Radical Ring-Opening Emulsion Polymerization of Vinylcyclopropanes

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ABSTRACT: Radical emulsion polymerizations of vinylcyclopropanes, 1,1-bis(ethoxycarbonyl)-2-vinylcyclopropane (ECVCP) and 1,1-dichloro-2-vinylcyclopropane (CVCP) were examined. ECVCP underwent soap-free and soap-in emulsion polymerizations satisfactorily to afford the ring-opened polymer in good yields. Polymer emulsions were obtained in a spherical shape with single particle size distribution. Meanwhile, emulsion polymerization of CVCP proceeded in only a low conversion. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 497–501, 1998

Key words: radical ring-opening polymerization; emulsion polymerization; vinylcyclopropane

INTRODUCTION

Polymer emulsion is widely used in the field of materials such as paint, adhesives, papers, fibers, and construction materials.[1–4] Polymer emulsion has been synthesized by emulsion polymerization of vinyl monomers, such as styrene, methyl methacrylate, vinyl acetate, and butadiene. Emulsion polymerization has considerable processing advantages over bulk, suspension, and solution polymerizations. Polymerization temperature in emulsion polymerization can be easily controlled to afford high molecular weight polymers. Control of particle size, size distribution of polymer emulsion, and soap-free polymerization technique are attracting a great interest from the industrial, as well as academic, points of view. Meanwhile, ring-opening polymerization has superior characteristics to vinyl polymerization. Ring-opening polymerization can introduce functional groups, such as olefin, ester, carbonate, ether, and ketone into the polymer main chain, whereas vinyl polymerization can afford only polymers with polyethylene main chains. Various 1,1-disubstituted 2-vinylcyclopropanes have been reported to undergo radical ring-opening polymerization to give polymers bearing mainly 1,5-ring-opened unit (Scheme 1).[5] Synthesis of novel polymer emulsion is expected by using radical ring-opening polymerization. In this article, radical ring-opening emulsion polymerization behavior of vinylcyclopropanes, 1,1-bis(ethoxycarbonyl)-2-vinylcyclopropane (ECVCP; $X = CO_2Et$) and 1,1-dichloro-2-vinylcyclopropane (CVCP; $X = Cl$), is described.

EXPERIMENTAL

Measurements

^{1}H-NMR spectra of the monomers and polymers were recorded on JEOL EX-90 and EX-400 spectrometers using tetramethylsilane as an internal standard in chloroform-*d* at 27°C. Elemental anal-
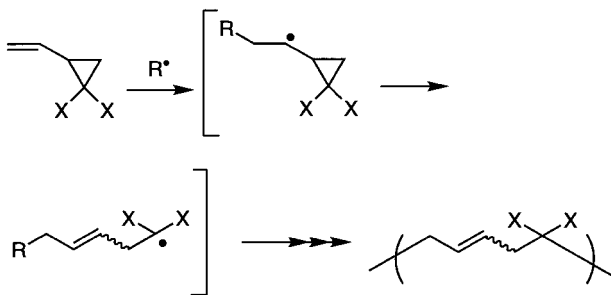
Scheme 1

yses were performed on a Yanaco CHN Corder MT-5. Molecular weights ($\bar{M}n$) and the distributions ($\bar{M}w/\bar{M}n$) were estimated by gel permeation chromatography (GPC) on a Tosoh HPLC CCP & 8000 system with a data processor, equipped with a polystyrene gel column (TSK gel G4000H), using tetrahydrofuran as an eluent, a flow rate 1.0 mL min^{-1}, polystyrene calibration, and refractive index and ultraviolet detectors. Particle sizes of the polymer emulsions were measured by a Shimadzu laser diffraction particle analyzer SALD-2000A. Scanning electron micrographs were recorded on a JEOL JSM-T200.

