

The Copolymerization of the Vinyl Monomer with a Cyclic Compound.

I. The Cationic Copolymerization of Some Vinyl Monomers with 3,3-Bis(chloromethyl)oxetane*

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Several attempts to copolymerize the vinyl monomer with cyclic ether have been made. Recently, Tsuruta and Fujio¹⁾ prepared the copolymer of methyl vinyl ketone with propylene oxide or epichlorohydrin, using aluminum isopropoxide as an anionic catalyst. The acrylonitrile-ethylene oxide²⁾ and -propylene oxide³⁾ copolymers have been prepared in the radiation-induced copolymerization at a low temperature. The cationic copolymerizations of cyclic ethers with vinyl monomers have also been patented.^{4,5)} Höhr et al.⁶⁾ have reported a detailed mechanism of the cationic copolymerization of trioxane with styrene.

The present investigation was undertaken to evaluate the reactivities of vinyl monomers and cyclic ether in their copolymerizations by Lewis acids. Styrene (St), α -methylstyrene (α -MeSt) and isobutyl vinyl ether (IBVE), having different reactivities for cationic polymerization, were used as the vinyl monomers. 3,3-Bis(chloromethyl)oxetane (BCMO) was adopted as the cyclic ether, and boron trifluoride-diethyl etherate ($\text{BF}_3 \cdot \text{Et}_2\text{O}$), stannic chloride (SnCl_4) and triethylaluminum-water ($\text{AlEt}_3\text{-H}_2\text{O}$) were used as the cationic catalysts. The copolymerizations were carried out in methylene chloride at 0°C.

Experimental

Materials.—Commercial St, α -MeSt and IBVE were distilled over calcium hydride under reduced pressure. BCMO was prepared by the method described by Farthing⁷⁾ and distilled over calcium hydride under reduced pressure; b. p. 80.5–81.5°C/10 mmHg, n_D^{20} 1.4858 (lit.⁷⁾ b. p. 80.2–81.5°C/10 mmHg, n_D^{20} 1.4858).

* Vinyl Polymerization. CIV.

1) T. Tsuruta and R. Fujio, *Makromol. Chem.*, **64**, 219 (1963).

2) S. Okamura, K. Hayashi and H. Watanabe, *Isotopes and Radiation (Dokai to Hoshasen)*, **3**, 512 (1960).

3) S. Okamura, K. Hayashi and H. Watanabe, *J. Chem. Soc. Japan, Ind. Chem. Sec. (Kogyo Kagaku Zasshi)*, **65**, 740 (1962).

4) R. Merten, Ger. Pat. 1083055; *Chem. Abstr.*, **55**, 14998 (1961).

5) British Industrial Plastics, Ltd., Berg. Pat. 610580; *Chem. Abstr.*, **57**, 11401 (1962).

6) L. Höhr, H. Cherdron and W. Kern, *Makromol. Chem.*, **52**, 59 (1962).

7) A. C. Farthing, *J. Chem. Soc.*, 1955, 3648.

Commercial $\text{BF}_3 \cdot \text{Et}_2\text{O}$ and SnCl_4 were purified by distillation before use. AlEt_3 (Ethyl Corp.) was used without further purification. The $\text{AlEt}_3\text{-H}_2\text{O}$ catalyst was prepared in methylene chloride ($\text{AlEt}_3/\text{H}_2\text{O}=1$ in mole).

Methylene chloride was shaken with a sodium carbonate solution, washed with pure water, and then distilled over phosphorous pentoxide. The other materials were purified by ordinary methods.

