Macromolecules **2001,** *34,* 4737−4741

Kinetic and ESR Studies of Ring-Opening Radical Polymerization of 1,1-Bis(ethoxycarbonyl)-2-vinylcyclopropane

Tomohiro Hirano, Atsushi Tabuchi, Makiko Seno, and Tsuneyuki Sato*

Department of Chemical Science and Technology, Faculty of Engineering, Tokushima University, Minamijosanjima 2-1, Tokushima 770-8506, Japan

Received November 16, 2000

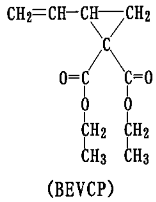
ABSTRACT: Ring-opening radical polymerization of 1,1-bis(ethoxycarbonyl)-2-vinylcyclopropane (BEVCP) with dimethyl 2,2′-azobisisobutyrate (MAIB) was investigated kinetically in benzene. The overall activation energy ($E_a = 94 \pm 4$ kJ/mol) was calculated from the polymerization rate (R_p) obtained at 30−60 °C. R_p (40 °C) is given by $R_p = k[\text{MAIB}]^{0.6\pm0.1}[\text{BEVCP}]^{1.0\pm0.1}$, which is similar to that of conventional radical polymerizations involving bimolecular termination. The present polymerization system involves ESR-observable polymer radicals under the actual polymerization conditions. The total polymer radical concentration ($[\text{P}^\bullet]$) was determined at different temperatures by ESR. Using R_p, $[\text{P}^\bullet]$, and the initiation rate obtained separately, the apparent rate constants of propagation (k_p) and termination (k_t) were estimated at different temperatures. The k_p (71 L/mol·s, 60 °C) and k_t (5.8×10^4 L/mol·s, 60 °C) values are much lower than those of typical vinyl monomers such as methyl methacrylate (MMA) and styrene. Owing to the markedly low k_t, BEVCP is more homopolymerizable than MMA. Analysis of the observed ESR spectrum suggests that the present polymerization system involves ring-opened type and cyclobutyl-type polymer radicals. This corresponds to the fact that the resulting poly(BEVCP) contains 1,5-adduct and cyclobutane structural units.

Introduction

Vinylcyclopropanes are readily polymerized by radical initiators to yield polymers carrying mainly a 1,5-ring-opened structural unit.[1−8] Such ring-opening polymerizations have received considerable attention because of less shrinkage during polymerization compared to those of typical vinyl monomers such as methyl methacrylate (MMA) and styrene (St).[2−5,8]

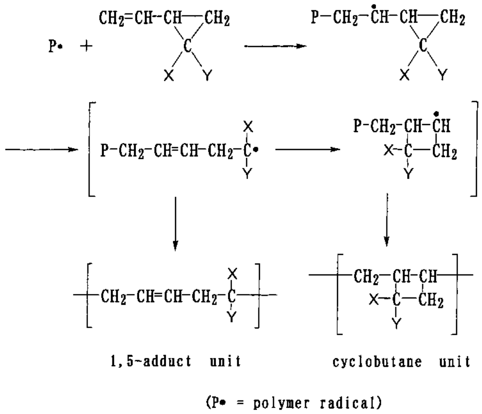
Polymerization of 1,1-disubstituted 2-vinylcyclopropanes was proposed to proceed with ring-opening and recyclization as shown in Scheme 1.[2,3,5,8] The resulting polymers carry 1,5-adduct units and cyclobutane units. The ratio of the structural units is substituent dependent. Efforts have been devoted to synthesis of such monomers and structural analysis of the resulting polymers. Conversely there have been few kinetic studies on ring-opening radical polymerizations of vinylcyclopropanes, although 1,1-bis(1-adamantyloxycarbonyl)-2-vinylcyclcopropane (BAVCP) reportedly shows the usual kinetics in its polymerization with azobis(isobutyronitrile) (AIBN) in benzene.[4]

1,1-Bis(ethoxycarbonyl)-2-vinylcyclopropane (BEVCP) yields ESR-observable polymer radicals under the actual radical polymerization conditions. This paper describes kinetic and ESR results on the radical polymerization behavior of BEVCP with dimethyl 2,2′-azobisisobutyrate (MAIB) in benzene.



