m, 2 H), 5.27–5.87 (m, 2 H) ppm; ^{13}C NMR ($CDCl_3$) δ 13.19, 25.54, 50.14, 118.31, 139.14, 172.31 ppm.

Synthesis of 1-Propyl *trans*-3-Hexenoate. To a solution of 1-propanol (0.601 g, 10.0 mmol) and pyridine (791 mg, 10.0 mmol) in dichloromethane (10 mL) was added dropwise a solution of *trans*-3-hexenoyl chloride (1.33 g, 10.0 mmol) in dichloromethane (5 mL) at 0 °C. The addition was followed by stirring at room temperature for 14 h. The reaction mixture was washed with 1 M hydrochloric acid (30 mL), a saturated solution of sodium hydrogen carbonate (30 mL), and then water (30 mL). The organic layer was dried over anhydrous sodium sulfate, and evaporated. The residue was distilled with a Kugelrohr apparatus under reduced pressure to yield a colorless oil: yield 1.31 g (84%); bp 140–150 °C/95 mmHg; ^1H NMR ($CDCl_3$) δ 0.84–1.07 (m, 6 H), 1.46–1.79 (m, 2 H), 1.85–2.20 (m, 2 H), 2.97–3.06 (m, 2 H), 4.04 (t, J = 6.6 Hz, 2 H), 5.50–5.63 (m, 2 H) ppm; ^{13}C NMR ($CDCl_3$) δ 10.37, 13.50, 22.04, 25.54, 38.16, 66.15, 120.80, 136.23, 172.33 ppm; IR (neat) 3039, 2966, 2937, 2879, 1739, 1461, 1164, 968 cm^{-1}. Anal. Calcd for $C_9H_{16}O_2$: C, 69.20; H, 10.32. Found: C, 68.75; H, 10.15.

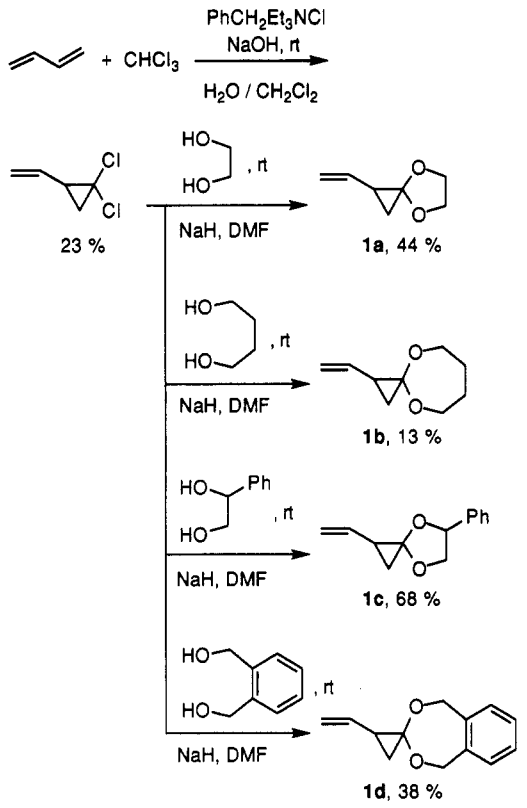
Synthesis of 1-Phenyl-1-propyl *trans*-3-Hexenoate. 1-Phenyl-1-propyl *trans*-3-hexenoate was prepared from 1-phenyl-1-propanol (1.36 g, 10.0 mmol) and *trans*-3-hexenoyl chloride (1.33 g, 10.0 mmol) similarly to 1-propyl *trans*-3-hexenoate: yield 2.02 g (87%), bp 120–135 °C/0.5 mmHg; ^1H NMR ($CDCl_3$) δ 0.87 (t, J = 7.4 Hz, 3 H), 0.97 (t, J = 7.3 Hz, 3 H), 1.62–2.18 (m, 4 H), 2.99–3.08 (m, 2 H), 5.31–5.78 (m, 2 H), 5.68 (t, J = 6.8 Hz, 1 H), 7.30 (s, 5 H) ppm; ^{13}C NMR ($CDCl_3$) δ 9.85, 13.47, 25.51, 29.38, 38.29, 77.35, 120.67, 126.53, 127.77, 128.35, 136.29, 140.61, 171.46 ppm; IR (neat) 3033, 2967, 2935, 2877, 1735, 1494, 1454, 1162, 968, 755, 700 cm^{-1}. Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.10; H, 9.08.

Synthesis of 2-Phenyl-1-propyl *trans*-3-Hexenoate. 2-Phenyl-1-propyl *trans*-3-hexenoate was prepared from 2-phenyl-1-propanol (1.36 g, 10.0 mmol) and *trans*-3-hexenoyl chloride (1.33 g, 10.0 mmol) similarly to 1-propyl *trans*-3-hexenoate; yield 1.97 g (85%); bp 140–145 °C/0.8 mmHg; ^1H NMR ($CDCl_3$) δ 0.97 (t, J = 7.4 Hz, 3 H), 1.29 (d, J = 7.0 Hz, 3 H), 1.87–2.19 (m, 2 H), 2.94–3.28 (m, 3 H), 4.16 (d, J = 7.0 Hz, 1 H), 4.18 (d, J = 7.0 Hz, 1 H), 5.43–5.57 (m, 2 H), 7.25 (s, 5 H) ppm; ^{13}C NMR ($CDCl_3$) δ 13.43, 17.99, 25.49, 38.10, 38.97, 69.43, 120.61, 126.68, 127.33, 128.46, 136.25, 143.19, 172.05 ppm; IR (neat) 3085, 3062, 3029, 2966, 1945, 1868, 1735, 1494, 1454, 1162, 761, 700, 534 cm^{-1}. Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.15; H, 8.65.

Synthesis of (2-Methylphenyl)methyl *trans*-3-Hexenoate. (2-Methylphenyl)methyl *trans*-3-hexenoate was prepared from (2-methylphenyl)methanol (1.22 g, 10.0 mmol) and *trans*-3-hexenoyl chloride (1.33 g, 10.0 mmol) similarly to 1-propyl *trans*-3-hexenoate: yield 1.95 g (89%); bp 140 °C/0.6 mmHg; ^1H NMR ($CDCl_3$) δ 0.98 (t, J = 7.3 Hz, 3 H), 1.89–2.19 (m, 2 H), 2.34 (s, 3 H), 3.02–3.10 (m, 2 H), 5.12 (s, 2 H), 5.50–5.63 (m, 2 H), 7.16–7.38 (m, 4 H) ppm; ^{13}C NMR ($CDCl_3$) δ 13.45, 18.88, 25.51, 38.06, 64.81, 120.52, 126.01, 128.48, 129.20, 130.35, 133.95, 136.49, 136.97, 172.00 ppm; IR (neat) 3029, 2964, 2933, 2873, 1737, 1608, 1461, 1157, 968, 744 cm^{-1}. Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.79; H, 8.69.

Polymerizations of 1. General Procedure. To a monomer (2 mmol) in a polymerization tube was introduced an initiator. The tube was cooled, degassed, sealed off, and heated at a set temperature for 48 h. The polymer was isolated from the resulting mixture by separation with a preparative HPLC (Nihon Bunseki Kogyo), equipped with two polystyrene gel columns (JAIGEL-

Scheme 3



H1 and JAIGEL-H2), using chloroform as an eluent (flow rate 3.8 mL/min, RI and UV detectors).

Measurement of Density. Densities of 1 and poly(1) were 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 IIci equipped with a 21 MIPS coprocessor board with use of SONY Tektronix CAChe system version 2.7. Geometries were optimized first with Molecular Mechanics using the CAChe MM2 program and second with Molecular Dynamics using CAChe MM2 force field parameters and finally with MOPAC version 6.00 (QCPE No. 455[9]) revised as version 6.10 for the CAChe system, using a 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).

Results and Discussion

1. Synthesis of Monomer 1. Vinylcyclopropanone cyclic acetals, **1a–d**, were prepared by the reaction of 1,1-dichloro-2-vinylcyclopropane with dialkoxides obtained from the corresponding diols and 2 equiv of sodium hydride referring to the synthesis of 1,1-dimethoxy-2-methyl-3-vinylcyclopropane as shown in Scheme 3.[10] 1,1-Dichloro-2-vinylcyclopropane was prepared from butadiene and chloroform by treatment with sodium hydroxide in the presence of benzyltriethylammonium as a phase transfer catalyst (Scheme 3).[8] **1a–d** are all new compounds. Yields of **1b** and **1d** (13 and 38%, respectively) having seven-membered rings were lower than those of **1a** and **1c** (44 and 68%, respectively) having five-membered rings. The low yields of **1b** and **1d** should come from a ring strain of the seven-membered ring larger than that of the five-membered ring, and advantage in entropy for cyclization to the seven-membered ring less than that of the five-membered ring should lower the yield. Intermolecular condensation would proceed more favorably than intramolecular cyclization in these cases. In fact, the lower

