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Free Radical Ring-Opening Polymerization of 1,1-Bis[(1-adamantyloxy)carbonyl]-2-vinylcyclopropane

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ABSTRACT: A new monomer 1,1-bis[(1-adamantyloxy)carbonyl]-2-vinylcyclopropane (**3**) was readily synthesized and polymerized by radical initiators. Monomer **3** afforded a 1,5-addition polymer selectively and in good conversion, even at high temperatures or low monomer concentrations. Poly(**3**) is soluble in common organic solvents, but insoluble in ether and methanol. Poly(**3**) (M_n = 51 000 estimated by GPC based on polystyrene standard) exhibited a grass transition at 34 °C and 10% weight loss at 377 °C under nitrogen. Monomer **3** showed a positive volume change (+4.5 ± 1.1%) upon polymerization. This phenomenon can be rationalized by several reasons, such as the depression of recyclization during propagation by bulky ester groups, conversion of the crystalline monomer to the amorphous polymer, and the fact that **3** contains a pair of large spreadable ester groups that may increase the free volume of the polymer matrix. The kinetics of the homopolymerization of **3** with AIBN was investigated in benzene. The rate of polymerization (R_p) can be expressed by $R_p = k[\mathrm{AIBN}]^{0.52}[\mathbf{3}]^{1.2}$, and the overall activation energy E_a has been calculated to be 20.8 kcal/mol.

Introduction

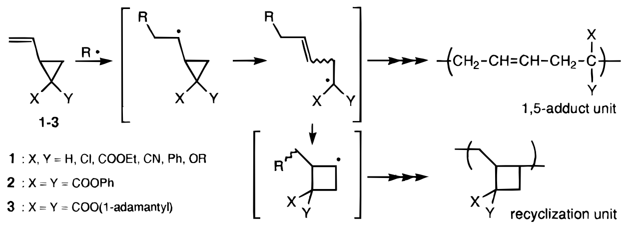
Since the monomers currently used in the manufacture of commercial potting and casting resins, molding resins, film coatings, etc. exhibit some degree of shrinkage during polymerization, the development of a volume-expanding monomer is desired.[1] Generally, in addition polymerization, cyclic monomers show a smaller degree of shrinkage than vinyl monomers, but there are few monomers that afford a high molecular weight polymer by radical initiation through ring opening. Vinylcyclopropane **1** is one candidate because it can afford relatively high molecular weight polymers through radical ring-opening polymerization (Scheme 1).[2−8] However, most show volume shrinkage upon polymerization. Recently, we have found that 1,1-bis(phenoxycarbonyl)-2-vinylcyclopropane (**2**) is a peerless high-volume-expanding monomer.[9] The volume expansion value of **2** ranged from 1.28% (obtained from solution polymerization at 120 °C) to 6.77% (obtained from bulk polymerization at 60 °C). The difference in the volume expansion value correlates with the composition of the polymer obtained, and we have proposed that overisomerization, such as recyclization in Scheme 1, may decrease the volume expansion.

The **2** is a capable monomer, but polymerization conditions for undergoing high volume expansion are restricted. To exclude the recyclization by steric hindrance, we thought a new monomer containing more bulky ester groups would be more amenable. This article describes the synthesis and polymerization of 1,1-bis[(1-adamantyloxy)carbonyl]-2-vinylcyclopropane (**3**), containing bulky substituents.

Experimental Section

Materials. Methylene chloride was purified by distillation over phosphorus pentoxide. Tetrahydrofuran was refluxed with sodium and benzophenone until the blue color of the ketyl of benzophenone was well established and then was distilled. Sodium hydride (60% in oil) was washed in *n*-hexane to remove oil and then dried *in vacuo*. Other reagents were obtained commercially and used as received.

Scheme 1



Measurements. IR spectra were recorded on a Hitachi I-5020 FT-IR spectrophotometer. NMR spectra were obtained on a JEOL JNM-EX270 (270 MHz) spectrometer. Molecular weights of polymers were determined by a gel permeation chromatograph (GPC) on the basis of standard polystyrenes using a JASCO TRIROTAR-III system equipped with Shodex KF-800P and KF-80M columns at 40 °C in tetrahydrofuran. Thermal properties were measured by a Seiko SSC 5000 thermal analyzer at a heating rate 10 °C/min for thermogravimetric analysis (TGA). Differential scanning calorimetry (DSC) of the samples was performed by the use of a Seiko SSC 5200 at a heating rate of 10 °C/min under nitrogen purge using preheated samples (300 °C).

Measurement of Density. Densities of the monomer and polymers were measured by the sink and float test at 25 °C, employing standard hydrometers. The samples of monomer and polymers were pressed at 300 kg/cm^2 for 1 min *in vacuo*.

Preparation of 1,1-Bis[(1-adamantyloxy)carbonyl]-2-vinylcyclopropane (3). To a suspension of oil-free sodium hydride (239 mg, 10.0 mmol), 1,4-dibromo-2-butene (573 mg, 2.7 mmol), and dry THF (25 mL) was added dropwise di-1-adamantyl malonate (1000 mg, 2.7 mmol) in THF (25 mL) at ambient temperature under nitrogen atmosphere, and the mixture was then heated at 70 °C. After 5 h, THF was removed under reduced pressure. The residue was dissolved in ether (50 mL), washed with aqueous sodium bicarbonate, and then dried over magnesium sulfate. After the removal of ether *in vacuo*, the crude product was purified by column chromatography [benzene/*n*-hexane = 4/1 (v/v) on silica gel] followed by recrystallization from ether. The yield of **3** was 775 mg (25%) as colorless columns (mp 104−105 °C): IR (KBr)

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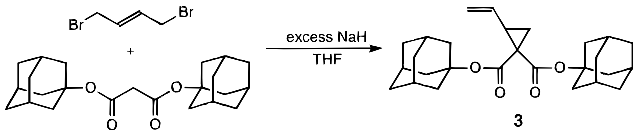
Scheme 2