(BEVCP)

Scheme 1



Experimental Section

Measurements. ^{1}H NMR spectra were obtained in $CDCl_3$ at 25 °C using a JEOL-EX400 (400 MHz) spectrometer with tetramethylsilane as the internal standard. Size exclusion chromatograms (SEC) were recorded at 38 °C by a TOSO−HLC 802A chromatograph [columns: Toso TSK gel G7000 HXL (pore size: 300 nm, bead size: 9 μm) + G5000 HXL (pore size: 65 nm, bead size: 9 μm) + G3000 HXL (pore size: 7.5 nm, bead size: 5 μm), [polymer] = 1 mg/mL, flow rate: 1 mL/min] with THF as the eluent. From the SEC results, the number-average ($\bar{M}_n$) and weight-average ($\bar{M}_w$) molecular weights of the resulting polymers were estimated after calibration with poly(St) standards. ESR spectra of the polymerization mixtures in a degassed and sealed ESR quartz tube of 2 mm diameter were recorded at a polymerization temperature on a JEOL−JES−FE2XG spectrometer operating at X-band (9.5 GHz) with a TE mode cavity. The concentration of polymer radical in a polymerization mixture was determined by double integration of observed first derivative ESR spectrum, using

---

* To whom all correspondence should be addressed.

10.1021/ma001962t CCC: $20.00

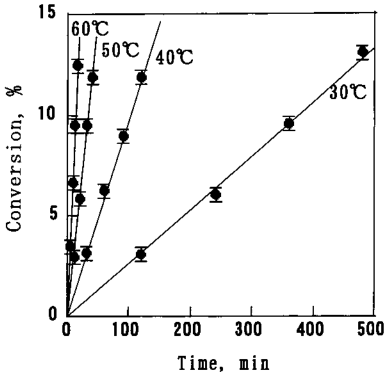


Figure 1. Time−conversion curves in the polymerization of BEVCP with MAIB at different temperatures in benzene. [BEVCP] = 1.55 M; [MAIB] = 20.0 mM.

2,2,6,6-tetramethylpiperidin-l-oxyl radical (TEMPO) as the standard in the same polymerization mixture without MAIB.

Materials. BEVCP was prepared by the reaction of 1,4-dibromo-2-butene with diethyl malonate in tetrahydrofuran (THF) in a presence of sodium hydride according to the literature method:[5,9] 56% yield, bp 95 °C/6 mmHg. Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.26; H, 7.60. Found: C, 62.08; H, 7.51. MAIB was recrystallized from methanol. Benzene was treated with sulfuric acid and distilled.

Polymerization. The polymerization of BEVCP was performed in a degassed and sealed tube at a temperature between 30 and 60 °C under shaking as in the following example. A benzene solution (3 mL) of BEVCP (1.55 M) and MAIB (20.0 mM) was placed in a glass tube, which was degassed several times by a freeze−thaw method and sealed off under a vacuum. After the polymerization was carried out at 40 °C for 90 min, the polymerization mixture was cooled to −50 °C and poured into a large excess (60 mL) of a water/methanol [1:9(v/v)] mixture. The precipitated polymer was filtered, dried in a vacuum, and weighed. The polymer yield was 9.0%. $\bar{M}_n$ of the polymer was 2.3 × 10^5. The experiments were run in quadruplicate for determination of a polymerization rate.

Results and Discussion

Kinetic Study of the Polymerization of BEVCP with MAIB in Benzene. Figure l presents the time−conversion plots obtained in the temperature range of 30−60 °C, where the concentrations of BEVCP and MAIB were 1.55 M and 20.0 mM, respectively. Polymer yields increased linearly with time without any induction period in the initial polymerization stage. The initial polymerization rate (R_p) at each temperature was estimated from Figure 1. From the Arrhenius plot of R_p values (Figure 2), the overall activation energy of the polymerization was calculated to be 94 ± 4 kJ/mol. The value is somewhat higher than those for the polymerizations of BAVCP (87 kJ/mol) and MMA (84 kJ/mol) with AIBN.[4,10] Similar activation energies were reported for decompositions of AIBN (126 kJ/mol) and MAIB (121 kJ/mol).[11,12]

Figure 3a shows the effect of the MAIB concentration on R_p observed at 40 °C, fixing the BEVCP concentration at 1.55 M. R_p increases in proportion to the 0.6 ± 0.1 power of the initiator concentration.

Figure 3b presents the relationship between R_p and the BEVCP concentration at 40 °C and a fixed MAIB concentration (20.0 mM). Thus, R_p is first (±0.1) order with respect to the monomer concentration.