Copolymerization Procedure.—The copolymerizations were carried out in a glass-stoppered tube, except in the case of the $\text{AlEt}_3\text{-H}_2\text{O}$ catalyst, for which a serum type-stoppered tube was used as the reaction vessel. The initial concentrations of the total monomer mixture and of the catalyst were kept constant at 3.0 and 0.07 mol./l. respectively. After the monomers and the solvent had been charged, dry nitrogen gas was flashed into the tube, which had previously been chilled in an ice-water bath. A known quantity of the catalyst solution in methylene chloride was then added to this tube, and it was sealed off. After it had been polymerized for a given time, the reaction mixture was poured into a large amount of methanol in order to stop the reaction and isolate the polymer produced. In the cases of SnCl_4 and $\text{AlEt}_3\text{-H}_2\text{O}$ catalysts, methanol containing a small amount of hydrochloric acid was used as the precipitant in order to avoid the precipitation of metal hydroxide. The resulting polymer was washed by methanol and dried under reduced pressure at room temperature.

The Analysis and Fractionation of the Polymer.—The compositions of the polymers were determined from their chlorine contents. In order to check whether or not the copolymer was obtained, the polymer was separated with chloroform into insoluble and soluble fractions. The chloroform-soluble fraction was then fractionated into several fractions by the successive addition of methanol.

The molecular weight of the polymer was determined by the cryoscopic method in benzene. The infrared spectra of the polymers were determined in a KBr disk.

Results

The St-BCMO- $\text{BF}_3 \cdot \text{Et}_2\text{O}$ System.—The results of the copolymerization of St and BCMO as catalyzed by $\text{BF}_3 \cdot \text{Et}_2\text{O}$ are tabulated in Table I. The rate of the polymerization (R_p) of St was remarkably lowered by the presence of BCMO. As is indicated in Table I, the reactivity of St for the copolymerization with BCMO

TABLE I. COPOLYMERIZATION OF St AND BCMO BY $\text{BF}_3 \cdot \text{Et}_2\text{O}$ IN METHYLENE CHLORIDE AT 0°C
([Monomer] = 3, $[\text{BF}_3 \cdot \text{Et}_2\text{O}] = 0.07 \text{ mol./l.}$)

Exp. No.	Monomer compn.*		Time min.	Conversion, %	R_p %/min.	Cl content in polymer, %	Polymer compn.*	
	St	BCMO					St	BCMO
11	0.00	1.00	35	3.9	0.11	(45.73)**	0.00	1.00
12	0.20	0.80	15	11.2	0.75	45.67	0.00	1.00
13	0.30	0.70	15	8.7	0.58	45.50	0.01	0.99
14	0.40	0.60	10	4.8	0.48	45.62	0.00	1.00
15	0.50	0.50	20	6.4	0.32	45.11	0.02	0.98
16	0.60	0.40	20	3.1	0.16	44.36	0.04	0.96
17	0.70	0.30	25	3.5	0.14	43.97	0.06	0.94
18	0.80	0.20	20	2.4	0.12	43.42	0.07	0.93
19	1.00	0.00	0.5	90.2	180	—	1.00	0.00

* In mole fraction

** Calculated value for BCMO

TABLE II. COPOLYMERIZATION OF α -MeSt AND BCMO BY $\text{BF}_3 \cdot \text{Et}_2\text{O}$ IN METHYLENE CHLORIDE AT 0°C
([Monomer] = 3, $[\text{BF}_3 \cdot \text{Et}_2\text{O}] = 0.07 \text{ mol./l.}$)

Exp. No.	Monomer compn.*		Time min.	Conversion, %	R_p %/min.	Cl content in polymer, %	Polymer compn.*	
	α -MeSt	BCMO					α -MeSt	BCMO
11	0.00	1.00	35	3.9	0.11	—	0.00	1.00
32	0.21	0.79	20	5.9	0.30	45.16	0.02	0.98
33	0.31	0.69	158	5.6	0.04	43.05	0.05	0.95
34	0.31	0.69	—	13.8	—	45.25	0.01	0.99
35	0.41	0.59	14	3.4	0.24	43.69	0.06	0.94
36	0.41	0.59	135	3.0	0.02	40.15	0.17	0.83
37	0.51	0.49	865	35.9	—	34.56	0.26	0.74
38	0.51	0.49	105	1.7	0.02	31.61	0.33	0.67
39	0.61	0.39	195	13.9	—	29.58	0.42	0.58
40	0.61	0.39	92	3.8	0.03	18.49	0.66	0.34
41	0.61	0.39	25	2.1	0.08	31.18	0.38	0.62
42	0.71	0.29	124	7.8	0.06	20.66	0.61	0.39
43	0.71	0.29	77	4.1	0.05	6.76	0.88	0.12
44	0.81	0.19	80	9.7	0.12	1.65	0.97	0.03
45	0.81	0.19	41	1.6	0.04	16.20	0.70	0.30
46	0.81	0.19	60	8.2	0.14	3.46	0.94	0.06
47	1.00	0.00	0.5	30.2	60	—	1.00	0.00

