[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

# A New Synthetic Polyampholyte—Poly-N-ethyleneglycine. Synthesis, Potentiometric Titration, Viscosity and Electrophoretic Mobility[1]

BY HARRY P. GREGOR, DANIEL H. GOLD AND GUENTHER K. HOESCHELE

RECEIVED APRIL 29, 1955

The preparation and characterization of poly-N-ethyleneglycine is described. This polyampholyte is highly polar, as evidenced by its high solubility in aqueous salt solutions over the entire *p*H range, including the region of the isoelectric point. Three characterization procedures, namely, titration, viscosity and electrophoretic mobility, locate the isoelectric point in the range *p*H 2.7–2.9.

## Introduction

The preparation and properties of several synthetic polymeric ampholytes have been described; some of the first work in this field was reported by Alfrey, Fuoss, *et al.*,[2–4] and by Wagner and Long.[5] Schloegl and Fabitschowitz[6] recently reported the synthesis of polyphenylalanine. Most of these substances were prepared by the copolymerization of a basic and an acidic monomer, and were usually of fairly high base molecular weight. As a result, these polyampholytes are often insoluble in the region of the isoelectric point.

This communication reports on the preparation and preliminary characterization of a new polyampholyte of relatively low base molecular weight (101) which is essentially polymeric glycine.

## Experimental

**Synthesis.**—The preparation of polymers similar to polymeric glycine was described by Bersworth[7] who treated ethylenediamine diacetate with ethylene chloride to prepare triethylenetetramine tetraacetic acid; higher homologs could presumably be prepared by this procedure, although probably not of high molecular weight. Another patent by Bersworth describes similar compounds.[8]

A method for preparing substituted α-amino acids was also described by Bersworth.[9] A primary or secondary amino group was carboxymethylated by treatment with formaldehyde and alkali cyanides in the presence of alkali; N-substituted glycines were obtained with nearly quantitative yields. This latter procedure was applied by us to a polymeric amine, polyethyleneimine. However, these polymers are usually highly branched (about 40%) and only the secondary amino groups in the chain are available for carboxymethylation. Further, the product dissolved only partially in alkaline solution, indicating that cross-linking with formaldehyde or with methylol groups had occurred. These polymers are of interest as ampholyte resins.

Poly-N-ethyleneglycine (PEG) was prepared by the polymerization of the methyl ester of N-ethyleneglycine. First, ethyleneimine was prepared after a modification of Wenker's method as described by Leighton, Perkins and Renquist.[10] The preparation of the methyl ester of N-ethyleneglycine as reported by Bestian[11] was followed. To a mixture of 33.8 g. of ethyleneimine and 160 g. of triethylamine (as solvent) was added 57 g. of methyl α-chloroacetate under stirring and cooling at 5–10°. After 15 minutes precipitation of triethylamine hydrochloride started. The reaction was completed after 16 hours (with continued stirring) at 5°. The filtered solution was evaporated *in vacuo* (100 mm.) and the residue vacuum distilled at 20 mm. through a short column. Redistillation gave a water-clear liquid, b.p. 67–69° (20 mm.); yield 46 g. (65% of theoretical).

The conditions for the polymerization of N-substituted ethyleneimine compounds as esters of N-ethyleneglycine are reported by Bestian.[12] In the procedure adopted, 40 g. of the methyl ester of N-ethyleneglycine was stirred with 0.2 g. of dibutyl sulfate at room temperature. Polymerization occurred after a few minutes with a constant evolution of heat. The temperature was maintained at 50–60° for 30 minutes, whereupon an additional 0.2 g. of dibutyl sulfate was added dropwise with vigorous stirring to the viscous oil. After 4 hours a highly viscous, nearly colorless oil was formed which was readily soluble in water.

The polymeric ester was saponified by dissolving 33 g. of the polymer mixture in 150 ml. of 2 *N* sodium hydroxide. Saponification was presumably complete within a few minutes as evidenced by the cessation of a strong evolution of heat. The cooled solution was passed through a column of a carboxyl cation-exchange resin in the acid state (Amberlite IRC 50); the *p*H was reduced to about 3.4. The column was rinsed with distilled water as long as a portion of the eluate gave a strong blue color with dilute copper(II) acetate solution, which indicated the presence of the polymer.

