Radical Polymerizaion Behavior of 1,1-Disubstituted 2-Vinylcyclopropanes

Fumio Sanda, Toshikazu Takata, and Takeshi Endo*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta-cho, Midori-ku, Yokohama 227, Japan

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ABSTRACT: Radical polymerizations of 1,1-disubstituted 2-vinylcyclopropanes (**1a–c**) were carried out, and the structures of the obtained polymers, mechanism of the polymerization, and volume change on polymerization were studied. From the detailed analyses of the ^{1}H and ^{13}C NMR spectra of the obtained polymers, a unit which was supposed to have a cyclobutane ring was confirmed in addition to the 1,5-type ring-opened unit. On the basis of the structure of the polymer, the selectivity in the direction of cleavage of the cyclopropane ring of **1a** was found not to be 100%. Molecular orbital calculations were carried out to discuss the mechanism of the polymerization. The results of the calculations suggested that the formation of the cyclobutane unit is thermodynamically possible, and the selectivity in the direction of cleavage of the cyclopropane ring of **1a** is lower than that of **1b** from the difference of two-center energies. The radical polymerization of **1a–c** showed a volume shrinkage larger than those of usual ring-opening monomers. This result was suggested to be due to the occurrence of polymerization other than the 1,5-type ring-opening polymerization.

Introduction

Vinylcyclopropane (1; X, Y = H) undergoes radical polymerization to give a polymer consisting of a 1,5-ring-opened unit (**2**) and an unidentified unit.[1] On the contrary, vinylcyclopropanes having chloro(X = H, Y = Cl)[2] and dichloro (X, Y = Cl)[3] groups as radical-stabilizing moieties are reported to undergo radical polymerization to afford only 1,5-ring-opened polymer **2**. Similar results are obtained with vinylcyclopropanes substituted by electron-withdrawing groups such as ester and/or cyano and phenyl groups (X = H, Y = CO_2Et;[4] X, Y = CO_2Et;[5] X = CO_2Et, Y = CN;[5] X, Y = CN;[5] X = H, Y = Ph;[6] X = CO_2Et, Y = Ph[4e]) (Scheme I).

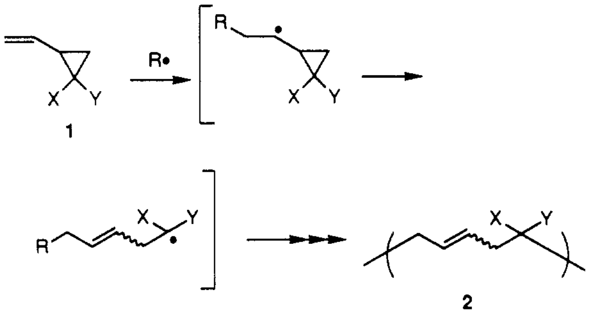
Since vinylcyclopropanes **1** are ring-opening monomers, they are expected to be applied to materials which show low shrinkage in volume on radical polymerization.[7] However, there are no reports on the volume change on polymerization of **1**. Furthermore, the structure of the produced polymer and the mechanism of the polymerization are not sufficiently investigated. In this paper, detailed studies of the radical polymerization of **1**, especially the structure of the obtained polymer, the mechanism of the polymerization, and the volume change on polymerization, are disclosed.

Experimental Section

Measurements. ^{1}H and ^{13}C NMR spectra of monomers and polymers were recorded at 27 °C on JEOL JNM-EX-90 and JNM-GX-500 spectrometers, using tetramethylsilane (TMS) as an internal standard in deuteriochloroform. FT-IR spectra were obtained with a JASCO FT/IR-3 at 25 °C. Molecular weight and its distribution (MWD, $\bar{M}_w/\bar{M}_n$) were determined by gel permeation chromatography (GPC) on a TOSO HPLC CCP & 8000 system with a data processor equipped with three polystyrene gel columns (TSK gel G2000H, G2500H, and G3000H), using tetrahydrofuran (THF) as an eluent (flow rate 1.0 mL/min), polystyrene calibration, and refractive index (RI) and ultraviolet (UV) detectors.

Materials. Chlorobenzene was dried and distilled by the usual method and stored over molecular sieves (4A). Initiators 2,2′-azobis(isobutyronitrile) (Wako Pure Chemical Industries, Ltd.), benzoyl peroxide (Koso Chemical Co.), and di-*tert*-butyl peroxide (Nacalai Tesque, Inc.) were used as received.

Scheme I



X, Y=Cl, CO_2Et, CN, Ph

Synthesis of 1,1-Dichloro-2-vinylcyclopropane (1a). 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 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.[3b] bp 48 °C/40 mmHg); yield 47.0 g (23%): ^{1}H NMR δ 1.26–1.90 (m, 2 H), 2.08–2.50 (m, 1 H), 5.03–5.58 (m, 3 H); IR (neat) 3060, 2980, 2810, 1630, 1418, 1218, 915, 759, 665 cm^{-1}.