* In mole fraction

TABLE III. FRACTIONATION OF THE POLYMER OBTAINED IN THE SYSTEM α -MeSt - BCMO - $\text{BF}_3 \cdot \text{Et}_2\text{O}$

Fraction	Wt. g.	Wt. %	Cl %	BCMO unit*	Wt. g.	Wt. %	Cl %	BCMO unit*	Wt. g.	Wt. %	Cl %	BCMO unit*
Sample	0.9752	—	34.56	0.70	0.4980	—	29.58	0.58	0.0964	—	18.49	0.34
1 (CHCl ₃ -insol.)	0.7303	74.89	44.02	0.95	0.3170	63.65	45.97	1.00	0.0290	30.08	42.96	0.92
2	0.0054	0.55	39.05	0.82	0.0504	10.12	20.09	0.37	0.0657	68.15	12.89	0.23
3	0.1054	10.81	11.04	0.20	0.0698	14.02	2.11	0.04	—	—	—	—
4	0.0186	1.91	7.60	0.13	0.0205	4.12	—	—	—	—	—	—
5	0.0248	2.54	1.29	0.02	—	—	—	—	—	—	—	—
6	0.0029	0.29	—	—	—	—	—	—	—	—	—	—
Total	0.8874	90.99	—	—	0.4577	91.91	—	—	0.0947	98.23	—	—

* In mole fraction

** Molecular weight of CHCl₃-soluble part was 724 (Cl: 5.07%), while that of homopoly α -MeSt (Exp. No. 47) was 1270.

was extremely low, and the homopolymer of BCMO was obtained.

The α -MeSt-BCMO- $\text{BF}_3 \cdot \text{Et}_2\text{O}$ System.—The results of the copolymerization of α -MeSt and BCMO by $\text{BF}_3 \cdot \text{Et}_2\text{O}$ are summarized in Table II. The rate of copolymerization decreased as compared with the respective homopolymerization rates. Colorless, powdered polymers, composed of both monomer units, were obtained. The monomer-polymer composition curve in this system is shown in Fig. 1.

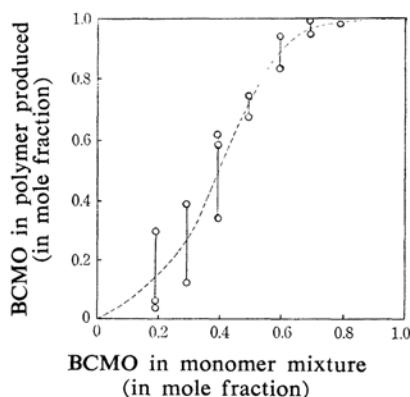


Fig. 1. Monomer-polymer composition curve for the copolymerization of α -MeSt and BCMO by $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in methylene chloride at 0°C .

Since the molecular weights of the polymers obtained under the present conditions were low (see Table III), it may be assumed that the low molecular weight polymer mainly consisted of α -MeSt units is partly soluble in methanol as a precipitant. Accordingly, the curve in Fig. 1 should be shifted in a small extent, however, any further discussion will be not disturbed.

