[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, PLASTICS DIVISION, MONSANTO CHEMICAL CO.]

A Study of Polymethacrylic Acid by the Light Scattering and Osmometric Methods

BY Q. A. TREMENTOZZI

RECEIVED JUNE 2, 1954

Four sharp fractions of polymethacrylic acid were examined by light scattering and osmotic pressure measurements as a function of concentration of polyelectrolyte and simple, supporting electrolyte. An appreciable Donnan membrane effect is demonstrated for the case of pure ethanol as the solvent. In the presence of 0.125–0.250 *M* LiBr, the Donnan effect is shown to be eliminated. Use of pure ethanol instead of alcoholic LiBr as the solvent has little if any effect on the molecular weight determined from angular light scattering measurements. The molecular weights by the two methods are found to be in excellent agreement over a tenfold range. The second virial coefficients and μ values are found to be in accord, also.

Introduction

In recent years numerous investigations have been carried out on various solution properties of linear polyelectrolytes in the presence and absence of supporting, simple electrolytes. Much valuable knowledge has been acquired with respect to the fundamental behavior of charged polymers by means of conductance and transference,[1–4] potentiometric titration,[5–6] viscometric,[7–9] osmometric[10–12] and light scattering[13–15] studies of linear polyelectrolytes. However, unambiguous evidence of the reliability of molecular weights of charged polymers has not been presented, although an indirect proof has been established.[13]

With respect to neutral polymers, the approach to the problem of proving the accuracy of molecular weights obtained has been to compare the molecular weights of sharp polymer fractions by two or more of the direct methods. The agreement in molecular weights which has been obtained through these comparative studies involving direct methods[16–18] has been of great value not only in establishing the reliability of the different methods but, also, in advancing the theory of polymer kinetics and the thermodynamics of dilute polymer solutions.

It was the purpose of this investigation to contribute to the present knowledge of solution properties of polyelectrolytes by comparing the results of light scattering and osmotic pressure studies of fractions of polymethacrylic acid.

Experimental

Polymerization of Methacrylic Acid.—Methacrylic acid purified by fractional distillation of glacial methacrylic acid at 32° was polymerized by the solvent–precipitation technique in which distilled reagent grade benzene was employed as the solvent for the monomer and precipitant for the polyacid. A typical charge contained 16% methacrylic acid and 84% benzene. Benzoyl peroxide was employed as a catalyst at a concentration of 0.02–0.2% (based on the monomer content). The solution of methacrylic acid in benzene was swept free of air before addition of the catalyst and maintained under oxygen-free nitrogen during polymerization. The system was stirred throughout polymerization and the total reaction time was four hours at a temperature of 73–76°. Conversion was 49 and 54% for the two polyacids prepared.

The polyacid was steeped in benzene and filtered repeatedly to remove monomer. Vacuum drying at 65° for several days removed almost all of the remaining monomer.

Fractionation.—Prior to fractionation a sample of high and another of low molecular weight polymethacrylic acid (PMA) were freed of traces of monomer and catalyst by triple precipitation from methanol solutions employing ether as the precipitant. Fractionation was carried out essentially according to the method of Katchalsky and Eisenberg.[13] However, the homogeneity of the fractions was improved considerably by dissolving each fraction in 100 cc. of a mixture of methanol and ether of the same composition as that which had produced phase separation in the original fractionation followed by slow warming to 25° where phase separation occurred. The recovered fraction was subjected to the same treatment with a new mixture of methanol–ether and then recovered and dried in a vacuum oven at 65°. The low molecular weight polyacid was resolved into seven fractions representing 65% of the original sample weight. These fractions were designated series A. The high molecular weight polyacid was resolved into ten fractions constituting 75% of the original parent polymer. This was called series B.

Osmotic Pressures.—Measurements of the osmotic pressures of solutions of polymethacrylic acid fractions in ethanol and in alcoholic LiBr solution were made at 30.0 ± 0.005° in modified Fuoss–Mead osmometers. Gel-cellophene No. 600 membranes were employed in all the measurements. Equilibrium was attained in a period of eight to ten hours. It should be mentioned that these membranes were strictly semi-permeable for even the lowest molecular weight fraction for as long as 48 hours. The membrane dissymmetry correction was approximately 0.10 cm. and reproducible only to ±0.03 cm. Because of this, membrane dissymmetries were determined prior to the measurement of the osmotic pressure of each solution. For the lowest concentrations, the applied membrane correction was an average of two or three such determinations.