Synthesis of 1,1-Bis(ethoxycarbonyl)-2-vinylcyclopropane (1b). To a solution of 1,4-dibromo-2-butene (12.5 g, 58.4 mmol) and diethyl malonate (9.35 g, 58.4 mmol) in ethanol (50 mL) was added dropwise an ethanol solution of sodium ethoxide, which was prepared from sodium (2.69 g, 117 mmol) and ethanol (60 mL) at 70 °C. After the addition, 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, bp 90–96 °C/10 mmHg (lit.[8] bp 69–72 °C/0.5 mmHg); yield 3.22 g (26%): ^{1}H NMR δ 1.30 (t, J = 6.0 Hz, 6 H), 1.48–1.78 (m, 2 H), 2.30–2.75 (m, 1 H), 4.17 (q, J = 6.0 Hz, 4 H), 4.93–5.60 (m, 3 H); IR (neat) 3075, 2960, 1722, 1638, 1365, 1315, 1264, 1200, 1130 cm^{-1}.

Synthesis of 1,1-Dicyano-2-vinylcyclopropane (1c). To a solution of malononitrile (3.86 g, 58.4 mmol) and silver oxide (13.5 g, 58.4 mmol) in tetrahydrofuran (THF) (20 mL) was added dropwise 1,4-dibromo-2-butene (12.5 g, 58.4 mmol) with continuous THF refluxing. After the mixture was refluxed for 9 h, the resulting mass was filtered off and washed with THF. The combined filtrate was evaporated, and the residue was distilled under reduced pressure, bp 68 °C/0.8 mmHg (lit.[5c] bp 50–51 °C/

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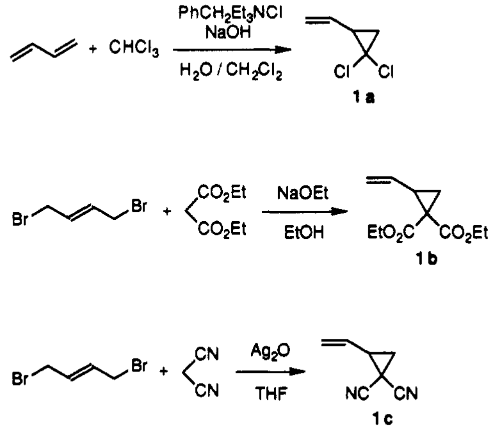
Table I
Radical Polymerization of **1a–c**[a]

								polymer structure[d] (%)		
run	monomer	init[b]	temp (°C)	solv[c] (mL)	conv[d] (%)	$\bar{M}_n$[e]	$\bar{M}_w/\bar{M}_n$[e]	**2**	**2′**	**3**
1	**1a**	AIBN	60		8	1260	1.53	68	24	8
2	**1a**	BPO	80		20	1250	1.74	55	21	24
3	**1a**	DTBP	120		21	960	1.93	40	26	34
4	**1b**	AIBN	60		72[f]	25260	2.38	94	0	6
5	**1b**	BPO	80		97[f]	16780	2.75	40	0	60
6	**1b**	DTBP	120		93[f]	13800	2.86	58	0	42
7	**1b**	DTBP	120	CB	84	7780	2.65	53	0	47
8	**1c**	AIBN	60		78					
9	**1c**	BPO	80		99					
10	**1c**	DTBP	120		87					

[a] Conditions: monomer, 3 mmol; 20 h. [b] 3 mol % AIBN (2,2′-azobis(isobutyronitrile)), BPO (benzoyl peroxide), or DTBP (di-*tert*-butyl peroxide). [c] CB = chlorobenzene, 2.82 M. [d] Estimated by ^{1}H NMR. [e] Estimated by GPC (based on PSt). [f] Estimated by GC.

Scheme II



0.3 mmHg); yield 1.52 g (22%): ^{1}H NMR δ 1.63–2.10 (m, 2 H), 2.40–2.78 (m, 1 H), 5.42 (s, 3 H); IR (neat) 3100, 3010, 1640, 1441, 1262, 1069, 930, 703 cm^{-1}.

Polymerizations of 1a–c. General Procedure. To a monomer (3 mmol) in a polymerization tube was introduced an initiator and subsequently dry solvent, if required. The tube was cooled, degassed, sealed off, and heated at a set temperature for 20 h. Polymer was isolated from the resulting mixture by separation with a preparative HPLC (Nihon Bunseki Kogyo) equipped with two polystyrene gel columns (JAIGEL-H1 and JAIGEL-H2), using chloroform as an eluent (flow rate 3.8 mL/min, RI and UV detectors).

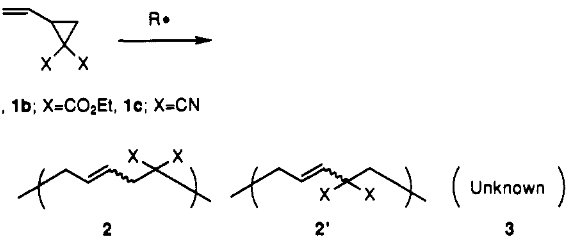
Measurements of Density. Densities of the monomers and polymers were measured by the density gradient tube method at 25 °C with a Shibayama Kagaku Seisakusho Model A.

Molecular Orbital Calculations. All computations were done on a Hitachi EWS 2050G with the use of MOPAC version 5.01 (QCPE No. 455).[9] The calculations were carried out by the PM3 program. Starting geometries were obtained by a Hitachi MODELMATE system. The energies of the compounds were calculated by the unrestricted Hartree–Fock (UHF) method. All calculations were done with full optimization of all geometrical variables (bond length, bond angles, and dihedral angles).