Materials

2,2′-Azobis(isobutyronitrile) (AIBN; Tokyo Chemical Industry Co., Tokyo, Japan), potassium persulfate (KPS; Mitsubishi Gas Chemical. Co.), and sodium lauryl sulfate (Kao Co.) were used as received. Styrene (St), acrylonitrile (AN), vinyl acetate (VA), and maleic anhydride (MAN) were used after purification by usual methods. ECVCP and CVCP were prepared according to the reported method.[6]
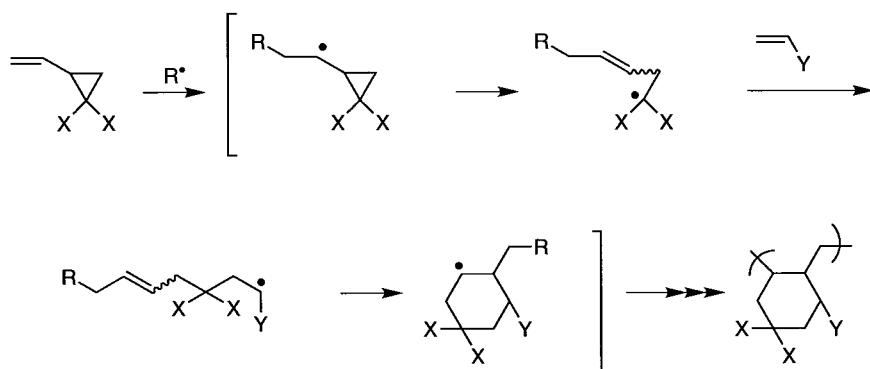
Bulk Polymerization

To the monomers in a polymerization tube was introduced AIBN (3 mol %). The tube was cooled, degassed, sealed off, and heated at 60°C for 20 h. The conversion of the monomer was determined by ^{1}H-NMR. The resulting mixture was diluted with chloroform and poured into a methanol/water-mixed solvent (80 : 20, v/v) to precipitate a solvent-insoluble polymer. Poly(ECVCP) ^{1}H-NMR δ (CDCl$_3$) 1.0–1.4 (m), 1.4–2.9 (m), 3.1–4.0 (m), 4.0–4.3 (m) ppm. Poly(CVCP) ^{1}H-NMR δ (CDCl$_3$) 1.8–3.2 (m), 1.4–2.9 (m), 5.7–6.1 (m) ppm. Poly(ECVCP$_4$-co-St$_{96}$) ^{1}H-NMR δ (CDCl$_3$) 1.2–2.2 (m), 6.3–6.8 (m), 6.9–7.3 (m) ppm. Poly(ECVCP$_{41}$-co-AN$_{59}$) ^{1}H-NMR δ (CDCl$_3$) 1.1–1.4 (m), 1.4–3.5 (m), 4.0–4.4 (m) ppm. Poly(ECVCP$_{72}$-co-VA$_{28}$) ^{1}H-NMR δ (CDCl$_3$) 1.1–1.4 (m), 1.4–2.8 (m), 3.9–4.3 (m), 4.7–5.3 (m) ppm. Poly(ECVCP$_{76}$-co-MAN$_{24}$) ^{1}H-NMR δ (CDCl$_3$) 1.1–1.4 (m), 1.7–2.9 (m), 3.9–4.3 (m), 5.3–5.5 (m) ppm.

Emulsion Polymerization

To a mixture of the monomers and deionized water was added KPS (1 mol %) at 70°C with vigorous stirring. After stirring at the temperature for a set time, the polymer was corrected and dried at 150°C.

RESULTS AND DISCUSSION

Radical copolymerizations of ECVCP with St, AN, VA, and MAN were conducted at 60°C in bulk in the presence of AIBN as an initiator. ECVCP showed good copolymerizability with AN, VA, and

X = CO$_2$Et, Y = Ph, CN, OCOMe, etc.