Light Scattering.—Angular scattering intensities of light were measured at approximately 25° C. by means of a Brice–Speiser light scattering photometer which had been calibrated by use of the Cornell standard polystyrene. A solution of 0.500 g. of standard polystyrene/100 cc. of toluene was found to have an excess scattering at 90° of 3.64×10^{-3} cm.$^{-1}$ for 4358 Å. mercury light. This compares favorably with the values reported in the literature.[19] The calibration of the photometer was checked further by means of several polystyrenes of known molecular weight.[20]

Alcoholic solutions of LiBr (0.125 *M*) were freed of larger foreign particles before use in the preparation of PMA solu-

---

[1] R. M. Fuoss and U. P. Strauss, *J. Polymer Sci.*, **3**, 246 (1948).

[2] J. R. Huizenga, P. F. Grieger and F. T. Wall, THIS JOURNAL, **72**, 2636 (1950).

[3] F. T. Wall, P. F. Grieger, J. R. Huizenga and R. H. Doremus, *J. Chem. Phys.*, **20**, 1206 (1952).

[4] F. T. Wall and R. H. Doremus, THIS JOURNAL, **76**, 1557 (1954).

[5] R. Arnold and J. Th. G. Overbeek, *Rec. trav. chim.*, **69**, 192 (1950).

[6] A. Katchalsky and J. Gillis, *ibid.*, **68**, 879 (1949).

[7] R. M. Fuoss and W. N. Maclay, *J. Polymer Sci.*, **6**, 305 (1951).

[8] R. M. Fuoss and U. P. Strauss, *Ann. N. Y. Acad. Sci.*, **51**, 836 (1949).

[9] H. Markowitz and G. E. Kimball, *J. Colloid Sci.*, **5**, 115 (1950).

[10] A. Dobry and F. Boyer-Kawenoki, *Makromol. Chem.*, **6**, 157 (1951).

[11] W. Kern, *ibid.*, **2**, 279 (1948).

[12] U. P. Strauss and R. M. Fuoss, *J. Polymer Sci.*, **4**, 457 (1949).

[13] A. Katchalsky and H. Eisenberg, *ibid.*, **6**, 145 (1951).

[14] A. Oth and P. Doty, *J. Phys. Chem.*, **56**, 43 (1952).

[15] F. T. Wall, J. W. Drenan, M. R. Hatfield and C. L. Painter, *J. Chem. Phys.*, **19**, 585 (1951).

[16] P. M. Doty, B. H. Zimm and H. Mark, *ibid.*, **12**, 144 (1944).

[17] R. S. Stein and P. Doty, THIS JOURNAL, **68**, 159 (1946).

[18] M. Wales, J. W. Williams, J. O. Thompson and R. H. Ewart, *J. Phys. Colloid Chem.*, **52**, 983 (1948).

[19] B. A. Brice, M. Halwer and R. Speiser, *J. Optical Soc.*, **40**, 768 (1950).

[20] Q. A. Trementozzi and R. Buchdahl, *J. Polymer Sci.*, **12**, 149 (1954).

tions by pressure filtration through No. 03 Selas porcelain candles. Final purification of solvent and polyacid solutions was accomplished by centrifugation at 25,000 g. for two hours. The solvent and the solution of the lowest molecular weight fraction were freed from most foreign particles by centrifugation at 50,000 g. for 90 minutes. Great care was employed in the removal of centrifuged solvent and polyacid solution. Carefully cleaned pipets, scattering cell and storage flask were rinsed several times with the appropriate centrifuged solvent or solution before transfers were made.

