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Radical Ring-Opening Polymerization of Novel Vinylcyclopropanes Designed as Low Shrinkage Monomers. Structure of the Polymer, Mechanism of the Polymerization, and Volume Change on the Polymerization

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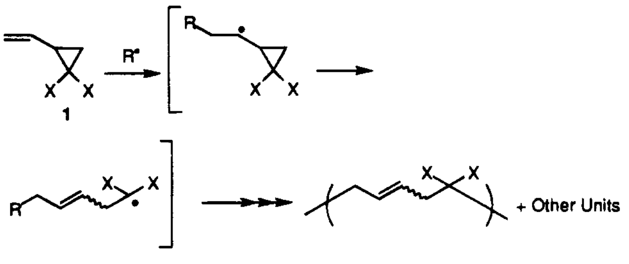
ABSTRACT: Synthesis and radical polymerization of new vinylcyclopropane derivatives, 1,1-bis(ethoxycarbonyl)-2-isopropenylcyclopropane (**4a**) and 1,1-bis(ethoxycarbonyl)-2-isopropenyl-2-methylcyclopropane (**4b**), were carried out. **4a** and **4b** were prepared by treating 1,4-dibromo-2-butene derivatives and diethyl malonate with sodium ethoxide. The radical polymerization of **4** was carried out in the presence of an appropriate initiator (3 mol % vs monomer) at 60–120 °C. The polymers which were insoluble in methanol/water (volume ratio = 80:20), were obtained as transparent solids. The conversion of **4a** in the polymerizations in both bulk and chlorobenzene was 95–99%. On the other hand, the conversion of **4b** was 40–48%. From the detailed analyses of ^{1}H and ^{13}C NMR spectra of the polymers obtained, poly(**4a**) was determined to consist of 1,5-ring-opened units in cis and trans configurations in the main chain and a cyclobutane-containing unit. The content ratio of poly(**4a**) in the trans configuration to that of the cis configuration increased as the polymerization temperature was raised. Poly(**4b**) was determined to consist of a 1,5-ring-opened unit in the trans configuration and a cyclobutane-containing unit. MM and MO calculations were carried out to examine the difference in the selectivity of radical ring-opening polymerizations of **4a** and **4b**. The results of examination of the conformation of **4** and activation energy in the addition reaction of the trimethylmethyl radical to **4** agreed well with the selectivity in the configuration of the main chain of the polymers. The degrees of volume shrinkage on the polymerization of **4a** and **4b** were 10.4 and 10.2%, and the T_g's of **4a** and **4b** were 24 and 3 °C, respectively.

Introduction

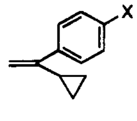
Cyclic monomers which undergo ring-opening polymerization are important in the field of materials such as precision materials, adhesives, and so on, since they show low shrinkage or sometimes expansion in volume on polymerization.[1] Many monomers and materials undergo polymerization and curing via a radical process. Since, generally, vinyl polymerization is accompanied by volume shrinkage larger than ring-opening polymerization, monomers and materials that show low shrinkage or some expansion in volume through radical ring-opening polymerization are specially useful. Vinylcyclopropanes are typical monomers which undergo radical ring-opening polymerization to give polymers bearing mainly a 1,5-ring-opened unit.[2] However, vinylcyclopropanes like **1a–c** show volume shrinkage (11–17%) larger than common cyclic monomers.[2n] In the course of our study on the development of monomers undertaking low volume shrinkage via the radical polymerization process, we have recently clarified the detailed structure of the polymer of **1**. Namely, the polymer involved not only the proposed 1,5-ring-opened unit but also another possible 1,5-ring-opened unit and cyclobutane unit. The somewhat large volume shrinkage of **1** was suggested to be due to the formation of the cyclobutane via ring formation during the polymerization process contributing to the volume shrinkage (Scheme 1).

Scheme 1

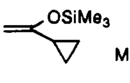


X = Cl (**1a**), CO$_2$Et (**1b**), CN (**1c**)

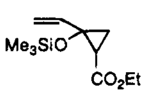
Meanwhile, vinylcyclopropanes having aryl (**2a–c**)[3] and trimethylsiloxy groups (**3a–c**)[4] have been reported to afford polymers bearing only a 1,5-ring-opened unit without any cyclobutane unit and the volume shrinkage



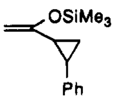
X = Cl (**2a**), H (**2b**), OMe (**2c**)



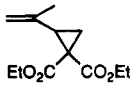
3a



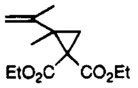
3b



3c



4a



4b

on polymerization of **2a–c** is considerably small (7.2–8.6%).[3] These monomers seem to have the essential structure suitable for low shrinkage monomers. However, the rate of polymerization of **2** is fairly slow probably because of the bulky aryl group on the vinyl

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moiety. Furthermore, handling of **3** is rather difficult since **3** as well as its polymers is sensitive to water because of the hydrolytic trimethylsiloxy group.[4] Recently, we have devised a candidate monomer **4** which can show high radical polymerizability, high stability against water, and small volume shrinkage on polymerization. In this paper, the radical ring-opening polymerization of **4**, structure of the polymer, mechanism of the polymerization, and volume change on polymerization are described.

Experimental Section

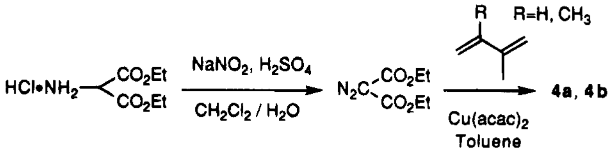
Measurements. ^{1}H and ^{13}C NMR spectra of monomers and polymers were recorded on a JEOL GSX-270 spectrometer using tetramethylsilane (TMS) as an internal standard in deuteriochloroform at 27 °C. IR spectra were obtained with a Hitachi Model 260-10 at 25 °C. Molecular weight and its distribution ($\bar{M}_w/\bar{M}_n$) were determined by gel permeation chromatography (GPC) on a Shimadzu LC-6A system with a data processor, equipped with three polystyrene gel columns (Shim-pack, HSG-20H, HSG-40H, and HSG-60S), using tetrahydrofuran as an eluent (flow rate 1.0 mL/min) and a refractive index detector by comparison to polystyrene standard samples. Thermal analyses were performed on a Rigaku Denki DSC8230. The glass transition temperature (T_g) by differential scanning calorimetry was taken as an inflection point on a trace. Densities of **4** and their polymers were measured by density gradient tubes at 25 °C with a Shibayama Kagaku Seisakusho model-A.

Materials. 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 was distilled over calcium hydride after washing with concentrated sulfuric acid, aqueous sodium hydrogen carbonate, and water and stored over molecular sieves (4 Å).

Synthesis of 4a. 1,4-Dibromo-2-methyl-2-butene (5a). To a solution of isoprene (68.1 g, 1.00 mol) in carbon tetrachloride (250 mL) was added dropwise a solution of bromine (160 g, 1.00 mol) in carbon tetrachloride (70 mL) and then water (200 mL) at 0 °C. The addition was followed by stirring at room temperature for 5 min. The mixture was extracted with carbon tetrachloride (200 mL × 2) and the organic layer was washed with a saturated solution of sodium hydrogen carbonate (100 mL). The organic layer was dried over anhydrous sodium sulfate and evaporated. The residue was distilled under reduced pressure to yield a colorless oil; yield 192 g (84%), bp 53–55 °C/3 mmHg (lit.[5] 45–47 °C/0.05 mmHg); trans:cis = 87:13. ^{1}H NMR (CDCl$_3$), δ: trans isomer 1.90 (d, J = 1.2 Hz, 3 H), 3.94–4.05 (m, 4 H), 5.93 (t, J = 7.3 Hz, 1 H); cis isomer 1.88–2.02 (m, 3 H), 3.94–4.05 (m, 4 H), 5.75 (t, J = 7.3 Hz, 1 H), ^{13}C NMR, δ (CDCl$_3$): trans isomer 14.65, 27.58, 39.23, 125.67, 138.20; cis isomer 16.36, 29.37, 42.17, 125.93, 140.84. IR (neat) 2980, 1655, 1442, 1395, 1241, 1205, 1000 cm^{-1}.

