Anionic Polymerization of Vinylidene Chloride. III.
Copolymerization Initiated by n-Butyllithium

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Although plans for the cationic coplymerizations of vinylidene chloride with styrene and with vinyl *n*-butyl ether have been announced by Florin1) and by Walling2), reports of their success have yet to be published.

The mechanism of the polymerization of vinyl monomers initiated by *n*-butyllithium has been generally recognized as anionic polymerization. However, there are some questions concerning the mechanism of the polymerization of a monomer such a vinylidene chloride, with a relatively low susceptibility to anionic catalysis.

In order to elucidate the mechanism of the vinylidene chloride polymerization initiated by *n*-butyllithium, a copolymerization study was undertaken because the proof of ionic mechanism can best be accomplished by the relative reactivity ratios in the copolymerization data3). Methyl acrylate, styrene and vinyl chloride were chosen as the comonomer for this study because vinylidene chloride is surrounded by the above three monomers in q-ε map4).

Experimental

The details of the preparation of *n*-butyllithium and of the purification of *n*-hexane and vinylidene chloride were given in a previous report5). Methyl acrylate and styrene were dried over calcium hydride and distilled under argon before use. Vinyl chloride produced by the Kureha Kasei Co. was repurified by drying over phosphorus pentoxide, followed by distillation under argon into a polymerization vessel in a closed system.

The polymerization apparatus and procedure were the same as before5). The catalyst was added to monomers in the polymerization vessel cooled at −70°C with dry ice-methanol, sealed, and then gradually warmed to the desired polymerization temperature. The polymerization was stopped by adding methanol and the mixture was poured into excess methanol or petroleum ether, and then the polymer was successively filtered, washed and dried to a constant weight in vacuo at 40°C.

All copolymerizations were stopped within a ten per cent conversion. The copolymers formed were repurified as follows: poly(vinylidene chloride *co* methyl acrylate)* was dissolved in acetone, filtered, precipitated by petrolum ether, washed, and dried in vacuo. Poly(vinylidene chloride *co* styrene) is only with difficulty soluble in common solvents and was therefore thoroughly allowed to swell in cyclohexanone and was then reprecipitated by methanol. Poly(vinylidene chloride *co* vinyl chloride) was successively redissolved in tetrahydrofuran, filtered and precipitated by methanol. The compositions of the copolymers were determined by chlorine analysis and some infrared spectroscopic data were added to qualify the copolymer, as is discussed below.

Results

Tables I—III and Figs. 1—6 show details of experiments which were employed to determine the monomer reactivity ratios. The monomer reactivity ratios for the three monomer pairs have been calculated using the intersection

TABLE I. REACTIVITY RATIO DATA FOR THE COPOLYMERIZATION OF VINYLIDENE CHLORIDE (M_1) AND METHYL ACRYLATE (M_2)
(See Figs. 1 and 2)

Total monomers, 1.0 mol.; *n*-BuLi, 0.005 mol.; *n*-hexane, 14.6 cc.; temp., 50°C; time, 3.0 hr.

Number	Charge, M_1 mole fraction	Conversion %	Anal. Cl %
1-1	0.900	2.2	9.09
1-2	0.700	2.1	5.03
1-3	0.500	2.3	2.13
1-4	0.300	3.2	0.892

TABLE II REACTIVITY RATIO DATA FOR THE COPOLYMERIZATION OF VINYLIDENE CHLORIDE (M_1) AND STYRENE (M_2)
(See Figs. 3 and 4)

Total monomers, 1.0 mol.; *n*-BuLi, 0.010 mol.; *n*-hexane, 122 cc.; temp., 26°C; time, 4.0 hr.

Number	Charge, M_1 mole fraction	Conversion %	Anal. Cl %
2-1	0.900	4.1	35.90
2-2	0.700	4.5	21.36
2-3	0.500	6.2	12.54
2-4	0.321	9.0	7.48

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1) R. E. Florin, *J. Am. Chem. Soc.*, **71**, 1867 (1949).
2) C. Walling, E. R. Briggs, W. Cummings and F. R. Mayo, ibid., **72**, 48 (1950).
3) C. E. Schildknecht, *Ind. Eng. Chem.*, **50**, 107 (1958).
4) A. Konishi, This Bulletin, **35**, 193 (1962).
5) A. Konishi, ibid., **35**, 197 (1962).

* Poly (A *co* B) means a copolymer between A and B. Cf., *J. Polymer Sci.*, **8**, 227 (1952).

