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.[8] 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[14] 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,[15] 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[16] 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.

BROOKLYN, N. Y.

RECEIVED JULY 27, 1951

[CONTRIBUTION OF THE POLYTECHNIC INSTITUTE OF BROOKLYN AND YALE UNIVERSITY]

Amphoteric Polyelectrolytes. II. Copolymers of Methacrylic Acid and Diethylaminoethyl Methacrylate[1]

BY TURNER ALFREY, JR.,[2] RAYMOND M. FUOSS, HERBERT MORAWETZ AND HARRY PINNER

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.[3] Previous publications[4,5] 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.

TABLE I

Copolymer	DEAM content, mole %	Copolymer	DEAM content, mole %
A	11.2	F	59.5
B	24.2	G	79.6
C	33.3	H	86.2
D	43.0	J	100.0
E	45.0		

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.[6] 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

---

[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).

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

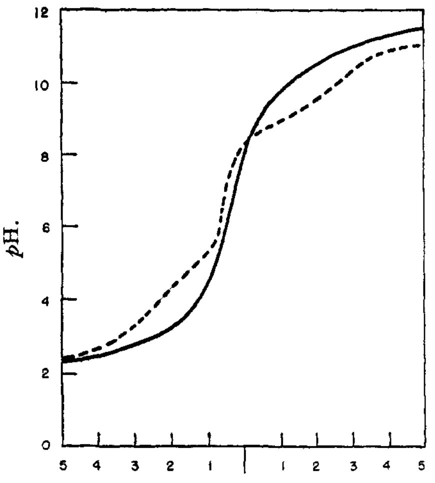


Fig. 1.—Titration curve for copolymer E: solid curve, in distilled water; broken curve, in $N/2$ NaCl solution.

stronger acid and a stronger base because the increased counter-ion density reduces the large electrical free energy of ionization of the polyion. It follows that the intersection of the two titration curves should be an indication of the isoelectric point, as observed by Soerensen with proteins.[7] This interpretation of the titration curves of copolymer E indicates an isoelectric point of 8.2–8.3.

At a resin concentration of 0.1 g. per 100 ml., the reduced viscosity (η_{sp}/c) exhibits a minimum at the isoelectric point, and maxima on the acid and alkaline sides.

The viscosity behavior in acid solution (Fig. 2) is similar to that expected for a cationic polymer. As the polymer is neutralized with HCl, it changes from a highly coiled zwitterion chain to a positively charged polycation, which is forced into a highly extended configuration by the interionic repulsions. Excess HCl, however, swamps this effect, and leads to a partial recoiling and reduction in viscosity.

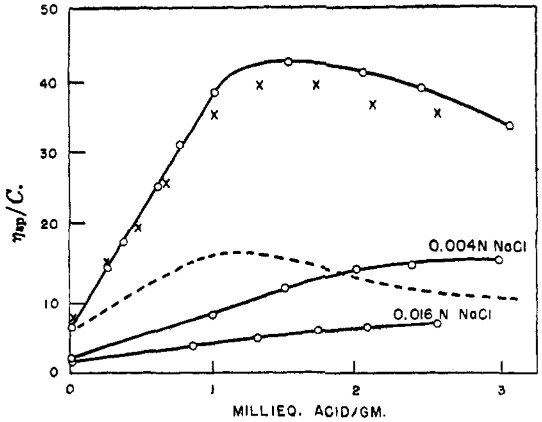


Fig. 2.—Reduced viscosity of dilute solutions of copolymer E, at different degrees of neutralization by acid: solid curves with circles, neutralization with HCl; crosses, neutralization with trichloroacetic acid; broken curve, neutralization with H_2SO_4.

The viscosities of these solutions are extremely sensitive to small concentrations of simple electrolytes, as shown in Fig. 2. Sodium chloride, in concentrations as low as 0.004 N, reduces sharply the effective charge of the polyion, and thus permits the charged polymer chains to coil up. Divalent anions are even more effective in this regard than chloride ion. The dotted line in Fig. 2 shows the changes in (η_{sp}/c) which occur on neutralization with H_2SO_4. The maximum reduced viscosity achieved with H_2SO_4 is only about $^1/_3$ that attained with HCl, and the maximum is shifted to a lower degree of neutralization. On the other hand, the curve for trichloroacetic acid is virtually identical with that for HCl.

On the alkaline side, considerable difficulty was encountered, because of the tendency of the solutions to absorb CO_2 from the atmosphere. Unless extreme precautions were taken, the pH would drift downward, and the solution viscosities would also drift. Some viscosity studies were therefore carried out in dilute buffer solutions. This led to stable and reproducible viscosity values; but it must be remembered that even dilute buffers have a pronounced influence on the configuration of the polymer chains in the anionic or cationic state. The magnitude of this swamping effect depends upon the nature of the buffer—specifically, upon the valences of the ions.

