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Copolymerization Behavior of Ionizable Monomers[1]

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The copolymerization reactivity of methacrylic acid, both with diethylaminoethyl methacrylate and with acrylonitrile, depends markedly upon the *p*H of the polymerizing system. This is interpreted in terms of the ionization of methacrylic acid at neutral and high *p*H's and a distinctive copolymerization behavior of the ionized monomer. In terms of the *Q–e* scheme, the double bond of the methacrylate anion possesses a negative *e*-value, whereas the double bond of un-ionized methacrylic acid possesses a positive *e*-value. Ionization of diethylaminoethyl methacrylate (at low *p*H) leads to a less pronounced change of the polymerization reactivity—presumably because of the larger distance separating the site of the charge from the double bond.

One of the factors leading to an alternation tendency in copolymerization reactions is the polarity of the double bond resulting from the electronegative or electropositive character of the substituent groups.[4–7] In spite of this polarity effect, it has been uniformly observed that copolymerization reactivities are quite insensitive to the nature of the medium, *e.g.*, to the dielectric constant of the solvent.[8]

It is to be expected that in the case of ionizable monomers, such as methacrylic acid, the copolymerization reactivities should depend upon *p*H, since at low *p*H methacrylic acid exists mainly as the undissociated acid whereas in neutral and alkaline solutions it exists principally as the anion. These two structures should differ considerably with respect to addition of a free radical to the double bond. In particular, we might expect the carboxylate anion to be an electron-donating substituent, in contrast to the undissociated carboxyl group which is electron-withdrawing. Likewise, the ionization of a basic monomer such as diethylaminoethyl methacrylate should alter the reactivity of the double bond. However, in this particular case the site of the positive charge is several atoms removed from the double bond, and hence a smaller effect is to be expected. Very pronounced alternation is to be expected when an acid and a basic monomer are copolymerized in aqueous solution, at a *p*H where both are ionized.

This paper describes the copolymerization of methacrylic acid with diethylaminoethyl methacrylate using media and *p*H ranges so selected as to test these suggestions. These conditions were as follows: (A) in 2 *M* aqueous solution adjusted to *p*H 1.2 with hydrochloric acid; (B) in 2 *M* aqueous solution adjusted to *p*H 7.2 with hydrochloric acid or sodium hydroxide solution; (C) in 2 *M* 50% aqueous methanol solution adjusted to *p*H 10.2 with sodium hydroxide solution; (D) in 2 *M* 50% aqueous dioxane solution adjusted to *p*H 10.2 with lithium hydroxide solution; (E) in bulk; (F) in 2 *M* 50% aqueous methanol solution or in aqueous solution without *p*H adjustment. In addition, methacrylic acid was copolymerized with acrylonitrile in aqueous solution adjusted to *p*H 7 with sodium hydroxide solution. Copolymer compositions are given in Tables I and II.

TABLE I

COMPOSITION OF DIETHYLAMINOETHYL METHACRYLATE (M_2) METHACRYLIC ACID (M_1) COPOLYMERS

Series[a]	Amine in monomer mixture (M_2), mole %[b]	N, %	Amine[c] in copolymer (M_2), mole %	Time, hr.	Conversion, %
A	9.6	1.55	11.2	0.66	23
A	24.0	2.85	24.2	.5	23
A	49.0	4.17	43.0	.25	12
A	74.0	5.65	76.7	.5	18
A	90.0	5.95	86.2	.33	24
A	100	6.32	100[d]	1	..
B	10.0	4.21	37.8	0.25	3.2
B	25.0	5.06	50.0	.16	16
B	49.0	5.80	60.0	.5	20
B	74.5	5.77	73.0	.125	7.1
B	91.0	5.67	77.5	.125	1.6
E	9.9	2.43	18.0	0.5	0.5
E	24.0	4.07	35.0	.08	2.5
E	49.0	5.37	53.0	.08	4.5
E	76.0	6.77	79.0	.25	9.0
E	90.5	6.97	83.0	.43	10.0
E	100	7.51	100[d]	.75	..
F	10.5	2.36	17.5	1.0	11
F	23.0	3.92	33.0	.83	18
F	24.2	4.06	35.0	.33	5
F	37.0	4.98	47.0	.5	18
F	40.4	5.01	47.5	.25	6
F	49.0	5.75	60.0	.5	20
F	49.5	5.80	61.0	24[e]	7
F	50.0	6.04	65.0	0.08	4
F	64.0	6.37	71.0	1	10
F	74.0	6.76	80.0	0.5[e]	9
F	92.0	6.80	81.0	1.5[e]	23

