Radical Copolymerization of 1,1-Bis(ethoxycarbonyl)-2-vinylcyclopropane and Methyl Methacrylate Accompanying Ring Opening and Cyclization

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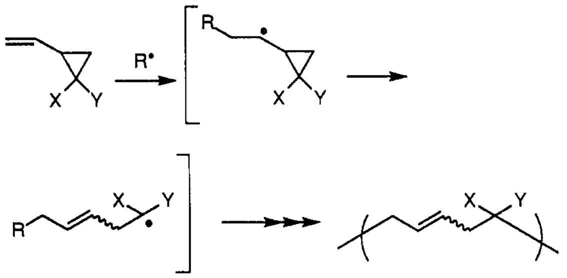
ABSTRACT: Radical copolymerization of 1,1-bis(ethoxycarbonyl)-2-vinylcyclopropane (ECVCP) and methyl methacrylate (MMA) was carried out in the presence of 2,2′-azobis(isobutyronitrile) (AIBN) at 60 °C in bulk or in chlorobenzene. Both the yields and molecular weights of the copolymers were lower than those of the homopolymers. Structural analysis of the copolymer suggested that radical copolymerization proceeded through ring opening followed by intramolecular cyclization. The copolymerization parameters were evaluated to be $r_1 = 0.11$, $r_2 = 21.49$ and $r_1 = 0.11$, $r_2 = 21.51$ (M_1, ECVCP; M_2, MMA) by Fineman–Ross and nonlinear least-squares methods, respectively. From the examination of the electron density of the olefinic carbon of ECVCP and its related compounds calculated by a semiempirical molecular orbital method (PM3), it was confirmed that the substituents on the cyclopropane ring of the vinylcyclopropanes affected the reactivity of the olefinic groups less than those on 1,1-disubstituted ethylenes did. The degree of volume shrinkage on the copolymerization decreased as the content of ECVCP increased. A similar tendency was observed in the glass transition temperature (T_g) of the copolymers.

Introduction

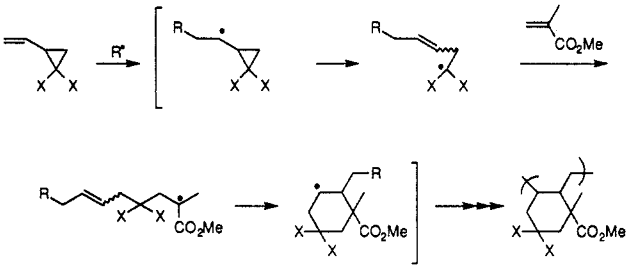
Cyclic monomers which undergo ring-opening polymerization are important in the fields of precision materials, adhesives, and so on, since they show low shrinkage or sometimes expansion in volume on polymerization.[1] Many monomers and materials undergo polymerization and curing through a radical process. Since vinyl polymerization is generally accompanied by larger volume shrinkage than ring-opening polymerization, monomers and materials that show low shrinkage or expansion through radical polymerization processes are especially desirable. Various 1,1-disubstituted 2-vinylcyclopropanes have been reported to undergo radical ring-opening polymerization to give polymers bearing mainly a 1,5-ring-opened unit (Scheme 1).[2]

On the contrary, few works on their radical copolymerization with usual vinyl monomers have been reported. Takahashi has reported that radical copolymerizations of 1,1-dichloro-2-vinylcyclopropane (CLVCP) with maleic anhydride (MAnh), methyl acrylate (MA), methyl methacrylate (MMA), and styrene afford copolymers containing a "ring-opened cyclized unit" through a radical 1,5-ring-opening reaction of CLVCP followed by addition of the propagating radical to MMA and an intramolecular cyclization reaction (Scheme 2, X = Cl, with MMA).[3] However, structures of the copolymers obtained were speculated only be elemental analyses and IR spectra, and their properties were not described at all. We have investigated this unique copolymerization in detail in the course of our study on radical ring-opening polymerizations, because it is an interesting copolymerization involving both ring opening and ring closing. In this paper, the radical copolymerization of 1,1-bis(ethoxycarbonyl)-2-vinylcyclopropane (ECVCP) and MMA (Scheme 2, X = CO_2Et), the structure of the copolymer obtained, the copolymerization parameters, the mechanistic aspects of the copolymerization, the volume change on copolymerization, and the glass transition temperature of the copolymer are disclosed.