Therefore, $R_p = k[\mathrm{MAIB}]^{0.6\pm0.1}[\mathrm{BEVCP}]^{1.0\pm0.1}$ at 40 °C. The rate equation is very similar to that of typical radical polymerization, indicating that the present polymerization involves bimolecular termination between propagating polymer radicals.

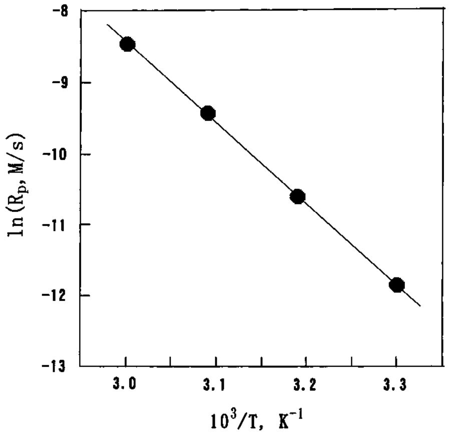


Figure 2. Temperature effect on the polymerization rate (R_p) in benzene.

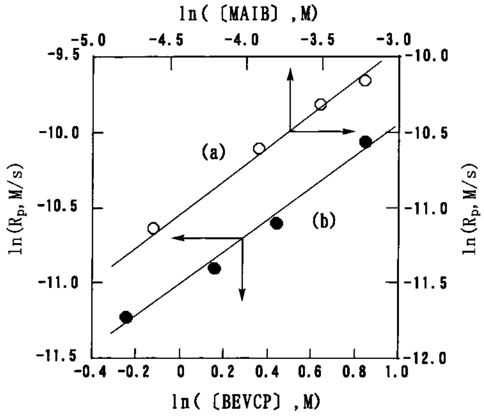


Figure 3. Dependence of the polymerization rate (R_p) on (a) the MAIB concentration and (b) the BEVCP concentration at 40 °C in benzene. Key: (a) [BEVCP] = 1.55 M; (b) [MAIB] = 20.0 mM.

Table 1. Molecular Weights and Polydispersities of Poly(BEVCP)[a]

temp (°C)	[MAIB][b] × 10^2 (mol/L)	[BEVCP] (mol/L)	$\bar{M}_n \times 10^{-5}$	$\bar{M}_w/\bar{M}_n$
30	2.0	1.55	3.7	1.9
40	2.0	1.55	2.3	2.2
50	2.0	1.55	1.8	2.3
60	2.0	1.55	1.4	2.0
40	1.0	1.55	2.6	1.9
40	3.0	1.55	2.1	2.3
40	4.0	1.55	2.2	2.1
40	2.0	0.78	1.0	1.9
40	2.0	2.33	3.1	2.0
40	2.0	4.66	6.8	2.3

[a] BEVCP = 1,1-bis(ethoxycarbonyl)-2-vinylcyclopropane. [b] MAIB = dimethyl 2,2′-azobisisobutyrate.

Characterization of the Resulting Poly(BEVCP). Table 1 summarizes the molecular weights of the resulting poly(BEVCP)s. The $\bar{M}_n$ value was in the range (1.0−6.8) × 10^5. Similar to typical radical polymerizations, the molecular weight of the polymer increases with increasing monomer concentration and tends to decrease with increasing temperature and increasing initiator concentration, although the effect of initiator concentration is smaller. The $\bar{M}_w/\bar{M}_n$ values range from 1.9 to 2.3, which are also similar to those of typical radical polymers.

Table 2. Fractions of 1,5-Adduct (Structure I) and Cyclobutane (Structure II) Units in Poly(BEVCP)[a]

temp (°C)	[BEVCP] (mol/L)	1,5-adduct units (%)	cyclobutane units (%)
30	1.55	71	29
40	1.55	69	31
50	1.55	68	32
60	1.55	66	34
40	0.78	67	33
40	2.33	68	32
40	4.66	71	29

[a] BEVCP = 1,1-bis(ethoxycarbonyl)-2-vinylcyclopropane.