Viscosity data in the vicinity of the isoelectric point are shown in Fig. 3. The isoelectric point, as indicated by the viscosity minimum, occurs at pH 8.0. At the isoelectric point, addition of small amounts of NaCl results in a very small viscosity *increase*. (The reduced viscosity of copolymer E, at 0.1 g./100 ml. concentration in a $M/400$ disodium phosphate buffer, changed from 1.15 to 1.20, 1.23 and 1.27 by making the solution $N/220$, $N/120$ and $N/70$ in NaCl.)

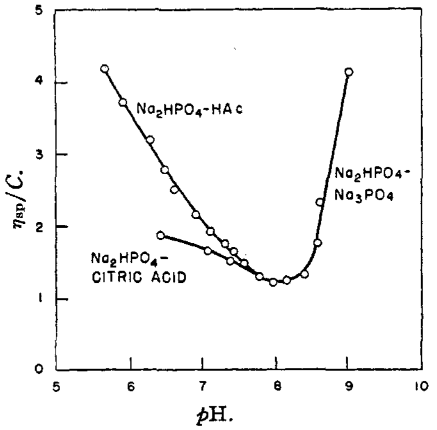


Fig. 3.—Reduced viscosity of copolymer E in the vicinity of the isoelectric point.

The electrophoretic mobility of copolymer E was studied at various pH's, in buffer solutions having an ionic strength of 0.057. The results are shown in Fig. 4. The isoelectric point, as indicated by reversal of mobility, occurs at pH 8.0 to 8.1, in good agreement with the values estimated from titration and viscosity data.

---

(7) S. P. L. Soerensen, *Compt. rend. trav. lab. Carlsberg*, **12**, 68 (1917).

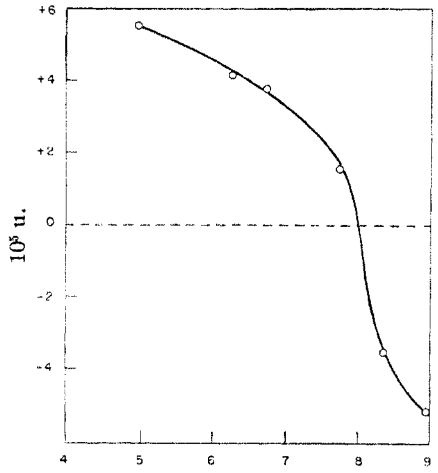
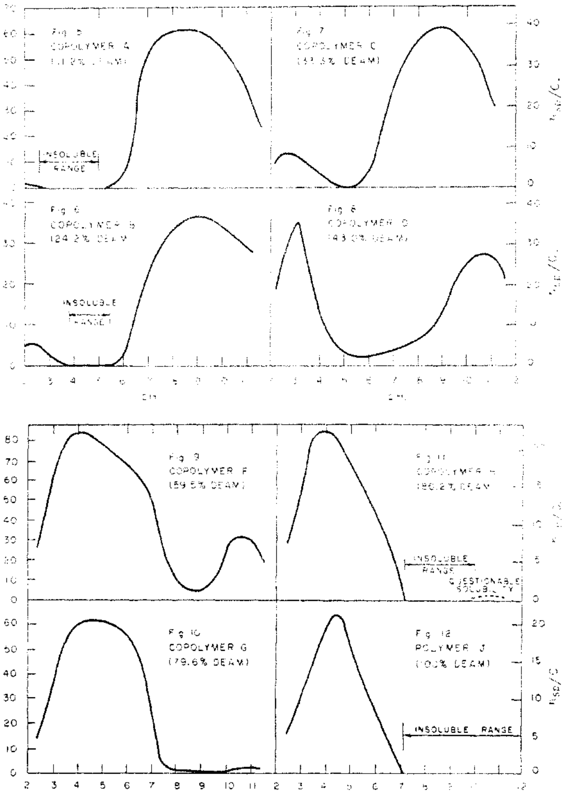


Fig. 4.—Electrophoretic mobility of copolymer E, as a function of *p*H.

Reduced viscosities *vs.* *p*H for copolymers A, B, C, D, F, G, H and J are shown in Figs. 5 to 12. Copolymer A (11.2% DEAM) and copolymer B (24.2% DEAM) exhibited insoluble ranges on the acid side. Likewise, copolymer H (86.2% DEAM) and copolymer J (100% DEAM) were insoluble on the alkaline side. Copolymers C, D, F and G (ranging from 33.3 to 76.7% DEAM) were soluble over the entire *p*H range covered. Increasing the amine/acid ratio raised the height of the viscosity maximum on the acid side, relative to the maximum on the alkaline side. (The absolute values of the viscosities exhibited by different copolymers are not strictly comparable, because of molecular weight differences and also because copolymers A, B, D and H were prepared as hydrochlorides).