1,1-Bis(ethoxycarbonyl)-2-isopropenylcyclopropane (4a). To a mixture of **5a** (91.2 g, 400 mmol) and diethyl malonate (64.1 g, 400 mmol) in ethanol (300 mL) was added dropwise an ethanol solution of sodium ethoxide at 70 °C, which was prepared from sodium (19.3 g, 840 mmol) and ethanol (400 mL). 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 19.3 g (bp 103 °C/2 mmHg). The liquid obtained was purified by column chromatography [solid support, silica gel (200 mesh); eluent, *n*-hexane/ethyl acetate = 50:1 (volume ratio)]; yield 15.3 g (17%). ^{1}H NMR, δ (CDCl$_3$): 1.18–1.33 (m, 6 H), 1.40–1.45 (m, 1H), 1.78–1.85 (m, 1 H), 1.81 (s, 3 H), 2.45–2.50 (m, 1H), 4.06–4.29 (m, 4 H), 4.71 (s, 1H), 4.86 (s, 1H). ^{13}C NMR, δ (CDCl$_3$): 14.10, 18.12, 22.88, 33.56, 36.45, 61.28, 61.63, 112.66, 139.13, 167.00, 170.23. IR (neat) 3100, 2950, 1732, 1656, 1455, 1378, 1323, 1282, 1209, 1139, 1104, 1029, 900, 862, 793 cm^{-1}. Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.73; H, 8.07.

Scheme 2



Synthesis of 4b. 1,4-Dibromo-2,3-dimethyl-2-butene (5b). The title compound (**5b**) was prepared from 2,3-dimethylbutadiene (72.6 g, 884 mmol) and bromine (141 g, 884 mmol) similarly to **5a** as mentioned above; yield 187 g (87%), bp 75–78 °C/3 mmHg (lit.[6] 77.5–79.5 °C/5 mmHg), trans:cis = 80:20. ^{1}H NMR, δ (CDCl$_3$): trans isomer 1.87 (s, 6 H), 4.00 (s, 4 H); cis isomer 1.84 (s, 6 H), 4.05 (s, 4 H). ^{13}C NMR, δ (CDCl$_3$): trans isomer 17.18, 35.06, 131.87; cis isomer 18.15, 33.34, 132.29. IR (neat) 2980, 1640, 1443, 1380, 1203, 1055, 920, 856 cm^{-1}.

1,1-Bis(ethoxycarbonyl)-2-isopropenyl-2-methylcyclopropane (4b). The title compound (**4b**) was prepared from **5b** (96.8 g, 400 mmol) and diethyl malonate (64.1 g, 400 mmol) similarly to **4a** as mentioned above, bp 95 °C/1 mmHg; yield 12.8 g (13%). ^{1}H NMR, δ (CDCl$_3$): 1.20 (t, J = 7.2 Hz, 3 H), 1.27 (t, J = 7.2 Hz, 3 H), 1.31 (s, 3 H), 1.44 (d, J = 4.9 Hz, 1 H), 1.76 (s, 3 H), 1.87 (d, J = 4.9 Hz, 1 H), 4.09 (q, J = 7.2 Hz, 2 H), 4.22 (q, J = 7.2 Hz, 2 H),4.83–4.86 (m, 2 H). ^{13}C NMR, δ (CDCl$_3$): 14.03, 14.19, 20.55, 20.87, 25.12, 38.49, 40.16, 61.19, 61.30, 113.15, 144.40, 168.03, 168.47. IR (neat) 3100, 2995, 1730, 1650, 1452, 1378, 1305, 1270, 1238, 1182, 1110, 1025, 902, 862, 785 cm^{-1}. Anal. Calcd for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 64.87; H, 8.33.

Polymerizations of 4. General Procedure. To the monomer (**4**, 3 mmol) in a polymerization tube was 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 20 h. The conversion of the monomer was determined by gas chromatography using anisole as an internal standard. The resulting mixture was diluted with chloroform (3 mL) and poured into methanol/water (volume ratio = 80:20, 60 mL) to precipitate a solvent-insoluble polymer.

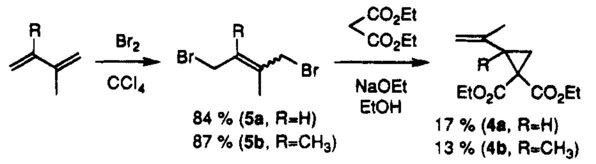
Molecular Mechanics and Molecular Orbital Calculations. All computations were done on an Apple Macintosh Quadra 700 equipped with a 28 MIPS coprocessor board with use of SONY Tektronix CAChe system version 3.0. Molecular mechanics (MM) calculations were done with the CAChe MM2 program. Molecular orbital (MO) calculations were done with MOPAC version 6.00 (QCPE No. 455[7]) revised as version 6.10 for the CAChe system, using the PM3 Hamiltonian by the restricted Hartree–Fock (RHF) method on nonradical compounds and by the unrestricted Hartree–Fock (UHF) method on radical compounds.

Results and Discussion

1. Synthesis of Monomer 4. First, coupling reactions of diethyl diazomalonate, prepared from diethyl aminomalonate hydrochloride, with isoprene and 2,3-dimethylbutadiene in the presence of copper acetyl acetonate as a catalyst were carried out to prepare **4a** and **4b** (Scheme 2). However, the yield of **4** was very low (<10%) and formation of many byproducts prevented the isolation of **4** with a satisfactory purity. Low reactivity of diethyl diazomalonate toward olefins without electron-donating groups should cause this unsatisfactory result.[8]

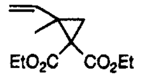
Second, a mixture of 1,4-dibromo-2-butene derivatives (**5**) and diethyl malonate was treated with sodium ethoxide. **5** was prepared by the addition reaction of bromine to butadiene derivatives (Scheme 3). Pure **4a** and **4b** were obtained by distillation followed by column chromatographic separation, although their overall yields were low (17 and 13%, respectively). Their

Scheme 3



structures were determined by ^{1}H NMR, ^{13}C NMR, and IR spectra besides elemental analyses.

Both trans and cis isomers were formed in the addition reaction of bromine to the dienes, but the separation of the isomers could not be performed by distillation. The ratios of trans and cis isomers were 87:13 for **5a** and 80:20 for **5b**, which were similar to the reported results.[5] Formation of 1,1-bis(ethoxycarbonyl)-2-methyl-2-vinylcyclopropane (**4c**) was not observed in the synthetic step from **5a** to **4a**. This probably results from the steric hindrance of the methyl group; i.e., the nucleophilic attack of the malonate anion selectively occurred at the 4-position but not at 1-position of **5a**.