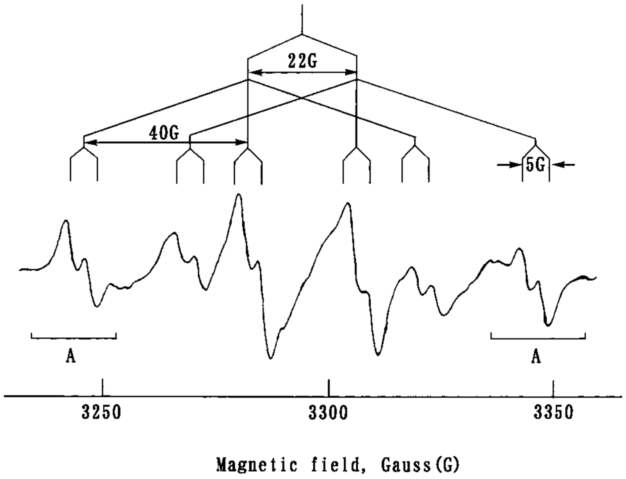
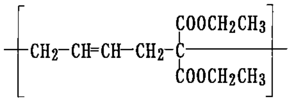


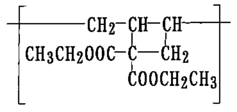
Figure 4. ESR spectrum observed in the polymerization of BEVCP with MAIB at 60 °C in benzene. [BEVCP] = 2.33 M; [MAIB] = 0.100 M; the modulation amplitude of 3.2 G was employed.

As expected from Scheme 1, poly(BEVCP) presumably contains both a 1,5-adduct structural unit (**I**) and a cyclobutane structural unit (**II**). The fractions of structures **I** and **II** in the polymers were determined by comparing the peak area of the olefinic protons (around 5.4 ppm) in structure **I** to that of the ethoxy methylene protons (around 4.2 ppm) in structures **I** and **II** (Table 2). Thus, the fraction of structure **I** (66−71%) seemed almost insensitive to temperature and the monomer concentration.



$$-\!\!\left[CH_2-CH{=}CH-CH_2-C(COOCH_2CH_3)_2\right]\!\!-$$

(I)

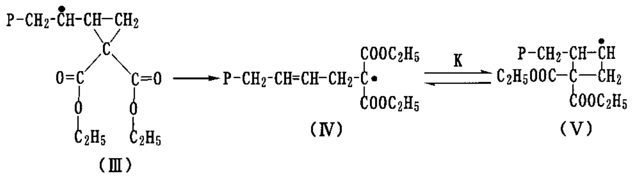


(II)

ESR Study of the Polymerization of BEVCP with MAIB. Figure 4 shows an ESR spectrum of the polymerization of BEVCP (2.33 M) with MAIB (0.100 M) at 60 °C in benzene. The spectrum apparently consists of a doublet (22 G) of 1:2:1 triplets (40 G) further split into doublets (5 G).

The present polymerization system should involve three types of polymer radicals **III**, **IV**, and **V** as shown in Scheme 2. If the rate of ring-opening of radical **III** is sufficiently rapid compared to propagation, the polymerization system involves radicals **IV** and **V** as persistent (ESR-observable) radicals. This assumption is reasonable based on the fact that cyclopropylmethyl radicals bearing conjugative substituents on the cyclopropyl ring undergo exceedingly fast ring-opening to yield homoallyl radicals.[13,14]

Scheme 2



(P = polymer chain)

The unusually large coupling constant (40 G) of two equivalent hydrogens for triplets in the ESR spectrum suggests a unique structure of the radical, probably a cyclobutyl radical; the β-hydrogens of the nonsubstituted cyclobutyl radical show a large coupling constant of 35.2 G.[15] Thus, the observed spectrum is assignable to cyclobutyl radical **V** in Scheme 2. Radical **V** is expected to be deformed by three substituents with restricted ring-flip, leading to different coupling constants of two geminal β-hydrogens. The two methylene hydrogens were reported to be nonequivalent to radical spin in propagating polymer radicals of some acrylates and methacrylates.[16−22] The estimated coupling constants for radical **V** are as follows: 40 G for β- and β'-hydrogens, 22 G for an α-hydrogen, and 5 G for a β-hydrogen.

However, there is some broadening in the central part of the spectrum in Figure 4, indicating the coexistence of another radical, probably radical **IV**. One of the β-hydrogens of radical **IV** may interact much more strongly with radical spin than the other as observed in the propagating radicals of methyl acrylate and *N*-methylacrylamide in which the small interaction of the latter β-hydrogen with unpaired electron can only contribute to broadening of the spectral lines.[16−18]

The propagating radicals of methyl α-deuterioacrylate and 1,1-diphenylethylene were observed as a broad doublet spectrum, indicating main interaction of the unpaired electron with one of the two methylene hydrogens.[16,19]

As a result, a doublet spectrum (splitting of ca. 25 G) of radical **IV** would overlap with the central two peaks due to radical **V**. This may be supported by the fact that the integrated area of parts A in Figure 4 constitutes only about 10% of that of the whole spectrum although it should be 25% in radical **V**.