δ 1713 (C=O), 1640 (C=C), 1456, 1335, 1273, 1206, 1140, 1053 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.37 (dd, 1H, J = 4.6 and 8.9 Hz, E-**H**CH< of cyclopropane), 1.51 (dd, 1H, J = 4.6 and 7.3 Hz, Z-**H**CH< of cyclopropane), 1.66 (s, 12H, 4,6,10-CH$_2$ of adamantyl), 2.1 (m, 12H, 2,8,9-CH$_2$ of adamantyl), 2.2 (m, 6H, 3,5,7-CH of adamantyl), 2.43 (ddd, 1H, J = 7.3, 8.3, and 8.9 Hz, CH< of cyclopropane), 5.11 (dd, 1H, J = 2.0 and 9.9 Hz, E-**H**CH=CH), 5.27 (dd, 1H, J = 2.0 and 17.2 Hz, Z-**H**CH=CH), 5.43 (ddd, 1H, J = 8.3, 9.9, and 17.2 Hz, CH$_2$=C**H**); ^{13}C NMR (CDCl$_3$) δ 19.8 (t), 30.0 (d), 30.8 (d, adamantyl), 36.2 (t, adamantyl), 37.8 (s), 41.3 (t, adamantyl), 81.5 (s, adamantyl), 117.6 (t, CH$_2$=), 133.7 (d, =CH), 166.4 and 168.7 (s, C=O).

Typical Procedure of the Radical Polymerization of 3. A mixture of **3** (400 mg, 0.94 mmol), azobis(isobutyronitrile) (AIBN) (3.1 mg, 2 mol %), and benzene (0.5 mL) was heated at 60 °C in a glass tube that was sealed after degassing. After 48 h, the reaction mixture was dissolved in methylene chloride (5 mL) and then poured into a 20-fold excess of methanol. The polymer was collected by filtration as a white powder and purified by reprecipitation from methylene chloride in methanol: yield, 384 mg (96%); IR (KBr) 1727 (C=O), 1458, 1248, 1184, 1103, 1057, 968 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.7 (br, 12H), 2.1 (br, 12H), 2.2 (br, 6H), 2.4 (br, 4H), 5.4 (br, 2H); ^{13}C NMR (CDCl$_3$) δ 30.8 (d), 36.3 (t), 41.3 (t), 41.3 (t), 58.5 (s), 80.9 (s), 128.5 (d), 169.7 (s).

Molecular Orbital Calculation. Computations were done on an Apple Macintosh Quadra 840AV and an IBM RISC System/6000 with the use of Sony Tektronix CAChe group server system version 3.6. Molecular orbital (MO) calculations were performed with MOPAC version 6.00, revised as CACheMOPAC version 94.1 for the CAChe system, using the PM3 hamiltonian by the unrestricted Hartree–Fock (UHF) method on all compounds.[10] All of the bond distances, bond angles, and dihedral angles were optimized except those of the adamantyl groups, which were locked to the parameters of optimized adamantanol. The optimized grand state structures were found from more than 20 candidates and calculated by using the PRECISE command. The polymers were optimized by using the transition vector (Tv) that is calculated by 0.002 Å. The optimized transition state structures were found from the maximum point of heat of formation in reaction coordinate curves by using the NLLSQ command, and then it was confirmed that the structure transformed into both reactant and product by the IRC method.

Results and Discussion

Radical Polymerization of 3. Monomer **3** was prepared from 1,4-dibromo-2-butene and di-1-adamantyl malonate by a previously reported method (Scheme 2).[9] Formation of a cyclopropane ring is supported by the presence of the peaks assignable to methylene (δ 1.37 and 1.51) and methyne (δ 2.43) in the ^{1}H NMR spectrum. Characteristic hydrogens of adamantyl groups are classified into three groups as 4-, 6-, and 10-positions of methylene (12H), the 2-, 8-, and 9-positions of methylene (12H), and the 3-, 5-, and 7-positions of methyne (6H).

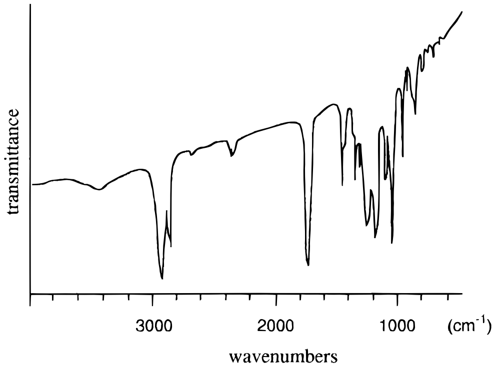


Figure 1. IR spectrum of the polymer obtained from run 2 (KBr).

Polymerization of **3** was carried out in a sealed, degassed tube in the presence of azobis(isobutyronitrile) (AIBN) or di-*tert*-butyl peroxide (DTBP). The results are summarized in Table 1. The polymer obtained was collected as a white powder insoluble in methanol. The polymer was soluble in methylene chloride, chloroform, DMF, and THF. The solubility of poly(**3**) was improved over that of poly(**2**), which may be explained by the introduction of bulky side chains. Number-average molecular weights (M_n) of the polymers were 2300–51 000, estimated by GPC in THF on the basis of polystyrene standard.