4c

2. Radical Polymerization of 4. Radical polymerization of **4a** and **4b** was carried out in the presence of a radical initiator under some different conditions in a degassed sealed tube. The polymer formed was isolated by precipitation with a methanol/water mixed solvent (volume ratio = 80:20). Colorless transparent solid polymers, which were soluble in dichloromethane, chloroform, THF, DMF, and DMSO, were obtained in any case. The conditions and results are summarized in Table 1. The conversion of **4a** was nearly the same (95–99%) independent of condition (Table 1, runs 1–6). The conversion of **4b** (40–48%) was lower than that of **4a** (Table 1, runs 7–12). Yield of poly(**4a**) was high (75–85%) in the polymerizations both in bulk and in solution (chlorobenzene) in accordance with the high conversion of **4a**. On the other hand, that of **4b** was 3–14% in bulk polymerizations and below 1% in solution polymerizations. The yield of poly(**4b**) being much lower than that expected from the conversion of **4b** should be caused by the formation of a low molecular weight polymer soluble in methanol/water. A single modal GPC curve was observed in any polymer. The molecular weight of the polymer decreased as the polymerization temperature was raised. The molecular weight in the bulk polymerization was higher than that in the solution polymerization. The molecular weight of poly(**4b**) was lower than that of poly(**4a**), probably due to the chain transfer reaction of **4b** being higher than that of **4a**, which corresponds to the formation of a large amount of low molecular weight monomer soluble in methanol/water.

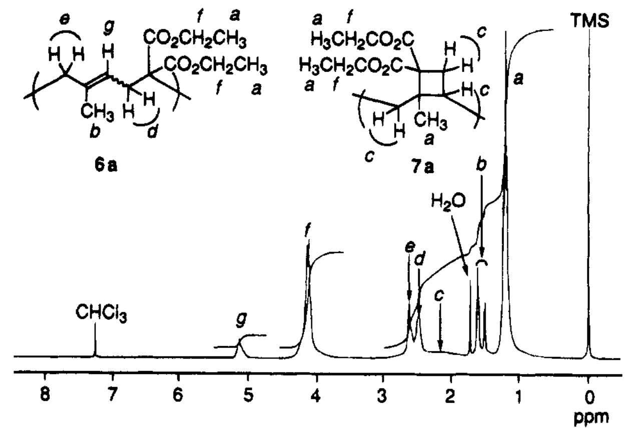


Figure 1. ^{1}H NMR spectrum (solvent CDCl$_3$, 270 MHz) of poly(**4a**) (run 1 in Table 1).

3. Structure of Poly(4a). The structure of poly(**4a**) was examined by the ^{1}H and ^{13}C NMR spectra. It was confirmed that no cyclopropane ring was incorporated into the polymer, by the absence of signals in the field of 1.41–1.45 and 1.80–1.86 ppm in the ^{1}H NMR spectrum (Figure 1). The main structure of the polymer was concluded to be a 1,5-ring-opened unit, as previously reported in the radical polymerization of 1,1-disubstituted-2-vinylcyclopropanes.[2] Namely, the integration ratio of the signals of the allylic methyl proton (Figure 1, *b*, 1.54 and 1.65 ppm, assignable to the signals of the cis and trans isomers, respectively) to the allylic methylene proton [Figure 1, *d*,*e*, 2.43–2.59 ppm and 2.59–2.71 ppm, corresponding to β- and α-protons of the olefin carbon substituted by the methyl group; the assignment was performed on the basis of the chemical shift values of the allylic methylene protons of poly(**1b**) (2.53 ppm)[2n] and those of poly(**4b**) (2.75 ppm) of which the structure is discussed later] is 3:4. Secondly, the integration ratio of the signals of the olefin proton (Figure 1, *g*, 5.05–5.21 ppm) to the allylic methylene proton (Figure 1, *d*,*e*) is 1:4. Thirdly, the intensities of the signals of two kinds of allylic methylene proton (Figure 1, *d*,*e*) are nearly equal each other. From these

Table 1. Radical Polymerization of 4a and 4b[a]

									polymer structure[g] (%)		
run	monomer	init[b]	temp (°C)	solv[c]	conv[d] (%)	yield[e] (%)	$\bar{M}_n$[f]	$\bar{M}_w/\bar{M}_n$[f]	6	(cis:trans)	7
1	**4a**	AIBN	60		97	84	13700	5.18	53	(33:67)	47
2	**4a**	BPO	80		95	77	4500	3.02	43	(46:54)	57
3	**4a**	DTBP	120		99	75	3000	2.30	29	(52:48)	71
4	**4a**	AIBN	60	CB	99	79	8700	2.75	36	(42:58)	64
5	**4a**	BPO	80	CB	99	85	4400	2.38	24	(53:47)	76
6	**4a**	DTBP	120	CB	99	77	2200	2.27	22	(70:30)	78
7	**4b**	AIBN	60		41	8	4100	1.39	92	(0:100)	8
8	**4b**	BPO	80		48	14	2600	1.38	72	(0:100)	28
9	**4b**	DTBP	120		48	3	2100	1.25	50	(0:100)	50
10	**4b**	AIBN	60	CB	40	1>					
11	**4b**	BPO	80	CB	47	1>					
12	**4b**	DTBP	120	CB	45	1>					

[a] Conditions; monomer 3 mmol, polymerization time 20 h. [b] Initiator 3 mol % *vs* monomer. AIBN, 2,2′-azobis(isobutyronitrile); BPO, benzoyl peroxide; DTBP, di-*tert*-butyl peroxide. [c] CB, chlorobenzene. [C] = 1 M. [d] Estimated by GC (internal standard; anisole). [e] Methanol–water (80:20, volume ratio)-insoluble part. [f] Estimated by GPC (based on polystyrene standard samples). [g] Estimated by ^{1}H NMR.

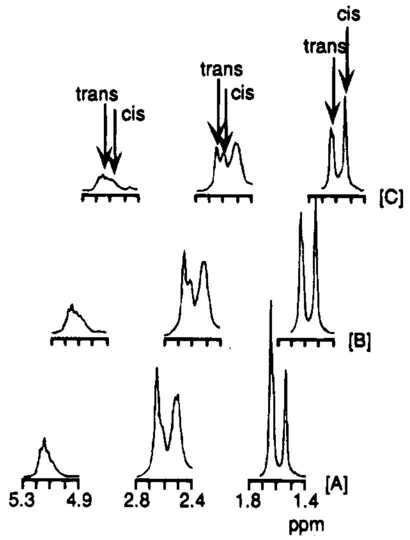
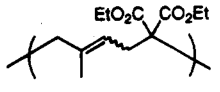
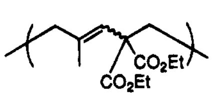


Figure 2. Partial ^{1}H NMR spectra (solvent CDCl$_3$, 270 MHz) of poly(**4a**). [A] Polymerization conditions: bulk, AIBN 3 mol %, 60 °C, 20 h (run 1 in Table 1). [B] Polymerization conditions: bulk, BPO 3 mol %, 80 °C, 20 h (run 2 in Table 1). [C] Polymerization conditions: bulk, DTBP 3 mol %, 120 °C, 20 h (run 3 in Table 1).

three NMR characteristics, the 1,5-ring-opened unit consists only of **6a** but not **6a′**.



6a



6a′

As described above, the signals corresponding to the allylic methyl protons observed at 1.54 and 1.65 ppm (Figure 1, *b*) are assigned as those of the cis and trans isomers of **6a**.[2d,9] The ratio of the cis:trans configuration was calculated to be 33:67. The ratio of the cis one increased as the polymerization temperature was raised (Figure 2). A similar relation was observed in the allylic methylene proton signal (2.60, 2.66 ppm) and olefin proton signals (5.0–5.2 ppm), as shown in Figure 2.[10] In the ^{13}C NMR spectrum, a few sets of two signals assigned to the allylic methyl carbon (Figure 3, *c*) and olefin carbons (Figure 3, *i,j*) can be also observed.[10,11] The cis:trans ratio increased as the polymerization temperature was raised (Figure 4), similarly to the ^{1}H NMR results. Solution polymerization (Table 1, runs 4–6) afforded cis polymer more than bulk polymerization (Table 1, runs 1–3) at the same polymerization temperature. A molecular mobility in solution polymerization larger than that in bulk polymerization would favor the cis configuration which is supposed to be thermodynamically more stable than the trans one.