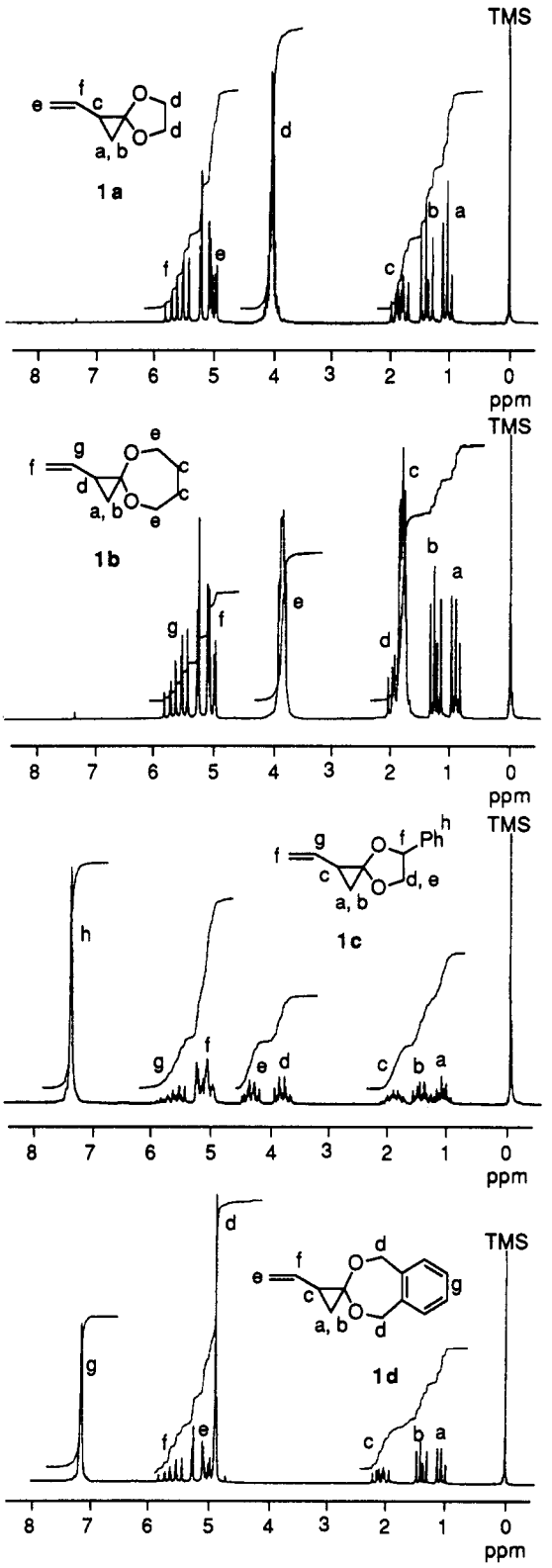
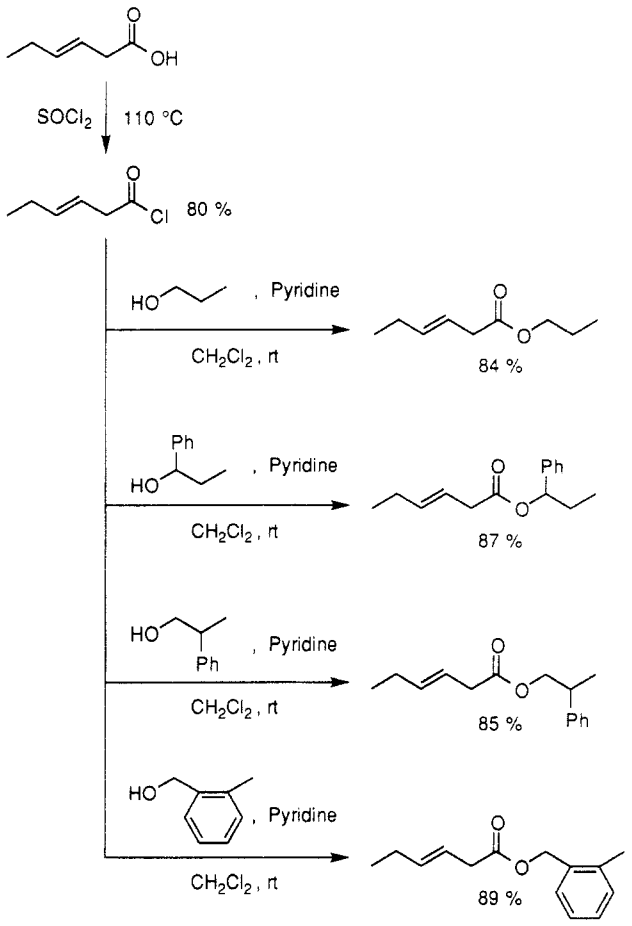


Figure 1. ^{1}H NMR spectra of **1a**, **1b**, **1c**, and **1d** (solvent, $CDCl_3$; 90 MHz).

the yield of the monomer was, the more the polymeric residue was formed in the distillation. Comparing **1b** with **1d**, both of which have the seven-membered rings, the yield of **1d** (38%) was larger than that of **1b** (13%). The result is probably from the flexibility of the 1,4-butanediol moiety being larger than that of the 1,2-benzenedimethanol moiety in the cyclization step. The structures of these monomers were determined by ^{1}H NMR, ^{13}C NMR, and IR spectra besides elemental analyses. The ^{1}H NMR spectra of the monomers are shown in Figure 1.

Scheme 4



2. Synthesis of Model Compounds of Polymers. Model compounds for the analysis of polymer structure were prepared by the reaction of *trans*-3-hexenoyl chloride with alcohols in high yields (Scheme 4). *trans*-3-Hexenoyl chloride was prepared from *trans*-3-hexenoic acid with thionyl chloride. The structures of the model compounds were determined by ^{1}H NMR, ^{13}C NMR, and IR spectra in addition to elemental analyses. The ^{1}H NMR spectra are shown in Figure 2.

3. Radical Polymerization of 1. Radical polymerization of **1** was carried out in the presence of an appropriate initiator (3 mol % vs monomer) in bulk for 48 h in a degassed sealed tube. Isolation of the polymer obtained was carried out with preparative HPLC. Polymeric materials, which were soluble in *n*-hexane, methanol, chloroform, ether, and THF, were obtained as a pale yellow transparent viscous oil, but the polymerizations of **1a** and **1b** with DTBP at 120 °C afforded gel materials which were insoluble in common organic solvents. Conversion of monomers in the polymerization with DTBP at 120 °C was higher than those with AIBN at 60 °C and BPO at 80 °C. Conversions of **1c** and **1d** having aromatic substituents in the acetal moiety were higher than those of **1a** and **1b** having no such substituents. Radical polymerizability of **1a–d** decreased with the following order: **1a** > **1b** ≫ **1c** > **1d**. The polymers obtained consisted of some units in addition to the double ring-opened unit that was first expected. The spectral analyses indicated that the radical polymerization of **1** proceeded in many modes, as shown in Scheme 5. Path A is a vinyl polymerization process. Path B is a process to afford cyclobutane-containing unit **3** through a fission of bond C or **R2** followed by a cyclization. Path C is a single ring-opening process. Path D is a double ring-opening process through a fission of bond D of **R4**. Path E is a process to

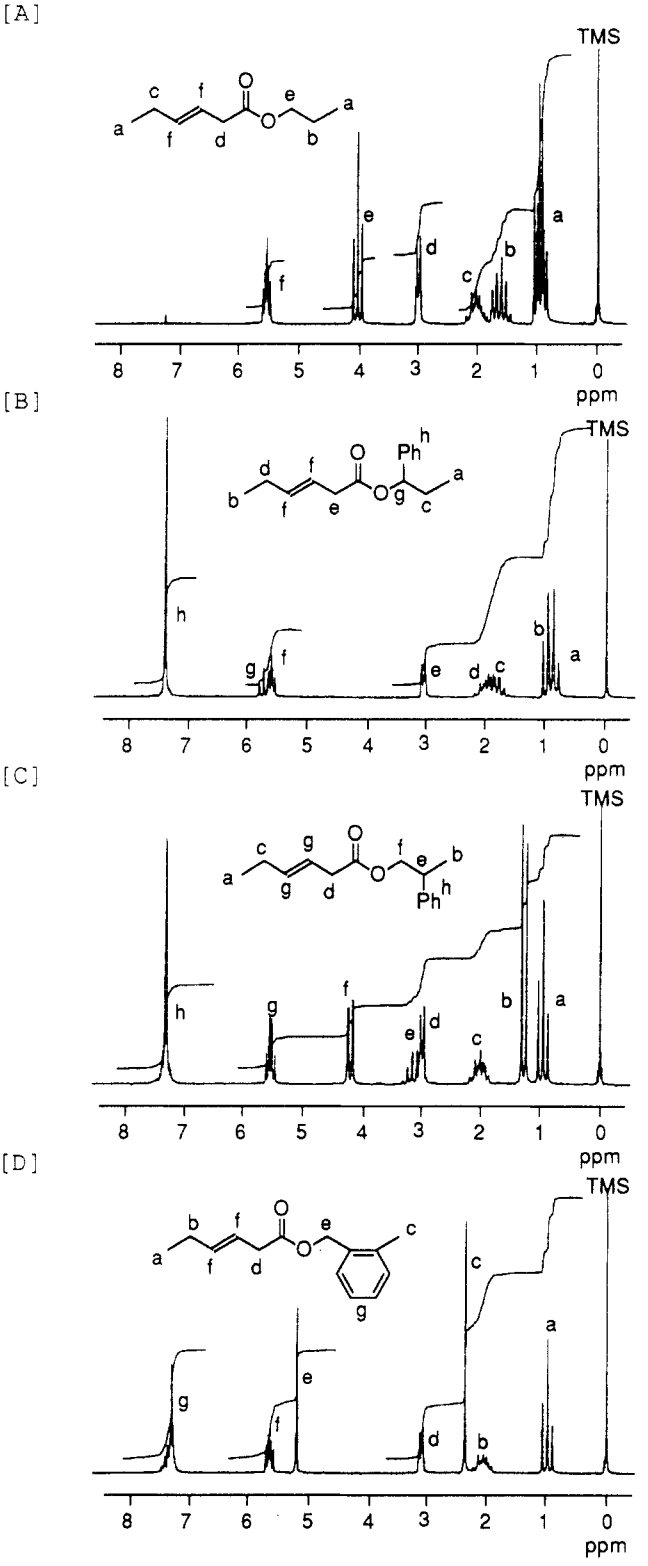
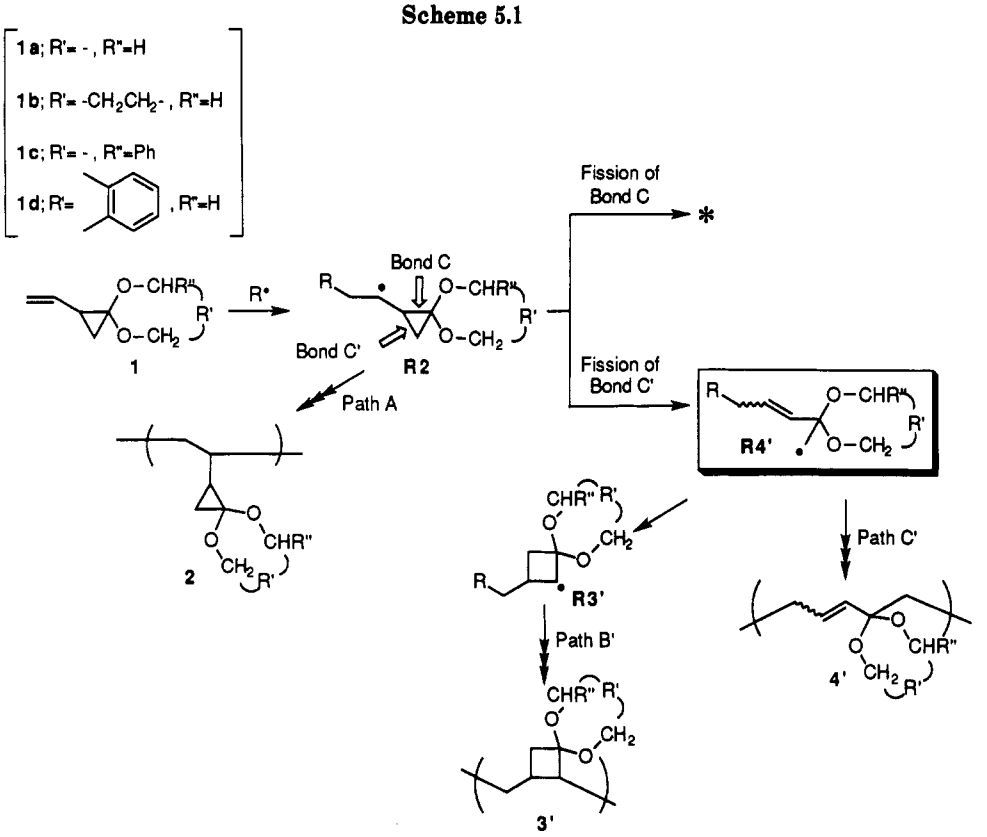