In order to minimize light scattering errors due to dust, etc., in the dilute concentration region, measurements were made first on the pure solvent medium. Known amounts of stock solution were then added to the scattering cell, mixed thoroughly and the light scattering data obtained until the desired concentration range had been covered. Refraction increments were measured in a Brice–Speiser differential refractometer at 25.0 ± 0.005°. The instrument was calibrated with concentrated NaCl solutions of known refractive indices[21] and with sucrose solutions. The refraction increment for solutions of polymethacrylic acid for 4358 Å. light was 0.154 for solutions in ethanol and in alcoholic LiBr.

Results and Discussions

Molecular Weights from Osmotic Pressures.—In the first attempt to determine the molecular weight by the osmometric method pure ethanol was employed as the solvent. The selection was based on its lower dielectric constant as compared to other known solvents for polymethacrylic acid. Consequently, ionization of polymethacrylic acid would be suppressed to a greater extent than in other pure solvents. With sufficient suppression of the dissociation of the polyacid, reliable molecular weights should be obtained, since the observed osmotic pressures would not include the contribution of the hydrogen ions. In Fig. 1 the reduced osmotic pressure, π/c, is plotted as a function of the concentration according to the basic equation

$$\pi/c = 1033RT/\bar{M}_n + Ac \qquad (1)$$

where π is the osmotic pressure in centimeters of solution, c is concentration of polyelectrolyte in g./1000 g. of solution, R is the gas constant, 0.0821 l. atm./°A., $\bar{M}_n$ is the number average molecular weight and A is a constant. It is apparent from curve 2 that PMA in pure ethanol constitutes a typical dissociating system. The osmotic pressure reflects not only the contribution of the polyelectrolyte but also that of the hydrogen ions originating from the dissociation of the polymethacrylic acid.[22]

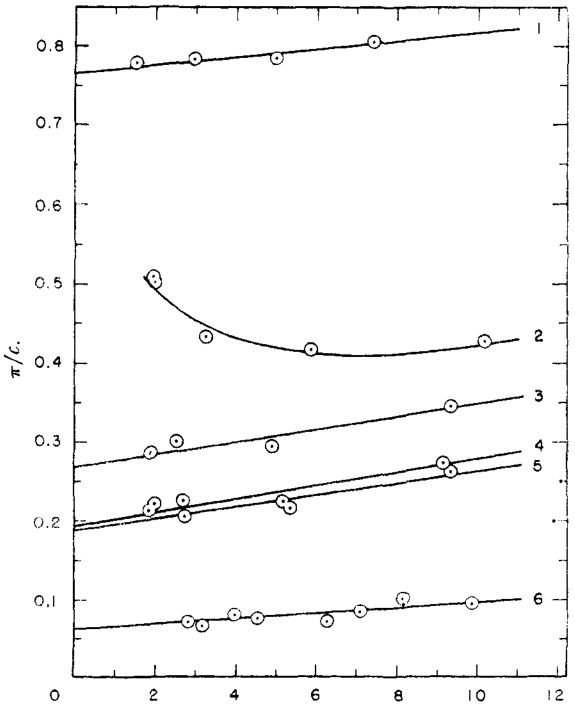

Fig. 1.—Reduced osmotic pressure curves of polymethacrylic acid fractions: 1, fraction 5A in 0.125 M LiBr in ethanol solution; 2, fraction 1A in pure ethanol; 3, fraction 2A in 0.125 M LiBr in ethanol solution; 4, fraction 1A in 0.125 M LiBr in ethanol solution; 5, fraction 1A in 0.250 M LiBr in ethanol solution; 6, fraction 6B in 0.125 M LiBr in ethanol solution.

A comparison of curve 2 with curves 4 and 5 clearly demonstrates the two cases of Donnan equilibria[23] involved. In the PMA–ethanol system the hydrogen ions resulting from the dissociation of the polymethacrylic acid are confined to the same side of the semi-permeable membrane as the non-diffusible polyion in order to preserve the electroneutrality of the system. The resulting osmotic pressure, therefore, is too high. In the presence of added LiBr (0.125 to 0.250 M), however, sufficient counter ions have been provided to suppress almost completely the contribution of the hydrogen ions to the osmotic pressure. The reduced osmotic pressure curve is then much like that of a typical neutral polymer in a moderately good solvent. Increasing the level of supporting simple electrolyte from 0.125 to 0.25 M appears to reduce the thermodynamic slope somewhat, but otherwise does not effect a significant change.