[a] See introduction for reaction conditions. [b] Where conversion exceeded 5%, the composition of the monomer mixture at the completion of the polymerization was calculated from the yield and composition of the copolymer and the arithmetic means of the initial and final compositions were used in this column. [c] Values were calculated after allowing for ionic chlorine or sodium which were independently determined when known to be present. [d] These quantitative results for the pure amine polymer show the complete lack of hydrolysis under these conditions. [e] Polymerized at 30°.

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[4] F. M. Lewis, F. R. Mayo and W. F. Hulse, THIS JOURNAL, **67**, 1701 (1945).

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[6] C. Walling, E. R. Briggs, K. B. Wolfstirn and F. R. Mayo, *ibid.*, **70**, 1537 (1948).

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[8] C. Walling and F. R. Mayo, *ibid.*, **3**, 895 (1948).

Table II

Composition of Acrylonitrile (M_2) Methacrylic Acid (M_1) Copolymers

Acrylonitrile[a] in monomer mixture (M_2), mole %	N, %	Acrylonitrile in copolymer (M_2), mole %	Time, hr.	Conversion, %
15.0	4.46	29.0	5	11
27.5	6.50	37.3	5	20
47.5	9.05	49.5	5	13
70.5	14.1	68.0	25	13
87.0	10.2	55.0	25	20
100	26.2	99.5	1	62

[a] See note *b*, Table I.

Experimental

Monomer Preparation.—Diethylaminoethyl methacrylate[12] was prepared by ester interchange between diethylaminoethanol and methyl methacrylate, using sodium as a catalyst and picric acid as a polymerization inhibitor, b.p. 70–74° (3 mm.), $n^{24}D$ 1.4424 (80° (10 mm.)).[12] *Anal.*[9] Calcd. for $C_{10}H_{19}O_2N$: C, 65.0; H, 10.32; N, 7.56; neut. equiv., 185. Found: C, 64.7; H, 10.32; N, 7.51; neut. equiv., 185.5. Methacrylic acid was purified from commercial 90% aqueous methacrylic acid by saturating with sodium chloride to separate the aqueous layer, drying over calcium chloride and finally distilling *in vacuo*. Calcd. for $C_4H_6O_2$: neut. equiv., 86. Found: neut. equiv., 86.7. Commercial acrylonitrile was purified by distillation *in vacuo*.

Polymerization.—The copolymerizations were carried out in screw-cap bottles at 70°, using 0.1–1.0% potassium persulfate, based on monomer, as catalyst for the aqueous solutions and 0.1–1.0% 2,2′-azo-bis-isobutyronitrile as catalyst for the non-aqueous solutions. At high *p*H, induced decomposition of the persulfate catalyst occurred, so the polymerizations were carried out at room temperature (see Table 1F). The rates of polymerization were generally much greater in aqueous solutions at intermediate *p*H and with intermediate compositions. The polymerization was terminated when the solution became viscous, by pouring into a non-solvent (see below).

Copolymer Purification.—These amphoteric copolymers had considerable affinity for water and alcohols, and separation from solvent and monomers was difficult. In general, the water-soluble copolymers were dissolved in water, methanol or aqueous methanol and precipitated into acetone or ether, frequently at low temperatures (minus 50°). The water-insoluble copolymers were dissolved in ether and acetone and precipitated into hexane or Skellysolve B at −50°. The thrice-precipitated copolymers were then dissolved in water, benzene or dioxane, freeze-dried overnight at less than 1 mm. pressure, and finally dried for 24 hours, at 55° and 1 mm. pressure.

