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Amphoteric Polyelectrolytes. III. Copolymerization of Allylamine and Methacrylic Acid[1,2]

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Allylammonium ion was copolymerized with methacrylic acid to high molecular weight products containing up to 6.91% nitrogen. The composition of the copolymer was sensitive to the degree of ionization of the acid monomer, with the amine content passing through a minimum when the methacrylic acid was half-ionized. This behavior was consistent with predictions based on the Alfrey–Price theory. The copolymers obtained from equimolar allylamine and methacrylic acid in neutral solution contained 15 weight % of lactam; the degree of lactamization was reduced by acidifying the monomer mixture and increased by raising the allylamine/methacrylic acid ratio.

The preparation of several types of amphoteric polyelectrolytes has been reported previously. Copolymers of 2-vinylpyridine with acrylic acid[3] and methacrylic acid,[4] respectively, were water insoluble in the absence of added acid or base and this was thought to be due to their uncharged, rather than zwitterionic, state. Although later studies of the ultraviolet[5] and infrared spectra[6] of the isoelectric gels indicated partial ionization, it is reasonable to postulate that the insolubility of the isoelectric copolymers is a consequence of insufficient charge density.

To obtain polyampholytes, which are fully ionized at the isoelectric point, the uncharged base residues must be stronger bases than the anionic groups,[7] a condition which is satisfied in the copolymerization of carboxylic acids with aliphatic amines. Such copolymers were prepared from methacrylic acid and diethylaminoethyl methacrylate[8] and infrared studies revealed the expected zwitterionic behavior.[6] However, the attachment of the basic function to the polymer by a hydrolyzable ester linkage is rather unsatisfactory, particularly in view of the demonstrated attack of γ-carboxylate on ester groups.[9] This disadvantage was eliminated in the synthesis of a vinylamine–acrylic acid copolymer by a fairly complex reaction sequence.[10]

The ready availability of allylamine makes it an attractive monomer for polyampholyte preparation. It probably has not been previously considered, because of the "degradative chain transfer" of allylic monomers[11] which prevent them from forming polymers of high molecular weight. However, the mutual electrostatic repulsion of allylammonium radicals and monomers should work powerfully against chain transfer when the allylamine is fully ionized, in analogy with the inhibition of the polymerization of carboxylic acid monomers in the ionized state.[12,13]

Experimental

Polymer Preparation.—Glacial methacrylic acid (Rohm and Haas Co.) was freed from inhibitor by distillation under reduced pressure. Allylamine (Fisher Scientific Co.) was distilled collecting the middle fraction boiling at 57°. Titration showed 5 ml. to contain 66.5 meq. of base. Both monomers were stored at 3°. To 0.2 mole of allylamine in 30 ml. of methanol cooled in an ice-bath 0.3 mole of methacrylic acid was added dropwise with stirring. The state of ionization of the monomers was adjusted by addition of HCl or NaOH in 30 ml. of water. In a second series of experiments 0.1 mole of methacrylic acid was used with increasing amounts of allylamine, neutralizing the excess allylamine with HCl. After addition of 0.045 g. of azo-bis-isobutyronitrile initiator, the solution was degassed by repeated freezing in liquid nitrogen and thawing under vacuum and polymerized in sealed tubes at 60°. All polymerizations were held to low conversion. The polymers were precipitated twice into dioxane, dialyzed until the spec. resistivity of the dialyzate was above 200,000 ohm cm., and freeze-dried.

Analysis of Copolymers.—Nitrogen, chlorine and ash determinations were obtained from the Ritter Laboratories in Basel, Switzerland. Amine and carboxyl was determined by conductometric titration of 20 mg. of polymer in 150 ml. of water with 0.024 *N* HCl and 0.076 *N* NaOH, respectively, using an Industrial Instruments Co. conductivity bridge. The lactam nitrogen content of the polymer was calculated as the difference between total and amine nitrogen. Intrinsic viscosities were measured in 2 *N* NaOH at 30°.

Results and Discussion

The dependence of the copolymer properties on the polymerization conditions is summarized in Table I. Here α_A and α_B are the degrees of ionization of methacrylic acid (MA) and allylamine (AA) while r is the molar ratio AA/MA in the monomer mixture.

Considering the copolymerization of equimolar amounts of the two monomers as a function of the degree of ionization of MA, it is found that the amine content of the polymer passes through a deep minimum for $\alpha_A = 0.5$ (Fig. 1). This result is consistent with the interpretation of the copolymerization behavior of methacrylic acid proposed by Alfrey, Overberger and Pinner.[13] They applied to their results the Alfrey–Price theory[14] in which the relative reactivity of two monomers with a given radical is expressed as

$$\frac{k_{11}}{k_{12}} = \frac{Q_1}{Q_2} \exp\,[-e_1(e_1 - e_2)]$$

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[1] Abstracted from the M.S. thesis of A. Drucker.

[2] Financial support by the Office of Ordnance Research is gratefully acknowledged.

[3] H. L. Wagner and F. A. Long, *J. Phys. Colloid Chem.*, **55**, 1512 (1951).

[4] T. Alfrey, Jr., and H. Morawetz, THIS JOURNAL, **74**, 436 (1952).

[5] A. Katchalsky and I. R. Miller, *J. Polymer Sci.*, **13**, 57 (1954).

[6] G. Ehrlich, THIS JOURNAL, **76**, 5263 (1954).

[7] E. J. Cohn and J. T. Edsall, "Proteins, Amino Acids and Peptides," Reinhold Publ. Corp., New York, N. Y., 1943, Chapter 4.

[8] T. Alfrey, Jr., R. M. Fuoss, H. Morawetz and H. Pinner, THIS JOURNAL, **74**, 438 (1952).