The number average molecular weights, the second virial coefficients, A_2, and the interaction constants, μ, are listed in Table I. A_2 is equal to A/RT where A has the same meaning as in equation 1, provided π, c and R are expressed in the proper units. The values of μ were calculated from the Flory–Huggins equations.[24–25]

Light Scattering Data and Weight Average Molecular Weight.—The reduced intensity of scattered light at 90° and the dissymetry from excess scattering intensities at 45 and 135° were measured as a function of concentration of the PMA solution. These data are plotted in Fig. 2 in a form consistent with the basic scattering equation of Debye.[26]

$$H(c/\tau)\ P(90) = 1/\bar{M}_w + 2Bc \qquad (2)$$

H = proportionality constant
c = g. polymethacrylic acid/cc. of soln.
τ = turbidity of the soln. minus that of the solvent
$\bar{M}_w$ = the wt. av. mol. wt.
B = the second virial coefficient
$P(90)$ = the correction factor for the turbidity due to internal interference of scattered light

---

[21] A. Kruis, *Z. physik. Chem.*, **B34**, 13 (1936).

[22] In an osmotic pressure study of polymethacrylic acid in methanol solution, this effect was not reported. See N. W. Wiederhorn and A. Brown, *J. Polymer Sci.*, **8**, 651 (1952). Due to the higher dielectric constant of methanol, as compared to ethanol, one would expect a greater Donnan effect.

[23] F. G. Donnan, *Trans. Faraday Soc.*, **31**, 80 (1935).

[24] P. J. Flory, *J. Chem. Phys.*, **9**, 660 (1941); **10**, 51 (1942).

[25] M. L. Huggins, *ibid.*, **9**, 440 (1941); *Ann. N. Y. Acad. Sci.*, **43**, 1 (1942).

[26] P. Debye, *J. Phys. Colloid Chem.*, **51**, 18 (1947).

TABLE I

Fraction	Solvent medium	$\bar{M}_n$	$\bar{M}_w$	$A_2 \times 10^4$	$B \times 10^4$	$\mu_{\text{o.p.}}$	$\mu_{\text{L.S.}}$
5A	0.125M LiBr in ethanol	34,000	42,000	4.9	5.2	0.456	0.455
2A	0.125M LiBr in ethanol	96,000	108,000	4.0	3.3	0.465	0.471
2A	Ethanol (pure)		101,000				
1A	0.125M LiBr in ethanol	133,000	151,000	4.3	2.8	0.463	0.476
1A	0.250*M* LiBr in ethanol	135,000		2.5		0.479	
6B	0.125*M* LiBr in ethanol	421,000	383,000	1.8	2.3	0.486	0.480

Av. $A_2 = 3.8 \times 10^{-4}$ cc. moles/g.^{2}; av. $B = 3.4 \times 10^{-4}$ cc. moles/g.^{2}

For random coils, the correction factor at any angle θ has the form[26]

$$P(\theta) = 2/x^2 \left[e^{-x} - (1 - x)\right] \qquad (3)$$

where

$$x = \kappa^2 s^2 R^2$$

The turbidity correction factors for the various measured dissymmetries were derived from the solution of equation 3 for 90°. The reciprocal specific turbidity plots of the various polyelectrolyte fractions in alcoholic LiBr solution are seen to be quite like those of a neutral polymer in a moderately good solvent. A comparison of curves 2 and 3 (of Fig. 2) reveals that the supporting simple electrolyte has little or no effect on the light scattering molecular weight, whereas in the osmometric method, the added simple electrolyte is indispensable in obtaining accurate molecular weights. For the case of pure ethanol as the solvent, the turbidity and the fluctuations in concentration of polyanions are independent of the simple ions to all practical purposes. It is reasonable to expect that the behavior of other polycarboxylic acids would be analogous in these solvents. It is to be anticipated, also, that this turbidimetric behavior of polymethacrylic acid and similar polyelectrolytes is not confined to ethanol and ethanol plus LiBr. The observed agreement should extend to all weak polyelectrolyte systems in which the solvent has a reasonably low dielectric constant.[27–28]