In the ^{1}H NMR spectrum of poly(**4a**), the integration ratios of the allylic methyl proton (Figure 1, *b*), allylic methylene proton (Figure 1, *d,e*), and olefin proton (Figure 1, *g*) to the methylene proton of the ester group (Figure 1, *f*, 3.85–4.35 ppm) were all smaller than those expected from the 1,5-ring-opened unit **6a** (3:4, 4:4, and 1:4, respectively). Moreover, a broad signal which cannot be assigned to any protons of **6a** was observed at 1.8–2.9 ppm (Figure 1, *c*). In the ^{13}C NMR spectrum, the unassignable signal was observed at 172.90 ppm (Figure 3, *l*). These signals appear to be derived from a unit which has no olefin moiety. Since the polymers are soluble in many organic solvents and show unimodal GPC curves, the disappearance of the olefin moiety would not be caused by intermolecular reactions such as cross-linking but by an *intramolecular* reaction. The enhanced ratio of the unit which has no olefin moiety in solution polymerization rather than in bulk polymerization does not contradict this assumption. This unit is assumed to cyclobutane-containing unit **7a**, which is similar to that reported in the radical polymerization of vinylcyclopropanes.[2b,n] Since in the ^{13}C NMR, the

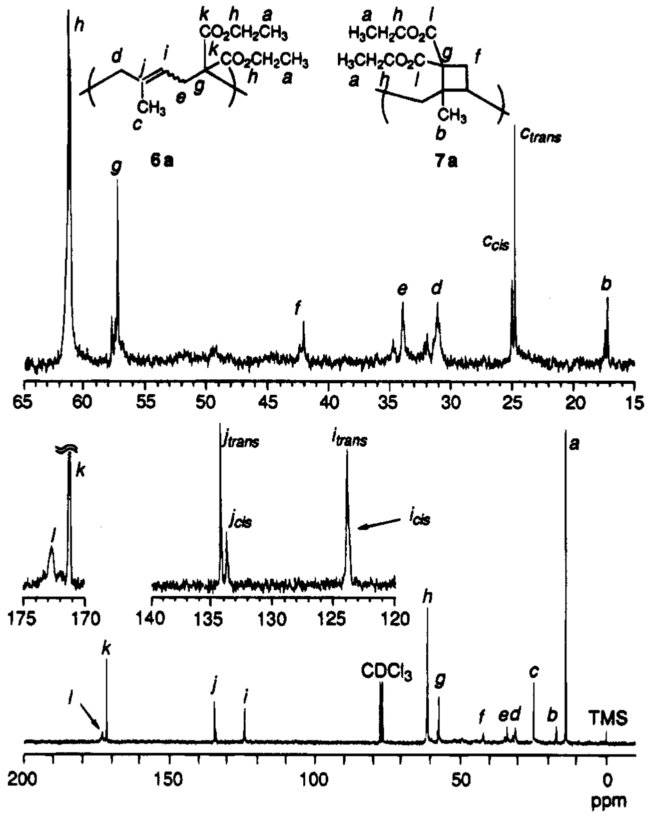


Figure 3. ^{13}C NMR spectrum (solvent CDCl$_3$, 67.5 MHz) of poly(**4a**) (run 1 in Table 1).

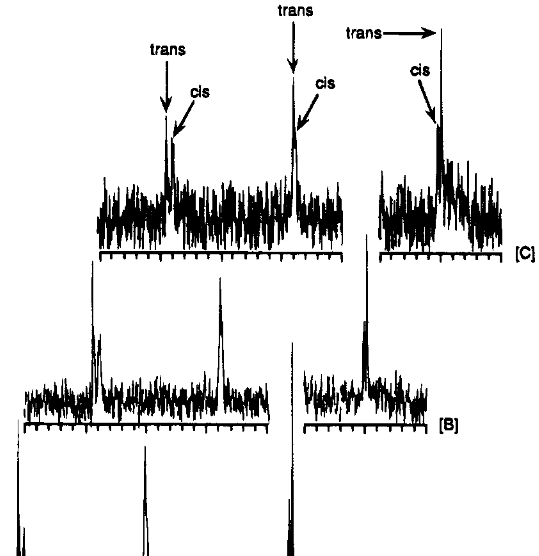
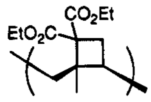
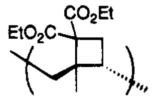


Figure 4. Partial ^{13}C NMR spectra (solvent CDCl$_3$, 67.5 MHz) of poly(**4a**). [A] Polymerization conditions: bulk, AIBN 3 mol %, 60 °C, 20 h (run 1 in Table 1). [B] Polymerization conditions: bulk, BPO 3 mol %, 80 °C, 20 h (run 2 in Table 1). [C] Polymerization conditions: bulk, DTBP 3 mol %, 120 °C, 20 h (run 3 in Table 1).

methyl carbon (Figure 3, *b*, 17.27 and 17.43 ppm) or methylene carbon (Figure 3, *f*, 42.09 and 42.49 ppm) can be observed as two signals, formation of two stereoisomers **7a** (syn) and **7a** (anti) is a certainty. Each signal at a higher field is assigned to the syn isomer.[12] The ratio of **7a** to **6a** increases as the polymerization temperature is raised (Table 1, runs 1−6), probably due to the thermodynamic stability of **7a** being larger than that of **6a**.

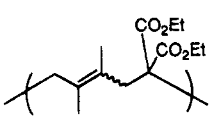


7a (syn)

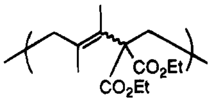


7a (anti)

4. Structure of Poly(4b). The structure of poly(**4b**) was similarly examined by the ^{1}H and ^{13}C NMR spectra. It was confirmed that no cyclopropane ring was incorporated into the polymer from the ^{1}H NMR spectrum (Figure 5). The main structure of the polymer is the 1,5-ring-opened unit similar to poly(**4a**). Since the integration ratio of allylic methyl protons (Figure 5, *b*, 1.58 ppm) to allylic methylene protons (Figure 5, *c*, 2.75 ppm) is exactly 6:4, the 1,5-ring-opened unit consists only of **6b**. No another unit **6b′** is contained in poly(**4b**).



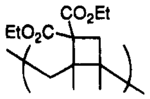
6b



6b'

There was no signal at 1.58 ± 0.1 ppm, where the signal of another stereoisomer can be observed, other than the methyl signal of **6b** (Figure 5, *b*). Moreover, the signals of the allylic methylene proton (Figure 5, *c*) and allylic methyl carbon (Figure 6, *b*) were singlets. From these results, **6b** consists only of one stereoisomer. The trans isomer is more probable because the mutual steric repulsion of its two methyl groups is smaller than that of the cis isomer. A detailed examination by MM and MO calculations for this point is discussed later.