Scheme 2

Table I Radical Copolymerization of ECVCP and with Vinyl Monomers

Comonomer	Conversion[a] (mol %)	Yield[b] (%)	$\bar{M}n^c$	$\bar{M}w/\bar{M}n^c$	ECVCP in Copolymer[a] (mol %)	Olefin Content in Copolymer[a] (mol %)
None	71	63	30,500	1.26	100	59
St	45	30	9,600	1.66	4	—
AN	73	41	5,200	1.90	41[d]	23
VA	60	29	4,200	1.43	72	46
MAN	63	10	8,900	1.78	76	20

Conditions: polymerization was conducted in bulk in the presence of AIBN (3 mol %) at 60°C for 20 h.
[a] Determined by ^{1}H-NMR.
[b] MeOH/H$_2$O (80 : 20)-insoluble part.
[c] Estimated by GPC basd on polystyrene standards.
[d] Determined by elemental analysis.

MAN but did not with St, probably due to the nonconjugated character.[7] Decrease of the olefin contents in the copolymers were confirmed by ^{1}H-NMR spectra. Cyclization to form five- and/or six-membered rings seemed to proceed similarly in the radical copolymerization of ECVCP and methyl methacrylate (as illustrated in Scheme 2)[7] (see also Table I).
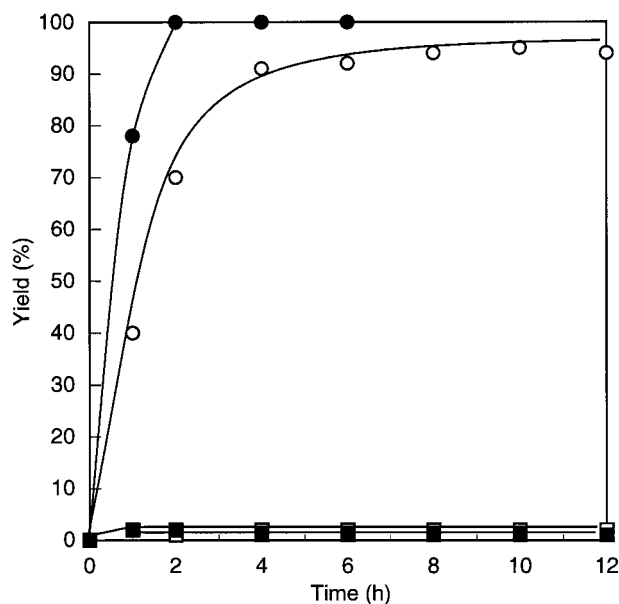
Figure 1 illustrates the time–yield relation-

Figure 1 Relationships between the polymerization time and the yields of the polymers obtained in the emulsion polymerizations of ECVCP and CVCP. Conditions: initiator KPS (1 mol %), 70°C. Sodium lauryl sulfate (0.5 wt %) was used for the soap-in polymerizations. (●) ECVCP in soap-in emulsion polymerization; (○) ECVCP in soap-free emulsion polymerization; (■) CVCP in soap-in emulsion polymerization; (□) CVCP in soap-free emulsion polymerization.

ships in the emulsion polymerizations of ECVCP and CVCP in the presence (soap-in) and absence (soap-free) of sodium lauryl sulfate. ECVCP showed good polymerizability both in soap-in and soap-free polymerizations, whereas CVCP did not. The lower solubility of CVCP in water, as well as radical polymerizability, may cause the result.[6]

Figure 2 illustrates the relationship between the polymerization time and the particle size of the emulsion formed. The particle size increased in accordance with the time progress similarly to common emulsion polymerizations. Formation of polymer emulsions in spherical shape with single particle size distribution was con-
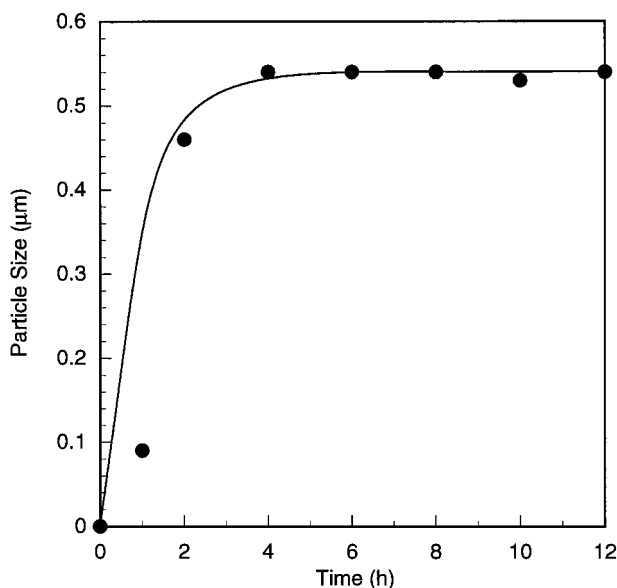