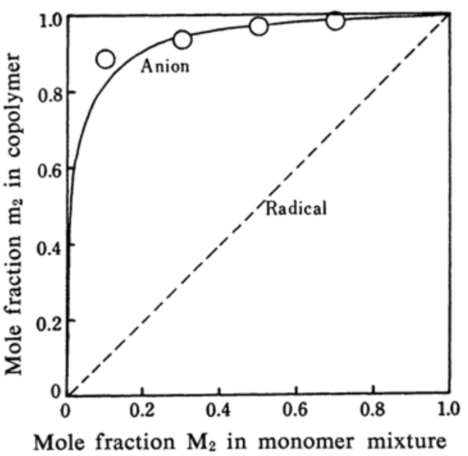

Fig. 1. Copolymer composition curve. Vinylidene chloride (M_1)-methyl acrylate (M_2)

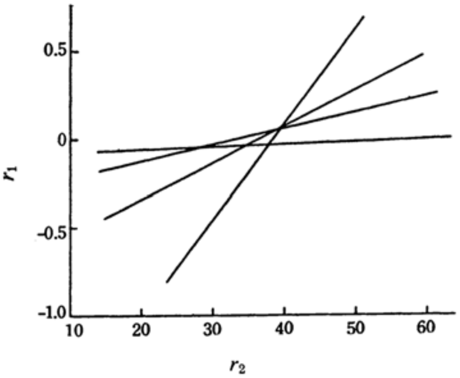

Fig. 2. Reactivity ratio diagram. Vinylidene chloride (M_1)-methyl acrylate (M_2)

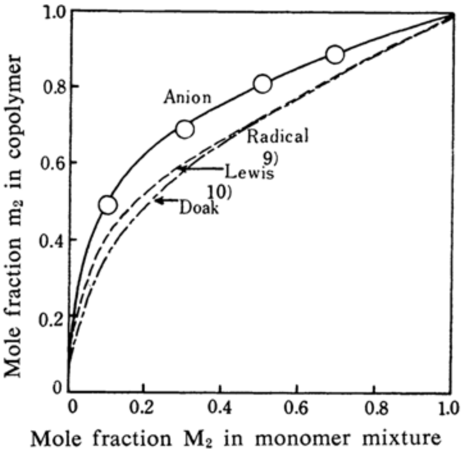

Fig. 3. Copolymer composition curve. Vinylidene chloride (M_1)-styrene (M_2)

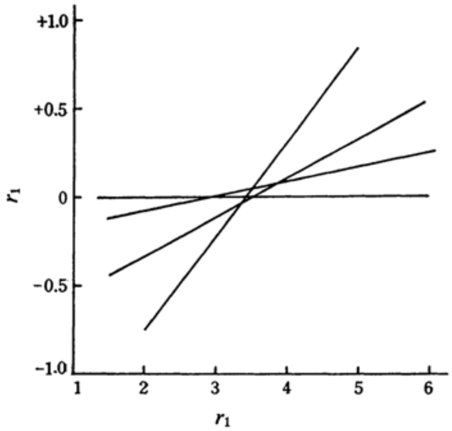

Fig. 4. Reactivity ratio diagram. Vinylidene chloride (M_1)-styrene (M_2)

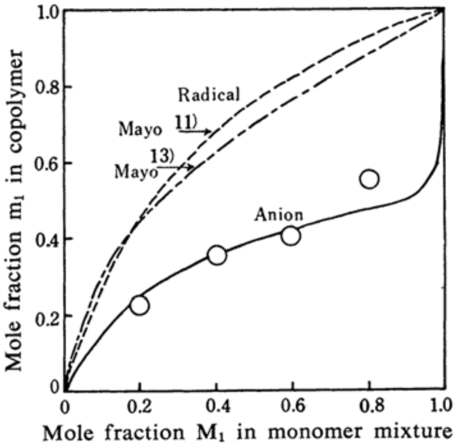

Fig. 5. Copolymer composition curve. Vinylidene chloride (M_1)-vinyl chloride (M_2)

TABLE III. REACTIVITY RATIO DATA FOR THE COPOLYMERIZATION OF VINYLIDENE CHLORIDE (M_1) AND VINYL CHLORIDE (M_2)
(See Figs. 5 and 6)

Total monomers, 1.0 mol.; *n*-BuLi, 0.010 mol.; *n*-hexane, 8.8 cc.; temp., 25°C; time, 1.0 hr.

