

[CONTRIBUTION FROM THE POLYMER RESEARCH INSTITUTE, POLYTECHNIC INSTITUTE OF BROOKLYN]

Amphoteric Polyelectrolytes. I. 2-Vinylpyridine-Methacrylic Acid Copolymers<sup>1,2</sup>BY TURNER ALFREY, JR., AND HERBERT MORAWETZ<sup>3</sup>

Three copolymers of 2-vinylpyridine and methacrylic acid were prepared. These were soluble in some organic solvents and in aqueous acid or base solutions above a critical degree of neutralization. Dilute solution viscosity behavior of one of the copolymers was studied. Both titration and viscosity behavior resembled, in acid solution, that of polyvinylpyridine and, in basic solution, that of polymethacrylic acid. The behavior of the copolymers indicates that they are uncharged, rather than dipolar, ions at their isoelectric points. This is probably due to the weak basicity of the pyridine group.

Many natural substances of biological importance are amphoteric polyelectrolytes, and this has stimulated interest in the investigation of their synthetic analogs.

Polymeric acids such as polyacrylic acid<sup>4-6</sup> and cationic polymers such as polyvinylamine,<sup>7</sup> polyvinylpyridine and quaternary polyvinylpyridinium salts<sup>8</sup> have been prepared and studied by a number of investigators. The titration behavior of polymeric acids has been interpreted in terms of (1) the electrical free energy change associated with the removal of protons from the field of the poly-ion and (2) the entropy change accompanying the chain uncoiling which is caused by electrostatic repulsion among the ionic charges.<sup>5,9</sup> The dependence of the chain extension on the number of attached ionic charges, and the density of the counterion atmosphere, can be followed conveniently by viscosity measurements. The observed effects have been accounted for fairly satisfactorily by a number of theoretical treatments.<sup>9,10</sup>

The present communication reports an extension of the study of synthetic polyelectrolytes to copolymers carrying both cationic and anionic groups. Such materials behave as polyanions in alkaline solution, and as polycations in acid solution. Particular interest attaches to their behavior near the isoelectric point, and this is determined by the strengths of the ionizing groups.

## Experimental

**Monomers.**—2-Vinylpyridine (Reilly Tar and Chem. Co.) was vacuum distilled under nitrogen (b.p. 61° at 10 mm.). Because of the tendency of the uninhibited monomer to polymerize slowly even at low temperature, it was always distilled immediately before use.

Commercial methacrylic acid (Rohm and Haas) was shaken with sodium chloride, the aqueous layer separated and the acid dehydrated over calcium chloride. It was then vacuum distilled under nitrogen (b.p. 73° at 20 mm.) and stored at 0°.

(1) This research was supported by the Office of Naval Research, as Project NR-054-022.

(2) Abstracted from the doctoral dissertation presented by H. M. to the Graduate School of the Polytechnic Institute of Brooklyn, September, 1950.

(3) Harvard Univ. Lab. of Phys. Chem. Related to Medicine and Public Health, Boston, 15 Mass.

(4) W. Kern, *Z. physik. Chem.*, **A181**, 283 (1938).

(5) W. Kuhn, O. Kunze and A. Katchalsky, *Helv. Chim. Acta*, **31**, 1984 (1948).

(6) A. Katchalsky and P. Spitnik, *J. Polymer Sci.*, **2**, 432 (1947).

(7) D. D. Reynolds and W. O. Kenyon, *THIS JOURNAL*, **69**, 911 (1947).

(8) R. M. Fuoss and G. I. Cathers, *J. Polymer Sci.*, **2**, 12 (1947); **4**, 97, 121 (1949); R. M. Fuoss and U. P. Strauss, *ibid.*, **3**, 246 (1948); **4**, 457 (1949).

(9) A. Katchalsky and J. Gillis, "Proceedings of the International Colloquium on Macromolecules," Centen's, Amsterdam, 1950, p. 277.

(10) J. J. Hermans and J. T. G. Overbeek, *Bull. soc. chim. Belges*, **67**, 154 (1948).

**Preparation of Copolymers.**—The copolymers were prepared by bulk polymerization under nitrogen at 70° in presence of 0.05% azo-bis-isobutyronitrile catalyst (du Pont). Conversions of less than 25% were aimed at, in order to obtain copolymers of reasonably homogeneous composition. The copolymers were precipitated and purified by redissolving twice and reprecipitating in a large excess of non-solvent. They were finally dried to constant weight under vacuum at 70°. Copolymer compositions calculated from carbon and nitrogen analyses agreed within 2% in all cases and the average of the two values was used. The following resins were prepared:

**Copolymer I.**—2-Vinylpyridine 28.4 mole % in monomer, 39.3 mole % in polymer. Conversion 12.2% in four hours. Purified by precipitation from dimethylformamide solution into dioxane.