Figure 2. ^{1}H NMR spectra of model compounds (solvent, $CDCl_3$, 90 MHz).

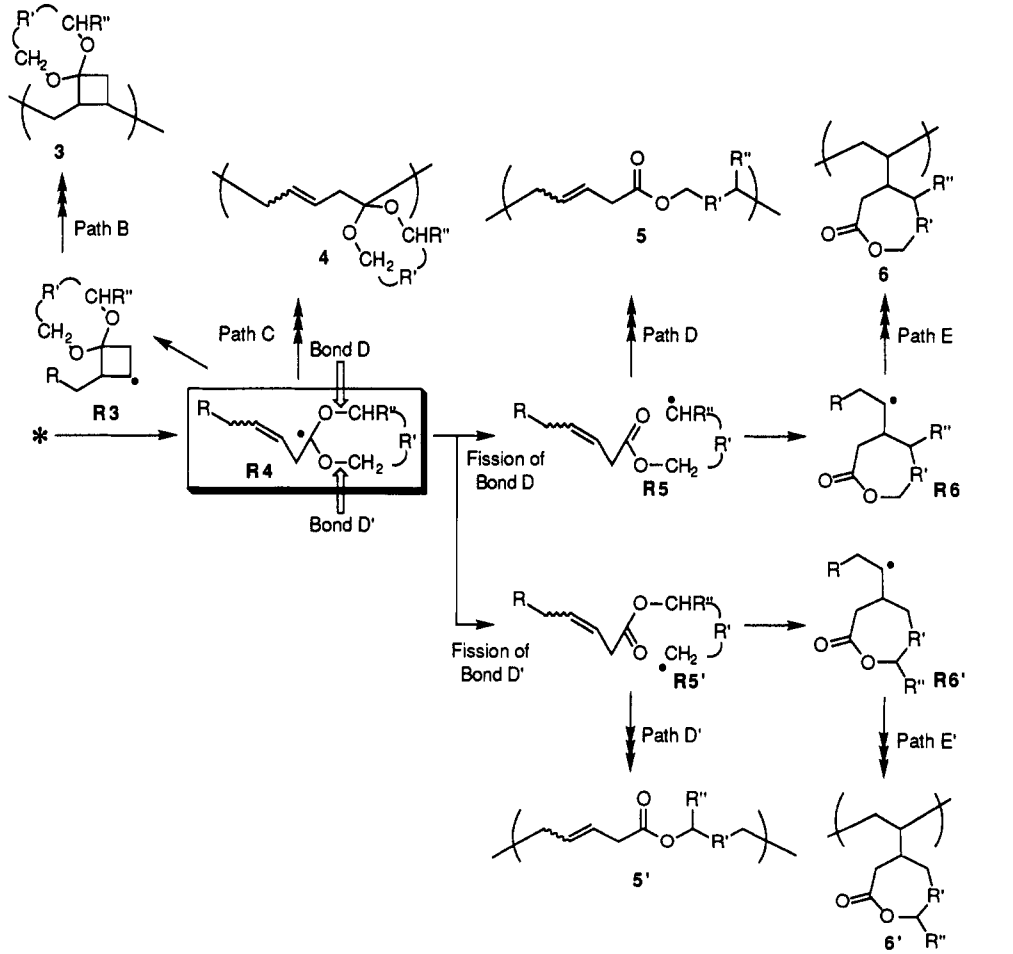
afford lactone-containing unit **6** through a double ring-opening process followed by a cyclization. Paths B′ and C′ are processes through a fission of bond C′ or **R2** to afford another cyclobutane-containing unit **3′** and single ring-opened unit **4′**, respectively. Paths D′ and E′ are processes through a fission of bond D′ or **R4** to afford another double ring-opened unit **5′** and lactone containing unit **6′**, respectively. Paths D′ and E′ are the same as paths D and E in the polymerizations of **1a**, **1b**, and **1d** having the symmetrical cyclic acetal moiety.

Detailed ^{1}H NMR and IR analyses resulted in the

Scheme 5.1

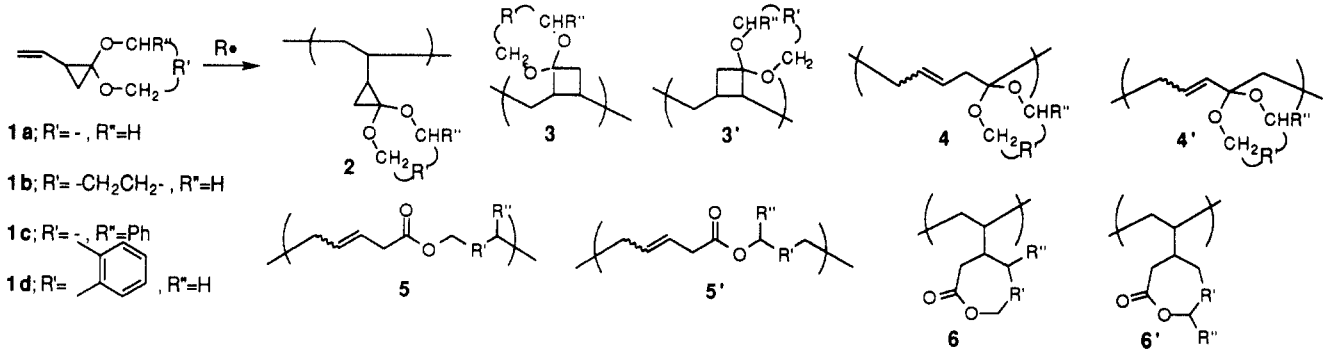


Scheme 5.2



following structural determination of the polymers of 1. Poly(**1a**) was suggested to consist mainly of single ring-opened units **4a** and **4a'**. On the other hand, poly(**1b**) consisted mainly of double ring-opened unit **5b**. **1c**, which has the structure of phenyl-substituted **1a**, contained double ring-opened unit **5c** besides single ring-opened unit **4c'**. **1d**, which has the structure of benzo-substituted **1b**, mainly had double ring-opened unit **5d**. The results of the radical polymerizations of **1a–d** are summarized in Table 1.

Table 1. Radical Polymerization of 1a–d[a]



							polymer structure[e] (%)							
run	monomer	init[b]	temp (°C)	conv[c] (%)	$\bar{M}_n$[d]	$\bar{M}_w/\bar{M}_n$[d]	2	3 + 3'	4	4'	5	5'	6	6'
1	1a	AIBN	60	50	3800	2.7	0	11	22	67	0		trace	
2	1a	BPO	80	24	1300	1.4	0	18	14	50	0		18	
3[f]	1a	DTBP	120	96[g]										
4	1b	AIBN	60	28	4700	4.4	8	0	31	15	46		0	
5	1b	BPO	80	26	5600	3.1	8	8	25	0	59		0	
6[f]	1b	DTBP	120	61[g]										
7	1c	AIBN	60	15	2100	1.8	0	0	0	74	19	0	7	0
8	1c	BPO	80	18	3100	1.4	0	0	0	67	21	0	12	0
9	1c	DTBP	120	70	3100	4.9	0	0	0	26	36	0	38	0
10	1d	BPO	80	7	800	1.5	7	29	4	14	46		0	
11	1d	DTBP	120	20	1700	4.5								

[a] Conditions: bulk, monomer 2 mmol, 48 h. [b] Initiator, 3 mol %: AIBN, 2,2'-azobis(isobutyronitrile); BPO, benzoyl peroxide; DTBP, di-*tert*-butyl peroxide. [c] Estimated by GPC. [d] Estimated by GPC in which only two peaks corresponding to polymer and monomer were observed in any case. [e] Determined by ^{1}H NMR. [f] Cross-linked polymer was obtained. [g] Determined by GC with *n*-hexadecane as an internal standard.