Scheme 1



Scheme 2



Experimental Section

Measurements. ^1H NMR spectra of the monomers and polymers were recorded on a JEOL GSX-270 spectrometer operating in the pulsed FT mode, using tetramethylsilane (TMS) as an internal standard in deuteriochloroform at 27 °C. Molecular weight and its distribution ($\bar{M}_w/\bar{M}_n$) were evaluated 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, a flow rate of 1.0 mL/min, polystyrene calibration, and a refractive index detector. Thermal analysis was performed on a Rigaku Denki DSC8230 system. The glass transition temperature (T_g), determined by differential scanning calorimetry, was taken as the inflection point on the

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Table 1. Radical Copolymerization of ECVCP (M_1) and MMA (M_2)[a]

run	M_1 in feed (mol %)	solv[b] (conc)	yield[c] (%)	$\bar{M}_n$[d]	$\bar{M}_w/\bar{M}_n$[d]	M_1 in copolymer[e] (mol %)	olefin content in copolymer[e] (mol %)
1	100	none	87	53600	2.48	100	53[f]
2	75	none	47	6300	2.01	55	1
3	50	none	54	8400	3.29	28	0
4	25	none	71	29900	2.58	12	0
5	0	none	96	54800	3.80	0	0
6	100	CB (1 M)	75	22400	2.36	100	53[f]
7	75	CB (1 M)	4	5200	1.95	17	0
8	50	CB (1 M)	12	5600	1.87	6	0
9	25	CB (1 M)	53	5600	3.17	3	0
10	0	CB (1 M)	84	7500	2.57	0	0

[a] Polymerization was performed using AIBN (3 mol %) at 60 °C for 20 h. [b] CB, chlorobenzene. [c] Methanol/water (volume ratio = 4:1)-insoluble part. [d] Estimated by GPC (based on PSt). [e] Determined by ^{1}H NMR. [f] Lowering of olefin content of the polymer is caused by formation of a cyclobutane-containing unit.

trace at a heating rate of 10 °C/min under a nitrogen atmosphere. Densities of monomers and polymers were measured by the density gradient tube method at 25 °C with a Shibayama Scientific Co., Ltd., Model A.

Materials. 2,2′-Azobis(isobutyronitrile) (AIBN, Tokyo Kasei Kogyo Co.) was used as received. MMA was distilled over calcium hydride after washing with 5% sodium hydroxide solution. ECVCP was prepared according to the reported method.[2a] Chlorobenzene was distilled over calcium hydride after washing with concentrated sulfuric acid, aqueous sodium hydrogen carbonate, and water and stored over molecular sieves (4A).

Polymerization. General Procedure. To a monomer in a polymerization tube were introduced AIBN and, subsequently, a dry solvent, if required. The tube was cooled, degassed, sealed off, and heated at 60 °C. The resulting mixture was diluted with chloroform and poured into methanol/water mixed solvent (volume ratio = 80:20) to precipitate a solvent-insoluble polymer. Copolymerization parameters r_1 and r_2 of ECVCP (M_1) and MMA (M_2) were examined by the copolymerizations in chlorobenzene (1 M) using AIBN (3 mol %) as an initiator at 60 °C for 0.5–2.0 h. The conversions of the monomers were kept below 9% in this case.

Molecular Orbital Calculations. All computations were done on an Apple Macintosh IIci equipped with a 21 MIPS coprocessor board with the use of the SONY Tektronix CAChe system version 3.0.4. Geometries were optimized first with molecular mechanics using the CAChe MM2 program and second with MOPAC version 6.00 (QCPE No. 455[4]) revised as version 6.10 for the CAChe system, using the PM3 Hamiltonian. The calculations were carried out by the restricted Hartree–Fock (RHF) method. All calculations were done with full optimization of all geometrical variables (bond lengths, bond angles, and dihedral angles).

Results and Discussion

1. Radical Copolymerization of ECVCP and MMA.

Radical copolymerization of ECVCP and MMA was carried out in the presence of AIBN both in bulk and in chlorobenzene. Isolation of the copolymer obtained was performed by reprecipitation with methanol/water mixed solvent to afford a colorless polymer, which was solbule in dichloromethane, chloroform, THF, DMF, and DMSO. The results of the copolymerizations are summarized in Table 1. A single-modal GPC curve observed for any polymer obtained suggested the occurrence of the radical copolymerization of ECVCP. Both the yields and molecular weights of the copolymers were lower than those of the homopolymers either in bulk or in chlorobenzene.