Number	Charge, M_1 mole fraction	Conversion %	Anal. Cl %
3-1	0.800	3.8	67.50
3-2	0.592	3.6	65.12
3-3	0.400	2.5	64.36
3-4	0.200	4.2	62.87

method of Mayo and Lewis[6]. The r_1 and r_2 values listed in Table V have been determined from Figs. 2, 4 and 6.

The copolymer composition curves are calculated from the values in Tables V and IV.

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[6] F. R. Mayo and F. M. Lewis, *J. Am. Chem. Soc.*, **66**, 1594 (1944).

TABLE IV. LITERATURE VALUES FOR VINYLIDENE CHLORIDE REACTIVITY RATIOS IN RADICAL COPOLYMERIZATION

M_1	M_2	r_1	r_2	Temp., °C	Ref.
Vinylidene chloride	Methyl acrylate	1	1	60	7
Vinylidene chloride	Methyl acrylate	1	1	70	7
Vinylidene chloride	Methyl acrylate	0.99	0.84	60	8
Styrene	Vinylidene chloride	2.00	0.14	60	9
Styrene	Vinylidene chloride	1.85	0.085	60	10
Vinylidene chloride	Vinyl chloride	3.2	0.3	60	11
Vinylidene chloride	Vinyl chloride	Large	0.14	68	12
Vinylidene chloride	Vinyl chloride	1.8	0.2	45	13

TABLE V. MONOMER REACTIVITY RATIOS IN THE ANIONIC COPOLYMERIZATION OF VINYLIDENE CHLORIDE

M_1	M_2	r_1	r_2
Vinylidene chloride	Methyl acrylate	0.005	38
Vinylidene chloride	Styrene	0.015	3.4
Vinylidene chloride	Vinyl chloride	0.001	0.5

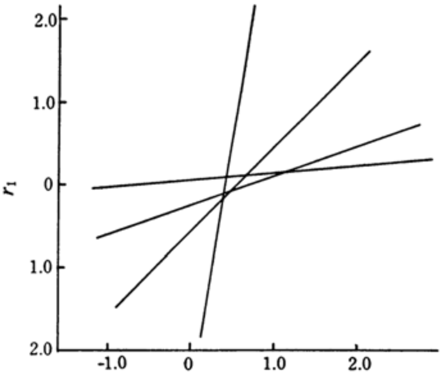

Fig. 6. Reactivity ratio diagram. Vinylidene chloride (M_1)-vinyl chloride (M_2)

The difficulties in determining accurate copolymer compositions arise from the side reaction which is thought to take place during the polymerization reaction and which causes the elimination of chlorine from the copolymer, as has been reported before⁵⁾.

In order to confirm the copolymerization and to estimate the copolymer compositions of the copolymers, the infrared spectra given in Figs. 7 and 8 were studied.

The spectra of poly(vinylidene chloride *co* styrene) shown in Fig. 7–a (initiated by *n*-BuLi) and Fig. 7–b (initiated by dibenzoyl peroxide) have common bands at 906 and 842 cm^{-1} whose absorptions increase with an

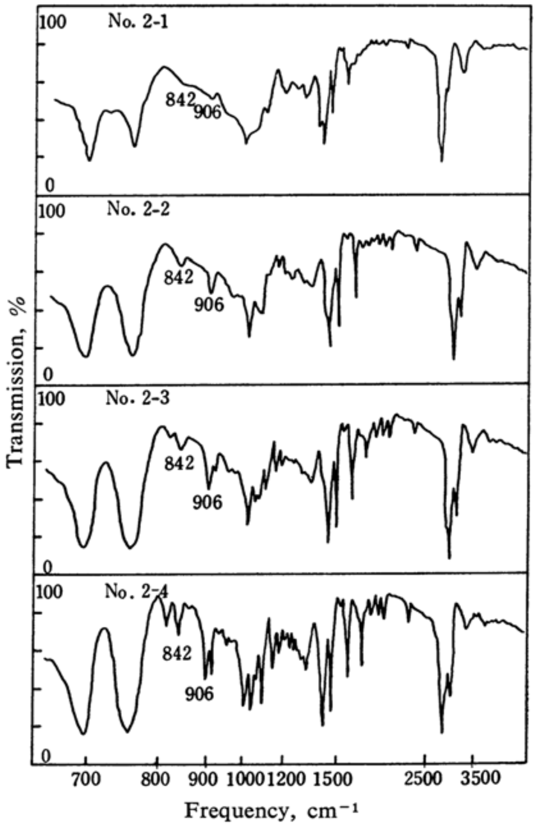

Fig. 7–a. Infrared spectra of poly(vinylidene chloride *co* styrene) initiated by *n*-BuLi.