Results and Discussion

1. Syntheses of 1a–c. Monomer **1a** was prepared from butadiene and chloroform by treatment with sodium hydroxide in the presence of benzyltriethylammonium chloride as a phase transfer catalyst,[3b] monomer **1b** was prepared by treating 1,4-dibromo-2-butene and diethyl malonate with sodium ethoxide,[8] and monomer **1c** was prepared by the reaction of 1,4-dibromo-2-butene and malononitrile with silver oxide,[10] according to the previously reported methods (Scheme II).

2. Radical Polymerizations of 1a–c. The radical polymerization of **1** was carried out in the presence of 2,2′-azobis(isobutyronitrile) (AIBN), benzoyl peroxide (BPO), or di-*tert*-butyl peroxide (DTBP) as the radical initiator. The results and conditions are summarized in Table I.



Colorless transparent liquid polymers, which were soluble in chloroform, THF, *n*-hexane, and methanol, were obtained by the polymerization of **1a** and **1b**. A pale yellow opaque solid polymer, which was insoluble in dichloromethane, chloroform, acetonitrile, THF, DMF, and DMSO, was obtained by the polymerization of **1c**. In the previously reported paper, poly(**1c**) is commented to be not completely soluble in DMSO at 25 °C.[5b]

In the polymerizations of **1a** and **1b**, the molecular weight of the obtained polymer decreased while the molecular weight distribution increased as the polymerization temperature increased. In the polymerization of **1b**, both the conversion of **1b** and the molecular weight of the polymer were larger than those in the case of **1a**, probably because the radical-stabilizing effect of the ethoxycarbonyl group (see Scheme I) is larger than that of the chloro group in the propagating end. The tendency of the above molecular weight change agrees with the previously reported results.[3b,5c]

It has been reported that a 1,5-type ring-opened polymer unit **2** is predominantly formed in the polymerization of 1,1-disubstituted 2-vinylcyclopropanes (**1**).[3–5] However, we have concluded that the radical polymerization of **1** is more complicated to afford polymer units other than **2** from the following structural analysis of the polymers.

The structure of the polymers (poly(**1a**) and poly(**1b**)) was examined by their ^{1}H NMR and ^{13}C NMR spectra (Figures 1–4). The absence of signals based on cyclopropane ring protons (1.3–1.8 ppm for **1a** and 1.5–1.8 ppm for **1b**, respectively) in the ^{1}H NMR spectra confirmed that no cyclopropane ring structure was incorporated into the polymer.

From the ^{1}H NMR spectra of poly(**1a**) (Figure 1), it is clear that some polymer unit other than the 1,5-type ring-opened unit **2a** is present, because of the existence of the broad signal a around 2.5 ppm. Furthermore, the ratio of methylene protons b to olefinic protons c was not exactly 2:1. This suggests that the polymer contains not only **2a** but also **2a′**, which is formed by cleavage of another bond

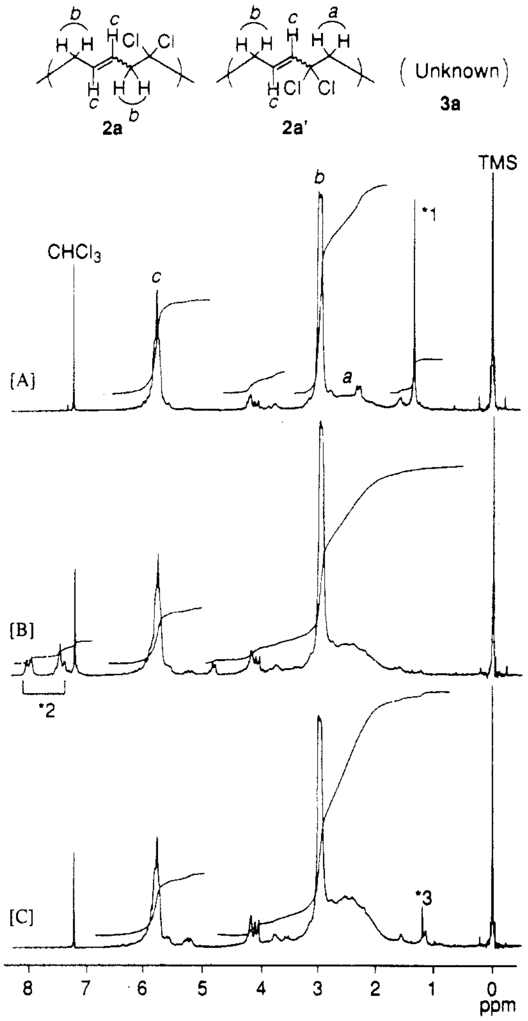


Figure 1. ^{1}H NMR spectra of poly(1a) (solvent $CDCl_3$, 90 MHz). (A) Polymerization conditions: bulk, 3 mol % AIBN, 60 °C, 20 h (run 1 in Table I). *1 is the signal derived from AIBN. (B) Polymerization conditions: bulk, 3 mol % BPO, 80 °C, 20 h (run 2 in Table I). *2 is the signal derived from BPO. (C) Polymerization conditions: bulk, 3 mol % DTBP, 120 °C, 20 h (run 3 in Table I). *3 is the signal derived from DTBP.