In order to check whether or not the copolymer was produced, some of the polymers obtained were fractionated into several frac-

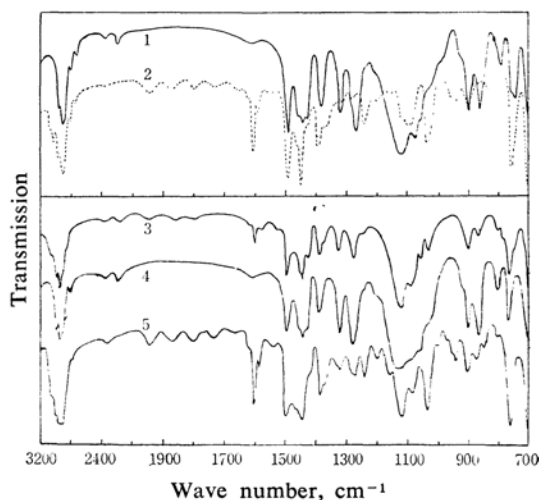


Fig. 2. Infrared spectra of the polymer (Exp. No. 37) obtained in the system of α -MeSt-BCMO- $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in methylene chloride at 0°C . 1. PolyBCMO, 2. Poly α -MeSt, 3. Unfractionated polymer, 4. Chloroform-insoluble fraction, 5. Chloroform-soluble fraction

tions. The analytical results of these fractions are shown in Table III, while their infrared spectra are indicated in Fig. 2.

Because the infrared spectra and chlorine contents of the chloroform-insoluble fractions were nearly identical with those of polyBCMO, it was obvious that this fractions were homopolymers of BCMO. On the other hand, the infrared spectrum of the chloroform-soluble fraction showed the absorption bands due to the α -MeSt unit and the C-O-C band at 1120 cm^{-1} from the BCMO unit, as is shown in Fig. 2. This fraction was, therefore, further fractionated into several fractions which contained considerable amounts of chlorine. The molecular weight of the chloroform-soluble fraction (Exp. No. 37) was found to be 724 (Cl: 5.07%). This value corresponds approximately to the calculated value (746) of the

TABLE IV. COPOLYMERIZATION OF α -MeSt AND BCMO BY SnCl_4 IN METHYLENE CHLORIDE AT 0°C ([Monomer]=3, $[\text{SnCl}_4]=0.07\text{ mol./l.}$)

Exp. No.	Monomer compn.*		Time min.	Conversion, %	R_p %/min.	Cl content in polymer, %	Polymer compn.*	
	α -MeSt	BCMO					α -MeSt	BCMO
51	0.00	1.00	2460	0.02	0.000	—	0.00	1.00
52	0.21	0.79	685	0.10	0.000	—	—	—
53	0.31	0.69	450	0.8	0.002	2.67	0.95	0.05
54	0.41	0.59	410	3.9	0.01	1.73	0.97	0.03
55	0.51	0.49	405	9.9	0.02	2.03	0.97	0.03
56	0.61	0.39	350	24.9	0.07	—	—	—
57	0.71	0.29	300	41.8	0.14	—	—	—
58	0.81	0.19	15	11.8	0.79	0.83	0.98	0.02
59	1.00	0.00	1	84.2	84	—	1.00	0.00

* In mole fraction

TABLE V. COPOLYMERIZATION OF α -MeSt AND BCMO BY $\text{Al}(\text{C}_2\text{H}_5)_3\text{-H}_2\text{O}$
IN METHYLENE CHLORIDE AT 0°C
([Monomer] = 3, $[\text{Al}(\text{C}_2\text{H}_5)_3] = 0.07$ mol./l.)