The structure of the polymer obtained from Table 1 was confirmed to be the expected ring-opening product by IR, ^{1}H NMR, and ^{13}C NMR spectra. The IR spectrum of the polymer from run 2 showed the absence of an absorption at 1640 cm^{-1}, assignable to the vinyl group of monomer **3**, and the presence of an absorption at 1727 cm^{-1}, assignable to the carbonyl of the aliphatic adamantyl ester, as shown in Figure 1. No extra peaks were found in the ^{1}H NMR and ^{13}C NMR spectra of the polymer, clearly indicating the formation of a 1,5-adduct unit (Figure 2). Although inherent viscosities decreased when polymerizations were carried out at high temperature or low monomer concentration, all of the polymers in Table 1 are consistent with the 1,5-adduct structure. In previous radical polymerizations of vinylcyclopropanes **1** and **2**, the composition of the 1,5-adduct unit decreased with increasing reaction temperature and in the solvent.[8,9] Decreasing the 1,5-adduct unit has been explained by the reason of propagating terminal radical attack on the *endo*-olefin through the recyclization path, as shown in Scheme 1. Therefore, depression of recyclization in the polymerization of **3** may be due to effective steric hindrance between the bulky bis[(1-

Table 1. Radical Polymerization of 3[a]

run	initiator	temp (°C)	solvent	molarity[c] (mol/L)	yield[d] (wt %)	M_n	M_w/M_n[e]	η_{inh}[f] (dL/g)
1	AIBN	60	PhH	1	86	33000	2.8	0.23
2	AIBN	60	PhH	2	96	51000	5.8	0.32
3	AIBN	60	PhH	10	95	35000	6.3	0.52
4	AIBN	60	PhCl	0.05	trace			
5	AIBN	60	PhCl	0.1	49	4800	3.1	0.07
6	DTBP	120	PhCl	0.05	trace			
7	DTBP	120	PhCl	1	96	6300	6.5	0.15
8	DTBP	120	Bulk		92	2300	4.4	0.09

[a] Heated for 48 h in a sealed tube. [b] 2 mol %. [c] Ratio of monomer (mol) to solvent (mL). [d] Insoluble in methanol. [e] Estimated by GPC (based on polystyrene). [f] Inherent viscosity, measured in chloroform (0.5 g/dL) at 30 °C.

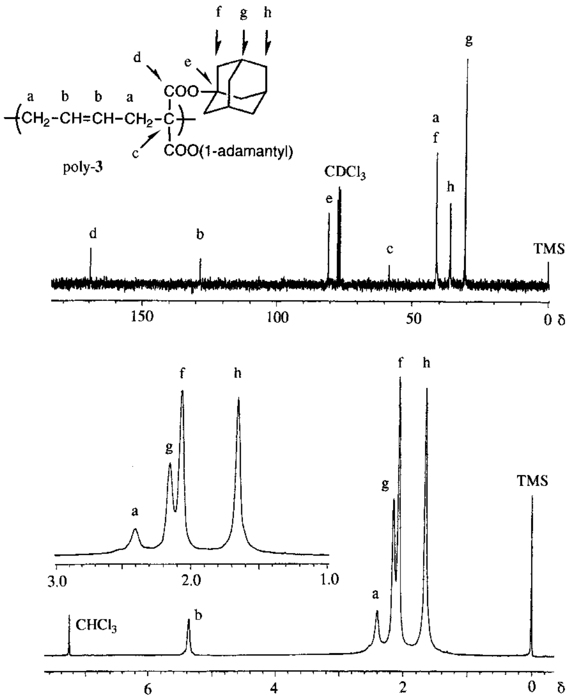


Figure 2. ^1H and ^{13}C NMR spectra of the polymer obtained from run 2: (top) ^{13}C NMR; (bottom) ^1H NMR spectrum.

Table 2. Thermal Properties and Volume Change of Polymers

polymer[a]	T_g[b] (°C)	T_d[c] (°C)	density[d] (g/mL)	vol change[e] (%)
run 1	31	376	1.129	+4.00
run 2	34	377	1.128	+4.08
run 3	23	361	1.110	+5.61
run 5	*f*	369	1.129	+4.00
run 7	*f*	354	1.122	+4.81
run 8	*f*	375	1.123	+4.72

[a] Prepared in Table 1. [b] Measured by DSC. [c] Measured by TGA (temperature at 10% weight loss with a heating rate of 10 °C/min under N_2). [d] Measured by the sink and float test; density of monomer **3** is 1.176 g/mL. [e] [Density(monomer) − density(polymer)]/density(monomer × 100. [f] Obvious T_g was not found.

adamantyloxy)carbonyl]methyl radical and the *endo*-olefin.

Thermal Properties of the Polymers. The thermal properties of poly(**3**) were examined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). All of the poly(**3**) runs exhibited a degradation temperature (T_d) above 350 °C (Table 2). Glass transition temperatures (T_g) of poly(**3**) obtained from runs 1−3 were detected at 23−34 °C. T_g of poly(**3**) is lower than T_g of poly(**2**) (ca. 76 °C). The higher T_g of poly(**2**) has been explained by aromatic−aromatic interactions of the side chains; thus, the absence of phenyl esters might decrease T_g of poly(**3**). This means the interaction among polymer chains became weaker than in poly(**2**) and agrees with the increasing solubility described earlier. The wide range of T_g values can be explained by the assumption that the polymer has various compositions of *cis* and *trans* forms around the double bond of the main chain. In NMR and IR spectroscopy, there are no characteristic signals of *cis* and *trans* forms to use for the determination; thus, it could not be estimated.

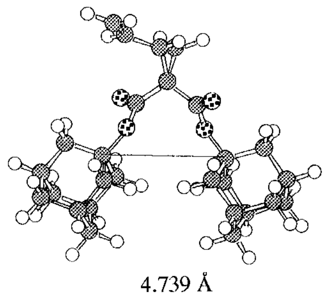
Volume Change upon Polymerization. Densities of the monomer and polymers were measured by the sink and float test. The results are summarized in Table 3. By using the density of monomer **3** (1.176 g/mL), the volume change ratio was estimated as [density(monomer) − density(polymer)]/density(monomer) × 100. All of the polymerizations in Table 3 showed positive volume expansion as +4.5 ± 1.1%. Consequently, **3** is a volume-expandable monomer. The reason for the expansion during polymerization can be rationalized by the bond change between the monomer and polymer forms and the conversion of the crystalline monomer to the amorphous polymer.