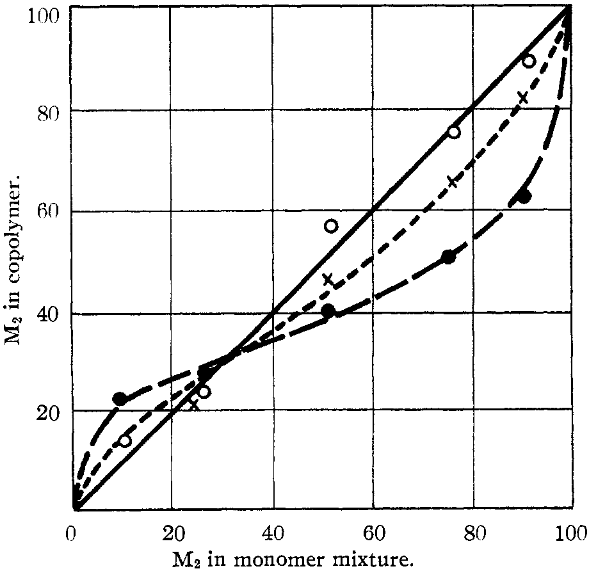

Fig. 1.—Copolymer composition curve for methacrylic acid (M_1) with diethylaminoethyl methacrylate (M_2): O, in aqueous solution at *p*H 1.2; ●, in aqueous solution at *p*H 7.2; ×, in bulk.

Analysis.—The compositions of the copolymers were determined from the nitrogen contents. The nitrogen contents were determined by the microanalytical Dumas method or by a semi-micro Kjeldahl method using (Eimer and Amend) Hengar selenized capsules as a digestion catalyst. Results obtained by the two methods agreed well, and theoretical results for polyacrylonitrile and polydiethylaminoethyl methacrylate were obtained by the Kjeldahl method. In addition, the compositions of many of the copolymers were checked by micro-electrometric titrations, by the Volhard method for ionic chloride when this was known to be present, and by the Perkin–Elmer flame photometer for sodium when this was known to be present.

Results and Discussion

Figure 1 shows that the composition of copolymers from the same mixture of ionizable monomers may differ markedly if the *p*H is varied. This *p*H dependence is also evident for the acrylonitrile–methacrylic acid system shown in Fig. 2. Quantitative character was given to these observations by computing reactivity ratios from the data, using the graphical method of Mayo and Lewis[10] (Table III). Similar computations could not be made for series E and F, in which the *p*H differed for each initial mixture depending on the proportion of

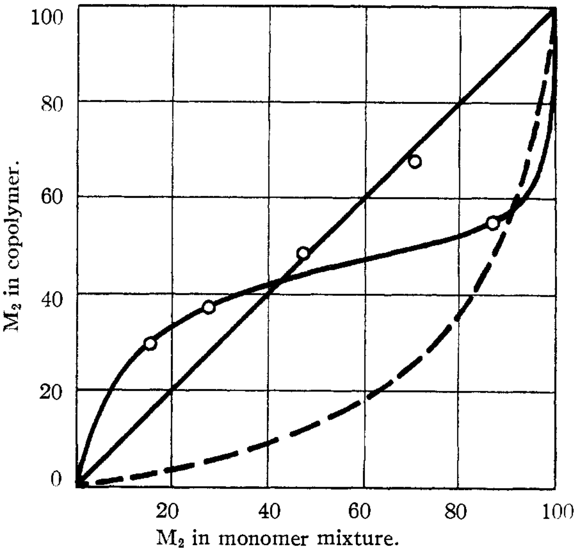

Fig. 2.—Copolymer composition curve for methacrylic acid (M_1) with acrylonitrile (M_2) in aqueous solution at *p*H 7: O, experimental points; solid line, theoretical curve for methacrylate anion; broken line, theoretical for undissociated methacrylic acid.

Table III

Monomer Reactivity Ratios at Different *p*H Values

*p*H	Acid, r_1	Amine, r_2	r_1r_2
1.2	0.98 ± 0.16	0.90 ± 0.23	0.88
7.2	.08 ± .015	.65 ± .03	.05

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(9) Analysis by Drs. Weiler and Strauss, Oxford, England.