Figs. 5–12.—Reduced viscosities *vs.* *p*H, for copolymers, A, B, C, D, F, G, H and J.

The location of the isoelectric point (viscosity minimum), and also of the acid and alkaline viscosity maxima, shifted toward higher *p*H values as the amine/acid ratio was increased. This is shown in Fig. 13. All *p*H values on the alkaline side are subject to some error, since the data in Figs. 5–12 were obtained with unbuffered solutions. The accurately determined isoelectric point of copolymer E falls well above the curve plotted in Fig. 13. However, the expected trend of the isoelectric point to higher *p*H values with increasing amine/acid ratio is beyond question.

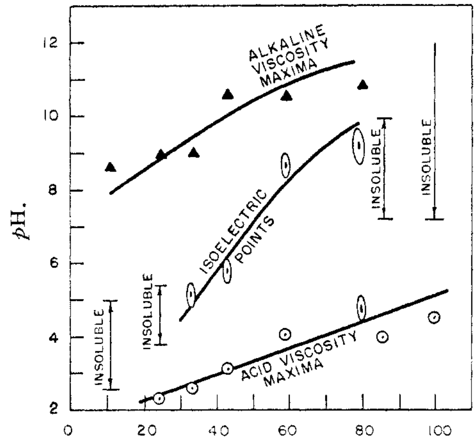


Fig. 13.—Effect of copolymer composition upon isoelectric point and upon acid and alkaline viscosity maxima.

The limits of the insolubility ranges are less sharply defined than Fig. 13 indicates. Intervening between indisputable solubility and formation of a definite aggregated precipitate, there often lies a *p*H range which is difficult to classify. Particularly since the solutions studied here were of quite low resin concentration (0.1 g./100 ml.), it was sometimes difficult to establish whether a given system should be considered as a true solution or as a colloidal suspension. This was especially true in the case of copolymer H at *p*H values above 10. Other experimental methods, such as light scattering, ultracentrifugal analysis, etc., must be employed if the nature of these solutions is to be definitely established.

Experimental

N,N-Diethylaminoethyl methacrylate (DEAM) was prepared by ester interchange of methyl methacrylate and diethylaminoethanol (Sharples). 250 g. of methyl methacrylate, 90 g. of diethylaminoethanol, 10 g. of toluenesulfonic acid and 10 g. of *t*-butylcatechol were refluxed in a nitrogen atmosphere under an efficient fractionation column packed with copper gauze. The column was heated so as to allow the azeotrope of methanol and methyl methacrylate (b.p. 54°) to distil over as fast as methanol was formed. After 24 hours the charge was fractionated under vacuum. Diethylaminoethyl methacrylate distilled at 80° at 10 mm., yield 50%. Methacrylic acid was purified by the method previously described.[5]

Copolymer E was prepared by solution polymerization, at 50% by volume in methanol, of an equimolar mixture of the two monomers. Azo-bis-isobutyronitrile (0.05%) was used as catalyst; the polymerization temperature was 70°. After 80 minutes, the viscous polymer solution was diluted with methanol, cooled and precipitated into an excess of acetone. The resin was washed with methyl ethyl ketone, and purified by twice redissolving in a 90–10 methanol–water mixture, precipitating in acetone, and hardening the precipitate by washing with methyl ethyl ketone. The polymer was finally vacuum dried. Conversion to polymer was 11%.

Copolymers C, G and F were prepared by solution polymerization in 50% aqueous methanol, using potassium persulfate as catalyst. Copolymers A, B, D and H were prepared by polymerization in dilute aqueous HCl solution (*p*H 1.2), using potassium persulfate as catalyst. Conversions were not permitted to exceed 25%. These copolymers were purified in essentially the same manner as copolymer E, minor variations being required because of solubility differences. Copolymer composition was determined by Kjeldahl analysis for nitrogen. Copolymers A, B, D and H were isolated as the hydrochlorides.

The viscosity data of Figs. 2 and 3 were determined in a dilution viscometer of the type previously described.[5] These curves were obtained at constant resin concentration; successive dilutions were made with a solution having the same resin concentration as that in the viscometer, but differing in the concentration of HCl, NaCl, buffer or other component undergoing variation. In the vicinity of the isoelectric point, solutions exhibited a very pronounced foaming tendency, which could be completely eliminated by addition of traces of 2-ethylhexanol. Another surface phenomenon, which affects the viscosity results to some extent, is a small amount of adsorption of the resin on glass surfaces.