**Copolymer II.**—2-Vinylpyridine 50.3 mole % in monomer, 62.1 mole % in polymer. Conversion 24.8% in six hours. Purified by precipitation from methanol-benzene solution into excess methyl ethyl ketone.

**Copolymer III.**—2-Vinylpyridine 63.2 mole % in monomer, 73.1 mole % in polymer. Conversion 22.2% in four hours. Purified by precipitation from methanol solution into excess methyl ethyl ketone.

The two monomer reactivity ratios<sup>11</sup> were computed; the values obtained were  $r_1 = 1.55 \pm 0.1$  and  $r_2 = 0.58 \pm 0.05$ , where the subscript 1 refers to 2-vinylpyridine.

All three copolymers were soluble in nitromethane, dimethylformamide, pyridine and acetic acid. They were all insoluble in acetone, methyl ethyl ketone, ethyl acetate, ether, dioxane, isopropyl alcohol, benzene, toluene, hexane and carbon tetrachloride. Polymer III dissolved in methanol. Polymer II dissolved in methanol-benzene mixtures containing 25 to 65% methanol by volume, and in methanol-water mixtures containing 10 to 25 volume % of water. All resins were insoluble in water and in sodium chloride solutions, but dissolved in dilute aqueous acid or alkali.

**Titration.**—Samples of 0.25 g. of resin in 80 ml. of water containing two milliequivalents of HCl were titrated with 0.1 N NaOH, using a Beckman glass electrode pH meter. The titration curves are shown on Fig. 1. It can be seen that each of the resins has an insoluble region. The conditions of solubility are summarized in Table I.

TABLE I  
CONDITIONS OF SOLUBILITY OF 2-VINYLPYRIDINE-METHACRYLIC ACID COPOLYMERS

Mole % 2-vinylpyridine	Minimum HCl, millieq./g.	Minimum NaOH, millieq./g.	pH range of insolubility
39.3	1.6	2.8	3.0-6.3
62.1	1.5	1.7	3.9-6.6
73.1	1.6	1.3	4.2-7.0

The pyridine residues are apparently very weakly basic, and no break appears in the titration curve on the acid side. On the alkaline side of the titration curve a break due to the methacrylic acid end-point is observed, but occurs before stoichiometric equivalence is attained (at 91, 85 and 84% of equivalence for copolymers I, II and III, respectively).

The dissociation constants for monomeric methacrylic acid and the 2-vinylpyridinium cation were determined:  $pK_a = 4.65$  and  $pK_a = 5.10$ , respectively. Pyridinium cations in the copolymers are much more strongly acidic

(11) T. Alfrey, Jr., F. R. Mayo and F. T. Wall, *J. Polymer Sci.*, **1**, 581 (1946).

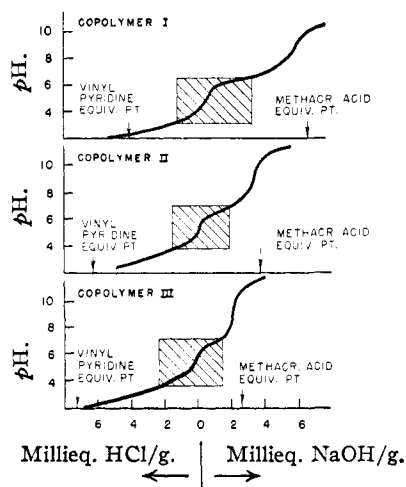


Fig. 1.—Titration curves and solubility ranges of copolymers I, II and III.

than the corresponding monomeric vinyl pyridinium ion; on the other hand, methacrylic acid groups in the copolymer are less acidic than monomeric methacrylic acid. When the titration of the copolymer was carried out in presence of 5% sodium chloride, it was found that the pH values were increased in acid and reduced in alkaline solution. The insoluble range was broadened for copolymer II to extend from pH 3.7 to pH 7.3 (3.1 millieq. HCl/g. and 2.7 millieq. NaOH/g., respectively).

**Dilute Solution Viscosity.**—A modified Ostwald viscosimeter was used. This viscosimeter had a large bulb in which the resin solution could be diluted by addition of measured amounts of solvent.<sup>12</sup> All viscosities were measured at 30°. Copolymer II was chosen as a representative member of the series for detailed investigation of its dilute solution viscosity.

In dimethylformamide, a non-ionizing solvent, the reduced viscosities were low, and decreased very slightly on dilution (0.112, 0.108 and 0.106 at concentrations of 1.0, 0.5 and 0.25 g./100 ml., respectively).