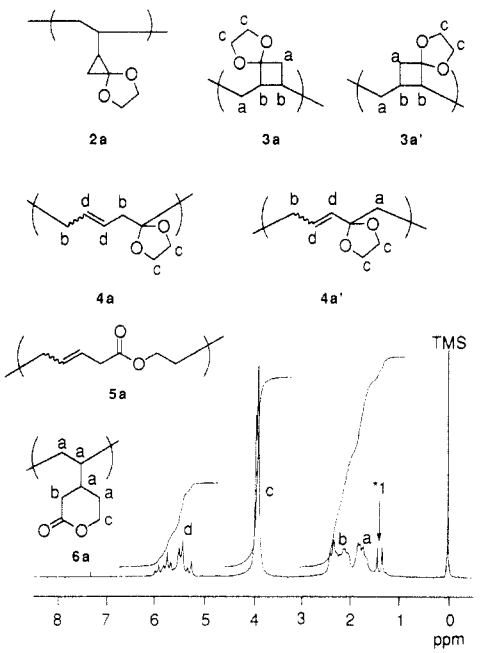


Figure 3. ^{1}H NMR spectrum of poly(**1a**) (solvent, $CDCl_3$; 90 MHz). Polymerization conditions: bulk, 3 mol % AIBN; 60 °C, 48 h (run 1 in Table 1). *1: Signal derived from $(CH_3)_2CCN$ attached to the polymer end.

^{1}H NMR and IR spectra of poly(**1a**) obtained by the polymerization with AIBN at 60 °C (Table 1, run 1) are shown in Figures 3 and 4, respectively.

Since absence of the cyclopropane ring was confirmed by the ^{1}H NMR spectrum (Figure 3) of poly(**1a**) in which there was no signal corresponding to cyclopropane protons at 0.5–0.9 ppm, unit **2a** obtained by vinyl polymerization was not contained in the polymer. Double ring-opened unit **5a** was not formed, since no signal corresponding to methylene protons α to the ester carbonyl group at 3 ppm was observed. The main structure of the polymer involved

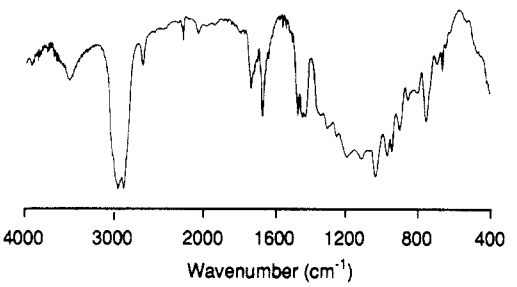


Figure 4. IR spectrum of poly(**1a**). Polymerization conditions: bulk, 3 mol % AIBN; 60 °C, 48 h (run 1 in Table 1).

two single ring-opened units **4a** and **4a'**. A weak carbonyl absorption around 1733 cm^{-1} was observed in the IR spectrum of poly(**1a**) (Figure 4). Further, the integration ratio of olefin protons *d* of this polymer was smaller than that expected for a polymer that consists only of **4a** and **4a'**; so, another polymer unit should be contained. The most probable structure other than **4a** and **4a'** seems to be the following two units. Namely, one is the cyclobutane-containing unit **3a** and/or **3a'** which are similar to that reported in the radical polymerization of vinylcyclopropane.[3,11] The other is δ-valerolactone-containing unit **6a** which is reported to be formed in the radical copolymerization of vinylcyclopropane and maleic anhydride.[12] The cleavage of the cyclopropane ring favorably proceeded in the bond which does not contain the spiro center carbon, since the content of **4a'** was larger than that of **4a**. The acetal moiety would increase the bond energy of the adjacent bond of the cyclopropane ring (Scheme 5, bond C of **R2**). The ^{1}H NMR spectrum of poly(**1a**) obtained by the polymerization with BPO at 80 °C showed nearly the same pattern as that of Figure 3. **5a** was not contained at all similar to the polymerization at 60 °C. The ratio of **6a** was larger than that of the polymer obtained with AIBN at 60 °C. So, the ratio of double ring-opening to single ring-opening processes increased at higher polymerization temperatures. The ratio of **4a** and **6a** to **4a'** increased

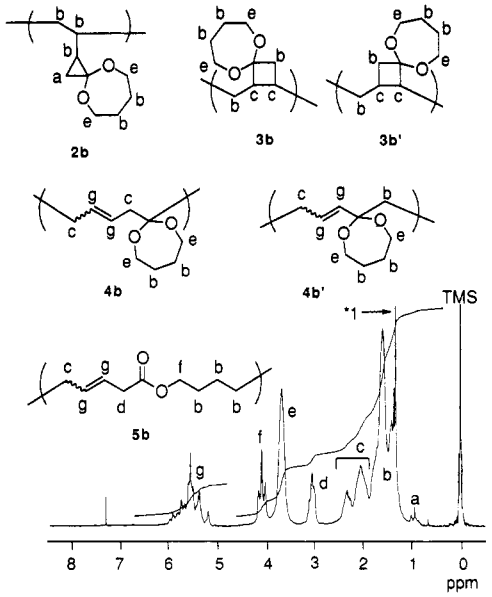


Figure 5. ^{1}H NMR spectrum of poly(**1b**) (solvent, $CDCl_3$; 90 MHz). Polymerization conditions: bulk, 3 mol % AIBN 60 °C, 48 h (run 4 in Table 1). *1: Signal derived from $(CH_3)_2CCN$ attached to the polymer end.

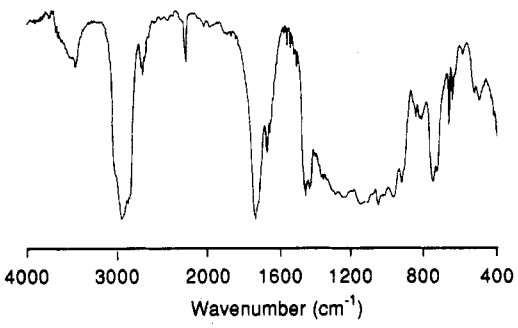


Figure 6. IR spectrum of poly(**1b**). Polymerization conditions: bulk, 3 mol % AIBN; 60 °C, 48 h (run 4 in Table 1).

more than that of polymerization at 60 °C. It is interesting that the selectivity in cleavage of the cyclopropane ring depends on the polymerization temperature. A polymer insoluble in common organic solvents was obtained by the polymerization with DTBP at 120 °C. The cross-linking reaction should proceed under this condition probably due to the double bonds in the polymer main chain.

^{1}H NMR and IR spectra of poly(**1b**) obtained by the polymerization with AIBN at 60 °C (Table 1, run 4) are shown in Figures 5 and 6, respectively.

Since the presence of the cyclopropane ring was observed in the ^{1}H NMR of poly(**1b**) (Figure 5), in which there was signal *a* corresponding to cyclopropane protons at 0.8–1.2 ppm, vinyl polymerization unit **2b** was contained in the polymer. Double ring-opened unit **5b** was contained, because signal *d* corresponding to methylene protons α to the ester carbonyl group at 3 ppm in the ^{1}H NMR spectrum, a strong absorption of the ester carbonyl group at 1733 cm^{-1} in the IR spectrum (Figure 6), and a signal of the ester carbonyl carbon at 172 ppm in the ^{13}C NMR spectrum were observed. However, since both ratios of signals *d* and *f* assigned to the methylene protons of **5b** to signal *g* assigned to the olefin proton were about 50% in the ^{1}H NMR spectrum (Figure 5), the content of **5b** in the obtained polymer is about 50%, and single ring-opened units **4b** and **4b'** which were confirmed in the polymerization of **1a** were also contained (their ratio was 46%). The lactone unit confirmed in poly(**1a**) was not contained, probably because cyclization of an eight-membered ring hardly proceeds owing to the entropically unfavorable ring

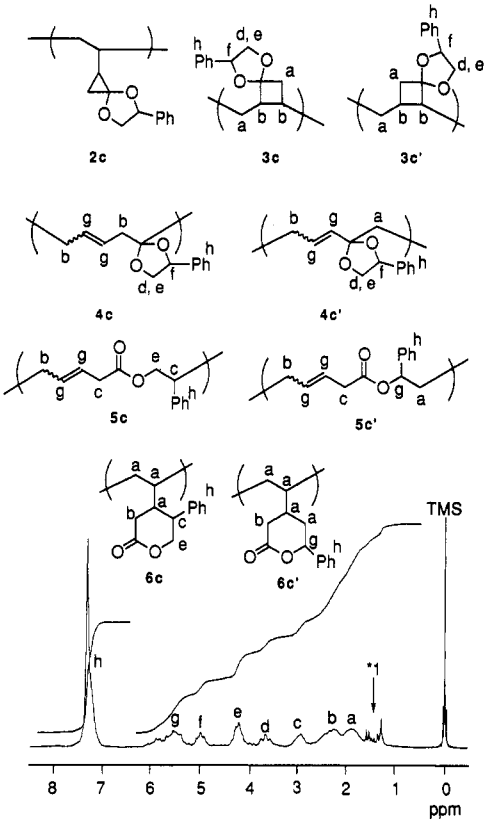


Figure 7. ^{1}H NMR spectrum of poly(**1c**) (solvent, $CDCl_3$; 90 MHz). Polymerization conditions: bulk, 3 mol % AIBN; 60 °C, 48 h (run 7 in Table 1). *1: Signal derived from $(CH_3)_2CCN$ attached to the polymer end.

system. The ^{1}H NMR integration strongly indicated the absence of cyclobutane-containing unit **3b** and/or **3b'**. The ^{1}H NMR spectrum of poly(**1b**) obtained by the polymerization with BPO at 80 °C showed nearly the same pattern as that of Figure 5. Double ring-opened unit **5b** was the main unit, and formation of cyclobutane-containing unit **3b** and/or **3b'** and single ring-opened unit **4b** was confirmed. However, another single ring-opened unit **4b'** was not confirmed. A polymer obtained by the polymerization with DTBP at 120 °C was insoluble in common organic solvents, as was that of **1a** obtained at 120 °C.