Table 3. Relationship between R_p and Initiator Concentration[a]

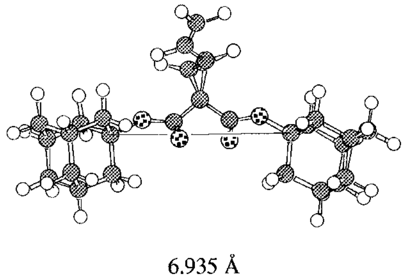
[AIBN] ($\times 10^3$ mol/L)	time (min)	yield (%)	R_p ($\times 10^6$ mol/L·s)
1.04	120	10.2	4.80
2.45	90	11.1	6.96
4.89	60	10.5	9.86
7.08	30	7.2	13.54

[a] Reacted at 60 °C in benzene, [**3**] = 0.34 mol/L.

Chart 1



A

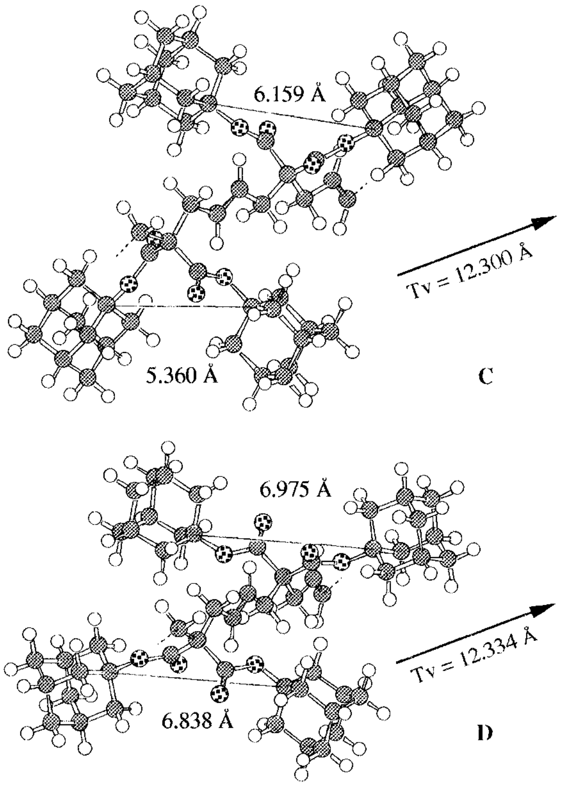


B

Endo and Ogasawara reported that there is a linear relationship with a positive slope between the volume shrinkage upon polymerization and the reciprocal of the monomer's molecular weight.[11] This idea is based on the fact that the greater the molecular weight, the lower the shrinkage.[1,12] This theory could explain the small shrinkage of a large monomer, but the volume expansion would not be explained. Similarly, if volume expansion is based on the assumption that ring-opening isomerization of cyclopropane increases the volume of the polymer repeating unit rather than the volume of the monomer molecule that has a compressed ring with high strain, then the larger molecular weight will be a disadvantage because the volume ratio of the expanding part becomes smaller with increased molecular weight. Consequently, a simple increment in molecular weight should cause close to no volume change, either shrinkage or expansion.

To consider the structures of both monomer **3** and poly(**3**), MO calculation was carried out. The optimized conformation of monomer **3** using the PM3 (UHF) method is shown in Chart 1. The structure **A** is found to be the most stable conformer, whose heat of formation (HOF) is estimated to be −161.11 kcal/mol. In spite of the large adamantyl esters, it is less crowded around

Chart 2



the polymerizable vinyl group. This means that the ring-opened terminal radical has large steric hindrance, but the monomer does not; therefore, polymerization goes smoothly. The conformer **A** also shows that the large ester groups are close, and the distance between the 1- and 1′-carbons of the adamantyls is 4.725 Å. The other conformation **B**, whose adamantyl esters are spread to 6.935 Å, is given with a HOF of −159.10 kcal/mol. The difference in HOF between **A** and **B** is 2.01 kcal/mol. This value indicates that if the only conformers are **A** and **B** and the existence ratio obeys Boltzmann's distribution, then **A**/**B** is 95/5 at 60 °C; thus, the contribution of conformer **B** may be small. Similarly, two optimized structures of poly(**3**) using the transition vector (Tv) in Chart 2 also show that the closed-ester conformation **C** (−317.75 kcal/mol) is more stable than the spread-ester conformation **D** (−294.81 kcal/mol). The noteworthy thing is that the difference between the adamantyl groups of structure **C** (5.360−6.159 Å) is elongated compared to monomer **A**. There is not enough evidence to determine the exact conformations of **3** and poly(**3**), but one explanation for volume expansion may be that the ring-opening isomerization of cyclopropane causes the split of the two large ester groups, and then the free volume of the polymer may increase.

Kinetic Study. Because in previous polymerizations of vinylcyclopropanes the composition of the polymer obtained had been affected by the temperature and concentration, the kinetics had not been elucidated. However, the composition of poly(**3**) is not influenced by these extrinsic factors; thus, it is suitable for kinetic study.

