Chain Characteristics of Poly(2-acrylamido-2-methylpropanesulfonate) Polymers. 1. Light-Scattering and Intrinsic-Viscosity Studies

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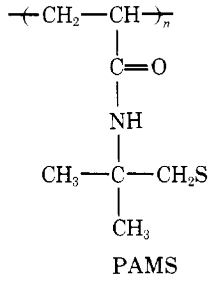
ABSTRACT: Dilute solution behavior of poly(2-acrylamido-2-methylpropanesulfonate) polymers has been investigated by light scattering and intrinsic viscosity. The acid (H–PAMS) and the sodium, cesium, and tetrabutylammonium salts (Na–PAMS, Cs–PAMS, and TBA–PAMS) are highly expanded in aqueous salt solutions and cannot be precipitated with added NaCl (>5 N). Similar measurements were also made for the TBA salt in isobutanol, acetone, and dichloroethane as well as in aqueous salt media. The constant value for $\langle s^2\rangle_z/\overline{N}_z$, where $\langle s^2\rangle_z$ and $\overline{N}_z$ are the z-average mean-square radius of gyration and the degree of polymerization, respectively, suggests that these polymers are coillike in dilute solutions. A linear relation was observed between the intrinsic viscosity and the reciprocal of the square root of ionic strength. The calculated Flory viscosity constants (Φ) are smaller for Na–PAMS in aqueous salt solutions than those for TBA–PAMS in organic media.

It has been generally assumed in previously published theoretical treatments of chain flexibility[1,2] that chain dimensions of a polymer in a theta condition are insensitive to the nature of the solvent or to the degree of ionization of the charged groups. Although this generalization has been found valid for most nonionic polymers in single nonpolar solvents,[1,3] exceptions have been found not only for some of these simple systems,[3–13] but also for copolymers[14,15] and polyelectrolytes.[16–23]

Only a limited number of results have been reported, however, for polyelectrolytes in different solvents. Differences in the unperturbed dimensions were found for poly(methacrylic acid) (PMAA)[16] and for a copolymer of methacrylic acid and methyl methacrylate[15] in mixed solvents. The earlier work of Flory and Osterheld[17] indicated that the unperturbed dimensions of poly(acrylic acid) (PAA) are identical in dioxane and in aqueous NaCl solutions, but calculations based on the more extensive data of Takahashi and Nagasawa[18] showed that fully ionized PAA has much larger unperturbed dimensions in aqueous NaBr solutions than does the un-ionized form in dioxane.[17] More recent data for a copolymer of acrylic acid and ethyl acrylate[22] reported from these laboratories also showed different unperturbed dimensions for the un-ionized form in organic media and the ionized form in aqueous NaCl solutions. In view of the recent review by Morawetz,[23] it would seem theoretically correct to expect changes in the unperturbed dimensions of polyelectrolytes with changes in the degree of ionization and the ionic strength of the media.

Sulfonic acid containing polymers represent a class of strong polyelectrolytes which typically have high degrees of ionization and extensive coil expansion in aqueous media. Although substantial thermodynamic and viscosity data in aqueous media have been reported for the salts of poly(vinylsulfonic acid)[24] and poly(styrenesulfonic acid),[25,26] very little is known about the effect of the nature of counterions and solvents on chain characteristics of these polymers. In the present work, we investigated solution behavior of a sulfonate-containing polymer, poly(2-acrylamido-2-methylpropanesulfonate) (PAMS). Solution properties were measured for this polymer with a variety of counterions (H$^+$, Na$^+$, Cs$^+$, and tetrabutylammonium (TBA$^+$)) in aqueous salt solutions. Studies in organic media were possible when this polymer was in the TBA salt form. In this paper, we report experimental results obtained from light-scattering and viscosity measurements. Comparison of the unperturbed dimensions and the persistence lengths of these polymers in various media, using the wormlike chain model, are presented in a subsequent publication (part 2).



PAMS

Experimental Section

Polymer Preparation and Fractionation. Poly(2-acrylamido-2-methylpropanesulfonic acid) (H–PAMS) was prepared by R. C. Sutton of these Laboratories. The monomer (Lubrizol Chemicals Co.) was polymerized in water at 60 °C under a nitrogen atmosphere for 16 h using 0.5% azobis(isobutyronitrile) as the catalyst. The whole polymer (H–PAMS) was fractionated by a stepwise precipitational-fractionation technique using ethanol as the solvent and *n*-heptane as the precipitant. The fractions were recovered by freeze drying from water and were oven dried exhaustively under vacuum at 40 °C for several days. Measurements of the molecular weight distribution of the fractions were made by aqueous exclusion chromatography[27] (AEC) on five stainless steel columns packed with porous glass of nominal pore sizes of 1250, 720, 500, 200, and 75 Å. The chromatographic solvent was 0.2 M Na_2SO_4 with the polymer eluting at a flow rate of 0.5 mL/min.