As described above, the fractions of structures **I** and **II** are independent of the monomer concentration, suggesting that polymer radical **IV** is in equilibrium with radical **V** as shown in Scheme 2 under the actual polymerization conditions.

The observed ESR spectrum did not change in shape or intensity during the ESR measurement, indicating that the polymer radicals reached a stationary state. Thus, as shown in Figure 5, the total concentration of polymer radicals was almost independent of time in the actual polymerization of BEVCP (1.55 M) with MAIB (20.0 mM) at 40 °C.

The total polymer radical concentration ([P$^\bullet$]) was determined by ESR under different temperatures and the results are listed in Table 3; they have an error of less than ±15%. Using R_p and [P$^\bullet$], the apparent rate constant of propagation(k_p) was determined according to eq 1 and is also presented in Table 3; the k_p values have an error of less than ±20%.

$$R_p = k_p[P^\bullet][BEVCP] \qquad (1)$$

Table 3. Total Polymer Radical Concentration ([P•]), Apparent Rate Constants of Propagation (k_p) and Termination (k_t), and the k_df Value in the Polymerization of 1,1-Bis(ethoxycarbonyl)-2-vinylcyclopropane (BEVCP) with Dimethyl 2,2′-Azobisisobutyrate (MAIB) at Different Temperatures[a]

temp (°C)	[P•] × 10^6 (M)[b]	k_p (L/mol•s)[c]	$k_t \times 10^{-3}$ (L/mol•s)[d]	$k_df \times 10^8$ (s^{-1})
30	1.23	3.8	1.8	6.80
40	1.52	10.5	5.0	29.1
50	1.84	28.0	17	139
60	1.92	71.0	58	535

[a] [BEVCP] = 1.55 M; [MAIB] = 20.0 mM. [b] [P•] values have an error of less than ±15%. [c] k_p values have an error of less than ±20%. [d] k_t values have an error of less than ±30%.

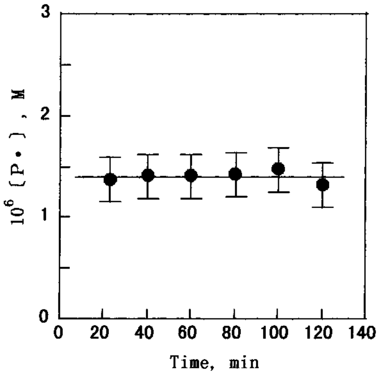


Figure 5. Relationship between the total polymer radical concentration ([P•]) and time in the polymerization of BEVCP with MAIB at 40 °C in benzene. [BEVCP] = 1.55 M; [MAIB] = 20.0 mM.

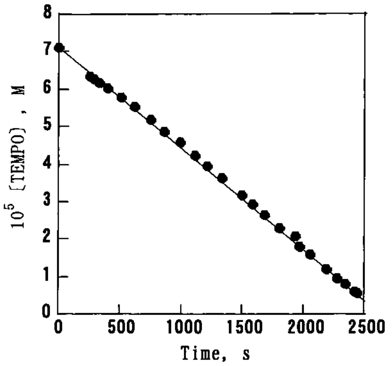


Figure 6. Relationship between the TEMPO concentration and time in the polymerization of BEVCP with MAIB at 60 °C in benzene. [BEVCP] = 1.55 M; [MAIB] = 2.50 mM; [TEMPO] = 7.13 × 10^{-2} mM.

To estimate the apparent rate constant of termination (k_t), the k_df value was determined using the same manner described in a previous paper,[23] where k_d = rate constant of the MAIB decomposition and f = initiator efficiency. The decrease in the TEMPO concentration was followed by ESR in the polymerization of BEVCP with MAIB in benzene in the presence of TEMPO. Figure 6 shows the relationship between the TEMPO concentration and time observed at 60 °C, where the initial concentrations of BEVCP, MAIB, and TEMPO were 1.55 M, 2.50 mM, and 7.13 × 10^{-2} mM, respectively. The k_df value was estimated from the slope of the straight line. Then the k_t value was calculated by eq 2 because bimolecular termination is apparently also involved in the present polymerization. The results obtained at different temperatures are also summarized in Table 3; the k_t values have an error of less than ±30%.