The combined solutions were concentrated at 50° *in vacuo* to 50 ml. and 200 ml. of acetone added. PEG precipitated as a yellowish, resinous mass. The liquid was decanted and the residue was dried in a vacuum desiccator to give a brittle, porous solid. The yield was 23.2 g. (80% theoretical on basis of monomer).

*Anal.* Calcd. for $C_4H_7O_2N$: C, 47.52; H, 6.98; N, 13.82. Found: C, 48.32; H, 7.8; N, 12.69.

The high percentage of carbon and the low percentage of nitrogen found probably result from the use of a dialkyl sulfate as a catalyst, because it is supposed to enter into the chain initiation and termination steps.

The polymer as prepared in this manner is free of salts and low molecular weight contaminants. A qualitative test for sulfur and chlorine by sodium fusion[13] gave negative results; a benzidine test for sulfate also gave negative results. Also, the polymer was dialyzed through cellophane tubing against pure water. Part of the polymer dialyzed through the membrane slowly; the *p*H of the polymer solution changed but slightly, the final value being 3.48 for a 0.01 *M* (base moles) solution. When base was added to the polymer solution followed by dialysis against pure water, the *p*H dropped sharply toward the former value. Also, the titration curves of undialyzed and dialyzed polymer were the same.

**Titration.**—The titration of PEG as purified by the ion-exchange procedure without subsequent dialysis was carried out as follows: Identical 40-ml. solutions of 0.01 *M* (base moles) PEG were titrated by adding acid to one solution,

---

[1] A portion of this work is abstracted from the Dissertation of Daniel H. Gold, to be submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry, Polytechnic Institute of Brooklyn.

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

[3] T. Alfrey, Jr., and H. M. Morawetz, *ibid.*, **74**, 436 (1952).

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

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

[6] K. Schloegl and H. Fabitschowitz, *Monatsh. Chem.*, **85**, 1223 (1954).

[7] F. C. Bersworth, U. S. Patent 2,564,092 (August 14, 1951).

[8] F. C. Bersworth, Brit. Patent 723,317.

[9] F. C. Bersworth, *et al.*, *J. Org. Chem.*, **14**, 355 (1949); *ibid.*, **15**, 46 (1950); *ibid.*, **15**, 255 (1950).

[10] P. A. Leighton, W. A. Perkins and M. L. Renquist, THIS JOURNAL, **69**, 1540 (1947).

[11] H. Bestian, *Ann.*, **566**, 233 (1950).

[12] H. Bestian, U. S. Patent 2,626,931 (Jan. 27, 1953).

[13] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

base to another, and the two titration curves joined. Curves were obtained in the absence of neutral salt.

Titrations were performed at 25.0 ± 0.1° in a jacketed cell kept $CO_2$ free during the titration by passing nitrogen over the solution in the cell. If the gas was passed through the solution foaming occurred with a shift in *p*H. A Beckman Model G *p*H meter utilizing a glass electrode with a sleeve-type saturated calomel electrode was used; the salt leak was found to be less than $10^{-3}$ *M* under the conditions employed. The solutions were stirred with a glass-encased magnetic stirring bar; stirring was stopped during a *p*H reading. The data are presented in Fig. 1.