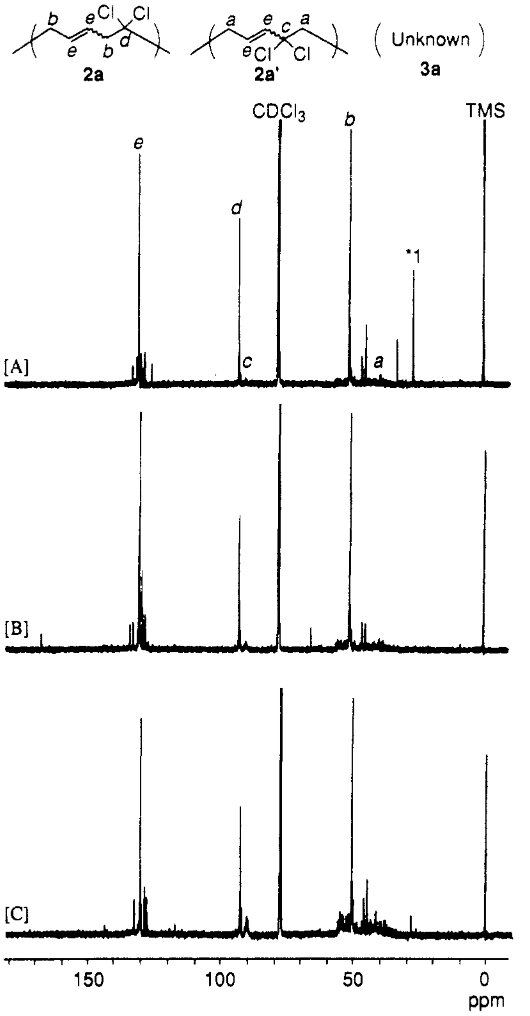
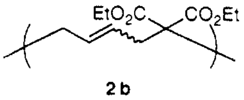


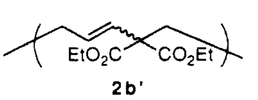
Figure 2. ^{13}C NMR spectra of poly(1a) (solvent $CDCl_3$, 125 MHz). (A) Polymerization conditions: bulk, 3 mol % AIBN, 60 °C, 20 h (run 1 in Table I). *1 is the signal derived from AIBN. (B) Polymerization conditions: bulk, 3 mol % BPO, 80 °C, 20 h (run 2 in Table I). (C) Polymerization conditions: bulk, 3 mol % DTBP, 120 °C, 20 h (run 3 in Table I).

of the cyclopropane ring. Since the integration ratio of the signal c of this polymer is smaller than that expected for a polymer that consists only of 1,5-type ring-opened units **2a** and **2a′**, another polymer unit should be present. In the ^{13}C NMR spectra of poly(**1a**) (Figure 2), signals which cannot be assigned to **2a** and **2a′** were observed at 35–55 ppm, and the ratio of these signals increased as the polymerization temperature increased. This tendency was the same as that in the ^{1}H NMR spectra (Figure 1).

On the other hand, in the ^{1}H NMR spectra of poly(**1b**) (Figure 3), a broad signal at 1.5–2.5 ppm, which could not be assigned to **2b**, was much more clearly observed in the polymers obtained by the polymerization with BPO and DTBP than in the polymer obtained with AIBN. This signal is derived from a unit which has no olefinic proton, because the ratio of olefinic proton is smaller than that for polymer which consists only of a 1,5-type ring-opened unit (**2b**). Since the ratio of the signals b:d is 2:1, **2b′** would not be contained in poly(**1b**). In the ^{13}C NMR spectra of poly(**1b**) (Figure 4), a signal other than those of **2b** is also observed at 30–45 ppm (broad) and 170–172 ppm.

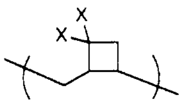


2b

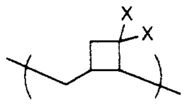


2b′

As mentioned above, in the polymerization of either **1a** or **1b**, an unidentified unit which has no olefinic proton should be formed. If the disappearance of the olefinic structure occurs by an intermolecular reaction such as grafting or cross-linking, the ratio of this unknown unit should decrease in the solution polymerization. However, this ratio did not decrease (runs 6 and 7 in Table I). Therefore, this unknown unit would be formed by an *intramolecular* reaction. The most probable structure seems to be cyclobutane-containing unit **4** or **4′**, which is similar to that reported in the cationic polymerization of vinylcyclopropane.[2] However, the detailed structure is not yet clear because of the difficult characterization of the cyclobutane structure by NMR spectra.



4



4′

In the polymerization of **1a**, both the ratio of the unknown unit and the ratio of **2a′** against **2a** increased as the polymerization temperature increased. In the polymerization of **1b**, unit **2b′** could not be observed in the polymer. The higher radical-stabilizing effect of the ethoxycarbonyl group in the propagating end might cause