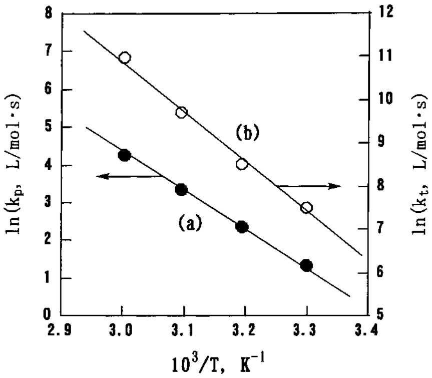


Figure 7. Temperature effect on (a) k_p and (b) k_t values.

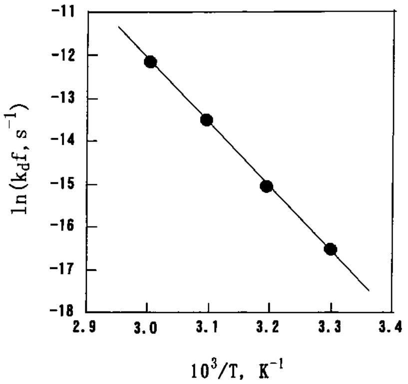


Figure 8. Temperature effect on k_df value.

$$2k_df[\mathrm{MAIB}] = k_t[\mathrm{P}^\bullet]^2 \qquad (2)$$

Figure 7 shows the Arrhenius plots of k_p and k_t. From the plots, the apparent activation energies of propagation (E_p) and termination (E_t) were calculated to be 82 ± 4 kJ/mol and 98 ± 8 kJ/mol, respectively. The E_p and E_t values are much higher than those of MMA (E_p = 18.2 and E_t = 2.7 kJ/mol) and St (E_p = 29.5 and E_t = 9.2 kJ/mol).[24] The E_p of BEVCP is probably high because propagation is a slow reaction of resonance-stabilized (**IV**) or sterically hindered (**V**) polymer radicals with a nonconjugative monomer (BEVCP). Since the termination reaction is generally diffusion-controlled in radical polymerizations, the high E_t may be due to restricted segmental motion of the rigid propagating poly(BEVCP) radical that contains double bonds and cyclobutyl moieties in the main chain.

From the Arrhenius plot of k_df (Figure 8), the activation energy of the initiation (E_i) is 123 ± 4 kJ/mol. The overall activation energy (E_a) of the radical polymerization involving bimolecular termination is given by $E_a = (E_i - E_t)/2 + E_p$. E_a is thus approximately 95 kJ/mol, which is nearly identical to that obtained above from the Arrhenius plot of R_p (94 kJ/mol).

As compared in Table 4, the values of k_p (71 L/mol•s, 60 °C) and k_t (5.8 × 10^4 L/mol•s, 60 °C) of BEVCP are much lower than those of typical monomers such as MMA, methyl acrylate (MA), St, acrylonitrile (AN), and vinyl acetate (VAc).[25] However, the $k_p/k_t^{1/2}$ value of BEVCP is large, indicating its homopolymerizability. Thus, BEVCP monomer has a higher homopolymerizability than MMA and St. This is because the k_t value of BEVCP is remarkably low.

Table 4. k_p, k_t, and $k_p/k_t^{1/2}$ Values of Some Vinyl Monomers

monomer	temp (°C)	K_p (L/mol·s)	$k_t \times 10^{-4}$ (L/mol·s)	$k_p/k_t^{1/2}$	ref
BEVCP[a]	60	71.0	5.81	0.29	this work
MMA[b]	60	705.6	2500	0.14	25
MA[c]	60.2	11 680	19 400	0.84	25
St[d]	60	176	7200	0.021	25
AN[e]	60	1960	78 200	0.070	25
VAc[f]	20	1100	8000	0.12	25

[a] BEVCP = 1,1-bis(ethoxycarbonyl)-2-vinylcyclopropane. [b] MMA = methyl methacrylate. [c] MA = methyl acrylate. [d] St = styrene. [e] AN = acrylonitrile. [f] VAc = vinyl acetate.