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7) T. Alfrey, Jr., J. J. Bohrer and H. Mark, "Copolymerization", Interscience, New York (1954), p. 34.

8) G. M. Burnett, "Mechanism of Polymer Reactions", Interscience, New York (1954), p. 263.

9) F. M. Lewis, F. R. Mayo and W. F. Hulse, *J. Am. Chem. Soc.*, **67**, 1701 (1945).

10) K. W. Doak, ibid., **70**, 1525 (1948).

11) F. R. Mayo, F. M. Lewis and C. Walling, ibid., **70**, 1529 (1948).

12) P. Agron, T. Alfrey, Jr., J. Bohrer, H. Haas and H. Wechsler, *J. Polymer Sci.*, **3**, 157 (1948).

13) F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 191 (1950).

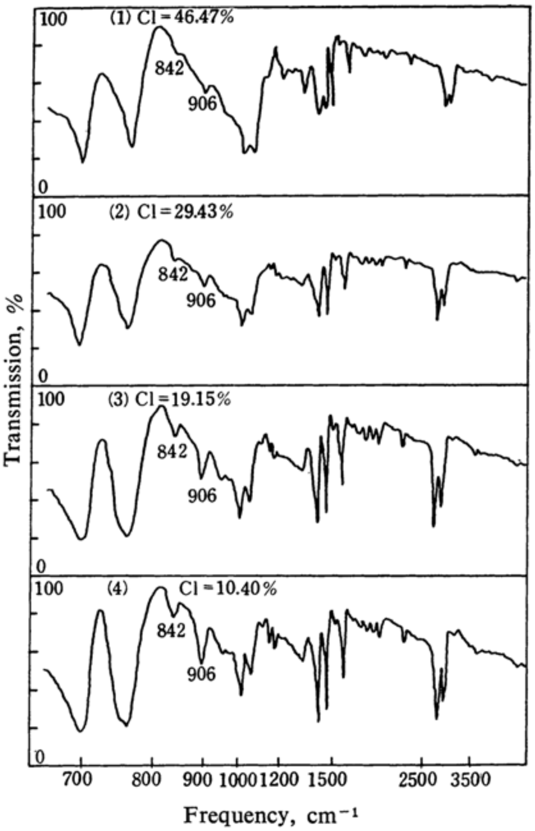

Fig. 7-b. Infrared spectra of poly(vinylidene chloride *co* styrene) initiated by BPO at 60°C.

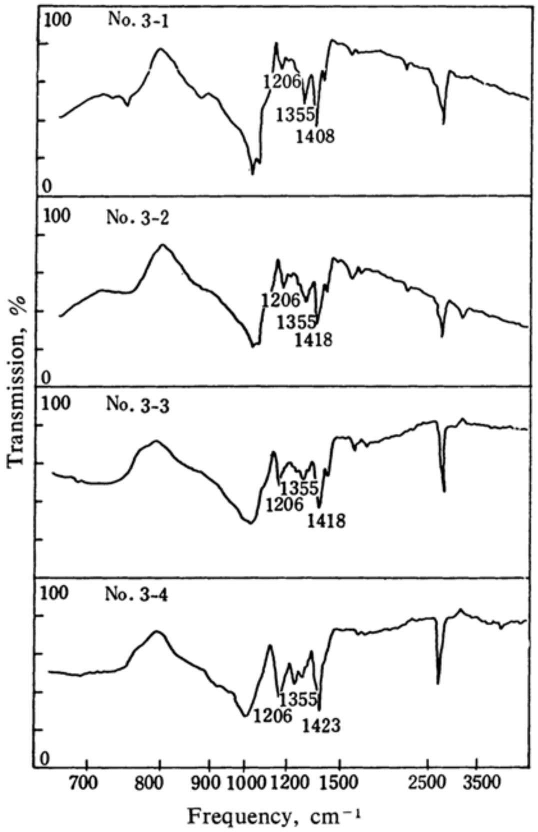

Fig. 8. Infrared spectra of poly(vinylidene chloride *co* vinyl chloride) initiated by *n*-BuLi.

increase in the styrene content; this is thought to be a proof of the copolymerization.

In the spectra of poly(vinylidene chloride *co* vinyl chloride), the shift of the strong CH_2-bending frequency from 1407 to 1428 cm^{-1} and optical density ratio of 1206 to 1355 cm^{-1} have been used for the characterization of the copolymer by Narita(14). Although the determination of the vinyl chloride fraction in the copolymer is rather difficult in the case of a high vinyl chloride content, the spectra agreed qualitatively with the results obtained from chlorine analysis.