The viscosity data of Figs. 5–12 were obtained in a similar dilution viscometer. Dilution was made with concentrated acid or alkali solutions; hence the resin concentration changed slightly during each dilution experiment. This was corrected for. Acid and base additions were run separately, in order to avoid the introduction of neutral electrolyte. Small concentrations of neutral salt were present, of course, in the cases of copolymers A, B, D and H, which had been isolated as the hydrochlorides. It would have been preferable to have measured the *p*H of the solutions inside the viscometers at the time of the viscosity measurement. Because this was difficult to arrange, parallel neutralizations were run outside the viscometers for *p*H determination. Since no buffers were used in this series of experiments, extreme care had to be taken to avoid absorption of CO_2, which would have resulted in sizable *p*H and viscosity drifts. All air taken into the viscometers was drawn through a Caroxite CO_2 absorption bulb.

Electrophoresis data were obtained with a Tiselius apparatus (Perkin-Elmer Company). The acetate–diethyl barbiturate buffer-system recommended by Michaelis[8] was used, since it covers a wide range of *p*H without introducing multivalent ions. Resin solutions containing 0.6 g./100 ml. were prepared in the buffers, and were dialyzed for 4 days against large volumes of buffers with an ionic strength of 0.057. Cell currents were 4.0–6.2 milliamps. at 6.3–7.9 volts/cm. Both ascending and descending boundaries were photographed and the mobility u (cm.^{2}/volt sec.) was calculated from their average displacements.

[8] L. Michaelis, *Biochem. Z.*, **234**, 139 (1931).

MIDLAND, MICHIGAN RECEIVED JULY 27, 1951

[CONTRIBUTION FROM THE COAL RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

The Nature of Oxygen in Coal: Preparation and Properties of Phthalan[1]

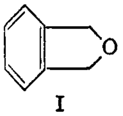
BY JACOB ENTEL, CLARENCE H. RUOF AND H. C. HOWARD

Phthalan has been produced in yields of 89% by dehydration of phthalyl alcohol over alumina at 300°. It readily absorbs oxygen from the atmosphere to form a crystalline peroxide, $C_{16}H_{14}O_4$; reacts with stannic chloride to form a crystalline adduct containing two molecules of the ether for each molecule of the tin salt; and readily adds hydrogen over Raney nickel catalyst at 150° to form hexahydrophthalan. It has been subjected to hydrogenolysis over copper–chromium oxide catalyst at 250, 300 and 350° and the products determined quantitatively by infrared and ultraviolet spectra and other physical properties; 2-methylcyclohexanemethanol and *o*-methylbenzyl alcohol were synthesized for comparison purposes. The similarity of the properties of phthalan to those of coal and its degradation products suggest that a part of the oxygen in coal may occur in phthalan type structures.

The controlled oxidation of suspensions of bituminous coals in aqueous alkali converts about 50% of the carbon to a mixture of water-soluble polycarboxylic acids. In addition to the benzenecarboxylic acids which have been definitely identified, there are present acids in which the nuclei are larger than the benzene ring and in which part of the oxygen is in non-determinable groups. Oxygen-rich fractions of the hydrogenolysis products of the esters of the acids have many chemical and physical properties characteristic of the cyclic ether structures, benzofuran and dihydrobenzofuran, but possess a few properties inconsistent therewith, which suggests the isomeric structure, phthalan.[2] The present work was undertaken to provide information necessary for definite characterization of phthalans and to test their amenability to hydrogenolysis. Such knowledge has hitherto been unavailable.

Discussion

Phthalan (I) has been prepared previously[3,4] in poor yield by heating *o*-xylylene bromide with potassium hydroxide.



I

In the present work phthalan has been prepared in 89% yields by the dehydration of phthalyl alcohol over alumina at 300° in analogy to the formation of methyltetrahydrofuran from 1,4-pentanediol.[5] Attempts to dehydrate phthalyl alcohol at 145° (3 mm.) by distillation or by refluxing with sirupy phosphoric acid yielded unchanged phthalyl alcohol and a red resin, respectively.

The phthalyl alcohol was prepared in 94% yield

---

[1] Presented before the Fuel, Gas and Petroleum Chemistry Section of the XIIth International Congress of Pure and Applied Chemistry, Sept., 1951, New York, N. Y.

[2] C. H. Ruof, T. R. Savich and H. C. Howard, THIS JOURNAL, **73**, 3873 (1951).

[3] R. Willstätter and H. Veraguth, *Ber.*, **40**, 965 (1907).

[4] For a discussion of phthalan and its homologs, *cf.* R. C. Elderfield, "Heterocyclic Compounds," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1951, pp. 83–91.

[5] E. Beati and G. Mattei, *Ann. chim. applicata*, **30**, 21 (1940).