Exp. No.	Monomer compn.*		Time min.	Conversion, %	R_p %/min.	Cl content in polymer, %	Polymer compn.*	
	α -MeSt	BCMO					α -MeSt	BCMO
62	0.21	0.79	300	1.2	0.004	43.65	0.06	0.94
63	0.31	0.69	300	0.6	0.002	43.41	0.07	0.93
64	0.51	0.49	470	0.9	0.002	46.42	0.00	1.00
65	0.61	0.39	360	1.3	0.004	40.88	0.13	0.87
66	0.71	0.29	460	0.2	0.001	43.37	0.07	0.93
67	0.81	0.19	240	0.2	0.001	—	—	—
68	1.00	0.00	18	4.4	0.24	—	1.00	0.00

* In mole fraction

TABLE VI. COPOLYMERIZATION OF IBVE AND BCMO BY $\text{BF}_3\cdot\text{Et}_2\text{O}$ IN METHYLENE CHLORIDE AT 0°C
([Monomer] = 3, $[\text{BF}_3\cdot\text{Et}_2\text{O}] = 0.07$ mol./l.)

Exp. No.	Monomer compn.*		Time sec.	Conversion, %	Cl content in polymer, %	Polymer compn.*	
	IBVE	BCMO				IBVE	BCMO
11	0.00	1.00	210	3.9	—	0.00	1.00
72	0.20	0.80	120	5.0**	7.97	0.89	0.11
73	0.30	0.70	30	—	2.84	0.96	0.04
74	0.40	0.60	30	19.6	0.27	1.00	0.00
75	0.50	0.50	30	31.4	0.21	1.00	0.00
76	0.60	0.40	45	32.9	0.22	1.00	0.00
77	0.70	0.30	15	40.5	0.07	1.00	0.00
78	0.80	0.20	10	46.7	0	1.00	0.00
79	1.00	0.00	10	69.3	—	1.00	0.00

* In mole fraction

** CHCl_3 -insoluble part: 18.42 wt.% (Cl: 41.74%); CHCl_3 -soluble part: 81.58 wt.% (Cl: 0.68%)

polymer, which consisted of five α -MeSt units and one BCMO unit (Cl: 9.5%). Therefore, this soluble fraction may be taken as a mixture of the homopolymers of α -MeSt and of poly- α -MeSt containing one terminal BCMO unit.

The α -MeSt - BCMO - SnCl_4 System.—The results of the copolymerization of α -MeSt and BCMO with SnCl_4 as the catalyst are tabulated in Table IV. BCMO was hardly polymerized at all by SnCl_4 , and only a poly- α -MeSt was obtained in this system.

The α -MeSt - BCMO - $\text{AlEt}_3\text{-H}_2\text{O}$ System.—The results of the copolymerization of α -MeSt and BCMO by the $\text{AlEt}_3\text{-H}_2\text{O}$ catalyst are tabulated in Table V. The polymer, mainly consisting of BCMO units, was obtained in the copolymerization of various monomer compositions, though the homopolymerizations of both α -MeSt and BCMO proceeded without difficulty when this catalyst system was used.

The IBVE-BCMO- $\text{BF}_3\cdot\text{Et}_2\text{O}$ System.—The results of the copolymerization of IBVE and BCMO by $\text{BF}_3\cdot\text{Et}_2\text{O}$ are tabulated in Table VI. Tacky and pale yellow polymers were obtained from this system. The homopolyIBVE was obtained in the copolymerization at a higher concentration of IBVE, while a polymer con-

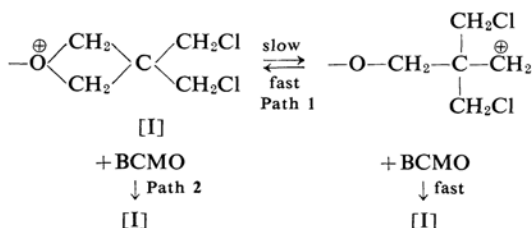
taining both IBVE and BCMO units was obtained through the system which used a higher concentration of BCMO. This polymer, containing both IBVE and BCMO units, was fractionated with chloroform, and a polymer mainly consisting of BCMO units and homopolyIBVE were separated.