In the ^{1}H NMR spectrum of poly(**4b**), the integration ratios of the allylic methyl protons (Figure 5, *b*) and methylene protons (Figure 5, *c*) to the methylene protons of the ester group (Figure 5, *d*, 4.02−4.25 ppm, 6:4 and 4:4, respectively) were smaller than those expected from 1,5-ring-opened unit **6b**. These ratios decreased as the polymerization temperature was raised. Therefore, cyclobutane-containing unit **7b** should be formed similarly to the polymerization of **4a**. The content of **7b** is smaller than that of **7a** under the same polymerization conditions. The steric hindrance around the olefin moiety of **6b** being bigger than that of **6a** would lower the intermolecular cyclization reaction, which forms **7b**.



7b

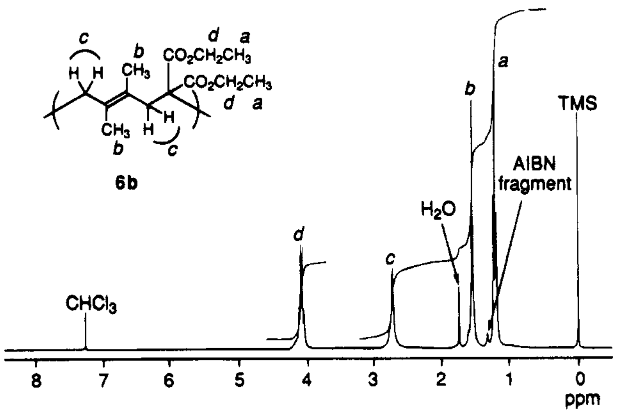


Figure 5. ^{1}H NMR spectrum (solvent $CDCl_3$, 270 MHz) of poly(**4b**) (run 7 in Table 1).

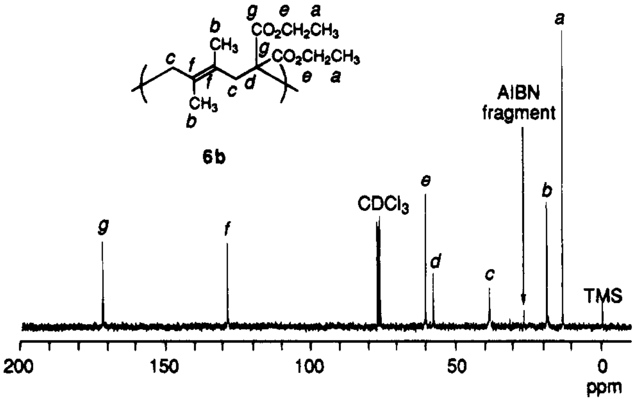
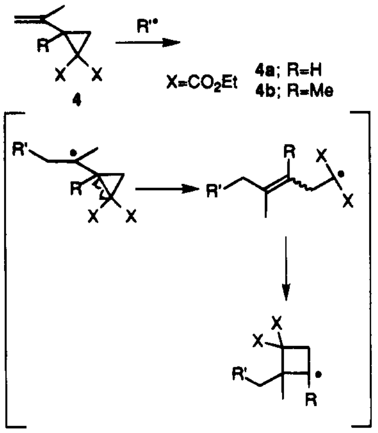


Figure 6. ^{13}C NMR spectrum (solvent $CDCl_3$, 67.5 MHz) of poly(**4b**) (run 7 in Table 1).

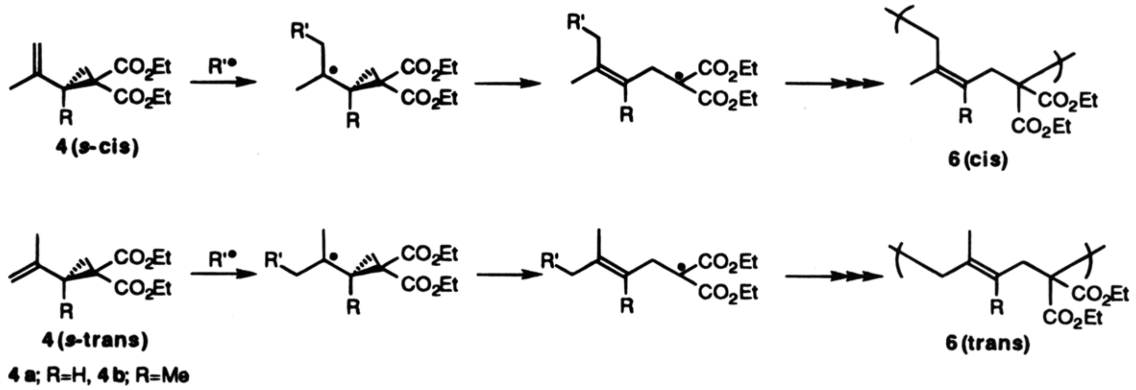
Scheme 4



5. Mechanism of Polymerization. The proposed mechanism of the polymerization of **4** is shown in Scheme 4. The 1,5-type ring-opened unit **6** is formed through selective cleavage of the C−C bond containing a carbon substituted by two ester groups. The electron-withdrawing ester groups of **4** should contribute to this selectivity, as reported in the radical polymerization of **1b**.[2n] The cyclobutane-containing unit **7** is formed via intramolecular radical addition to the double bond formed by the C−C bond cleavage. Contrary to the beginning expectation, formation of the cyclobutane-containing unit could not be suppressed despite the introduction of methyl groups into vinylcyclopropane. Bulky substituents such as the aryl[3] or trimethylsiloxy group,[4] more than methyl group, seem necessary for complete suppression of the formation of the cyclobutane-containing unit.

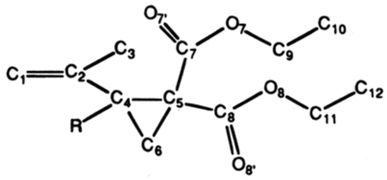
6. Comments on the Mechanism of Polymerization by MM and MO Calculations. 6.1. Conformation Analysis of Monomer. As described in the NMR analyses of poly(**4a**) and poly(**4b**), **4a** afforded both cis and trans isomers [**6a** (cis) and **6a** (trans), respectively], while **4b** did not afford the cis isomer [**6b** (cis)] but

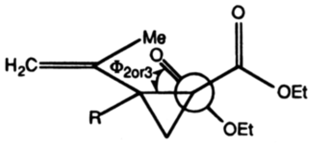
Scheme 5



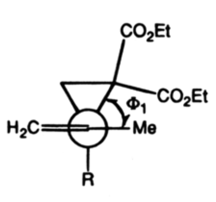
afforded the polymer supposed to be in the trans configuration [**6b** (trans)]. This drastic difference is sure to come from the existence of a methyl group on the cyclopropane ring. The activation energy of the ring-opening reaction of the cyclopropylmethyl radical to the 3-butenyl radical is small (5.90 kcal/mol) and this reaction is faster by 10^4 times than its reverse reaction.[13] Therefore, if the conformation of the isopropenyl group on the cyclopropane ring is assumed to be kept during the addition of a propagating end radical to the double bond of the monomer and following ring-opening of cyclopropane ring, **4**(*s*-cis) and **4**(*s*-trans) afford **6**(cis) and **6**(trans), respectively, as a result (Scheme 5).

The conformation analyses of **4a** and **4b** were carried out by MM and MO calculations as shown below. First, the bond (C_2-C_4) between the isopropenyl group and cyclopropane of **4a** was constrained at its dihedral angle Φ_1 ($C_3-C_2-C_4-C_5$) = −180°, and the MM2 rigid search for the bonds between the cyclopropane ring and ethoxycarbonyl groups [C_5-C_7, dihedral angle Φ_2 ($C_4-C_5-C_7-O_7$); C_5-C_8, dihedral angle Φ_3 ($C_4-C_5-C_8-O_8$)] from −180 to +180° with 30° increments was carried out to obtain the most stable conformation among 144 conformers. The most stable conformers of which Φ_1's were constrained at −150 to +180° with 30° increments were obtained similarly in the rigid searches for Φ_2 and Φ_3. The relationship of Φ_2, Φ_3, and the steric energy of **4a** and **4b** obtained by the MM2 rigid search is illustrated in Figure 7, in which Φ_1 is constrained at −90°. A trans zigzag conformation was adopted for ester groups ($C_7-O_7-C_9-C_{10}$ and $C_8-O_8-C_{11}-C_{12}$) in these searches.