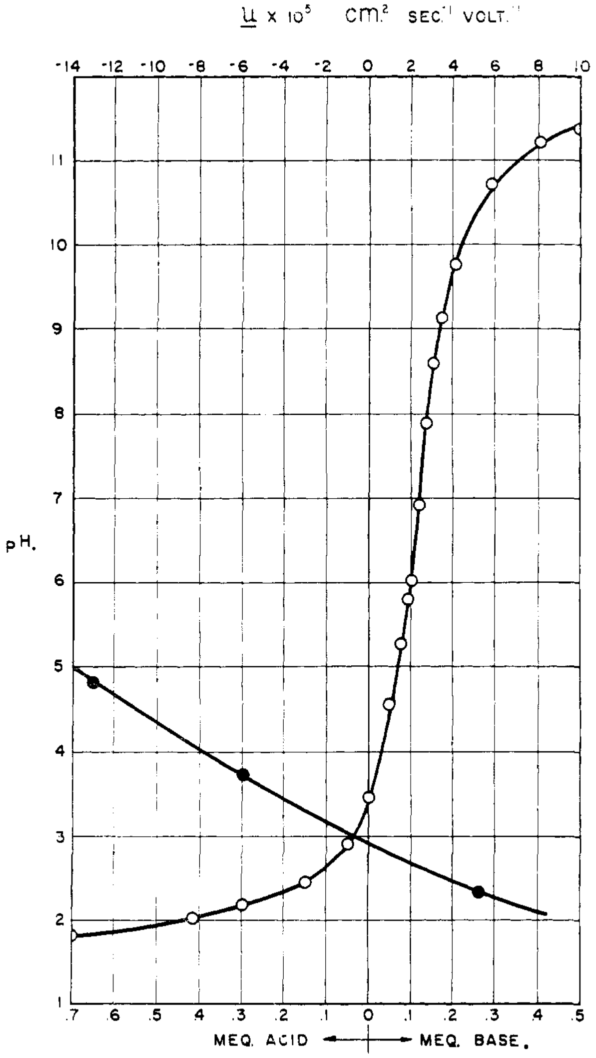


Fig. 1.—Titration of 0.4 mmole of 0.01 *M* PEG with sodium hydroxide and with nitric acid (○), and the electrophoretic mobility of PEG in acetate buffers (●).

**Viscometric Behavior.**—The viscosity minimum of PEG solutions of two different concentrations (0.01 and 0.05 *M* (base moles)) as determined with a Ubbelohede viscometer[14] is shown in Fig. 2. This viscometer permits dilutions to be effected directly in the bulb without affecting the pressure gradient. The water-flow time was such that kinetic energy corrections were negligible.[15] Viscosity measurements were taken at 24.95 ± 0.03°. The *p*H was measured as before.

**Electrophoretic Mobility.**—The electrophoretic mobility of PEG (Fig. 1) was determined using an Aminco portable electrophoresis apparatus with a double channel optical cell.

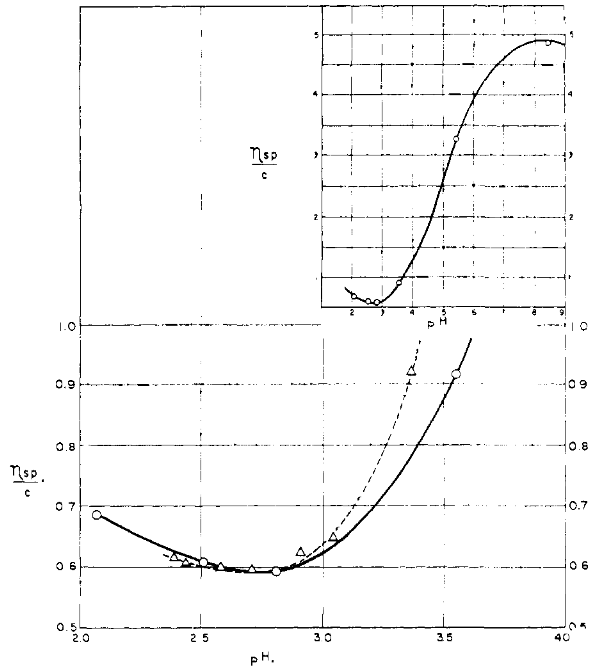


Fig. 2.—Reduced specific viscosity of 0.01 *M* PEG (○) and 0.05 *M* PEG (△) as a function of *p*H.