The structure of the copolymers was examined by their ^{1}H NMR spectra. The ^{1}H NMR spectrum of the copolymer obtained in the copolymerization of ECVCP and MMA (feed ratio = 50:50, Table 1, run 3) is shown in Figure 1, together with those of the homopolymer (poly(ECVCP) and poly(MMA)). The composition of the copolymer was determined as ECVCP:MMA = 28:72 from the integration ratio of the methylene protons (4.15 ppm) of the ester group derived from ECVCP to that of the methyl protons (3.60 ppm) of the ester group derived from MMA (Figure 1,C). No olefinic signal (5.32 ppm) or allylic methylene proton signal (2.50 ppm) based on the 1,5-ring-opened unit (Figure 1A) was observed in spectrum C, but a broad signal around 1.6–2.7 ppm suggesting the occurrence of some reaction exhausting the olefinic part was observed.

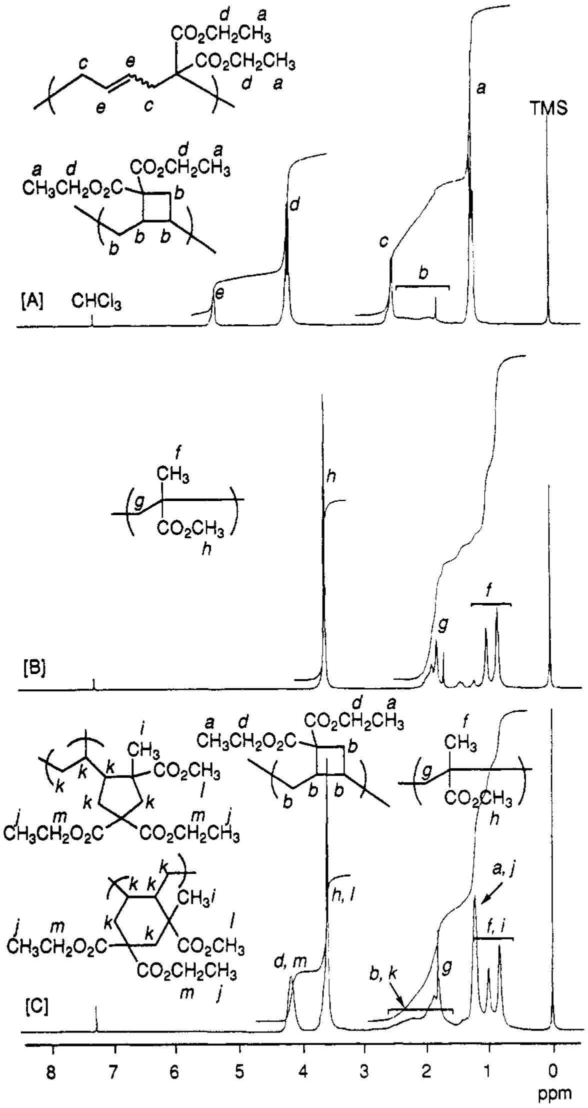
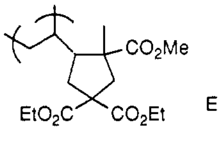


Figure 1. ^{1}H NMR spectra of polymers (solvent, $CDCl_3$; 270 MHz): (A) poly(ECVCP) (run 1 in Table 1); (B) poly(MMA) (run 5 in Table 1); (C) poly(ECVCP)-*co*-MMA) (run 3 in Table 1).

The copolymer showed a good solubility in many organic solvents and a unimodal GPC curve ($\bar{M}_n$ = 8400, $\bar{M}_w/\bar{M}_n$ = 3.29); therefore, the disappearance of the olefinic part would not be caused by an intermolecular reaction such as cross-linking but rather by some *intramolecular* reaction. Consequently, the radical copolymerization is supposed to proceed through ring opening of ECVCP followed by intermolecular cyclization with MMA (Scheme 2, X = CO_2Et). This result strongly supports the results of the radical copolymerization of CLVCP and MAnh, MA, MMA, and styrene as reported by Takahashi.[3] That is, as shown in Scheme 2, addition of initiator radical to ECVCP is followed by 1,5 ring opening to yield homoallyl radical which further attacks at MMA to give a δ-unsaturated MMA end radical. Cyclization of this radical proceeds via two possible pathways, i.e., six- and five-membered ring-forming processes. Only six-membered ring formation was illustrated in Takahashi's report (Scheme 2); however, detailed analysis of the ^1H NMR spectrum does not unambiguously establish which pathway is followed. Judging from general reactivity of δ-unsaturated radical,[5] the five-membered ring-forming pathway to afford unit 1 seems to be more favorable than the six-membered one and affords unit 2. In addition to units 1 and 2, the cyclobutane-containing unit 3 should also be contained in the copolymer because the olefin content of the homopolymer of ECVCP was 53% (run 1 in Table 1). If the formation ratio of unit 3 in the copolymerization is assumed to be similar to that of the homopolymerization of ECVCP, this copolymer composition can be calculated to be (1 + 2):3:poly(MMA) = 17:15:67.[6] The reactivity of the ECVCP radical and MMA radical in this copolymerization is discussed in the following paragraph.