Figure 2 Relationship between the polymerization time and particle size obtained by the soap-free emulsion polymerization of ECVCP. Conditions: initiator KPS (1 mol %), 70°C.
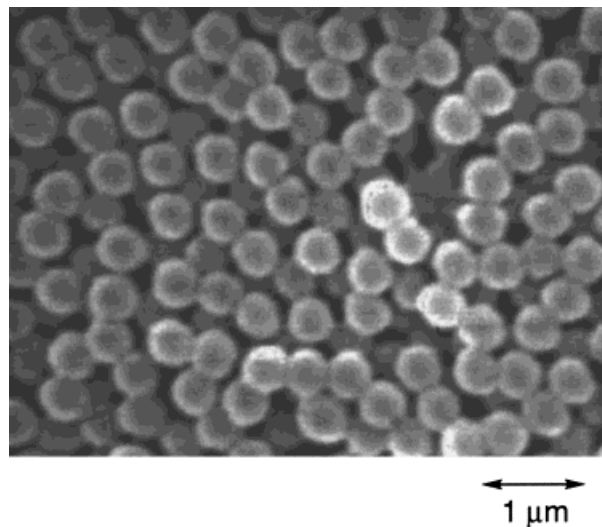
Figure 3 Scanning electron micrograph of the emulsion obtained in the soap-free emulsion polymerization of ECVCP initiated by KPS (1 mol %) at 70°C for 12 h (Table II). Particle size = 0.53 μm.
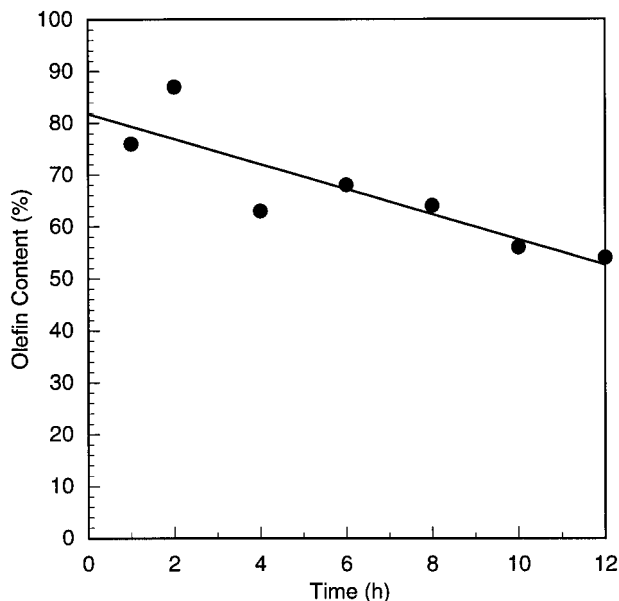

Figure 4 Relationship between the polymerization time and olefin content in the polymer obtained by the soap-free emulsion polymerization of ECVCP. Conditions: initiator KPS (1 mol %), 70°C.

firmed by scanning electron micrography (as shown in Figure 3).

Conditions and results of the bulk and emulsion polymerizations are summarized in Table 2. The soap-in emulsion polymerization afforded a higher molecular weight polymer with lower olefin content than the bulk and soap-free emulsion polymerizations. This may be explained by the difficult occurrence of a termination reaction in the soap-in polymerization. Figure 4 illustrates the change of the olefin content during the soap-free emulsion polymerization. The olefin content decreased as the time progressed, which might be caused by some intramolecular back-biting reactions.[6,8–12] Intermolecular propagating reaction

might be preferred to the intramolecular cyclization to decrease the olefin content in the first stage of the polymerization because of the larger monomer concentration, whereas the opposite occurred in the final stage of polymerization.