Discussion

In the cationic copolymerizations of the St-BCMO- $\text{BF}_3\cdot\text{Et}_2\text{O}$, α -MeSt - BCMO - SnCl_4 and α -MeSt - BCMO - $\text{AlEt}_3\text{-H}_2\text{O}$ systems, only the homopolymer of a vinyl or a cyclic compound was obtained (Tables I, IV and V). On the other hand, in the copolymerization of α -MeSt or IBVE by $\text{BF}_3\cdot\text{Et}_2\text{O}$, the composition analyses showed that the resulting polymer contained both monomer units (Tables II and VI, and Fig. 1). The S-shaped monomer-polymer composition curve in the copolymerization of α -MeSt and BCMO (Fig. 1) indicated that both monomer reactivity ratios (r_1 and r_2) were larger than unity, and that the homopropagating reactivities of both growing chain ends were very important. Furthermore, from the fractionation experiments of the resulting polymers

(see Table III), it was clarified that no copolymer was obtained, although a mixture of the homopolymers of BCMO and α -MeSt, and of poly α -MeSt containing one BCMO unit which might be attached as an end group, was obtained. Similar results were obtained in the case of IBVE-BCMO copolymerization (see Table VI). The phenomenon in which a mixture of homopolymers was produced through the copolymerization (this is expressed in terms of independent copolymerization) may be observed when the reactivities of the two monomers are close to each other.

The following two paths may be considered in the propagation of BCMO:

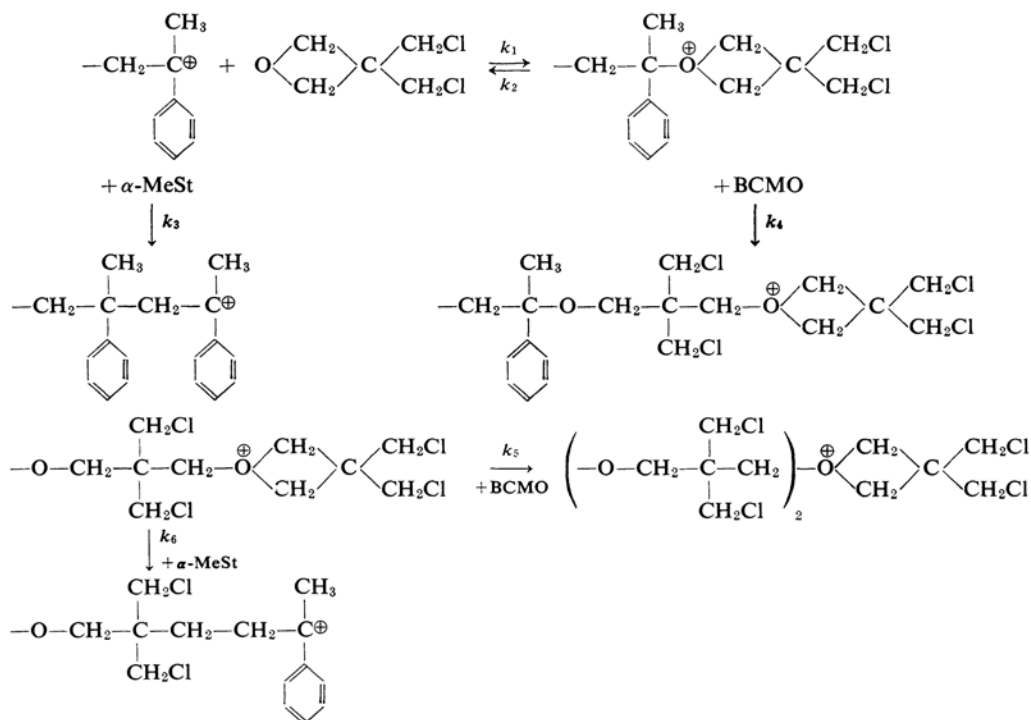


The rate of propagation should be proportional to the concentration of the propagating cation in path 1 and to the concentrations of both the propagating cation and the monomer in path 2. Penczek and Penczek⁸⁾ proved kinetically that the propagation in BCMO

polymerization was a bimolecular reaction of the propagating cation and the monomer. Therefore, path 1 may be eliminated. The propagation takes place through the reaction of the terminal oxonium ion with the monomer molecule.