4a; R=H, 4b; R=Me



4a; R=H, 4b; R=Me

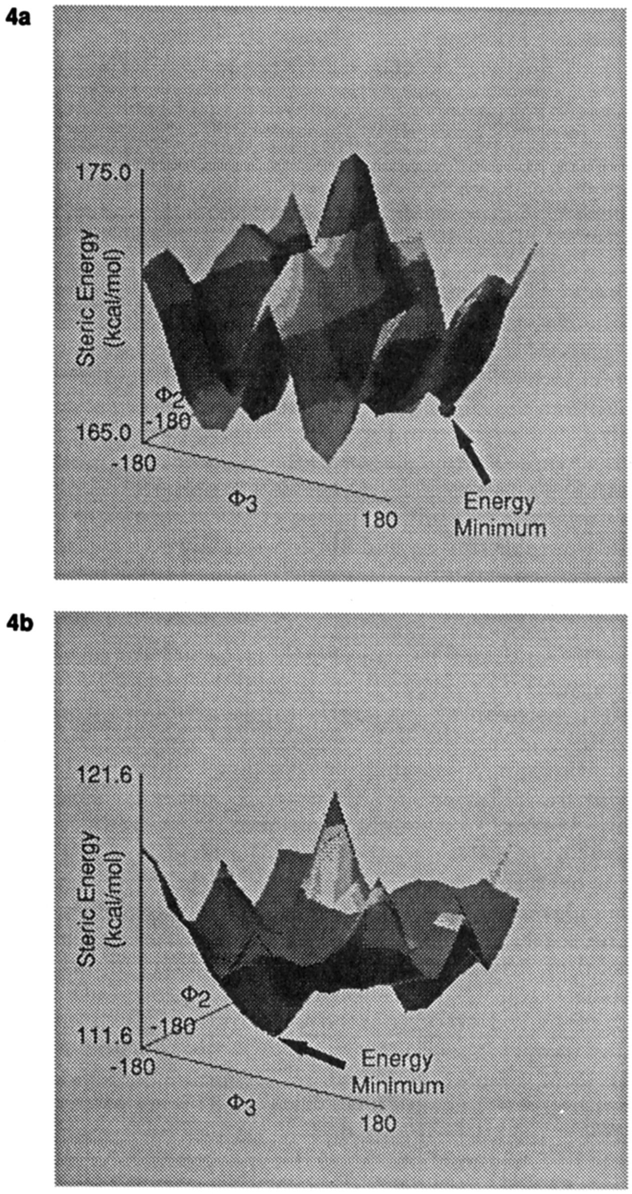


Figure 7. Energy maps obtained by an MM2 rigid search for rotation about Φ_2 ($C_4-C_5-C_7-O_7$) and Φ_3 ($C_4-C_5-C_8-O_8$) in **4a** and **4b**. Φ_1 ($C_3-C_2-C_4-C_5$) in **4a** and **4b** is constrained at −90°. Arrows indicate the energy minimum conformations.

Twelve conformers optimized by MM2 for Φ_2 and Φ_3 obtained as described above were further optimized by

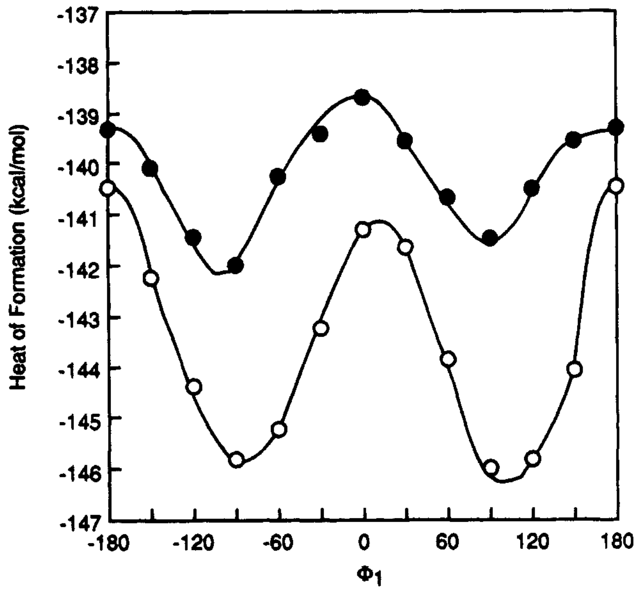


Figure 8. Energy relationships obtained by the PM3-optimized search for rotation about Φ_1 ($C_3-C_2-C_4-C_5$) in **4a** and **4b**: (●) **4a**; (○) **4b**. Φ_1 in **4a** and **4b** is constrained from −180 to +180° with 30° increments.

the PM3 method for bond length, bond angles, and dihedral angles except for Φ_1 (constrained at −180 to +180° with 30° increments for each conformer). Similar calculations were carried out for **4b**. The relationships between Φ_1 and the heat of formation (HOF) of **4a** and **4b** are illustrated in Figure 8. The conformers of which Φ_1's were 0 and 180 (=−180°) showed the maximum values, and those of which Φ_1's were −90 and +90° showed the minimum values. The conformer of which Φ_1 was −90° for **4a** and 90° for **4b** showed the smallest HOF, respectively. The most stable conformer of **4b** positioned its two methyl groups apart from each other to minimize the steric hindrance.

The rotational barrier of bond C_2-C_4 of **4b** (4.51−4.67 kcal/mol) was larger than that of **4a** (2.15−2.67 kcal/mol), because of the steric hindrance caused by the methyl group on the cyclopropane ring of **4b**. The rotational barriers about most single bonds are so small that free rotation essentially occurs at room temperature.[14] For example, the rotational barrier of the center C−C bond of 2,3-dimethylbutane [$(CH_3)_2CH-CH(CH_3)_2$] has been reported to be 4.22 ± 0.10 kcal/mol,[15] and the calculated value by MM2 method is nearly the same.[16] The restriction of internal rotation of the center C−C bond of 2,3-dimethylbutane can be observed only just below −160 °C. Therefore, the free rotation of bond C_2-C_4 of **4a** and **4b** undoubtedly occurs at the polymerization temperature in this work (60−120 °C), and **4a** and **4b** exist on average in two conformers which show the minimum values in HOF. Two conformers [**4a** (to cis), HOF −142.01 kcal/mol, Φ_1 −86.65°; **4a** (to trans), HOF −141.48 kcal/mol, Φ_1 95.17°] were obtained by the full optimization of conformers of **4a** which showed the minimum value in HOF. From the difference in HOF in these two conformers (0.53 kcal/mol), Boltzmann's distribution of the two at 120 °C was calculated to be **4a** (to cis): **4a** (to trans) = 66:34 (Table 2). Since **6** (cis) is considered to be formed from the conformers with Φ_1 = −180 to −30° and Φ_1 = 150−180°, while **6** (trans) is considered to be formed from the conformers with Φ_1 = −30−150°, **6** (cis) should be predominately formed under thermodynamic conditions. The ratio of **6** (cis):**6**(trans) (70:30) in polymerization in chlorobenzene at 120 °C (Table 1, run 6), which is supposed to be mostly effected by the thermodynamic factors, showed good accordance with the result calculated by Boltzmann's distribution.