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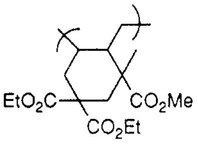

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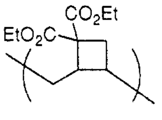


3

This "radical ring-opening cyclocopolymerization" is of particular interest for its unique mechanism involving both radical ring opening and ring closing steps, which has never been seen in radical copolymerizations and cyclopolymerizations reported so far. In the polymer with ECVCP composition larger than 50% (Table 1, run 2), small olefinic signals based on the homopolymer of ECVCP were observed in the ^1H NMR spectrum as expected.

To examine the radical copolymerizability of ECVCP exactly, the copolymerization parameters r_1 and r_2 of ECVCP (M_1) and MMA (M_2) were determined by the copolymerizations in chlorobenzene (1 M). Conversions of the monomers were kept below 9% in every case to facilitate the determination of the parameters. Compositions of the copolymers obtained were determined by their ^1H NMR spectra. Since the copolymerization in this work is different from a usual vinyl copolymerization, cyclization of the radical intermediate and addition of the cyclized radical to monomers should be considered as additional processes.[3,7] However, application of rate equations for usual radical copolymerizations of vinyl monomers to this system would not cause a big problem because the cyclization almost quantitatively proceeds as described above. The copolymerization parameters r_1 and r_2 calculated by the Fineman–Ross method[8] were 0.11 and 21.49, respectively. The monomer feed ratio–copolymer composition curve calculated using these parameters is shown in Figure 2 with the plots of the experimental data obtained. The copolymerization parameters were also calculated to be $r_1 = 0.11$ and $r_2 = 21.51$ by the nonlinear least-squares method.[9] These values showed good correspondence each other. r_1 and r_2 for ECVCP and MMA are close to those of vinyl acetate/MMA ($r_1 = 0.03$, $r_2 = 26.0$) and vinyl benzoate/MMA ($r_1 = 0.07$, $r_2 = 20.3$).[10] M_1 end radical adds to MMA faster than ECVCP 9.1 (=1/0.11) times, and M_2 end radical adds to MMA faster than ECVCP 21 times; the copolymer always has its composition enriched in MMA relative to the feed. ECVCP works as a nonconjugated monomer similarly to vinyl acetate and vinyl benzoate toward conjugated monomer MMA in the radical copolymerizations.

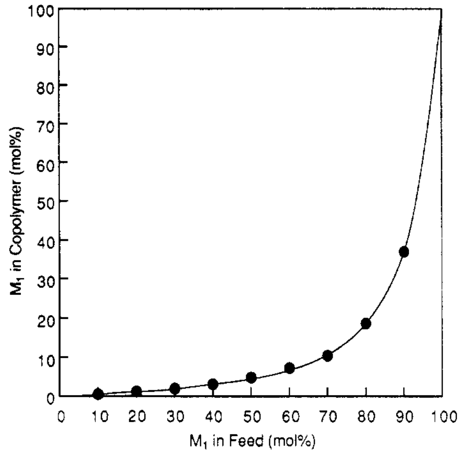


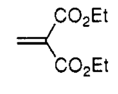
Figure 2. Copolymer composition curve of ECVCP (M_1) and MMA (M_2): (●) experimental points; (—) calculated curve using the copolymerization parameters $r_1 = 0.11$ and $r_2 = 21.49$.

Table 2. Calculated Net Atomic Charge of Olefinic Carbon of ECVCP, CLVCP, ECE, and CLE

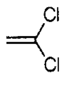
	net atomic charge[a] (e)	
	α-carbon	β-carbon
ECVCP	+0.025	+0.067
CLVCP	−0.128	−0.135
ECE	+0.020	+0.809
CLE	−0.228	−0.158

[a] Calculated by MOPAC version 6.10 using the PM3 Hamiltonian.