Descending and ascending boundaries were recorded by the Svensson crossed slit schlieren method on Kodak Ortho Process Contrast film at from 25–39° angles. The horizontal magnification was 1.95 ×. The solution temperature was maintained at 1.5°.

The mobility of 0.1–0.2 *M* (base moles) PEG was measured in acetate buffers of 0.04–0.06 ionic strength and in 1 *M* acetic acid of ionic strength 0.004. The potential gradients were 4–11 volts/cm., and the distance of migration was 1–3 cm. Both ascending and descending boundaries were fairly well defined, and the mobility *u* (cm.²/volt sec.) was calculated from average displacements.

## Discussion

This polyampholyte has an estimated molecular weight in the range 5,000–15,000 as indicated by diffusivity through membranes and moving boundary experiments. It is soluble over the *p*H range 1 to 12 at polymer concentrations as high as 1 *M* (base moles); dilute polymer solutions are not salted out by ordinary 1-1 electrolytes at concentrations as high as 1 *M*. The high solubility is the result of its high charge density, since the base molecular weight is 101. This polymer is highly soluble even at the isoelectric point, in contrast to many other polyampholytes. Higher molecular weight fractions are being prepared and will be reported on later.

The isoelectric point of the polymer as determined by the viscosity minimum is 2.7–2.8, and from the electrophoretic mobility is 2.9; the agreement is reasonable. The isoionic point or the *p*H of the pure ampholyte in water is 3.45. Ordinarily, isoionic and isoelectric points are nearly the same; however, in this case the isoionic *p*H is so low as to make for a considerable difference in the two values. This point has been noted by Edsall and co-workers.[16] The slower rise of the specific reduced viscosity on the acid side of the isoelectric point is a

---

(14) L. Ubbelohede, *Ind. Eng. Chem.*, **9**, 84 (1937).

(15) M. R. Cannon and M. R. Fenske, *Ind. Eng. Chem.*, *Anal. Ed.*, **10**, 297 (1938).

(16) J. T. Edsall, H. Edelhoch, R. Lontie and P. R. Morrison, This Journal, **72**, 4641 (1950).

consequence of the relatively high ionization constant of the carboxyl groups; the base side behaves normally as shown in the inset of Fig. 2.

A series of further papers on the potentiometric behavior of this polymer, ion-binding by the polymer and other studies is in preparation.

The authors wish to thank Professor K. G. Stern who performed the electrophoresis experiments.

This investigation was supported in part by the Office of Naval Research and by a research grant, RG 2934(C3) from the Division of Research Grants of the National Institutes of Health, Public Health Service.

BROOKLYN, N. Y.

---

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF NEW YORK UNIVERSITY]

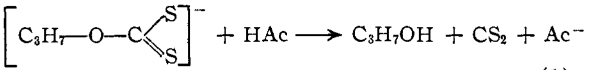
# Kinetics of the Decomposition of *n*-Propylxanthic Acid[1]

BY MELVIN L. SCHOCHET AND CECIL V. KING

RECEIVED APRIL 12, 1955

The rate of decomposition of *n*-propylxanthic acid has been determined at five temperatures from 0 to 60°, in dilute acetic acid–sodium acetate buffers containing up to 30% 1,4-dioxane to vary the dielectric constant. Electrostatic effects on the observed rates are small, because primary effects (on the kinetics of the rate-controlling process) and secondary effects (on the buffer equilibrium) are about equal and opposite in sign. Activation energies and entropies are discussed.

The decomposition reaction of *n*-propyl xanthate in acetic acid buffers may be written



(1)

While the xanthic acids are not quite fully ionized,[2] essentially only the ions are present in these buffers. Equation 1 does not represent the mechanism, since the rate depends on the buffer ratio, not on the acid component alone.[3] There is no general acid or base catalysis which can be detected in dilute aqueous solution. In previous studies of ethylxanthic acid[3,4] both salt and dielectric constant effects were found to be small, if the low dielectric constant region of ion pair formation is avoided.

The present work was undertaken partly in order to compare another xanthic acid with methyl-[2] and ethylxanthic[2–4] acids, with respect to absolute decomposition rates and general behavior, partly to extend the temperature range of such measurements. No appreciable change in activation energy was found over the 60° range explored.