Viscosities were measured in aqueous solutions of various concentrations and degrees of neutralization and, since the resin was insoluble in water below a critical degree of acid or base neutralization, data were also obtained for 90% methanol-10% water solution containing different amounts of acid or base. Figure 2 is a plot of the specific viscosities

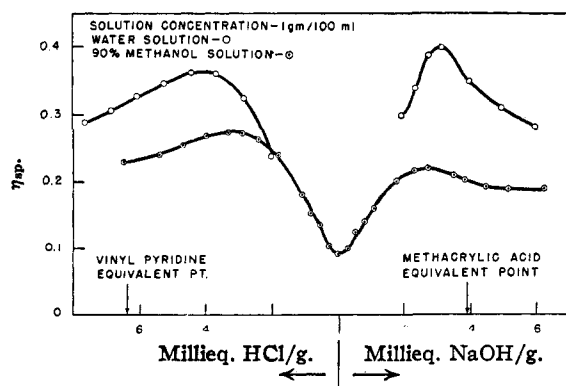


Fig. 2.—Solution viscosity of copolymer II as function of degree of neutralization.

at constant polymer concentration, as a function of the acid/resin and base/resin ratios. The aqueous methanol solutions have a viscosity minimum when neither acid nor base is added. The viscosity increase on acid addition is ascribed to the expansion of the chain due to repulsion of the pyridinium cations, while in alkaline solution the polymer expands because of the negatively charged carboxy groups. This charge reversal has been demonstrated previously by electrophoretic measurements.<sup>13</sup> The viscosity maxima in water solution correspond to 72% neutralization of the pyridine residues and to 84% neutralization of carboxyl groups. On the basic side the viscosity maximum coincides with the break in the titration curve. It is not unexpected that the viscosity maximum on the acid side should occur at a lower degree of neutralization, since the titration curve shows that the basic strength of the pyridine residues is very low.

Figures 3 and 4 are plots of the reduced viscosities

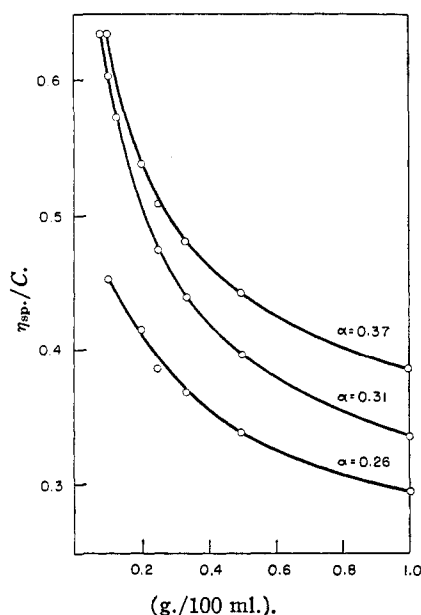


Fig. 3.—Viscosities of basic solutions of copolymer II at three different degrees of neutralization.

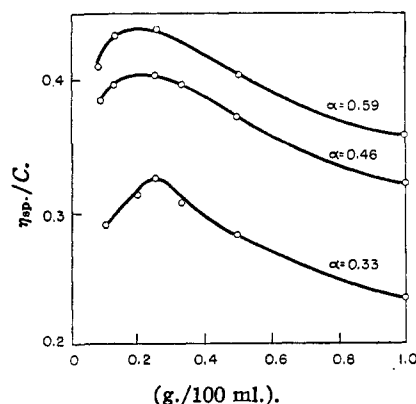


Fig. 4.—Viscosities of acid solutions of copolymer II at three different degrees of neutralization.

(12) T. Alfrey, Jr., A. I. Goldberg and J. A. Price, *J. Colloid Sci.*, **5**, 251 (1950).

(13) T. Alfrey, Jr., H. M. Morawetz, E. B. Fitzgerald and R. M. Fuoss, *THIS JOURNAL*, **72**, 1884 (1950).

of copolymer II in basic and acid solutions, respectively, as a function of dilution. In basic solutions, the reduced viscosity increases on dilution with water in a manner characteristic of strong polyelectrolytes (due to the thinning of the counter-ion atmosphere), and the data fit the relation proposed by Fuoss and Cathers.<sup>8</sup> On the other hand, if the resin is partially neutralized with acid, the reduced viscosity has a maximum at 0.25 g./100 ml., and falls off on further dilution. This behavior can be attributed to hydrolysis of the pyridinium cations.

Both the titration behavior and the dilute solution viscosities of the copolymers resemble in acid solution those of polyvinylpyridine and in basic solution those of polymethacrylic acid. This suggests strongly, that the polymer is uncharged in the isoelectric region rather than being a dipolar ion.