The reaction scheme of the cationic copolymerization of α -MeSt and BCMO is expressed below.

The reactions of k_3 and k_5 are the homopolymerizations of α -MeSt and BCMO respectively; their rates must be larger than that of cross propagation, if only a mixture of both homopolymers is produced. The stability of the α -MeSt cation participates in this copolymerization fairly importantly. If the growing carbonium ion from the vinyl monomer is unstable, it is very easy in the reaction with ether to form a stable oxonium ion, and the polymerization of the vinyl monomer is inhibited by the presence of ether. It is understandable, in view of this, that the greater reactivity of α -MeSt for cationic polymerization by $\text{BF}_3 \cdot \text{Et}_2\text{O}$ was much depressed, being it close to that of BCMO in its copolymerization with BCMO. In the St-BCMO system, the polymerization reactivity of St by $\text{BF}_3 \cdot \text{Et}_2\text{O}$ was also greatly depressed, and scarcely any polymers containing St units were obtained. The inhibiting effect of ethers in the cationic



8) I. Penczek and S. Penczek, *Makromol. Chem.*, **67**, 203 (1963).

polymerization of St has been reported previously.⁹⁾

The phenomenon that the copolymer was not obtained in the cationic copolymerization of α -MeSt and BCMO may result from the difference in reactivity based on the structures of the propagating cations; namely, the poly- α -MeSt cation is the carbonium ion, while the polyBCMO cation is the oxonium ion. A similar consideration was postulated by Yamashita et al.¹⁰⁾ for the cationic copolymerization of BCMO and β , β -dimethyl- β -propiolactone.

In the SnCl_4 -catalyzed copolymerization, only a homopolymer of α -MeSt was obtained, because the polymerization reactivity of BCMO by this catalyst is quite small. In the AlEt_3 - H_2O -catalyzed copolymerization, homopoly-BCMO was obtained, though the homopolymerization of α -MeSt proceeded without difficulty when this catalyst system was used. Recently it was proposed by Furukawa et al.¹¹⁾ that this catalyst system could act as does Lewis acid for the polymerization of BCMO.

These differences in the results according to the kind of catalyst may result from the fact that the effect of the gegen ion in the cationic polymerization is very important.

The relationship between the monomer and the resulting polymer compositions in the copolymerization is expressed by Eq. 1¹²⁾;

$$\frac{[m_1]}{[m_2]} = \frac{[M_1]}{[M_2]} \frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]} \quad (1)$$

where m_1 and m_2 are the monomer units in the copolymer, and M_1 and M_2 are those in the monomer mixture. If r_1 and r_2 are infinity, Eq. 1 is converted into Eq. 2:

$$\frac{[m_1]}{[m_2]} = \frac{[M_1]^2}{[M_2]^2} \quad (2)$$

However, if absolutely no cross propagation occurs (independent copolymerization), $[m_1]/[m_2]$ must be proportional to the ratio of the rates of homopolymerizations of M_1 and M_2 . On the basis of the postulations of the rate equations and the rate constants, including the term of the catalyst concentration in the homopolymerizations of M_1 and M_2 , the relation between monomer and polymer compositions in the independent copolymerization is shown in Fig. 3a—c.

As can be seen from Fig. 3, the relation of Eq. 2 is only an example of independent copolymerization; the S-shaped composition

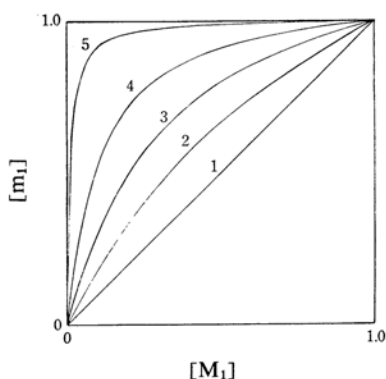


Fig. 3a. Relation between monomer and polymer compositions in independent copolymerization.