[9] H. Morawetz and P. E. Zimmering, *J. Phys. Chem.*, **58**, 753 (1954).

[10] M. Vrancken and G. Smets, *J. Polymer Sci.*, **14**, 521 (1954).

[11] P. D. Bartlett and R. Altschul, THIS JOURNAL, **67**, 812, 816 (1945).

[12] A. Katchalsky and G. Blauer, *Trans. Faraday Soc.*, **47**, 1360 (1951).

[13] T. Alfrey, Jr., C. G. Overberger and S. H. Pinner, THIS JOURNAL, **75**, 4221 (1953).

[14] T. Alfrey, Jr., and C. C. Price, *J. Polymer Sci.*, **2**, 101 (1947).

TABLE I

PREPARATION AND CHARACTERIZATION OF ALLYLAMINE-METHACRYLIC ACID COPOLYMERS

Polymerization conditions				Copolymer characterization					
α_A	α_B	r	% conversion/hr.	Wt. % AA	Wt. % MA	Ash, %	N, %	Cl, %	[η]
1.0	1.0	1	0.8	20.5	64.5	0.0	6.91		0.660
0.80	1.0	1	0.7	17.8	71.4	.0	4.88	0.0	1.678
.65	1.0	1	0.8	6.6	89.4	.0	1.73	0.5	
.50	1.0	1	1.9	2.8	97.2	.9	0.73		
.35	1.0	1	1.6	3.6	92.5	.0	0.85	0.5	
.20	1.0	1	1.6	16.4	84.3	.8	4.12		
1.0	0.8	1	0.6	15.3[a]	71.9[a]	15.2	5.01		0.812
1.0	0.5	1	0.03	0.0[a]	87.2[a]	6.0	2.80		
1.0	1.0	2	2.8	11.7	63.6		5.18		
1.0	1.0	3	1.1[b]	2.8[c]	58.4		4.74	0.2	
1.0	1.0	4	1.3[b]	1.7[c]	57.2		5.03	0.0	

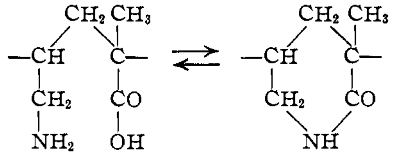
[a] Weight % of organic material calculated from titration data assuming the ash to consist of Na_2CO_5. [b] Precipitated into acetone. [c] Became water insoluble on freeze-drying; dissolved in base and back-titrated with acid.

and found for methacrylic acid $Q = 2.0$, $e = +0.7$, while for methacrylate ion $Q = 0.9$, $e = -1.0$. The opposite polarity factors e for ionized and un-ionized MA render the competition of the acid monomer with a given comonomer most favorable, if it involves addition of un-ionized acid to the anionic radical, or, *vice versa*, addition of the acid anion to the un-ionized acid radical. The probability of these processes is obviously at a maximum when the acid monomer is half-ionized. It is worth noting that the present results contradict the explanation proposed by Katchalsky and Blauer[12] for the *p*H dependence of the homopolymerization rate of methacrylic acid. According to these authors, the radical is very weakly acidic, virtually un-ionized and incapable of adding an ionized monomer. This interpretation would lead to the predictions that at full ionization of the acid monomer no copolymer could contain more than 50 mole % of the acid, and that the acid content of the copolymer would increase monotonically with decreasing ionization of the acid monomer. Both predictions are at variance with results reported above.

The high intrinsic viscosities of the copolymers obtained justify the assumption that chain transfer with allylammonium monomer is negligible. It was surprising that even with 20% of the allylamine un-ionized no lowering of the intrinsic viscosity of the copolymer was observed. However, the polymerization rate decreased sharply with increasing basicity of the medium and with 80% of the allylamine un-ionized, no polymer was obtained.

When equimolar amounts of AA and MA are copolymerized in a neutral medium, the polymer contains 15% by weight of lactam rings. As shown in Fig. 1, the difference between total nitrogen and amino nitrogen decreases rapidly as the polymerization medium becomes more acid. This is consistent with previous observations of the *p*H dependence of amino acid–lactam equilibria.[15]

It may be assumed, that the equilibrium is established under the conditions of polymerization at



60° and that the reaction rates are too slow at room temperature to produce any changes in the subsequent treatment of the copolymers.

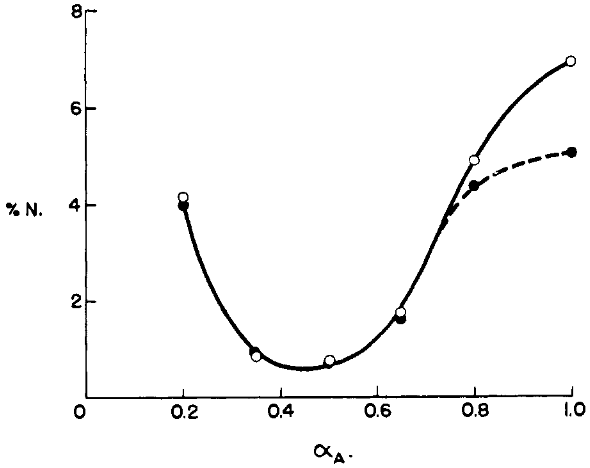


Fig. 1.—Copolymerization of allylamine with methacrylic acid: O, total N; ●, amino N.

Attempts to increase the amine content of the copolymer by increasing the AA/MA ratio, with both monomers fully ionized, was not successful and an increasing allylamine content of the mixed monomer resulted merely in increased lactamization of the copolymer. The cause of this strange behavior is not apparent.

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(15) H. P. Frank, *J. Polymer Sci.*, **12**, 565 (1954).