The ^{1}H NMR spectrum of poly(**1c**) obtained by the polymerization with AIBN at 60 °C (Table 1, run 7) is shown in Figure 7.

Similarly to the cases of **1a**, no cyclopropane ring signal was observed at 0.5–0.9 ppm in the ^{1}H NMR spectrum of the polymer. So, vinyl polymerization unit **2c** was not contained in that polymer. Double ring-opened unit **5c** was contained, since signal *c* corresponding to methylene protons α to the ester carbonyl group at 3 ppm was observed. However, the integration ratio of signal *c* to signal *g* assigned to olefin protons (5.2–6.2 ppm) is about 30%, and therefore, the content of the unit formed through only the ring-opening of the cyclopropane should be larger than that of the double ring-opened unit. Analysis of the ^{1}H NMR of poly(**1c**) is more complicated than of those of **1a** and **1b**, because of the unsymmetrical structure of the acetal ring. From the ^{1}H NMR spectra of the model compounds (Figure 2B,C), the ^{1}H NMR chemical shifts of each unit can be assigned as shown in Figure 7. The main structure (74%) of the polymer was determined to be single ring-opened unit **4c'** by solving the simultaneous equations obtained from the eight signals in the ^{1}H NMR spectrum. Although two different double ring-opened

units **5c** and **5c'** can be formed, only **5c** was contained in the polymer. This result means that the double ring-opening polymerization is achieved only when the benzyl radical type propagation end is formed by C–O bond cleavage (from **R4** to **R5** but not to **R5'**, Scheme 5). This selectivity corresponds to that of the radical ring-opening polymerization of 2-methylene-4-phenyl-1,3-dioxolane having the same cyclic acetal ring as **1c**; which is reported to undergo ring-opening polymerization only through a similar propagating benzyl radical.[13] The phenyl group would decrease the bond energy of the benzyl C–O bond (Scheme 5, bond D of **R4**). A detailed examination of this matter using molecular orbital calculations is discussed later. Neither cyclobutane-containing units **3c** and/or **3c'** nor **4c**, which would be formed through a cleavage of bond C, was contained in the polymer. The ^{1}H NMR spectrum of the poly(**1c**) by the polymerization with BPO at 80 °C (Table 1, run 8) showed nearly the same pattern as that of Figure 7.

In the ^{1}H NMR spectrum of the polymer obtained by the polymerization with DTBP at 120 °C (Table 1, run 9), the integration ratios of the broad signals at 1.2–2.1 and 2.1–2.6 ppm were obviously larger than those of the polymers obtained at 60 and 80 °C. This agrees with the fact that the olefin proton ratio of the polymer obtained at 120 °C is less than those of the polymers obtained at 60 and 80 °C. δ-Valerolactone-containing unit **6c** (38%) and double ring-opened unit **5c** (36%) were the two major units of the polymer. The content of the single ring-opened unit **4c'** (26%) was much smaller than those of the polymers obtained at 60 and 80 °C. The relative intensity of the ester carbonyl absorption at 1733 cm^{-1} in the IR spectrum was larger than those of the polymers obtained at 60 and 80 °C. So, the higher the polymerization temperature, the more the double ring-opening is accelerated in the polymerization of **1c**, and the more the ratio of δ-valerolactone-containing unit **6c** increases. The cleavage of bond C should occur more favorably than that of bond C' at high temperatures. Namely, both the cleavage of bond C and the formation of the δ-valerolactone-containing unit should be thermodynamically advantages. Detailed examination of this point is also discussed later.

Since the melting point of **1d** was 61–62 °C, bulk polymerization of **1d** with AIBN at 60 °C was not carried out. The ^{1}H NMR spectrum of poly(**1d**) obtained by the polymerization with BPO at 80 °C (Table 1, run 10) is shown in Figure 8.

Since the cyclopropane ring signal was observed at 0.8–1.2 ppm in the ^{1}H NMR spectrum of the polymer, vinyl polymerization unit **2d** was formed in the polymerization of **1d**, as seen in the polymer, similarly to the polymerization of **1b** which also had the seven-membered cyclic acetal ring. Double ring-opened unit **5d** was also contained, since both signal *d* assigned to methylene protons α to the ester carbonyl group at 3 ppm and signal *f* and 5.1 ppm assigned to methylene protons adjacent to the ether oxygen of the ester group were present. Furthermore, the strong absorption of the ester carbonyl group at 1733 cm^{-1} in the IR spectrum and the signal of ester carbonyl carbon at 172 ppm in the ^{13}C NMR spectrum supported the presence of the unit **5d**.

In the ^{1}H NMR spectrum of poly(**1d**) obtained by the polymerization with DTBP at 120 °C (Table 1, run 11), all signals were so broad that the microstructure of the polymer could not be determined. A similar IR spectrum of the polymer including a strong absorption at 1733 cm^{-1} undoubtedly suggests that the main structure is double ring-opened unit **5d**. However, since a broad signal at 1.0–2.0 ppm is observed, cyclobutane-containing units **3d** and/or **3d'** are possibly contained.

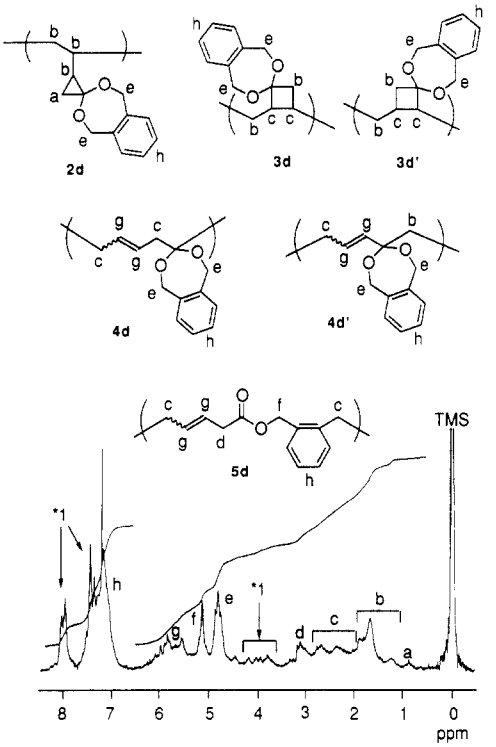
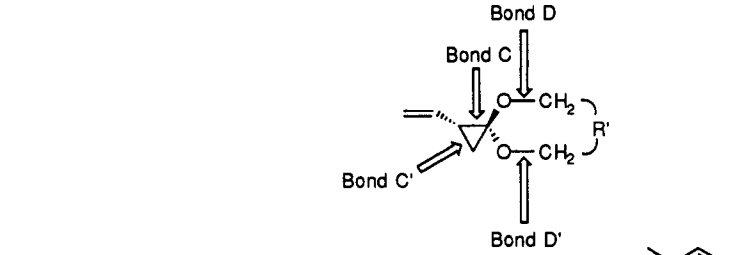


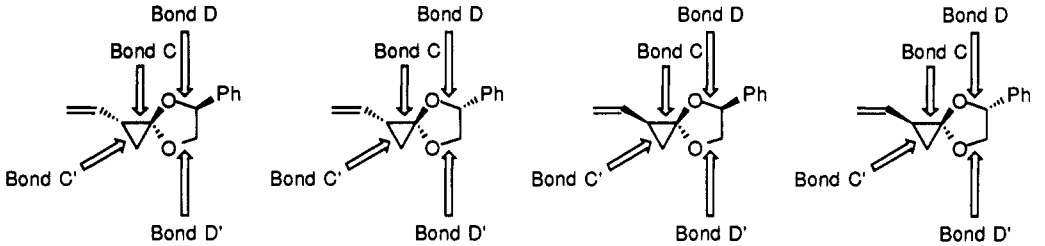
Figure 8. ^{1}H NMR spectrum of poly(**1d**) (solvent, $CDCl_3$; 90 MHz). Polymerization conditions: bulk, 3 mol % BPO; 80 °C, 48 h (run 10 in Table 1). *1: Signal derived from $PhCO_2$ attached to the polymer end.

4. Comments on the Mechanism of the Polymerization Using Molecular Orbital Calculations. As described above, the structures of the polymers obtained in the polymerization of **1a–d** have been clarified to somewhat vary according to the structure of the monomer and the polymerization conditions. For example, a certain clear relation between the structure of the polymer and the polymerization temperature was observed in the case of **1c**, being caused by a change in selectivity of the bond cleavage (bond C or C' and bond D or D'). Calculations of the two-center energies of bonds C, C', D, and D' and formation energies of **1a–d** were carried out by the semiempirical molecular orbital method (PM3). The two-center energy between two atoms, which are bound each other, is an energy term which corresponds to the bond energy of this bond. Therefore, the more negative this energy term is, the more stable the bond is.[14] The results are summarized in Table 2. The bond cleavage of either bond D or D' affords the structurally same polymer in the cases of **1a**, **1b**, and **1d**; however, the two-center energies of these two bonds are calculated for these monomers, since they are not equivalent to each other. As for **1c**, two-center energies and formation energies of its four stereoisomers, **1c**$_{-+}$, **1c**$_{--}$, **1c**$_{++}$, and **1c**$_{+-}$ as defined in Table 2, were calculated. The *s-trans* form of the vinyl group and cyclopropane ring, which was reported to be the most stable configuration for vinylcyclopropane by ab-initio calculation,[15] was used for the starting configuration in any case. The starting geometry used for another part of the monomers was preliminary optimized by MM2 calculation followed by MD calculation. Finally, full optimization of all geometrical variables (bond lengths, bond angles, and dihedral angles) was carried out by the PM3 method.