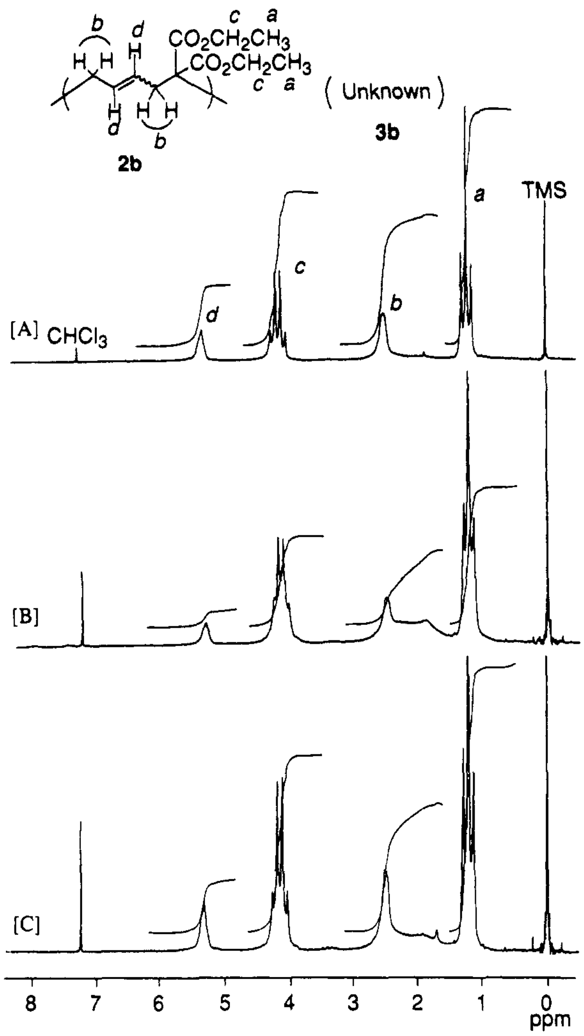


Figure 3. ^{1}H NMR spectra of poly(**1b**) (solvent $CDCl_3$, 90 MHz). (A) Polymerization conditions: bulk, 3 mol % AIBN, 60 °C, 20 h (run 4 in Table I). (B) Polymerization conditions: bulk, 3 mol % BPO, 80 °C, 20 h (run 5 in Table I). (C) Polymerization conditions: bulk, 3 mol % DTBP, 120 °C, 20 h (run 6 in Table I).

the selective cleavage of the cyclopropane ring of **1b**. Molecular orbital calculations were carried out to examine this point. Details of the calculations are discussed later in this paper. The ratio of the unknown unit in the polymerization of **1b** was higher than that in the polymerization of **1a**. If the cyclobutane unit **4** and/or **4′** is actually formed, the increase of the ratio of the cyclobutane unit can be caused by the stabilized propagation end, since the intramolecular reaction leading to **4** or **4′** favorably occurs with a long-lived propagation end radical which is stabilized by the ethoxycarbonyl group of **1b**.

3. Comments on the Polymerization Mechanism. If the unknown unit is assumed to have the cyclobutane structure **4** and/or **4′**, the mechanism of the polymerization of **1** is considered as shown in Scheme III.

1,5-Type ring-opened units **2** and **2′** are formed through paths A and A′, respectively. The cyclobutane units **4** and **4′** are formed through paths B and B′ (ring expansion via a 1,2-alkyl shift) and/or paths C and C′ (cyclobutanation via intramolecular radical addition to the double bond). A 1,2-shift of hydrogen and a simple alkyl group hardly ever occurs, probably because it needs a very large activation energy (30–35 kcal/mol),[11] and therefore paths C and C′ are thought to be more feasible than paths B and B′ as courses for the cyclobutane unit. Path D, which gives a simple vinyl polymerization unit **8**, is also possible,

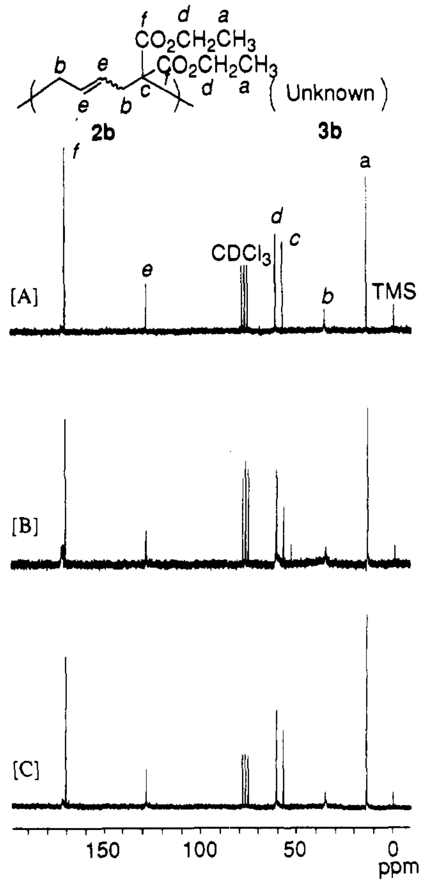
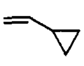


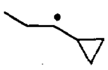
Figure 4. ^{13}C NMR spectra of poly(**1b**) (solvent $CDCl_3$, 22.5 MHz). (A) Polymerization conditions: bulk, 3 mol % AIBN, 60 °C, 20 h (run 4 in Table I). (B) Polymerization conditions: bulk, 3 mol % BPO, 80 °C, 20 h (run 5 in Table I). (C) Polymerization conditions: bulk, 3 mol % DTBP, 120 °C, 20 h (run 6 in Table I).

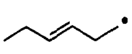
although **8** is not observed in the polymerization.