(10) F. R. Mayo and F. M. Lewis, This Journal, **66**, 1594 (1944).

acidic to basic monomer. Since the reactivity ratios are *p*H-dependent, conformity with the binary copolymerization equation is not to be expected for unbuffered systems.

Series C and D were designed to yield information concerning the reactivity of the undissociated amine. These copolymers were found to be very low in nitrogen; an equimolar feed, for example, giving a copolymer containing less than 5 mole % amine. More extended tests on the polymerization of the pure amine revealed that the amine monomer underwent rapid hydrolysis or methanolysis at high *p*H even at room temperature. The results for series C and D were therefore completely unreliable. Hydrolysis was much slower at low and intermediate *p*H values and since the polymerization was also much more rapid under these conditions, series A, B and F were largely free from such errors, except possibly for unbuffered feeds very rich in amine.

It is noted that methacrylic acid with a reported *pK* of 4.36[11] is about 99.9% un-ionized at *p*H 1.2 and about 99% ionized at *p*H 7.2. The cation of the amine has a *pK* above 10, and hence the amine is completely ionized at both *p*H values.[12] It is therefore reasonable to regard series A as a copolymerization between the substituted ammonium cation and methacrylic acid, and series B as a copolymerization between the ammonium cation and the methacrylate anion. The latter may be expected to reveal strong alternation and indeed this is so, as shown in Table III and Fig. 2.

Q and *e* values for methacrylic acid, tested against styrene, have been given as 2.0 and +0.7, respectively.[13] These were used to calculate *Q* and *e* values for the diethylaminoethyl methacrylate cation from the reactivity ratios at *p*H 1.2. We then used these values to calculate *Q* and *e* for the methacrylate anion, using the reactivity ratios at *p*H 7.2. The results are shown in Table IV.

TABLE IV

TABULATION OF *Q* AND *e* VALUES

	Q	*e*
Methacrylic acid[a]	2.0	+0.7
Methacrylate anion	0.9	−1.0
Diethylaminoethyl methacrylate cation	1.95	+0.7

[a] See reference 13.

It was desirable to check the *Q* and *e* values for the methacrylate anion by an independent method. Accordingly methacrylic acid was copolymerized with acrylonitrile at *p*H 7. The theoretical copolymerization curve using *Q* and *e* values listed for methacrylic acid[13] and acrylonitrile[14] was calculated, and also the curve using the above *Q* and *e* values for methacrylate anion. The experimental points (Table II) corresponded more closely with the methacrylate anion curve, as seen from Fig. 2. This supplied reasonable confirmation that the reactivity of the methacrylate ion in copolymerization differs markedly from that of the un-ionized acid. (The slight difference in the *Q–e* reference base, as used by Price and by Chapin, *et al.*, is not significant in this calculation.)

We were unable to demonstrate a similar dependence of reactivity on ionization of the amine. Evidence from copolymerization on this point is scanty owing to hydrolysis of the amine at high *p*H, but other measurements show that the *rate* of polymerization of the pure amine is indifferent to *p*H, in contrast with methacrylic acid which polymerizes more slowly with increasing ionization. Comparison of the calculated *Q–e* values for the amine cation with the *Q–e* values of methyl methacrylate would indicate a small change in reactivity and polarity as the result of ionization; but the effect is small, and is not unambiguously demonstrated by the data reported here. We attribute the smallness of this effect to the chain of 4 atoms separating the charged center from the double bond. A monomer such as dimethylvinylamine may be expected to behave in an analogous manner to methacrylic acid (pronounced sensitivity of its copolymerization reactivity to *p*H).

Series F may be considered to be a 3-component copolymerization (amine, methacrylic acid and methacrylate ion). Solving the copolymerization equation for this case leads to r_1, r_2 values which are functions of the degree of ionization of the acid. The latter can be evaluated from the observed *p*H, and the resultant theoretical curve agrees reasonably well with the data of series F.

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