As described above, two possibilities are considered in the cleavage of the cyclopropane ring, i.e. the cleavage of

Table 2. Two-Center Energy of Bond C, C′, D, D′ and Heat of Formation of 1a–d[a]





	two-center energy (eV)						
	bond			bond			
monomer	C	C′	Δ(bond C–C′)	D	D′	Δ(bond D–D′)	heat of formation (kcal/mol)
1a	−11.71	−11.39	−0.32	−13.47	−13.46	−0.01	−36.45
1b	−11.65	−11.71	+0.06	−13.57	−13.60	+0.03	−42.60
1c$_{-+}$	−11.84	−11.39	−0.45	−13.50	−13.46	−0.04	−7.78
1c$_{--}$	−11.65	−11.42	−0.23	−13.48	−13.45	−0.03	−8.12
1c$_{++}$	−11.82	−11.39	−0.43	−13.50	−13.48	−0.02	−7.57
1c$_{+-}$	−11.70	−11.38	−0.32	−13.42	−13.47	+0.05	−7.50
1d	−11.65	−11.58	−0.07	−13.73	−13.71	−0.02	−6.50

[a] Calculated by MOPAC Ver. 6.10, PM3 (RHF) method. All calculations were done with full optimization of all geometrical variables (bond lengths, bond angles, and dihedral angles).

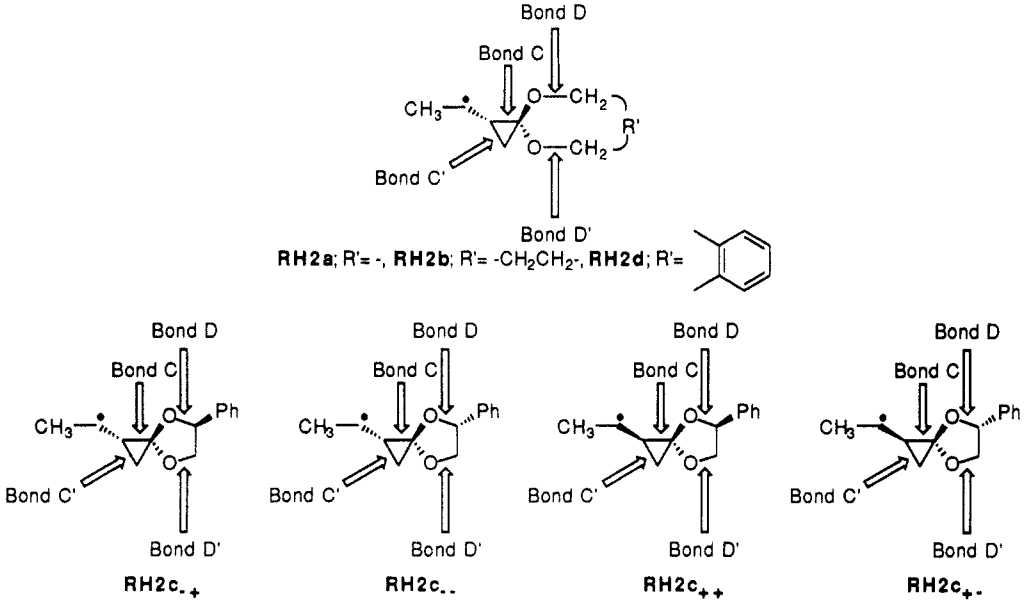
bonds C and C′ (Scheme 5). Two-center energies of bond C of **1** were negatively larger than those of bond C′ except for **1b**. The differences of the energy between these two bonds were 0.06–0.45 eV. So, bond C′ should be cloven more easily than bond C in the cases of **1a**, **1c**, and **1d**, and it is just opposite in the case of **1b**. These results well agree with the fact that the content of **4a′** formed through cleavage of bond C′ is larger than that of **4a** formed through cleavage of bond C. Moreover, the unit ratio of **4a′** to the sum of **4a** and **6a** (also formed through cleavage of Bond C) was lowered by increasing the polymerization temperature from 60 to 80 °C in the polymerization of **1a** (Table 1, runs 1 and 2). As shown in Table 1, the content of **4b′** formed through the cleavage of bond C′ is smaller than that of **4b** formed through the cleavage of bond C in the polymerization of **1b**. This result is also well-consistent with the tendency of two-center energy (Table 2).

Two-center energies of the isomers of **1c** are slightly different from one another. A mean value (−0.36 eV) of the difference in two-center energy between bonds C and C′ in the four isomers is larger than that of **1a**. The content of **4c′** formed by the cleavage of bond C′ in the polymerization of **1c** at 60 °C was the largest (74%, Table 1, run 7) among the four monomers, and therefore this is well-consistent with that fact that the selectivity in bond cleavage is larger than that observed in the polymerization of **1a** in which the difference was 0.32 eV. However, further investigation should be needed for this point because the ratio of the isomers of **1c** is not clear. In the polymerization of **1c**, the cleavage of only bond D containing a phenyl group attached carbon was confirmed to occur from ^{1}H NMR analysis. However, the two-center energy of bond D of only **1c**$_{+-}$ is larger than that of bond D′ among the four isomers of **1c**. So, is bond D′ cloven more easily than Bond D? Before extracting the conclusion, the following two points should be examined. One is that the differences in energy between them are very small 0.02–0.05 eV, and the other is that the difference in energy between radical intermediates should be precisely more important than those of the monomers. So, secondly, calculation of the two-center energy of bonds C, C′, D, and D′ and formation energy of radical intermediates (Scheme 5, **R2**) was carried out. In this case, the radicals for calculation were assumed to be formed by addition of a hydrogen radical to the exo carbon atom of the vinyl group of the monomers (indicated as **RH2**). The results are summarized in Table 3.

The tendencies of the two-center energies of bonds C and C′ of the radical intermediates **RH2** are the same as those of the corresponding monomers **1** except for **RH2c**$_{--}$ and **RH2d** (Tables 2 and 3). Therefore, the above discussions for **1a**, **1b** and **1c** should be also acceptable for **RH2a**, **RH2b** and **RH2c**, respectively. The two-center energies of bonds C and C′ of **RH2d** reveal that bond C is cloven more easily than bond C′ in contrast to the case of **1d**. Since the difference between the two energies of **1d** is small (0.07 eV) and the content of **5d** formed through cleavage of bond C is as large as 46% (Table 1, run 10), the ease of the cleavage of bond C compared with that of bond C′ in **1d** should be undoubtedly larger than that of **1a** which does not afford the unit **5a** on polymerization.

From above discussions, bond C′ is cloven more easily than bond C in the cases of **1a** and **1c** having a five-membered acetal ring, and this tendency decreases in **1b** and **1d** which have a seven-membered acetal ring. The reason for this difference observed between five- and seven-

Table 3. Two-Center Energy of Bond C, C', D, D' and Heat of Formation of RH2a, RH2b, RH2c, and RH2d[a]



	two-center energy (eV)						
	bond			bond			
compd	C	C'	Δ(bond C–C')	D	D'	Δ(bond D–D')	heat of formation (kcal/mol)
RH2a	−11.43	−11.29	−0.14	−13.47	−13.46	−0.01	−40.88
RH2b	−11.33	−11.73	+0.40	−13.62	−13.54	−0.08	−47.91
RH2c-+	−11.58	−11.49	−0.09	−13.34	−13.48	+0.14	−11.35
RH2c--	−11.45	−11.56	+0.11	−13.44	−13.45	+0.01	−13.87
RH2c++	−11.55	−11.36	−0.19	−13.48	−13.47	−0.01	−12.13
RH2c+-	−11.53	−11.20	−0.33	−13.50	−13.45	−0.05	−12.46
RH2d	−11.37	−11.51	+0.14	−13.73	−13.15	−0.58	−10.92

[a] Calculated by MOPAC Ver. 6.10, PM3 (UHF) method. All calculations were done with full optimization of all geometrical variables (bond lengths, bond angles, and dihedral angles).

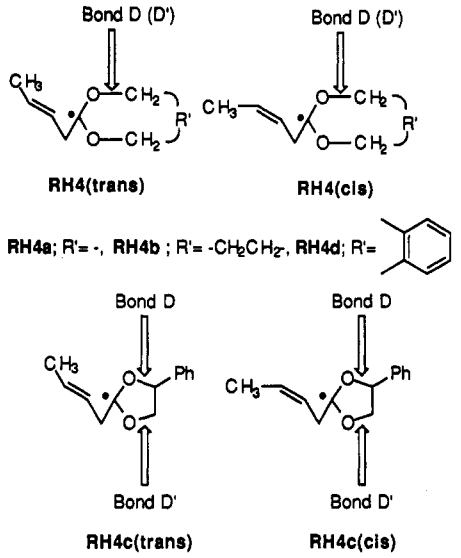
membered rings is not clear now. Precise examinations such as separate consideration of Coulomb and resonance terms in the two-center energy might solve the problem for which the difference comes from the electrostatic factor or overlaps of the orbitals.

Next, calculations of the two-center energies of bonds D and D' and formation energy of radical intermediate **RH4c** formed by the cleavage of bond C of **RH2c** were carried out. Results are summarized in Table 4, along with those of **RH4a**, **RH4b**, and **RH4d** corresponding to **1a**, **1b**, and **1d**, respectively. Calculations were carried out for both *trans* and *cis* isomers of **RH4**. Differences in the formation energies of the two isomers are only less than 0.2 kcal/mol in all intermediates. The *trans* isomer is slightly more stable than the *cis* isomer in the case of **RH4c**. The two-center energies of the *trans* and *cis* isomers are the same for **RH4a**, **RH4b**, and **RH4d** which have symmetrical structures. The difference in two-center energy between bonds D and D' is also just the same value (0.04 eV) for the *trans* and *cis* isomers of **RH4c** which has an unsymmetrical structure. This difference reveals that bond D of **RH4c** is cloven more easily than bond D'. Although bond D's of some isomers of **1c** (Table 2) and **RH2c** (Table 3) have, in turn, two-center energies smaller than those of bond D's, their differences are very small, only 0.01–0.05 eV. From the result of the most important radical intermediate **RH4c** for the determination of the ease of bond cleavage of bond D and/or D' of **1c**, bond D is determined to be cloven more easily than bond D'. This conclusion well corresponds to the fact that the polymer obtained in the polymerization of **1c** does not contain **5c'**, which is formed through cleavage of bond D', but **5c** which is formed through cleavage of bond D.