Generally, the production of polymer through radical chain polymerization consists of three steps: initiation, propagation, and termination. An additional reaction, an isomerization step, should be considered in the polymerization of **3**. Consequently the polymerization would obey eqs 1−5:

$$\mathrm{I} \xrightarrow{k_d} 2\mathrm{I}^\bullet \tag{1}$$

$$\mathrm{I}^\bullet + \mathrm{M} \xrightarrow{k_i} \mathrm{M_{in}}^\bullet \tag{2}$$

$$\mathrm{M_{op}}^\bullet + \mathrm{M} \xrightarrow{k_{ad}} \mathrm{M_{in}}^\bullet \tag{3}$$

$$\mathrm{M_{in}}^\bullet \xrightarrow{k_{iso}} \mathrm{M_{op}}^\bullet \tag{4}$$

$$2\mathrm{M}^\bullet \xrightarrow{k_t} \mathrm{P{-}P} \text{ or } \mathrm{P} + \mathrm{P}' \tag{5}$$

where I, $R^\bullet$, M, $M_{in}^\bullet$, and $M_{op}^\bullet$ are an initiator, its primary radical, a monomer, a ring-intact-form radical, and a ring-opened-form radical. k_d, k_i, k_{ad}, k_{iso}, and k_t are rate constants for the initiator dissociation, the addition of primary radical to the monomer, the addition of $M_{op}^\bullet$ radical to the monomer, the isomerization of $M_{in}^\bullet$ radical, and the termination by bimolecular coupling or disproportionation. The number of monomer molecules reacting in eqs 2 and 5 is far less than the number in eqs 3 and 4 for a process producing high polymer; therefore, the rate of polymerization R_p and $[M_{op}^\bullet]$ are given by eqs 3 and 4, with a very close approximation as follows:

$$\mathrm{R_p} \equiv -\frac{\mathrm{d[M]}}{\mathrm{d}t} = k_{ad}[\mathrm{M_{op}}^\bullet][\mathrm{M}] \tag{6}$$

$$\frac{\mathrm{d}[\mathrm{M_{op}}^\bullet]}{\mathrm{d}t} = k_{iso}[\mathrm{M_{in}}^\bullet] - k_{ad}[\mathrm{M_{op}}^\bullet][\mathrm{M}] \tag{7}$$

When the steady state assumption is made that the concentration of radicals instantaneously reaches a constant, the initiation and termination rates are equivalent or

$$2k_d f[\mathrm{I}] = k_t[\mathrm{M}^\bullet]^2 \tag{8}$$

where f is a factor of dissociation of the initiator. The total concentration of radicals $[M^\bullet]$ is

$$[\mathrm{M}^\bullet] = [\mathrm{M_{in}}^\bullet] + [\mathrm{M_{op}}^\bullet] \tag{9}$$

Under the steady state assumption, the left side of eq 7 is zero. Rearrangement of eqs 7 and 8 and substitution into eq 9 yield

$$\begin{aligned}\left(\frac{2k_d f[\mathrm{I}]}{k_t}\right)^{1/2} &= [\mathrm{M_{in}}^\bullet] + [\mathrm{M_{op}}^\bullet] \\ &= \frac{k_{ad}[\mathrm{M}]}{k_{iso}}[\mathrm{M_{op}}^\bullet] + [\mathrm{M_{op}}^\bullet] \end{aligned} \tag{10}$$

$$\therefore\ [\mathrm{M_{op}}^\bullet] = \left(\frac{2k_d f[\mathrm{I}]}{k_t}\right)^{1/2}\left(\frac{k_{iso}}{k_{ad}[\mathrm{M}] + k_{iso}}\right) \tag{11}$$

Consequently, the R_p yields

$$\begin{aligned} R_p &= k_{ad}\left(\frac{2k_d f}{k_t}\right)^{1/2}\left(\frac{k_{iso}}{k_{ad}[\mathrm{M}] + k_{iso}}\right)[\mathrm{I}]^{1/2}[\mathrm{M}] \\ &= \left(\frac{2k_d f}{k_t}\right)^{1/2}(k_{iso}^{-1} + (k_{ad}[\mathrm{M}])^{-1})^{-1}[\mathrm{I}]^{1/2} \end{aligned} \tag{12}$$

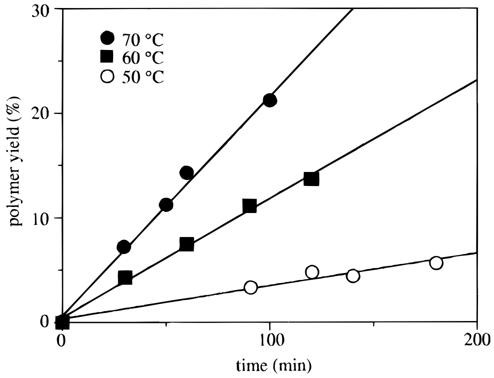


Figure 3. Relationship between time and polymer yield in the polymerization of **3** in benzene ([**3**] = 0.34 mol/L, [AIBN] = 2.45 × 10^{-3} mol/L).

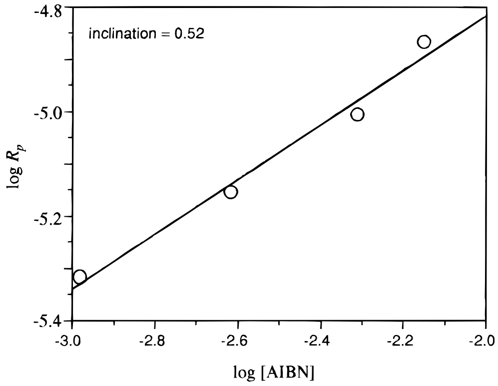


Figure 4. Relationship between log[AIBN] and log R_p in the polymerization of 3 ([**3**] = 0.34 mol/L).

If addition step (eq 3) is sufficiently faster than the isomerization step (eq 4), the second term of the right side in eq 10 is negligible. Hence, eq 12 yields

$$R_p = (2k_d f/k_t)^{1/2} k_{iso}[I]^{1/2} \tag{13}$$

Equation 13 means that $k_{iso} \ll k_{ad}[M]$ and R_p is independent of the concentration of monomer. On the contrary, if the addition is the rate-determining step in the propagation reaction, the first term of the right side in eq 10 is negligible. Hence, eq 12 yields

$$R_p = k_{ad}(2k_d f/k_t)^{1/2}[I]^{1/2}[M] \tag{14}$$

Equation 14 shows that $k_{iso} \gg k_{ad}[M]$ and R_p is proportional to first order in monomer concentration. It also agrees with the general vinyl monomer relationship to polymerize to first order in monomer concentration and undergo bimolecular termination.