## Experimental

Potassium *n*-propyl xanthate was prepared by mixing a solution of potassium hydroxide in the alcohol with carbon disulfide in ethyl ether. The salt was washed with ether and recrystallized from acetone with addition of ether. Its purity was confirmed by titrating weighed samples with standard iodine solution.

Acetic acid buffers, and pure dioxane, were prepared as described before.[4] Two solutions were made up and allowed to come to temperature in the thermostat: (a) the buffer, double strength, and (b) the xanthate in water or water–dioxane. Then 250-ml. portions of both were poured simultaneously into a larger flask mounted in the thermostat. In each run, seven to ten samples were withdrawn over a two- to five-hour period, quenched with sodium bicarbonate, and the remaining xanthate titrated with standard iodine solution.[2] The reaction was usually 75% complete in the time allowed.

Rate constants were calculated by means of the equation[3]

$$kK_0 = \frac{2.3}{(b-a)t}\left[(a+c)\log\frac{a}{a-x} - (b+c)\log\frac{b}{b-x}\right] \tag{2}$$

where *a*, *b*, *c*, are initial concentrations of xanthate, acetic acid and acetate, respectively, and $K_0$ is the thermodynamic dissociation constant of acetic acid.

Two to five runs were made at each concentration and temperature. The initial xanthate concentration was usually 0.012 to 0.015 *M*. The sodium acetate was made 0.01 to 0.04 *M*, and acetic acid–acetate ratios of 0.5 to 8 served to keep the rate in a convenient range. Rate constants showed no trend with extent of reaction; the average deviation in single runs and of several runs was usually less than 3.5%. Runs with added sodium chloride showed the salt effect to be small, as expected.

The dioxane mixtures were made by volume at room temperature, the weight concentrations and mole fractions calculated from the densities. The temperatures were maintained to ±0.02°, 0° referring to an ice-bath temperature of about +0.015°.

## Experimental Results

The rate constants obtained, without regard to $K_0$ for acetic acid, are summarized in logarithmic form in Table I.

TABLE I

LOG OF RATE CONSTANTS, $kK_0$, MIN.$^{-1}$

| Wt. % dioxane → | 0 | 10.2 | 20.2 | 30.1 | Eq. 3 |
|---|---|---|---|---|---|
| 0° | −3.44 | −3.47 | −3.40 | −3.50 | −3.47 |
| 15° | −2.81 | −2.78 | −2.75 | −2.76 | −2.76 |
| 30° | −2.14 | −2.14 | −2.12 | −2.10 | −2.12 |
| 45° | −1.57 | −1.48 | −1.43 | −1.44 | −1.52 |
| 60° | −0.99 | −1.11 | −1.05 | −0.99 | −1.00 |

Equation 3 is the least squares relation for the averages at each temperature *vs.* $1/T$

$$\log kK_0 = 10.24 - 17140/2.3RT \tag{3}$$

This equation represents all the data with an average deviation of 0.033 log unit. The maximum deviation of 0.11 log unit represents 22% in the value of $kK_0$.

The rate constants found are remarkably similar to those for the decomposition of ethyl xanthic acid in similar buffers,[4] for example at 30° the average value for the ethyl compound was log $kK_0 = -2.19$.

## Discussion

While equation 3 represents the rate constants $kK_0$ within the apparent over-all experimental error in this range, it is unsatisfactory from a theoretical view-point. Since values of $K_0$ are available, the bimolecular constants *k* may be calculated.

---

[1] From a Ph.D. thesis submitted by Melvin L. Schochet to the Graduate Faculty of New York University in April, 1954.

[2] H. v. Halban and W. Hecht, *Z. Elektrochem.*, **24**, 65 (1918).

[3] C. V. King and E. Dublon, THIS JOURNAL, **54**, 2177 (1932).

[4] A. Chatenever and C. V. King, *ibid.*, **71**, 3587 (1949).