It is reported that, in radical polymerization of 2-methylene-4-phenyl-1,3-dioxolane having the same acetal moiety as **1c**, the selective ring-opening yielding a benzylic radical end is owing to the high stability of the propagating benzylic radical end, like in the radical polymerization of styrenes.[13] In this work, formation energies of both radical intermediates **RH5c** having a benzyl radical end unit and **RH5c'** having an alkyl radical end unit were calculated, to confirm the stability of benzyl radical end unit. Results are summarized in Table 5, along with those of radical intermediates **RH5a**, **RH5b**, and **RH5d** formed from **RH4a**, **RH4b**, and **RH4d**, respectively, for comparison.

The highly stabilizing effect of the phenyl group on the radical end is confirmed, since *trans* and *cis* benzylic radical intermediates **RH5c** have formation energies above 15 kcal/mol smaller than those of alkyl radical intermediates **RH5c'**. Moreover, since the formation energy of **RH5c'** is 6.91–8.31 kcal/mol larger than that of its precursor **RH4c**, the isomerization of **RH4c** to **RH5c'** should be thermodynamically unfavorable. On the contrary, since the formation energy of **RH5c** is 8.16–8.43 kcal/mol smaller than that of their precursor **RH4c**, the isomerization of **RH4c** to **RH5c** should be thermodynamically favorable. The isomerization of **RH4a** to **RH5a** is an endothermic (about 4 kcal/mol) reaction, and those of **RH4b** to **RH5b** and **RH4d** to **RH5d** are exothermic reactions (about 1 and 9 kcal/mol, respectively). These thermodynamic data completely agree with the experimental results; no double ring-opened unit **5a** is contained in the polymer obtained in the polymerization of **1a** at 60 and 80 °C at all, whereas some double ring-opened units are included in all the polymers obtained in the polymerizations of **1b**, **1c**, and **1d**.

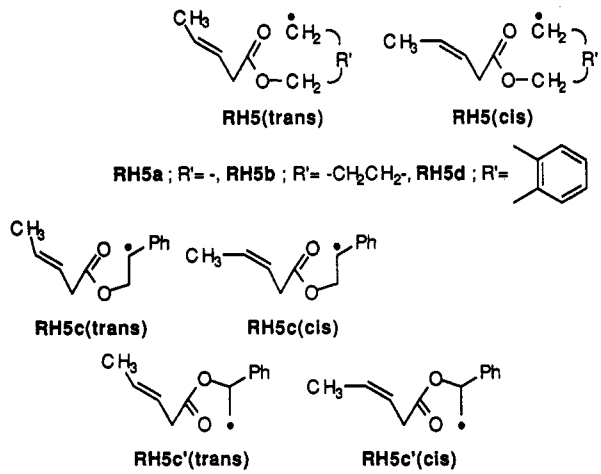
Table 4. Two-Center Energy of Bond D, D′ and Heat of Formation of RH4a, RH4b, RH4c, and RH4d[a]



compd	two-center energy (eV) bond D	bond D′	Δ(bond D–D′)	heat of formation (kcal/mol)	Δ(RH4-RH2)[b] (kcal/mol)
RH4a (*trans*)	−13.25			−58.99	−18.11
RH4a (*cis*)	−13.25			−58.86	−17.98
RH4b (*trans*)	−13.35			−64.24	−16.33
RH4b (*cis*)	−13.35			−64.20	−16.29
RH4c (*trans*)	−13.20	−13.24	+0.04	−31.95	−18.08
RH4c (*cis*)	−13.19	−13.23	+0.04	−31.77	−17.90
RH4d (*trans*)	−13.47			−27.85	−16.93
RH4d (*cis*)	−13.47			−27.75	−16.83

[a] Same as that of Table 3. [b] Data for **RH2** are in Table 3.

Table 5. Heat of Formation of RH5a, RH5b, RH5c, RH5c′, and RH5d[a]

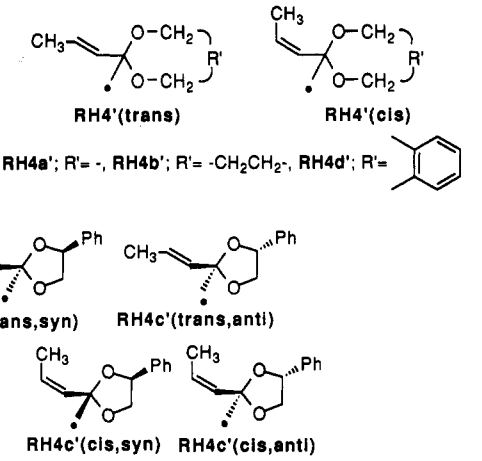


compd	heat of formation (kcal/mol)	Δ(RH5–RH4)[b] (kcal/mol)	Δ(RH5′–RH4)[b] (kcal/mol)
RH5a (*trans*)	−55.34	+3.65	
RH5a (*cis*)	−55.35	+3.51	
RH5b (*trans*)	−64.88	−0.64	
RH5b (*cis*)	−65.67	−1.47	
RH5c (*trans*)	−40.38	−8.43	
RH5c (*cis*)	−39.93	−8.16	
RH5c′ (*trans*)	−25.04		+6.91
RH5c′ (*cis*)	−23.46		+8.31
RH5d (*trans*)	−37.11	−9.26	
RH5d (*cis*)	−36.97	−9.22	

[a] Same as that of Table 3. [b] Data for **RH4** are in Table 4.

At last, calculations of the formation energy of radical intermediates **RH3**, **RH3′**, **RH4′**, **RH6**, **RH6′**, **RH7**, and **RH7′** were carried out to examine the selectivity in the formation of cyclobutane-containing units **3** and **3′**, the selectivity in proceeding through **RH4** or **RH4′** that affords δ-valerolactone-containing units **6** and **6′** (Scheme 5), and the possibility of formation of ε-caprolactone-containing units **7** and **7′** which are not shown in Scheme 5. Results are summarized in Tables 6–8.

Table 6. Heat of Formation of RH4′[a]



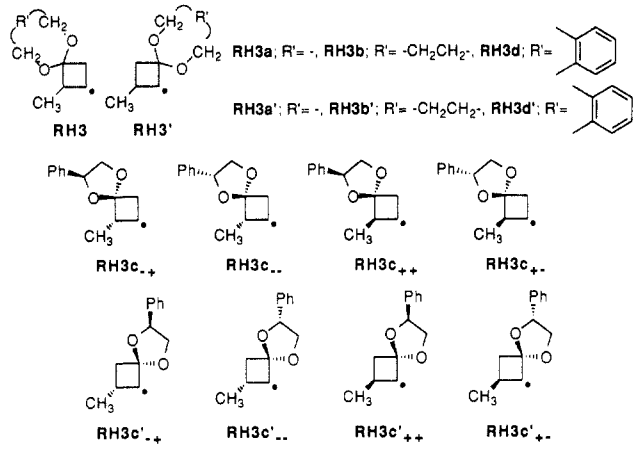
compd	heat of formation (kcal/mol)	Δ(RH4′–RH2)[b] (kcal/mol)
RH4a′ (*trans*)	−42.86	−1.98
RH4a′ (*cis*)	−40.98	−0.10
RH4b′ (*trans*)	−47.11	+0.80
RH4b′ (*cis*)	−45.34	+2.57
RH4c′ (*trans,syn*)	−13.84	+0.03
RH4c′ (*trans,anti*)	−13.00	+0.87
RH4c′ (*cis,syn*)	−11.93	+1.94
RH4c′ (*cis,anti*)	−12.72	+1.15
RH4d′ (*trans*)	−12.39	−1.47
RH4d′ (*cis*)	−10.34	+0.58

[a] Same as that of Table 3. [b] Data for **RH2** are in Table 3.

The formation energy of radical intermediate **RH4′** formed through cleavage of bond C′ which is not bonded directly to the acetal ring shows nearly the same value as that of its precursor **RH2** (Table 6). On the other hand, isomerization of **RH2** to **RH4** (competing reaction with isomerization of **RH2** to **RH4′**) is exothermic in 16.29–18.11 kcal/mol, as shown in Table 4. Accordingly, from the difference of the formation energies, that is only from the thermodynamic point of view, isomerization of **RH2** to **RH4** is more favorable than that of **RH2** to **RH4′**. However, from the examination of the two-center energy described in Table 3, bond C′ should be cloven more easily than bond C in ring-opening processes of **1a** and **1c** having a five-membered acetal ring. This tendency decreased in the cases of **1b** and **1d** having a seven-membered acetal ring, and the results of the examination of two-center energy are well-consistent with the experimental results as described before. In the polymerization of **1a**, the ratio of the content of **4a** to that of **4a′** increased as the polymerization temperature raised from 60 to 80 °C (Table 1, runs 1 and 2). This result strongly supports the conclusion from the examination of formation energy. So, the final conclusion is as follows; cleavage of bond C′ is kinetically more favorable than that of bond C, while cleavage of bond C is thermodynamically more favorable than that of bond C′ and therefore its ratio increases as the polymerization temperature raises.