The solution homopolymerization of **3** in benzene was studied with AIBN at temperatures ranging from 50 to 70 °C. The time vs conversion relationship could be fit to straight lines without any induction period (Figure 3). The experimental R_p for concentrations of monomer and initiator was investigated at 60 °C. Table 3 and Figure 4 show the relationship between R_p and initiator concentration. A plot of log R_p vs log[AIBN] is fit to a straight line with an inclination of 0.52, indicating a usual bimolecular termination. Similarly, Table 4 and Figure 5 show the relationship between R_p and monomer concentration. A plot of log R_p vs log[**3**] is fit to a straight line with an inclination of 1.2. The rate equation for the homopolymerization of **3** in benzene is given as

$$R_p = k_a[\mathrm{AIBN}]^{0.52}[\mathbf{3}]^{1.2} \tag{15}$$

where k_a is the experimental apparent whole rate constant. This equation indicates that monomer **3** seems to obey eq 14 rather than eq 13. Accordingly, monomer **3** also agrees with the general vinyl monomer relationship, where the contribution of the isomerization step is unrelated.

Table 4. Relationship between R_p and Monomer Concentration[a]

[**3**] (mol/L)	time (min)	yield (%)	R_p (×10^6 mol/L·s)
0.10	120	7.6	1.05
0.20	80	7.2	2.95
0.34	120	13.6	6.40
0.98	30	3.4	18.45

[a] Reacted at 60 °C in benzene, [AIBN] = 2.45 × 10^{-3} mol/L.

Table 5. Relationship between R_p and Reaction Temperature[a]

temp (°C)	1/T (×10^3/K^{-1})	R_p (×10^6 mol/L·s)	log R_p
50	3.10	1.78	−5.75
60	3.00	6.44	−5.19
70	2.92	11.99	−4.92

[a] Reacted in benzene, [**3**] = 0.34 mol/L, [AIBN] = 2.45 × 10^{-3} mol/L.

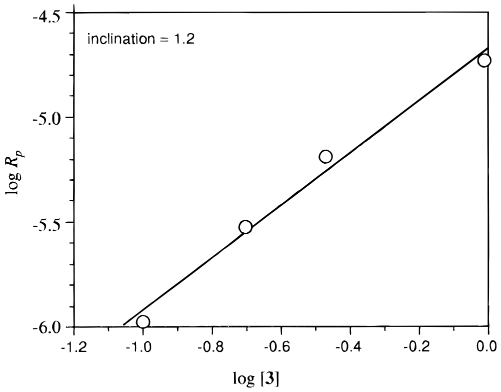


Figure 5. Relationship between log[**3**] and log R_p in the polymerization of **3** ([AIBN] = 2.45 × 10^{-3} mol/L).

It is known that the isomerization of cyclopropylmethyl radical to 3-butenyl radical is irreversible and its rate is very large (1.3 × 10^8 s^{-1}), but the isomerization of cyclopropylphenylmethyl is reversible and the ring-intact radical form is thermodynamically preferred over the ring-opened radical form.[13] In so far as **3** is concerned, it may safely be assumed that the ring-opening isomerization is apparently irreversible and that the k_{iso} in eq 12 may be sufficiently larger than $k_{ad}[M]$ because the ring-intact repeating unit is not detected.

Substitution of eq 14 into an Arrhenius-type relationship and rearrangement yield

$$\ln R_p = \ln((A_{ad}\, A_d^{1/2}/A_t^{1/2})(2f)^{1/2}[I]^{1/2}[M]) - (E_{ad} + {}^1/_2E_d - {}^1/_2E_t)\frac{1}{RT} \tag{16}$$

where each A is a collision frequency factor, each E is an activation energy, and T is the kelvin temperature. Equation 17 shows that the overall activation energy

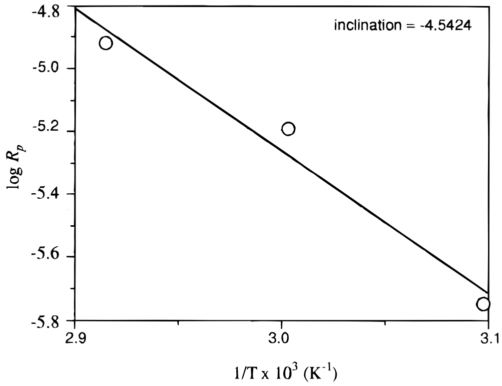


Figure 6. Relationship between $1/T$ and log R_p in the polymerization of **3** ([**3**] = 0.34 mol/L, [AIBN] = 2.45 × 10^{-3} mol/L).

E_a consists of

$$E_a = E_{ad} + {}^1/_2E_d - {}^1/_2E_t \tag{17}$$

which is found not to be influenced by E_{iso}.

From the inclinations of the lines in Figure 3, an Arrhenius plot is introduced (Figure 6). Experimental apparent whole active energy (E_a) is calculated as 20.8 kcal/mol. Rearrangement of eq 17 yields

$$E_a - {}^1/_2E_d = E_{ad} - {}^1/_2E_t \tag{18}$$

where the right side is the independent parameter of the monomer. By using 29.5 kcal/mol for the E_d of AIBN at 60 °C,[14c] $E_{ad}-E_t/2$ is estimated to be 6.0 kcal/mol. Compared with general monomers (vinyl acetate, 1.7; acrylonitrile, 2.0; methyl acrylate, 4.4; methyl methacrylate, 4.9; 2-vinylpyridine, 5.4; styrene, 5.3; and ethylene, 4.2 kcal/mol),[14] the value of monomer **3** is more similar. The result that **3** is similar to general vinyl monomers in spite of including an extra reaction, ring-opening isomerization, in the propagating step is not inconsistent with eq 17.