Molecular orbital calculations were carried out to examine the mechanism of the radical polymerization of **1**. For simplification, the calculation was performed for **1d** (X, Y = H) and a few radical intermediates (**5d**, **6d**(*trans*), **6d**(*cis*), and **7d**) which would be formed by the addition of methyl radical to the exo carbon atom of the vinyl group of **1d**. Thus the mechanism of the polymerization of **1d** can be simply illustrated as in Scheme IV.

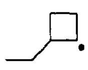
Heats of formation calculated for **1d** and the radical intermediates are listed in Table II.


1d


5d


6d(*trans*)

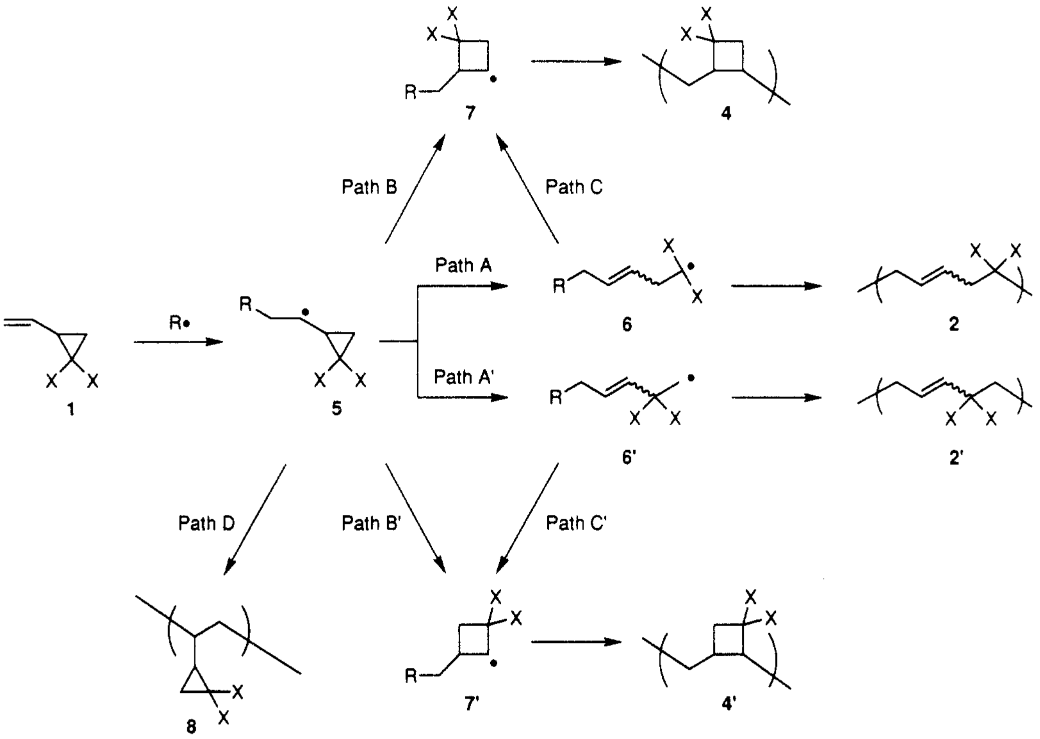

6d(*cis*)


7d

The heat of formation for **1d** was 33.8 kcal/mol. It seems to be relatively high, perhaps due to the ring strain of the cyclopropane ring. The heats of formation reported for **1d** so far[12] are compared with that obtained by this work in Table III. The value obtained by the PM3 method in this work agrees well with that obtained by the IMOA method. The value obtained by the MINDO/3 method is smaller than those obtained by the PM3 and IMOA methods, probably due to the tendency of the MINDO/3 method to underestimate the strain energy of the cyclopropane ring.[12]

The optimized geometries of **1d** and the intermediates are shown in Figure 5. The s-trans form is reported to be the most stable conformation of **1d** by an ab initio calculation.[13] Therefore, the s-trans form of **1d** was adopted for the conformation of **5d**, which was formed by

Scheme III



Scheme IV

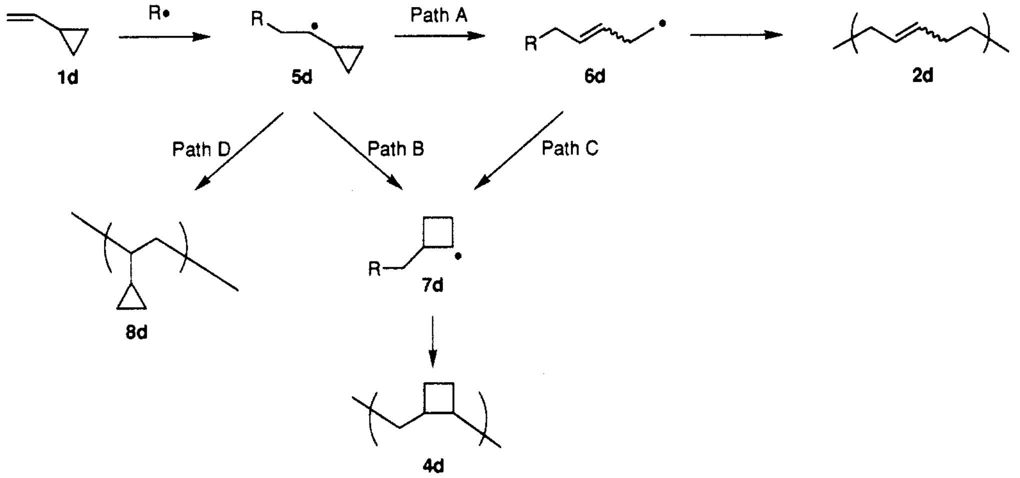


Table II
Calculated Heats of Formation for 1d, 5d, 6d(*trans*), 6d(*cis*), and 7d

compound	heat of formation[a] (kcal/mol)	compound	heat of formation[a] (kcal/mol)
1d	33.83864	**6d(*cis*)**	19.61931
5d	24.33042	**7d**	18.07876
6d(*trans*)	21.21033		

[a] Calculated by the PM3 (UHF) method, MOPAC Version 5.01.