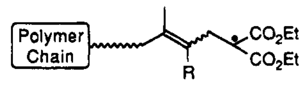
Table 2. Stable Conformers of 4a and 4b Obtained by PM3 Full Optimization

conformer	Φ_1[a]	heat of formation (kcal/mol)	Boltzmann's distribution[b] 60 °C	80 °C	120 °C
4a (to cis)	−86.65	−142.01	69	68	66
4a (to trans)	95.17	−141.48	31	32	34
4b (to cis)	−85.72	−146.21	45	46	46
4b (to trans)	102.69	−146.33	55	54	54

[a] Dihedral angle defined by $C_3-C_2-C_4-C_5$. [b] Calculated by $\exp(-\Delta E/RT)$.

On the other hand, two conformers of **4b** which showed the minimum HOF [**4b** (to cis), HOF −146.21 kcal/mol, Φ_1 −85.72°, **4b** (to trans), HOF −146.33 kcal/mol, Φ_1 102.69°] were obtained, and the Boltzmann distribution of the two at 120 °C was calculated to be **4b** (to cis) **4b** (to trans) = 46:54 (Table 2). The formation of **6b** (trans) was predominant under thermodynamic conditions in contrast to **4a**. This result agrees with the prediction by NMR analysis; however, the difference in HOF between **4b** (to cis) and **4b** (to trans) (0.12 kcal/mol) was smaller than that of **4a** (0.53 kcal/mol). Only from this calculated result is it hardly acceptable to explain the complete selectivity in configuration of the olefin moiety of **6b**. Since the cyclobutane-containing unit **7b** is also formed, the polymerization system is more complicated than the assumption described above; anyway, it is too hasty to extract the conclusion only from the thermodynamic examination. Therefore, the trial for calculation of the activation energy in the addition reaction of radical species to a monomer by simulation of the transition state by the MO method was carried out next.

6.2. Analysis of the Transition State in the Addition of Radical Species to a Monomer. The propagating step in the radical polymerization is the addition of a propagating end to the double bond of a monomer. Tertiary radical **8** is the propagating end in the polymerization of monomer **4**.



8 (R=H, Me)

Because of the limitation of architecutre of hardware and software of computers today, the MO simulation of the transition state in the addition reaction of **8** to **4** in both practical computation time and sufficient reliability is very difficult, although the polymer chain is replaced with one repeating unit. In this work, the simulation was carried out using the trimethylmethyl radical [$(CH_3)_3C^\bullet$] as the model of the propagating end because this radical has a symmetrical structure and atoms fewer than in reality, both of which are convenient for the MO simulation. Both π- and σ-complexes are presented for the transition state of radical addition to an olefin. Since the formation of the π-complex is thermally forbidden[17] and has a very large energy barrier (50−100 kcal/mol),[18] only the σ-complex was examined in this study. The procedure of the simulation is described below.

First, the trimethylmethyl radical approached the double bond of **4a** (to cis) from 3.0 to 1.5 Å distance with

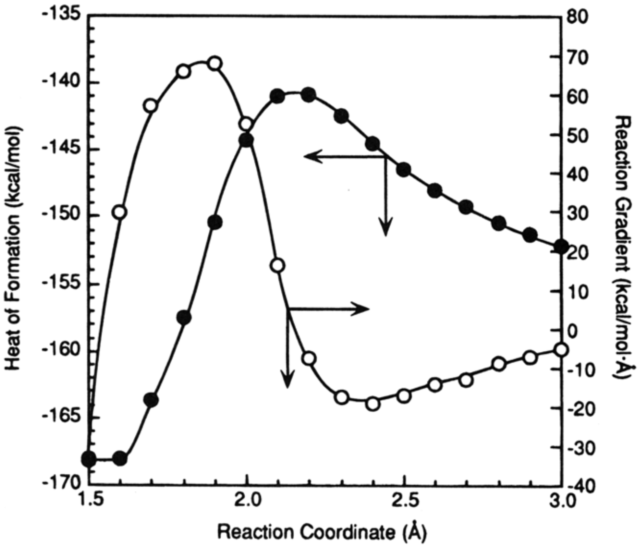
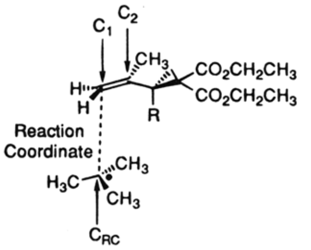


Figure 9. PM3(UHF) reaction coordinate and gradient for the addition reaction of the trimethylmethyl radical [$(CH_3)_3C^{\bullet}$] to **4a** (to cis).

0.1 Å increments between radical center carbon (C_{RC}) and exo carbon of the double bond (C_1) of **4a** (to cis). The set angle $C_2-C_1-C_{RC}$ was adopted for 110° referring to the reported value in the addition reaction of the methyl radical to ethylene.[19]



The geometry optimization by the PM3(UHF) method, other than the atomic distance C_1-C_{RC}, was carried out to obtain the HOF and reaction gradient at each point (reaction coordinate, C_1-C_{RC}). The potential and reaction gradient curves for C_1-C_{RC} in the system formed by **4a** (to cis) and the trimethylmethyl radical are illustrated in Figure 9. Since the point showing the largest HOF and zero reaction gradient, i.e., near 2.2 Å in C_1-C_{RC} distance, was regarded to be the transition state in this case, the optimized conformer at 2.2 Å in C_1-C_{RC} distance was treated by the nonlinear least squares gradient minimization routine (NLLSQ) to obtain the conformer in the transition state. Further, the vibrational calculation afforded 638.82i as the imaginary vibration frequency for this conformer obtained by NLLSQ, and the direction of the vibration vector corresponded to that of the reaction coordinate (C_1-C_{RC}). From this result, the conformation of the transition state was concluded to be obtained. Transition states in addition reactions of the trimethylmethyl radical to **4a** (to trans), **4b** (to cis), and **4b** (to trans) were obtained in a similar fashion. The results are summarized in Table 3, and the conformers of each transition state are illustrated in Figure 10.

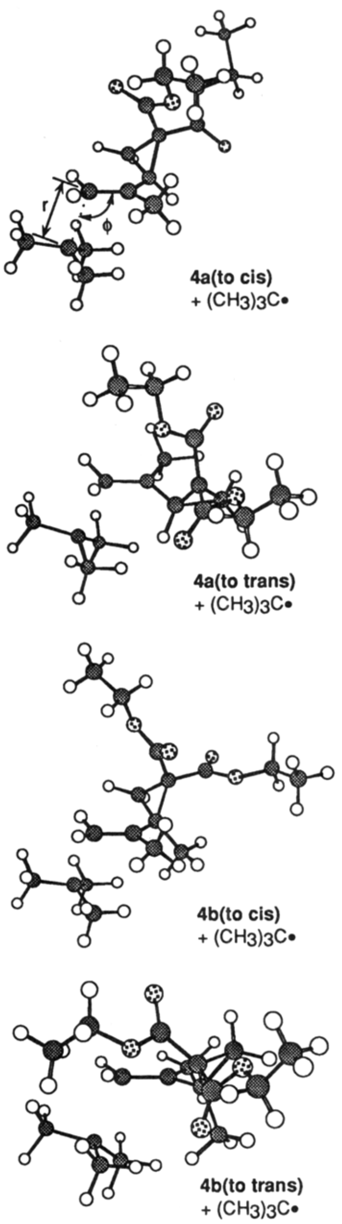


Figure 10. Transition states in the addition reaction of the trimethylmethyl radical [$(CH_3)_3C^{\bullet}$] to **4a** (to cis), **4a** (to trans), **4b** (to cis), and **4b** (to trans). Geometries were obtained by the nonlinear least squares gradient minimization routine (NLLSQ) using a PM3 Hamiltonian (UHF).