The formation energy of cyclobutane-containing radical intermediate **RH3** is 8.38–11.44 kcal/mol larger than that of its precursor **RH4**, as shown in Table 7. On the contrary, that of the other cyclobutane-containing intermediate

Table 7. Heat of Formation of RH3 and RH3′ [a]



compd	heat of formation (kcal/mol)	Δ(RH3–RH4 (*trans*))[b] (kcal/mol)	Δ(RH3′–RH4′ (*trans*))[c] (kcal/mol)
RH3a	−50.61	+8.38	
RH3b	−55.20	+9.04	
RH3c$_{-+}$	−22.78	+9.17	
RH3c$_{--}$	−22.11	+9.84	
RH3c$_{++}$	−22.00	+9.95	
RH3c$_{+-}$	−21.62	+9.33	
RH3d	−20.51	+11.44	
RH3a′	−48.79		−5.93
RH3b′	−54.38		−7.27
RH3c′$_{-+}$	−20.41		−6.57
RH3c′$_{--}$	−21.05		−7.21
RH3c′$_{++}$	−19.95		−6.11
RH3c′$_{+-}$	−19.79		−5.87
RH3d′	−18.70		−6.31

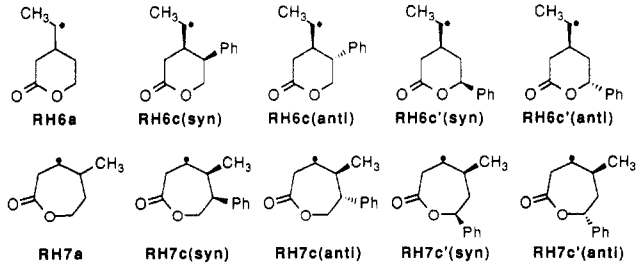
[a] Same as that of Table 3. [b] Data for **RH4** are in Table 4. [c] Data for **RH4′** are in Table 6.

RH3′ is 5.87–7.27 kcal/mol smaller than that of **RH4′**. So, the structure of the cyclobutane-containing unit would be **3′** formed through **RH3′**, although there is no evidence from the ^{1}H NMR spectra of the polymers because the determination of the ratio of **3** to **3′** is impossible due to their spectral similarity. Exothermic isomerization from **RH4′** to **RH3′** well explains the increase of cyclobutane-containing unit **3** and/or **3′** as the polymerization temperature raises from 60 to 80 °C (Table 1).

The data of Table 8 reveal that the formation energy of δ-valerolactone-containing radical intermediates **RH6** and **RH6′** is 7.52–24.72 smaller than that of their precursors **RH5** and **RH5′**, respectively. So, it is not unusual that once radical intermediates **RH5** and/or **RH5′** are formed, they are smoothly cyclized to **RH6** and/or **RH6′**, respectively. However, the content of double ring-opened **5** formed through propagating end radical **RH5** is larger than that of cyclized unit **6** in most cases in the polymerizations of **1a** and **1c**. Therefore, the activation energy of the radical cyclization must be larger than that of the radical addition to the monomer. **RH6** should be thermodynamically more stable than **RH5** because the ratio of **6c** to **5c** increased as the polymerization temperature rose (Table 1). On the other hand, since the formation energy of seven-membered cyclic radical intermediates **RH7** and/or **RH7′** is about 3–6 kcal/mol larger than that of corresponding six-membered intermediates **RH6** and/or **RH6′**, formation of the former intermediates would not be more favorable than that of the latter. However, since **RH7** and/or **RH7′** has a formation energy smaller than that of their precursors **RH5** and/or **RH5′**, formation of ϵ-caprolactone-containing unit **7** cannot completely be ruled out because **6** and **7** cannot be distinguished by the ^{1}H NMR spectrum. Anyhow, cyclization forming a seven-membered ring is much more unfavorable compared with the six-membered ring, as mentioned above, and from the viewpoint of the entropical factor and activation energy, **7** might not be formed in this case.

Examination of selectivity in the polymerization pathway of the radical polymerizations of **1** was carried out by calculation of the two-center energy and formation energy, as described above. Discussion with formation energy is only thermodynamic. However, discussion only by thermodynamic analysis is quite insufficient to examine the selectivity in a chemical reaction, especially in a radical reaction. Kinetic analysis is necessary and indispensable. Since the conclusion derived from the analysis of the two-center energy would reflect the activation energy of bond cleavage, it should contain the kinetic factor in a sense. The most essential and elegant method among the approaches to kinetic examination using molecular orbital theory is to directly calculate the activation energy of chemical reactions. However, generally, this method gives consistent results only when both starting and resulting systems are alike in structure, like in the Diels–Alder

Table 8. Heat of Formation of RH6, RH6′, RH7, and RH7′ [a]



compd	heat of formation (kcal/mol)	Δ(RH6–RH5(*trans*))[b] (kcal/mol)	Δ(RH6′–RH5′(*trans*))[b] (kcal/mol)	Δ(RH7–RH5(*trans*))[b] (kcal/mol)	Δ(RH7′–RH5′(*trans*))[b] (kcal/mol)
RH6a	−79.91	−24.57			
RH6c (*syn*)	−47.90	−7.52			
RH6c (*anti*)	−50.18	−9.80			
RH6c′ (*syn*)	−47.73		−22.69		
RH6c′ (*anti*)	−49.76		−24.72		
RH7a	−74.50			−19.16	
RH7c (*syn*)	−44.78			−4.40	
RH7c (*anti*)	−44.53			−4.15	
RH7c′ (*syn*)	−42.71				−17.67
RH7c′ (*anti*)	−45.05				−20.01

[a] Same as that of Table 3. [b] Data for **RH5**(*trans*) and **RH5′**(*trans*) are in Table 4.

Table 9. Volume Change on Radical Polymerization of 1c and 1d

monomer	density[a] monomer	density[a] polymer	volume change[b] (%)
1c	1.072	1.167[c]	−8.86
1d	1.173	1.210[d]	−3.15

[a] Measured by the density gradient tube method at 25 °C. [b] [Density(monomer) − density(polymer)]/density(monomer) × 100. [c] Run 9 in Table 1. [d] Run 11 in Table 1.

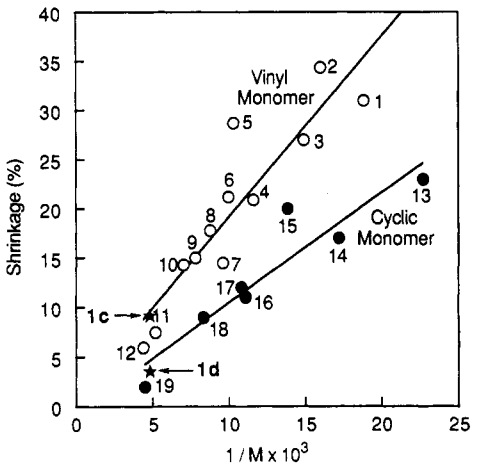


Figure 9. Relationship between volume shrinkage and reciprocal of molecular weight (M) (1, acrylonitrile; 2, vinyl chloride; 3, methacrylonitrile; 4, vinyl acetate; 5, vinylidene chloride; 6, methyl methacrylate; 7, styrene; 8, ethyl methacrylate; 9, n-propyl methacrylate; 10, n-butyl methacrylate, 11, N-vinylcarbazole; 12, 1-vinylpyrene; 13, ethylene oxide; 14, propylene oxide; 15, 2,2-dimethylethylene oxide, 16, 1,3,5-trioxane; 17, epichlorohydrin; 18, styrene oxide; 19, hexamethylcyclotrisiloxane).

reaction,[16] the Cope rearrangement,[17] the case of very simple calculation like assumption of rotational barrier, and so on, because of the limitation of not only the hardware but also the software of computer technology today. We hope the advancement of computer systems makes examination for transition states easier.

5. Volume Change on Polymerization. Densities of the monomers (1) and polymers formed were measured by the density gradient tube method at 25 °C. The results are summarized in Table 9. Volume shrinkage of **1c** and **1d** was 8.86 and 3.15%, respectively. **1d** showed the smallest volume shrinkage among radically polymerizable monomers.

Relationships between volume shrinkages on polymerization and the reciprocals of the molecular weights are shown for **1c** and **1d** as well as several ring-opening and vinyl monomers in Figure 9. Both the ring-opening and vinyl monomers are known to show linear relationships, and monomers which have larger molecular weights show smaller shrinkages.[18] Shrinkages of the vinyl monomers are about 2 times larger than those of the ring-opening monomers. This reason can be explained by the concept[5] of change in bond distance and distance between molecules on polymerization.

Degree of volume shrinkage of **1d** is usual, if **1d** can be regarded as an ordinary cyclic monomer. Meanwhile, **1c** shows shrinkage larger than that of **1d**. As for this reason, we can point out these two facts that the ratio of single ring-opened units (**3**, **3'**, **4**, **4'**, **6**, and **6'**) to double ring-opened units (**5** and **5'**) in poly(**1c**) is larger than that in poly(**1d**) and that the two monomers are different in phase; i.e. the density of **1d** is larger than that of **1c**, since **1d** is solid (mp 61–62 °C) but **1c** is liquid at room temperature.

Conclusion

In this paper, the radical polymerization of new hybrid monomers between vinylcyclopropanes and cyclic ketene acetals, vinylcyclopropanone cyclic acetals (1), was studied in detail. The structures of the polymers obtained were examined mainly by ^{1}H NMR and IR spectra in comparison with those of the model compounds of double ring-opened units. The structures of the polymers were dramatically changed according to ring size and substituent of the monomers. The results of the examination of the two-center energies and formation energies calculated by the MO method revealed the reason for this dramatic change in unit ratio of the polymers, i.e. the ratios of the single ring-opened, double ring-opened, cyclobutane-containing, and lactone-containing units. We are confident that the MO calculation is one of the most powerful tools to solve the mechanistic ambiguity not only for the radical polymerization of this work but also for various radical reactions and polymerizations. The volume expansion of polymerization of 1 was not observed, probably due to the occurrence of other processes causing volume shrinkage in addition to the double ring-opening polymerization which might result in volume expansion.

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