Table III
Calculated Heats of Formation for 1d by Different Methods

method	heat of formation (kcal/mol)
PM3 (this work)	33.8
MINDO/3	27.1
IMOA	34.7

the addition of methyl radical to **1d**. The conformations of **6d(*trans*)** and **6d(*cis*)** are considered as trans zigzag forms. The s-trans form of **5d** was also adopted for the conformation of **7d**, which contained the cyclobutane ring.

Although vinylcyclopropanes had been reported to undergo selectively 1,5-type ring-opening polymerization,[2-6] this work demonstrated the occurrence of another type of polymerization in addition to the 1,5-type ring-opening polymerization. If this new type of polymerization proceeds through paths B and B′ or paths C and C′ (Scheme III), we can make the following comments about the mechanism of the polymerization of vinylcyclopropanes according to the results of the PM3 calculation.

The main path of the polymerization is thought to be path A (Scheme IV) from the experimental results. This agrees with the fact that the heat of formation for **6d** is smaller than that for **5d**. It is reasonable that the isomerization of **5d** to **6d** proceeds smoothly. Since the heat of formation for **6d(*cis*)** is lower by 1.6 kcal/mol than that for **6d(*trans*)** (Table II), the cis isomer would be thermodynamically more likely to be formed than the trans isomer. However, it is reported that the double bonds of the polymers obtained from 1,1-disubstituted 2-vinylcyclopropanes have trans configurations from IR analysis,[5b]

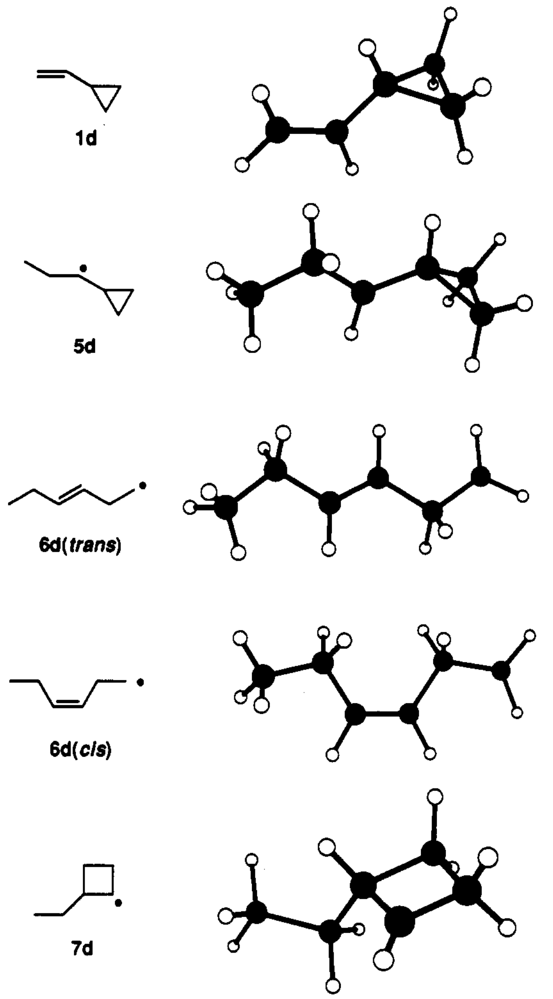
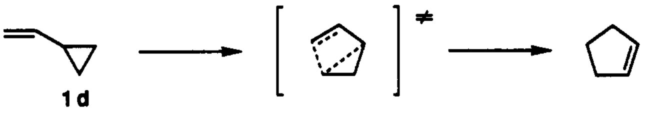


Figure 5. PM3-optimized geometries of **1d**, **5d**, **6d**(*trans*), **6d**(*cis*), and **7d**.

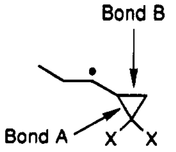
Scheme V



although it seems to be very difficult to estimate the configuration by IR analysis. It is easily conceivable that the 1–2 kcal/mol difference in heat of formation by the dependence on substituents can be observed. Further investigation is needed to make this point clear.

Since the heat of formation of cyclobutane-containing intermediate **7d** is smaller than that of **6d** (Table II), it is not strange that the polymerization proceeds to give **4d** through paths B or C, thermodynamically more favorable than path A. However, the polymerization actually proceeded mainly through path A, affording the 1,5-type ring-opened polymer **2**, rather than paths B or C (Scheme IV). Isomerization of vinylcyclopropane to cyclopentene (Scheme V) has been reported to require a large activation energy, 49.7 kcal/mol by experiment[14] and 63.6 kcal/mol by calculation by the AM1 method.[15] Since path B or C in Scheme IV resembles the path of Scheme V, they should require a large activation energy, too. So, the isomerization of **5d** or **6d** to cyclobutyl radical intermediate **7d** would hardly occur kinetically. This agrees with the experimental result that the ratio of the cyclobutane unit predicted increases as the polymerization temperature increase (Table I, runs 1–3).