Estimation of Elementary Reactions by the MO Method. In the preceding study, k_{iso} is assumed to be relatively large. To estimate the elementary reactions, we calculated the potential surface for the radical addition and ring-opening isomerization steps by using the MO method. The potential curves were estimated by HOF vs the reaction coordinate, as shown in Figure 7. A tertiary radical such as 1,1-bis(alkoxycarbonyl)ethyl was employed as the terminal radical of the propagating polymer. Instead of diadamantyl esters, corresponding dimethyl esters were employed since the degree of freedom in large ester groups would delay convergence in calculation. The total HOF of the radical and the monomer, which are calculated independently, is plotted at **O** where the two species separate to infinity.

The optimized structures in the radical addition step are shown in Chart 3, where the reaction coordinate is the decreasing atom distance between the radical center carbon, C•, and the β-carbon of vinylcyclopropane, C^β. The potential curve on the left in Figure 7 indicates that the radical addition is exothermic, with 17.8 kcal/mol enthalpy being released, the C–C bond forming in transition state **II** is 2.156 Å, and $\Delta H^\ddagger_{ad}$ based on **O** is 11.2 kcal/mol. The important thing in this result is that the product is not a ring-opened radical **VI**, but a ring-intact radical **III**. This means that the ring-intact radical **III** will be a metastable radical, and the formation of **VI** from **I** will occur not through concerted mechanism, but through a stepwise one.

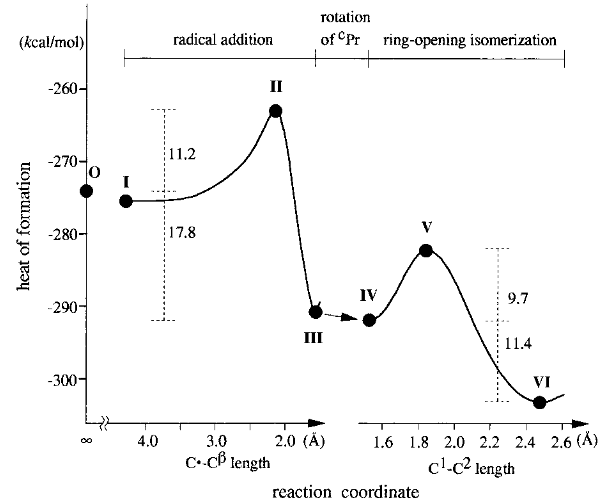


Figure 7. Potential curves of radical addition and ring-opeing isomerization obtained by PM3 (UHF) calculation.

The ring-intact radical **III** is not optimized completely because radical **IV** is found to be more stable. **IV** is obtained from the rotation of the cyclopropyl ring around the radical lobe, as shown in Scheme 3. The structure of the transition state between **III** and **IV** cannot be obtained because the $\Delta H^\ddagger$ of the rotation is too small (estimated to be <1.2 kcal/mol); therefore, deformation after radical addition may occur quickly.

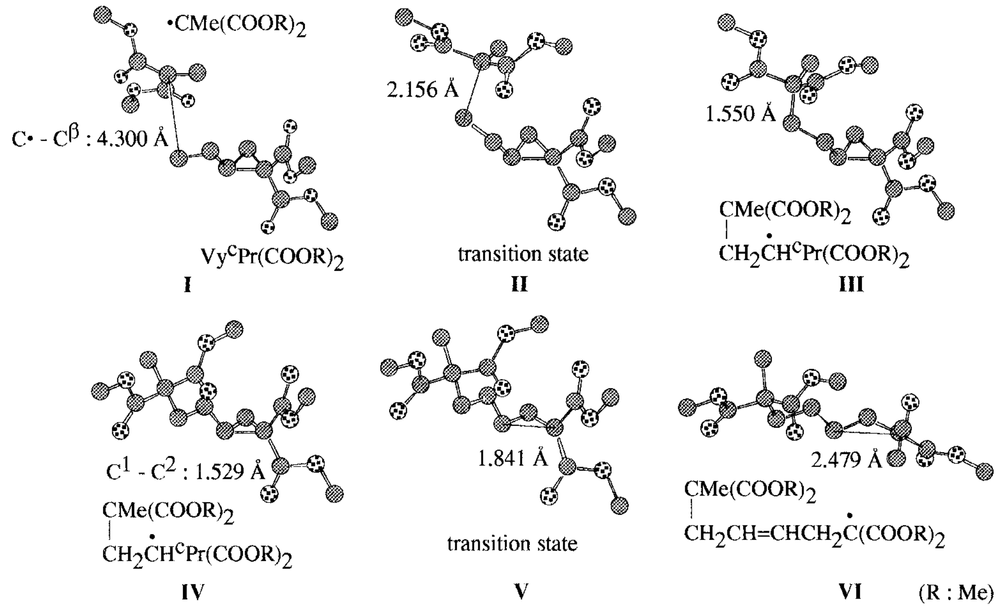
In the ring-opening isomerization step, the reaction coordinate was chosen as the increasing atom distance between the C^1 and C^2 carbons of cyclopropane. The potential curve is shown to the right in Figure 7. The $\Delta H^\ddagger_{iso}$ is estimated to 9.7 kcal/mol, where the C^1-C^2 distance is 1.841 Å. It indicates that the ring-opening isomerization step also shows exothermic reaction, with 11.4 kcal/mol enthalpy released.

Considering the two transition states **II** and **V**, thermodynamic quantities were calculated by using the THERMO command. The results are summarized in Table 6. Since $\Delta H^\ddagger$, $\Delta S^\ddagger$, ΔH, and ΔS are not changed at either 25 or 60 °C, these parameters are not influenced by temperature and can be dealt with as constants. $\Delta S^\ddagger_{ad}$ and ΔS_{ad} are negative because of the bimolecular addition reaction. On the other hand, $\Delta S^\ddagger_{iso}$ and ΔS_{iso} are estimated to be positive. This is attributable to the increasing degree of freedom by ring fission.