The case $R_{p1} = k_1[M_1]$; $R_{p2} = k_2[M_2]$

1. $k_1 = k_2$, 2. $k_1 = 2k_2$, 3. $k_1 = 4k_2$,

4. $k_1 = 10k_2$, 5. $k_1 = 100k_2$

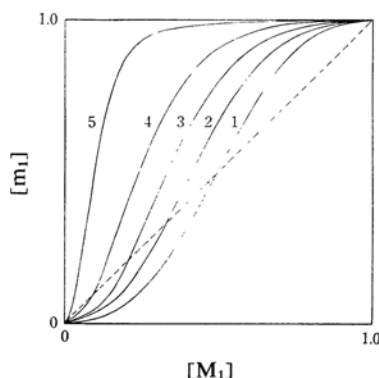


Fig. 3b. Relation between monomer and polymer compositions in independent copolymerization.

The case $R_{p1} = k_1[M_1]^2$; $R_{p2} = k_2[M_2]^2$

1. $k_1 = k_2$, 2. $k_1 = 2k_2$, 3. $k_1 = 4k_2$,

4. $k_1 = 10k_2$, 5. $k_1 = 100k_2$

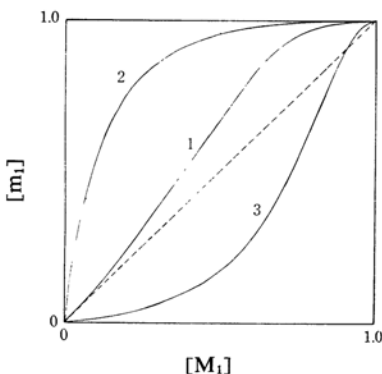


Fig. 3c. Relation between monomer and polymer compositions in independent copolymerization.

The case $R_{p1} = k_1[M_1]$; $R_{p2} = k_2[M_2]^2$

1. $k_1 = k_2$, 2. $k_1 = 10k_2$, 3. $k_1 = 1/10k_2$

9) M. Imoto and S. Aoki, *ibid.*, **63**, 141 (1963).

10) Y. Yamashita, T. Tsuda, Y. Ishikawa and T. Shimizu, *J. Chem. Soc. Japan, Ind. Chem. Sec. (Kogyo Kagaku Zasshi)*, **66**, 1493 (1963).

11) J. Furukawa, *Polymer*, **3**, 487 (1962); T. Saegusa, H. Imai and J. Furukawa, *Makromol. Chem.*, **65**, 60 (1963).

12) T. Alfrey, J. J. Bohrer and H. Mark, "Copolymerization," Interscience, New York (1952), p. 8.

curve is not essential. However, in actuality, no clear relation such as is shown in Fig. 3 is observed because of the complicated effects in the ionic polymerization.

It is known that the block copolymer is obtained occasionally in the ionic copolymerization. Tada, Saegusa and Furukawa¹³⁾ proved that this phenomenon occurs with the cationic copolymer of BCMO and β -propiolactone.

Equation 1 can be simply adopted for a copolymerization in which the monomer units are distributed statistically in the resulting copolymer chain. Therefore, if a block copolymer or a mixture of copolymer and homopolymer was obtained through the copolymerization, the resulting monomer reactivity ratios (r_1 and r_2), which indicate the ratio of the rate constants of homo- and cross-propagation, may become less significant.

13) K. Tada, T. Saegusa and J. Furukawa, *Makromol. Chem.*, **71**, 71 (1964).

Summary

The copolymerization of several vinyl monomers, such as styrene, α -methylstyrene and isobutyl vinyl ether, with 3,3-bis(chloromethyl)oxetane catalyzed by Lewis acids (boron trifluoride-diethyl etherate, stannic chloride and triethylaluminum-water) in methylene chloride at 0°C has been investigated. In these copolymerizations, the copolymers were not obtained, though a mixture of the corresponding homopolymers was obtained in some cases. The results have been explained on the basis of the differences in reactivity resulting from the structures of the two propagating chain ends.

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