The propagating ends of ECVCP and DCVCP correspond to those of 1,1-bis(ethoxycarbonyl)ethylene (ECE) and 1,1-dichloroethylene (CLE), respectively. The rate constant for addition of cyclohexyl radical to ECE is 225 times larger than that of CLE.[11] However, the difference in copolymerization parameters between ECVCP with MMA ($r_1 = 0.11$, $r_2 = 21.49$) and CLVCP with MMA ($r_1 = 0.07$, $r_2 = 11.0$)[3b] is very small. To obtain some information on the substituent effect, the electron density was calculated by a semiempirical molecular orbital method (PM3). The calculated electron densities (net atomic charges) of the olefinic carbons of ECVCP, CLVCP, ECE, and CLE are summarized in Table 2. The difference in electron density of the olefinic β-carbon between ECVCP and CLVCP (0.202 e) is smaller than that between ECE and CLE (0.967 e). Therefore, it was confirmed that the substituents on the cyclopropane ring of the vinylcyclopropanes affected the reactivity of the olefinic groups less than those on 1,1-disubstituted ethylenes did.



ECE



CLE

2. Volume Shrinkage on Copolymerization and T_g of the Copolymer. The densities of the monomer mixtures and copolymer were measured by the density gradient tube method at 25 °C. The relationship between the mixing ratio of the monomers and the density of the mixture is shown in Figure 3. The densities of the mixtures in which the molar ratio of ECVCP was below 25% could not be measured because of their solubilization in the

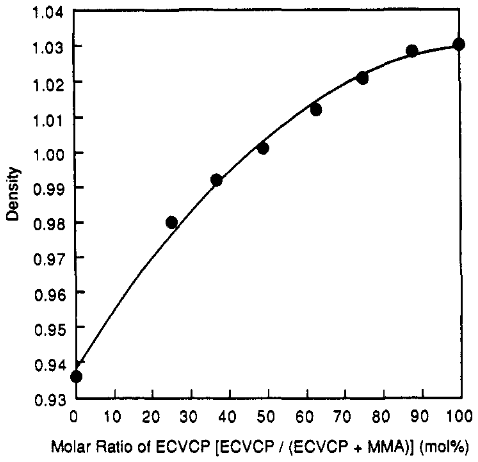


Figure 3. Relationship between monomer feed ratio and density of mixture of ECVCP and MMA.

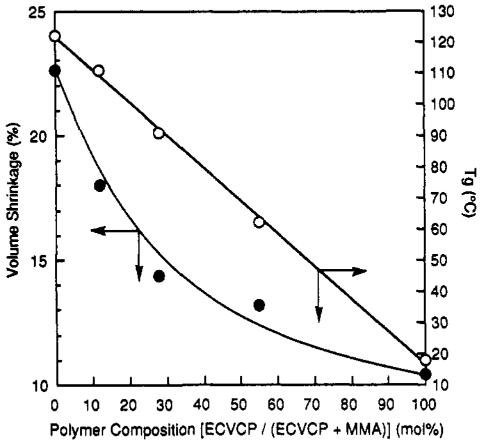


Figure 4. Volume shrinkage on polymerization and T_g of poly(ECVCP-*co*-MMA) vs copolymer composition.

density gradient liquid (calcium bromide solution in methanol/water). The degree of volume change during the copolymerization was calculated from the densities of the copolymer and the monomer mixture whose composition was same as that of the copolymer. The degree of volume change was plotted vs copolymer composition for a few copolymerizations with different feed ratios (Figure 4). The T_gs of the homopolymers and copolymers of ECVCP and MMA are also plotted in this figure. Additivity could be confirmed in both volume change and T_g. Both the volume shrinkage on polymerization and the T_gs of the copolymers decreased as the content of ECVCP increased.

Conclusion

Radical copolymerization of ECVCP (M_1) and MMA (M_2), the structures of the copolymers obtained, the volume change on polymerization, and the T_gs of the copolymers were studied. The unique "radical ring-opening cyclocopolymerization" was confirmed by this work. The copolymerization parameters were evaluated to be $r_1 = 0.11$ and $r_2 = 21.51$ (M_1, ECVCP; M_2, MMA) by the nonlinear least-squares method. From the MO study, it was confirmed that the substituents on the cyclopropane ring of the vinylcyclopropanes affected the reactivity of the olefinic groups less than those on 1,1-disubstituted ethylenes did. Both the degree of volume shrinkage on the copolymerization and the T_gs of the copolymers decreased as the content of ECVCP increased.

Supplementary Material Available: DSC thermograms of poly(ECVCP-*co*-MMA)s (1 page). Ordering information is given on any current masthead page.

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