The atom distance between vinyl $C^\alpha-C^\beta$ of **II** (1.376 Å) is intermediate, but slightly closer to reactant **I** (1.329 Å) than to product **III** (1.473 Å). The $C^\alpha-C^\beta$ bond order of **II** estimated by the BONDS command is 1.49. It seems reasonable to suppose that **II** possesses properties intermediate between the two extremes. In the isomerization step, the entropy of **V** closely resembles the entropy of reactant **IV**, but the atom distance for $C^\beta-C^2$ of **V** is 1.401 Å, which is also between 1.457 (**IV**) and 1.333 Å (**VI**) with a 1.29 bond order. It seems that **V** also possesses properties intermediate between the two extremes.

Although $\Delta H^\ddagger_{iso}$ is estimated to be close to $\Delta H^\ddagger_{ad}$, $\Delta H^\ddagger_{iso}$ is still smaller than $\Delta H^\ddagger_{ad}$. Furthermore, the ring-opening isomerization is intramolecular and the reaction progresses with a positive entropy change. Consequently, the order of k_{iso} may be estimated to be larger than that of k_{ad}. The adamantyl acrylate derivatives' propagation rate constant k_p, which corresponds to k_{ad} in this article, is 0.4–570 L/mol·s reported by

Chart 3



Scheme 3

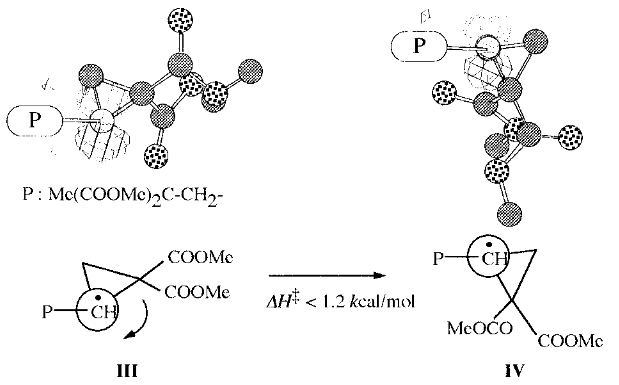


Table 6. Thermodynamic Quantities of the States Calculated by PM3[a]

	at 25 °C		at 60 °C	
state[b]	enthalpy (kcal/mol)	entropy (cal/mol)	enthalpy (kcal/mol)	entropy (cal/mol)
monomer	−123.7	124.6	−121.8	130.7
radical	−150.5	115.9	−149.0	120.8
O	−274.2	240.5	−270.8	251.5
I	−277.6	209.5	−274.1	220.8
II	−263.0	183.3	−259.6	194.3
III	−290.8	179.3	−287.4	190.3
IV	−292.0	181.8	−288.6	192.8
V	−282.3	182.1	−278.9	193.1
VI	−303.5	187.0	−300.0	198.1
$\Delta H^{\ddagger}_{ad}$ and $\Delta S^{\ddagger}_{ad}$	11.2	−57.3	11.2	−57.2
ΔH_{ad} and ΔS_{ad}	−17.8	−58.7	−17.8	−61.2
$\Delta H^{\ddagger}_{iso}$ and $\Delta S^{\ddagger}_{iso}$	9.7	0.3	9.7	0.3
ΔH_{iso} and ΔS_{iso}	−11.4	5.3	−11.4	5.3

[a] Calculated by THERMO on PM3 (UHF). [b] Monomer, 1,1-bis(methoxycarbonyl)-2-vinylcyclopropane; radical, 1,1-bis(methoxycarbonyl)ethyl; **O**, (monomer) + (radical); $\Delta H^{\ddagger}_{ad}$ and $\Delta S^{\ddagger}_{ad}$, **II**−**O**; ΔH_{ad} and ΔS_{ad}, **IV**−**O**; $\Delta H^{\ddagger}_{iso}$ and $\Delta S^{\ddagger}_{iso}$, **V**−**IV**; ΔH_{iso} and ΔS_{iso}, **IV**−**VI**.

Matsumoto, Otsu, *et al.*[15] This is consistent with the approximation of eq 14 not being an exaggeration.

Summary

The radical polymerization of 1,1-bis[(1-adamantyloxy)carbonyl]-2-vinylcyclopropane (**3**) undergoes through a 1,5-addition mode to afford a high molecular weight polymer in good yield. Selectivity in the direction of the ring-opening isomerization is quantitative at 60−120 °C, as estimated by ^{1}H NMR and ^{13}C NMR. In the poly(**3**), the cyclobutane skeleton formed by back-biting of the terminal radical was not detected because bulky adamantyl ester groups might depress recyclization by steric hindrance.

The new monomer **3** showed a positive volume change (+4.5 ± 1.1%) upon polymerization, in analogy with diphenyl ester **2**. This could be explained by the facts that recyclization during propagation is depressed by bulky ester groups and that **3** is crystalline at ambient temperature, which means that monomer is already compressed. Additionally, there is an explanation based on MO calculations that the ring-opening isomerization of cyclopropane causes the split of the two large ester groups, and then the free volume of the polymer may increase. The rate of polymerization (R_p) can be expressed by $R_p = k[\mathrm{AIBN}]^{0.52}[\mathbf{3}]^{1.2}$, and the apparent whole active energy is calculated to be 20.8 kcal/mol, which is similar to general vinyl monomers.

The di-1-adamantyl ester **3** is a peerless high-volume-expanding monomer, which can be polymerized by radical initiation at various temperatures and concentrations. Consequently, various applications for manufacture are expected.

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