The excellent agreement in molecular weight between the light scattering and osmotic pressure method is shown in Table I. The agreement is within ±7% except for the lowest molecular weight fraction (5A). The larger deviation in this case is due in part to an unexpected dissymmetry correction of 11%. Despite improved solution clarification efforts, there was evidence of contamination by dust, etc. It is felt that with prolonged centrifugation a considerable improvement could be made. From an over-all viewpoint, however, it is clear that the light scattering and osmometric methods are in complete accord with respect to molecular weights, second virial coefficient and μ values.

The change of the second virial coefficient with the molecular weight is somewhat greater than that of a typical, uncharged polymer in a good or moderately good solvent, *e.g.*, polystyrene in toluene,[29,30] or methyl ethyl ketone.[30] The effect is somewhat inconsistent for the osmotic pressure series, due to the lack of high precision inherent in this method and the number of data points obtained. The more precise data obtained from light scattering reveals a steady increase in the value of the second virial coefficient with decreasing molecular weight consistent with theory[31,32] and similar to experimental results for neutral random coil polymers,[29,30] although of a greater magnitude for the molecular weight range studied. Whether the greater variability of A_2 of the system studied is characteristic of PMA, or due to differences in sharpness of fractions or molecular structural differences, cannot be answered until more precise data are available.

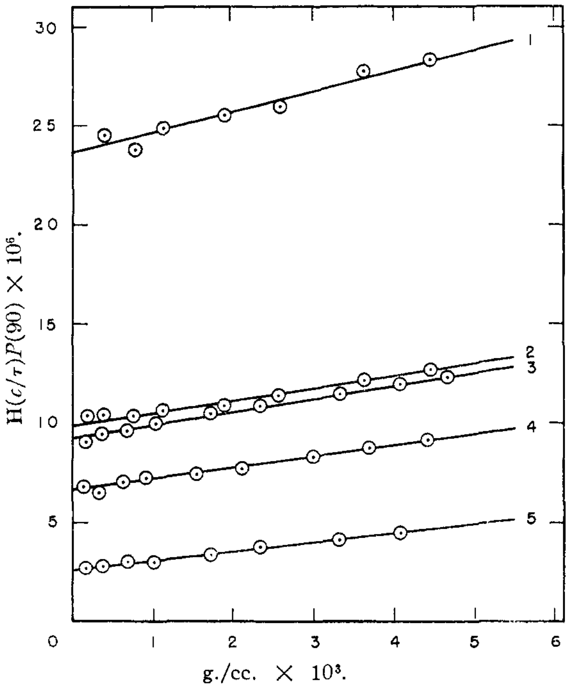

Fig. 2.—Reciprocal specific turbidity plots of polymethacrylic acid: 1, fraction 5A in 0.125 *M* LiBr in ethanol solution; 2, fraction 2A in pure ethanol; 3, fraction 2A in 0.125 *M* LiBr in ethanol solution; 4, fraction 1A in 0.125 *M* LiBr in ethanol solution; 5, fraction 6B in 0.125 *M* LiBr in ethanol solution.

Acknowledgment.—The writer is grateful to Mrs. Therese Laport who assisted with the fractionation and some of the light scattering measurements.

SPRINGFIELD, MASS.

---

(27) F. T. Wall, J. W. Drenan, M. R. Hatfield and C. L. Painter, *J. Chem. Phys.*, **19**, 585 (1951).

(28) Work now in progress substantiates this idea and will be published when the study of the effect of dielectric constant of the solvent (with and without added simple electrolytes) on the turbidimetric properties of polyelectrolytes has been completed.

(29) International Union of Pure and Applied Chemistry, *J Polymer Sci.*, **10**, 129 (1953).

(30) P. Outer, C. I. Carr and B. H. Zimm, *J. Chem. Phys.*, **18**, 830 (1950).

(31) P. J. Flory, *ibid.*, **13**, 453 (1945).

(32) B. Zimm, *ibid.*, **14**, 164 (1946).