Edsall<sup>14</sup> has shown that substances containing both carboxyl and amine groups will form dipolar ions only if the acidity of the carboxyl groups is greater than that of the cationic groups, and this condition is certainly not satisfied in copolymers of vinylpyridine and methacrylic acid. Since it is known that dipolar ions are much more water-soluble than their uncharged isomers,<sup>15</sup> the absence of ionic charges at the isoelectric point accounts for the insolubility of the copolymers. Copolymers of strongly basic monomers with methacrylic acid have been shown<sup>16</sup> to be soluble over the entire pH range, giving strong support for this interpretation.

(14) E. J. Cohn and J. T. Edsall, "Proteins, Amino Acids and Peptides," Reinhold Publishing Corp., New York, N. Y., 1943, chap. 4.

(15) *Ibid.*, chap. 8.

(16) T. Alfrey, Jr., R. M. Fuoss, H. Pinner and H. Morawetz, in preparation.

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## Amphoteric Polyelectrolytes. II. Copolymers of Methacrylic Acid and Diethylaminoethyl Methacrylate<sup>1</sup>

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Copolymers of methacrylic acid and N,N-diethylaminoethyl methacrylate exist as polycations at low pH, as polyanions at high pH, and probably as polyzwitterions at intermediate pH values. Each copolymer possesses a definite isoelectric point, characterized by a minimum in the solution viscosity and by a reversal in the electrophoretic mobility. The isoelectric point moves to higher pH values, as the amine/acid ratio in the copolymer is increased. If either the amine or the acid constituent is present in large excess, the isoelectric point broadens into a pH range in which the polymer is insoluble.

Synthetic vinyl copolymers containing both acid and basic groups may provide useful analogs to certain aspects of the solution behavior of proteins.<sup>3</sup> Previous publications<sup>4,5</sup> have discussed copolymers of methacrylic acid with vinylpyridine. The above copolymers were soluble in acid and in alkali, but exhibited water-insolubility in the neutral pH range. This was ascribed to the weakly basic character of the pyridine groups, which would preclude zwitterion formation.

This paper describes copolymers containing stronger basic groups, contributed by the monomer N,N-diethylaminoethyl methacrylate (DEAM). Electrophoretic and extensive viscometric studies were made on one member of the series, consisting of approximately 55% methacrylic acid and 45% DEAM. Solubility, titration and less extensive

viscometric studies were made on the complete series, ranging from 11 to 100% DEAM. Designations and compositions of these copolymers are given in Table I.

### Results and Discussion

Copolymer E (45 mole % DEAM) was soluble in water over the entire pH range studied (2.0 to 11.0), acting as a polyanion at high pH and as a polycation at low pH. Since the dissociation constant of the monomeric cation ( $pK_a$  10.04) is very much smaller than that of the acid monomer ( $pK_a$  4.60), it is reasonable to assume that the polymer is zwitter-ionic in the isoelectric range. The water solubility of the isoelectric resin appears to confirm this assumption, since it is known that zwitterionic materials are generally much more water soluble than their uncharged isomers.<sup>6</sup> The resin was also soluble in nitromethane, dimethyl formamide, pyridine, acetic acid and in methanol containing small amounts of water. It was insoluble in dry methanol, and in dioxane, ketones, benzene and higher alcohols.

On titration, copolymer E exhibits surprisingly little buffering action, and there are no breaks in the pH curve. If the titration is carried out in half-normal sodium chloride solution, slight inflections in the titration curve can be observed at points somewhat before the stoichiometric acid and basic end-points (see Fig. 1).

In the presence of salt, the resin behaves as a

(6) E. J. Cohn and J. T. Edsall, "Proteins, Amino Acids and Peptides," Reinhold Publishing Corp., New York, N. Y., 1943, chapter 8.

TABLE I

Copolymer	DEAM content, mole %	Copolymer	DEAM content, mole %
A	11.2	F	59.5
B	24.2	G	79.6
C	33.8	H	86.2
D	43.0	J	100.0
E	45.0		

(1) This investigation was supported by the Office of Naval Research, as Project NR-054-022, at the Polytechnic Institute of Brooklyn.

(2) Dow Chemical Company, Midland, Michigan.

(3) H. Staudinger, "Die Hochmolekularen Organischen Verbindungen," J. Springer, Berlin, 1932, p. 39.

(4) T. Alfrey, Jr., H. M. Morawetz, E. B. Fitzgerald and R. M. Fuoss, *THIS JOURNAL*, **72**, 1864 (1950).

(5) T. Alfrey, Jr., and H. Morawetz, *ibid.*, **74**, 436 (1952).