Table IV
Two-Center Energy of Bonds A and B of 5a–d



compound	two-center energy (eV) bond A	bond B	Δ(bond A − bond B)
5a (X = Cl)	−11.45	−11.67	0.22
5b (X = CO_2Et)	−10.90	−12.20	1.30
5c (X = CN)	−11.07	−12.03	0.96
5d (X = H)	−11.77		

Table V
Volume Change on Radical Polymerization of 1a–c

monomer	density[a] monomer	polymer	vol change[b] (%)
1a	1.167	1.360[c]	−16.54
1b	1.020	1.134[d]	−11.18
1c	0.998	1.136[e]	−13.83

[a] Measured by the density gradient tube method at 25 °C. [b] [Density(monomer) − density(polymer)]/density(monomer) × 100. [c] Run 3 in Table I. [d] Run 6 in Table I. [e] Run 10 in Table I.

As described above, **1b** shows a selectivity higher than **1a** in the cleavage of the cyclopropane ring. To examine this point, two-center energies of **5a–d** were calculated by the PM3 method (Table IV). The two-center energy between two atoms which are bound to 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.[16] Since bond B of **5a–c** has a negatively larger value than bond A in any case, bond B can be regarded to be more stable than bond A. The difference in the two-center energy between bonds A and B of **5b** is about 6 times larger than that of **5a** (Table IV), and, therefore, the ease of the cleavage of bond A in comparison with that of bond B, that is, the selectivity of the cleavage of bond A, is larger in **5b** than in **5a**. This result agrees well with the experimental results. **5c** would show nearly the same selectivity in the bond cleavage of the cyclopropane ring as was shown in the polymerization of **5b** from the difference of the two-center energies of bonds A and B, although there is no clear experimental evidence.

4. Volume Change on Polymerization. The densities of the monomers (**1**) and polymers (**2**) were measured by the density gradient tube method at 25 °C. The results are summarized in Table V. Volume shrinkage was ca. 15% on average.

The relationship between the volume shrinkage on polymerization and the reciprocal of the molecular weight is shown for **1a–c** as well as several ring-opening and vinyl monomers in Figure 6.[17] Both the ring-opening and vinyl monomers showed linear relationships. Monomers having larger molecular weights showed smaller shrinkage. Shrinkage of the vinyl monomers was about 2 times larger than that of the ring-opening monomers. This can be explained by the concept[18] of the change in bond distance and distance between molecules on polymerization.

1a–c showed a shrinkage larger than the usual ring-opening monomers. For this reason, we suggest that there is a contribution to the volume shrinkage of the occurrence of another kind of polymerization in addition to the 1,5-type ring-opening polymerization for **1a** and **1b**. In the case of **1c**, the reason is not clear because the structure of the polymer was not determined due to its insolubility in organic solvents. Judging from the shrinkage, **1c** is also

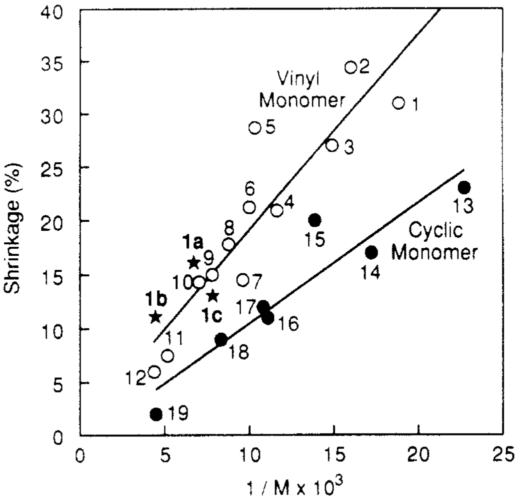


Figure 6. Relationship between shrinkage on volume and molecular weight (*M*) (1, acrylonitrile; 2, vinyl chloride; 3, methacrylonitrile; 4, vinyl acetate; 5, vinylidene chloride; 6, methyl methacrylate; 7, styrene; 8, ethyl methacrylate; 9, *n*-propyl methacrylate; 10, *n*-butyl methacrylate; 11, *N*-vinylcarbazole; 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).

suggested to undergo a polymerization similar to those of **1a** and **1b** as well as the formal 1,5-ring-opening polymerization.

Summary

In the radical polymerization of 1,1-disubstituted 2-vinylcyclopropanes, a new unit, which is supposed to have the cyclobutane structure, was formed in addition to the 1,5-type ring-opened unit. In addition, the selectivity in the direction of the cleavage of the cyclopropane ring of **1a** was not 100%. It was clarified that the formation of the cyclobutane unit is thermodynamically possible, and the lower selectivity in the direction of the cleavage of the cyclopropane ring of **1a** than that of **1b** can be proved by the molecular orbital calculation. The shrinkage in volume on polymerization of 1,1-disubstituted 2-vinylcyclopropanes was similar to those of usual vinyl monomers but larger than those of usual ring-opening monomers, and this extra shrinkage was suggested to be caused mainly by the contribution of the formation of the cyclobutane-containing unit.

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