Discussion

The monomer reactivity ratios of all the three monomer pairs initiated by *n*-butyllithium are distinctly different from those initiated by a radical initiator and present a proof of the anionic mechanism of the polymerization of vinylidene chloride initiated by *n*-butyllithium.

The poly(vinylidene chloride *co* styrene) here obtained are only with difficulty soluble, are only partly soluble or are nearly swollen in the common organic solvents, i. e., benzene, acetone, ethyl methyl ketone, tetrahydrofuran and cyclohexanone. On the contrary, the copolymers obtained by radical polymerization are easily soluble in benzene; this suggests that some structural differences may exist between these copolymers.

In Fig. 9 the known copolymer composition curves(15,16) of anionic copolymerizations are shown together with their known radical(7) and cationic copolymerization(15) curves. Comparing them with the curves shown in Figs. 1, 3 and 5, the mutual relationships between the curves obtained in the anionic and in the radical copolymerization of vinylidene chloride-methyl acrylate and vinylidene chloride-styrene pairs can be seen to be similar to the relationships in (2) methyl methacrylate-acrylonitrile, (3) methacrylonitrile-methyl methacrylate and (5) methyl methacrylate-styrene pairs. The curves of vinylidene chloride-vinyl chloride are

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14) S. Narita, S. Ichinohe and S. Enomoto, *J. Polymer Sci.*, **36**, 389 (1959).

15) D. C. Pepper, *Quat. Rev.*, **8**, 88 (1954).

16) N. L. Zutty and F. J. Welch, *J. Polymer Sci.*, **43**, 445 (1960).

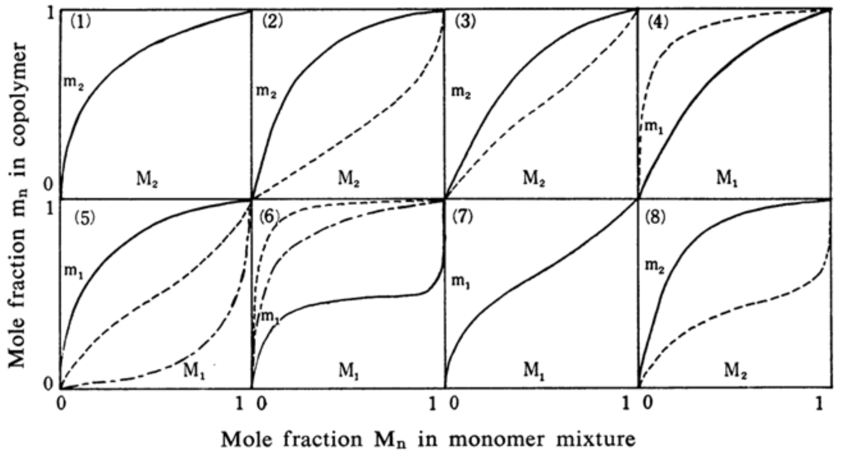

Fig. 9. Copolymer composition curves of known eight pairs; (1) Methyl methacrylate (M_1)-methyl acrylate(M_2), (2) methyl methacrylate(M_1)-acrylonitrile (M_2), (3) methyl methacrylate(M_1)-methacrylonitrile(M_2), (4) methyl methacrylate(M_1)-vinyl acetate(M_2), (5) methyl methacrylate(M_1)-styrene(M_2), (6) styrene(M_1)-vinyl acetate(M_2), (7) acrylonitrile(M_1)-butyl vinyl sulfone(M_2), (8) styrene(M_1)-acrylonitrile(M_2); Anionic ——, Radical ------, Cationic —·—·

similar to those of (4) methyl methacrylate-vinyl acetate and (6) styrene-vinyl acetate pairs.

The experimental results show that the susceptibility of methyl acrylate to anion is larger than that of vinylidene chloride. The copolymer composition curve of styrene-vinyl acetate resembles that of vinylidene chloride-vinyl chloride.

Summary

The copolymerization reaction of vinylidene chloride with methyl acrylate, styrene and vinyl chloride initiated by *n*-butyllithium has been studied. The monomer reactivity ratios have been found to be distinctly different from those of the radical copolymerizations. The results clearly showed that the nature of the polymerization of vinylidene chloride initiated by *n*-butyllithium is anionic, in accordance with the prediction from the *q*-*ε* or the *Q*-*e* map.

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