The approach of the trimethylmethyl radical to the exo olefin carbon proceeds outside from 18.85–22.28°

Table 3. Structures of the Transition State in the Addition Reaction of 4a and 4b with $(CH_3)_3C^{\bullet}$

transition state	r^a	ϕ^b	$\Phi_1{}^c$	charge (e)			charge change from ground state (e)			imaginary vibration frequency (cm^{-1})	activation[d] energy (kcal/mol)
				C_1	C_2	C_{RC}	C_1	C_2	C_{RC}		
4a (to cis)‡	2.15	108.85	−94.11	−0.1047	−0.1527	−0.1234	0.0419	−0.0462	0.0990	638.82i	11.72
4a (to trans)‡	2.15	109.02	87.24	−0.0996	−0.1522	−0.1239	0.0459	−0.0424	0.0985	648.18i	10.06
4b (to cis)‡	2.15	110.19	−89.80	−0.1107	−0.1391	−0.1214	0.0505	−0.0508	0.1010	668.01i	10.49
4b (to trans)‡	2.14	112.28	133.56	−0.1182	−0.1371	−0.1171	0.0272	−0.0308	0.1053	647.77i	9.96

[a] Interatomic distance of the exo carbon (C_1) of the olefin in **4** from the center carbon (C_{RC}) of the trimethylmethyl radical [$(CH_3)_3C^{\bullet}$]. [b] Angle $C_2-C_1-C_{RC}$. [c] Dihedral angle $C_3-C_2-C_4-C_5$. [d] Calculated by the following equation: $HOF_{\text{transition state}} - [HOF_4 + HOF_{(CH_3)_3C^{\bullet}}]$. HOF_4 of each conformer is summarized in Table 2. $HOF_{(CH_3)_3C^{\bullet}} = -9.29$ kcal/mol.

Table 4. Two-Center Energy, Bond Order, and Bond Length of C_4-C_5 and C_4-C_6 in 4a and 4b

	two-center energy (eV)		bond order		bond length (Å)	
	C_4-C_5	C_4-C_6	C_4-C_5	C_4-C_6	C_4-C_5	C_4-C_6
4a (to cis)	−11.449	−12.266	0.939	0.988	1.523	1.500
4a (to trans)	−11.413	−12.274	0.937	0.990	1.523	1.500
4b (to cis)	−11.424	−12.192	0.930	0.977	1.530	1.503
4b (to trans)	−11.412	−12.189	0.929	0.978	1.531	1.504

toward the vertical direction of the π-electron of the carbon. The interatomic distance of C_1-C_{RC} in the transition state was 2.14−2.15 Å. Although the Φ_1 values in the transition states were changed by 7.46−30.87° from those of the ground states, by the effect of the approach of the trimethylmethyl radical, every conformer in the transition state had the same conformation to afford the same configuration for the double bond in **6** as that in ground state. The charges of carbons C_1 and C_{RC} in the transition states decreased 0.0272−0.0505 and 0.0985−0.1053 e compared to those in the ground states, respectively, and that of carbon C_2 increased 0.0308−0.0508 e. These charge changes mean that the π-electron densities at carbons C_1-C_{RC} are decreasing (i.e., forming a σ-bond between C_1 and C_{RC}) and the π-electron of the radical is delocalizing from carbon C_{RC} to carbon C_2. The activation energies can be calculated from the HOF of the transition states and those of the monomers and trimethylmethyl radical in the ground states. The activation energy from **4a** (to trans) was smaller by 1.66 kcal/mol than that from **4a** (to cis), while that from **4b** (to trans) was smaller by 0.55 kcal/mol than that from **4b** (to cis). These results suggest that formation of **6** (trans) is kinetically more predominant than that of **6** (cis) for both **4a** and **4b**. **4a** thermodynamically predominately affords **6a** (cis) in contrast to that. As a result, **4a** predominately affords kinetically superior **6a** (trans) in the polymerization at lower temperatures and affords thermodynamically superior **6a** (cis) in the polymerization at higher temperatures. Meanwhile, formation of **6b** (trans) is more predominant in both kinetic and thermodynamic ways than that of **6b** (cis), which corresponds to the experimental result that only formation of **6b** (trans) was observed (Table 1, runs 7−9). The activation energy for the addition reaction of the trimethylmethyl radical to **4b** (trans) was smaller by 0.10 kcal/mol than that of **4a** (trans); however, on the other hand, the conversion of **4b** was smaller than that of **4a**. This is probably due to the fact that the overall rate of polymerization is also dependent on the frequency factor (Arrhenius constant), which would be different from each other for reagents, as well as the rates of chain transfer and termination reactions.

6.3. Selectivity of the Ring Cleavage of the Cyclopropane Ring. In the radical polymerization of **4**, C_4-C_5 bond of the cyclopropane ring selectively cleaves although bond C_4-C_6 of the ring also has a probability to cleave. To examine this point, the two-center energies,[20] bond order, the bond length of bonds C_4-C_5 and C_4-C_6 were calculated by the PM3 method (Table 4). As a result, the two-center energy of bond C_4-C_5 was larger than that of C_4-C_6 by 0.768−0.861 eV, the bond order of the former was smaller than that of the latter by 0.047−0.053, and the bond length of the former was longer than that of the latter by 0.023−0.027 Å. So, bond C_4-C_5 can be regarded to be more easily cleaved than bond C_4-C_6. This result agrees well with the experimental results. If the transition state in the radical ring-opening process becomes clear in the future, it is expected that discussion on the basis of kinetic factor will also be possible.

7. T_g of the Polymers and Volume Change on Polymerization. The glass transition temperatures (T_g) of poly(**4a**) and poly(**4b**) measured by DSC were 24 and 3 °C (polymers, Table 1, runs 1 and 7), respectively. No significant difference in the T_g's of the polymers obtained under different polymerization conditions was observed. The volume change during the polymerization of **4** was evaluated from the densities of **4** and poly(**4**). The densities of **4a** and **4b** were 1.019 and 1.000, respectively. The degrees of volume shrinkage of **4a** and **4b** were 10.4 and 10.2% (polymers, Table 1, runs 1 and 7), respectively. No significant difference in the densities of the polymers obtained under different polymerization conditions was observed, similarly to the T_g's. **4a** and **4b** showed shrinkage slightly smaller than **1b** (11.18%)[2n] but larger than **2a**−**c** (7.23 ~ 8.56%).[3] Formation of cyclobutane-containing units would probably contribute to the larger volume shrinkage than that for **2a**−**c**.

Conclusion

Synthesis and radical polymerization of 1,1-bis(ethoxycarbonyl)-2-isopropenylcyclopropane (**4a**) and 1,1-bis(ethoxycarbonyl)-2-isopropenyl-2-methylcyclopropane (**4b**) were carried out. Poly(**4a**) was determined to consist of 1,5-ring-opened units in cis and trans configurations in the main chain of the polymer and cyclobutane-containing unit. In the polymerization of **4a**, the content of thermodynamically favorable cis isomer increased in comparison to that of the kinetically favorable trans isomer as the polymerization temperature was raised. **4b** afforded no cis isomer but a trans isomer which was concluded to be kinetically as well as thermodynamically favorable by MM and MO study. **4a** and **4b** showed shrinkage slightly smaller than **1b** but larger than **2a**−**c**.

References and Notes

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