Conclusions

The polymerization of BEVCP with MAIB in benzene follows typical radical kinetics; that is, $R_p = k[\mathrm{MAIB}]^{0.6\pm0.1}[\mathrm{BEVCP}]^{1.0\pm0.1}$ (40 °C). The overall activation energy of the polymerization is 94 ± 4 kJ/mol. The $\bar{M}_n$ value [$(1.0-6.8) \times 10^5$] of the resulting poly(BEPVCP) increases with increasing monomer concentration and decreases with increasing initiator concentration and rising temperature. The polymerization system involves ESR-observable polymer radicals under the actual polymerization conditions. The ESR-determined apparent k_p (71 L/mol·s, 60 °C) and k_t (5.8×10^4 L/mol·s, 60 °C) values of BEVCP are much lower than typical vinyl monomers such as MMA and St. Owing to the very low k_t value, BEVCP has a higher homopolymerizability than MMA. Analysis of the observed ESR spectrum suggests that the present polymerization system involves ring-opened type **IV** and cyclobutyl type **V** polymer radicals. As a result, the resulting poly(BEVCP) contains 1,5-adduct (**I**) and cyclobutane (**II**) structural units.

Acknowledgment. The authors are grateful to the Center for Cooperative Research Tokushima University for NMR measurements. A part of this work was supported by the Satellite Venture Business Laboratory of Tokushima University.

References and Notes

(1) Takahashi, T.; Yamashita, I. *J. Polym. Sci.* **1965**, *3*, 251.
(2) Sugiyama, J.; Ohashi, K.; Ueda, M. *Macromolecules* **1994**, *27*, 5543.
(3) Sanda, F.; Takata, T.; Endo, T. *Macromolecules* **1995**, *28*, 1346.
(4) Sugiyama, J.; Kayamori, N.; Shimada, S. *Macromolecules* **1996**, *29*, 1943.
(5) Zeuner, F.; Moszner, N.; Rheinberger, V. *Macromol. Chem. Phys.* **1996**, *297*, 2745.
(6) Ozaki, T.; Sanda, F.; Endo, T. *Polym. Bull.* **1997**, *39*, 141.
(7) Sanda, F.; Murata, J.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 2037.
(8) Moszner, N.; Zeuner, F.; Volkel, T.; Rheinberger, V. *Macromol. Chem. Phys.* **1999**, *200*, 2173.
(9) Sanda, F.; Takata, T.; Endo, T. *Macromolecules* **1993**, *26*, 1818.
(10) Tobolsky, A. V.; Baysal, B. *J. Polym. Sci.* **1953**, *11*, 471.
(11) Otsu, T.; Yamada, B. *J. Macromol. Sci.—Chem.* **1969**, *A3*, 187.
(12) van Hook, J. P.; Tobolsky, A. V. *J. Am. Chem. Soc.* **1958**, *80*, 779.
(13) Maillard, B.; Forrest, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 7024.
(14) Newcomb, M.; Johnson, C. C.; Manek, M. B.; Varick, T. R. *J. Am. Chem. Soc.* **1992**, *114*, 10915.
(15) Fischer, H. Structure of Free Radicals by ESR Spectroscopy. In *Free Radicals*; Kochi, J. K., Ed.; Wiley & Sons: New York, 1973; Vol. II.
(16) Sugiyama, Y. *Chem. Lett.* **1996**, 951.
(17) Harris, J. A.; Hinojosa, O.; Arthur, J. C., Jr. *J. Polym. Sci., Polym. Chem.* **1974**, *12*, 679.
(18) Tanaka, H.; Sato, T.; Otsu, T. *Makromol. Chem.* **1979**, *180*, 267.
(19) Tanaka, H.; Sato, T.; Otsu, T. *Makromol. Chem.* **1980**, *181*, 2421.
(20) Kamachi, M.; Kuwae, Y.; Nozakura, S. *Polym. J.* **1981**, *13*, 919.
(21) Matsumoto, A.; Tanaka, S.; Otsu, T. *Macromolecules* **1991**, *24*, 4017.
(22) Keah, H. H.; Rae, I. D.; Hawthorne, D. G. *Aust. J. Chem.* **1992**, *45*, 659.
(23) Sato, T.; Takarada, A.; Tanaka, H.; Ota, T. *Makromol. Chem.* **1991**, *192*, 2231.
(24) McKenna, T. F.; Hamielec, A. E. In *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H. Eds.; Wiley & Sons: New York, 1989; p II-335.
(25) Berger, K. L.; Meyerhoff, G. In *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H. Eds.; Wiley & Sons: New York, 1989; p II-67.

MA001962T