Furthermore, soap-free emulsion copolymerizations of ECVCP with VA and AN were conducted (Fig. 5). Copolymerization of ECVCP with VA proceeded satisfactorily to afford the corresponding copolymer with $\bar{M}n(\bar{M}w/\bar{M}n) = 10,200$ (2.52) in 64% yield. The content of ECVCP, olefin content, and particle size of the copolymer emulsion were 89%, 33%, and 0.54 μm, respectively.

Table II Radical Polymerization of ECVCP

Type of Polymerization	Initiator	Time (h)	Temperature (°C)	Yield (%)	$\bar{M}n^a$	$\bar{M}w/\bar{M}n^a$	Olefin Content[b] (mol %)	Particle Size[c] (μm)
Bulk	AIBN[d]	20	60	63[e]	30,500	1.26	59	—
Soap-free emulsion	KPS[f]	12	70	94[g]	30,700	2.52	56	0.53
Soap-in emulsion	KPS[f]	12	70	100[g]	59,700	1.51	44	0.09

[a] Determined by GPC based on polystyrene standards.
[b] Determined by ^{1}H-NMR.
[c] Estimated by a laser diffraction particle analyzer.
[d] 3 mol %.
[e] Insoluble part in methanol/water (80 : 20, v/v).
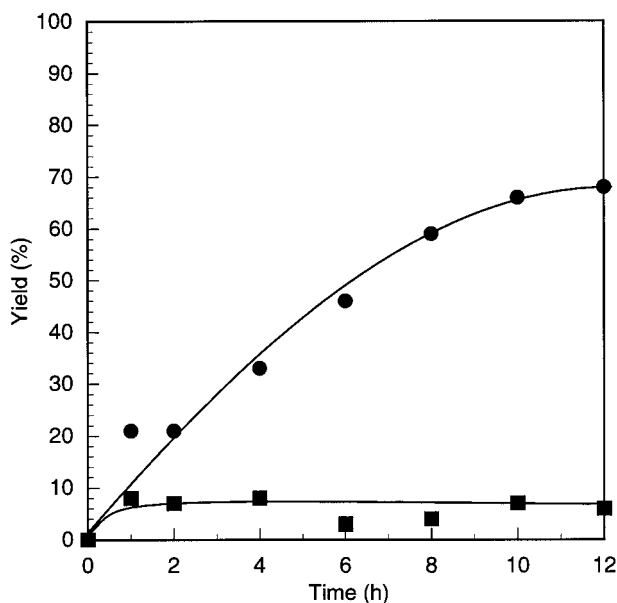[f] 1 mol %.
[g] Nonvolatile part.

Figure 5 Relationships between the polymerization time and the yields of the copolymers obtained in the soap-free emulsion copolymerizations of ECVCP with VA and AN. Conditions: initiator KPS (1 mol %), 70°C. (●) ECVCP with VA; (■) ECVCP with AN. Feed molar ratio of ECVCP : VA, AN = 1 : 1.

The molecular weight and ECVCP content of the copolymer obtained in the soap-free emulsion copolymerizations were larger than those obtained in bulk polymerization (Table I). Copolymerization of ECVCP with AN was unsatisfactory, which was different from bulk copolymerization (Table I). Different solubility of each monomer might cause the different polymerization behavior between bulk and soap-free emulsion polymerizations.

CONCLUSIONS

In this article, the first radical ring-opening emulsion polymerization of vinylcyclopropanes were examined. ECVCP underwent soap-free and soap-in emulsion polymerizations satisfactorily to af-

ford the 1,5-ring-opened polymer, whose yield and molecular weight were higher than those obtained in bulk polymerization. The emulsion copolymerization of ECVCP with VA afforded the copolymer in a high incorporation ratio of ECVCP. Decrease of olefin content in the copolymer was observed, which was caused by the intramolecular cyclization.

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