The various salts of H–PAMS, i.e., Na–PAMS, Cs–PAMS, and TBA–PAMS, were obtained by neutralization of the various fractions of H–PAMS in aqueous solutions with NaOH, CsOH, and TBA–OH, respectively. The neutralized solutions were dialyzed against water overnight and the solids were collected by freeze drying.

Light-Scattering and Viscosity Measurements. Light-scattering measurements were made for Na–PAMS fractions in aqueous NaCl solutions at ionic strengths ranging from 0.01 to 5 N. Measurements were made on a Sofica photometer using unpolarized light at 436 nm. Absolute scattering intensities were determined using benzene as the primary standard and Cornell Styron polystyrene in toluene as a working standard. All solutions were dialyzed for 2 to 4 days prior to light-scattering measurements. The d*n*/d*c* values were calculated from the measured difference in refractive indices of the dialyzed polymer solution and the dialyzate salt solution, divided by the polymer concentration *c*. The average values of d*n*/d*c* measured on the various fractions at a given ionic strength were used in determining weight-average molecular weights ($\overline{M}_w$), second virial coefficients (A_2), and z-average radii of gyration ($\langle s^2\rangle_z^{1/2}$), using the Zimm method of data treatment.[28] Experimental uncertainties in the determinations of molecular parameters were estimated to be d*n*/d*c*, ±2%; $\overline{M}_w$, ±5%; $\langle s^2\rangle_z^{1/2}$, ±10%; A_2, ±10%. Curvature in the Zimm plots did not allow the determination of $\langle s^2\rangle_z^{1/2}$ in 0.01 N NaCl.

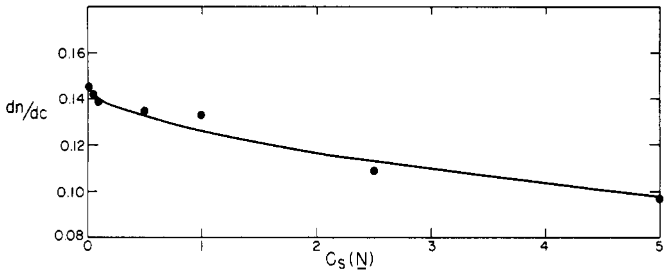


Figure 1. The refractive increment, dn/dc, vs. ionic strength for Na-PAMS in aqueous NaCl solutions.

The polymer solutions and dialyzates used for dilutions during the light-scattering determinations were filtered first through 5 μm and then through 0.22 μm Millipore filters prior to use. No significant change in polymer concentration occurred upon filtration as monitored by dn/dc determinations.

Intrinsic viscosity, $[\eta]$, was measured as a function of polymer concentration for H-PAMS, Na-PAMS, Cs-PAMS, and TBA-PAMS in various solvents at 25.0 °C (±0.05 °C) using Ubbelöhde semimicro viscometers. Solutions and solvents were filtered through ultrafine sintered-glass filters or 5 μm Teflon Millipore filters prior to use. In all cases, flow times exceeded 100 s. As a check for shear-rate dependence, a run was made on the highest molecular weight fraction of Na-PAMS at 0.01 N NaCl; results showed that no significant correction was necessary for this factor. Experimental uncertainties in $[\eta]$ determination were estimated to be ±2%.

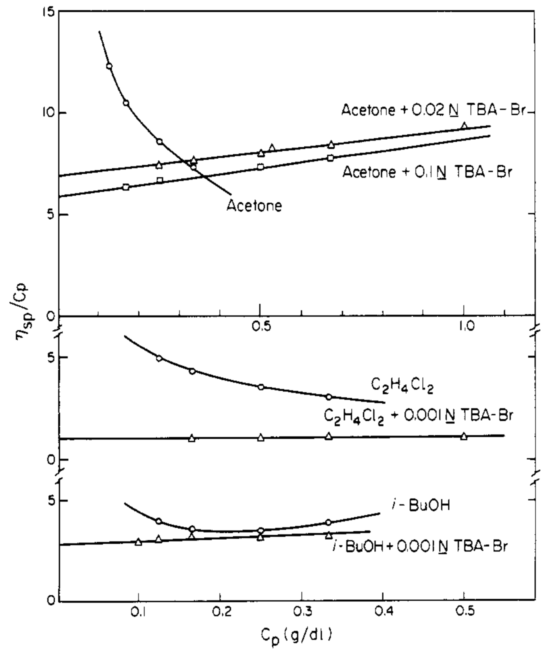


Figure 2. The reduced viscosity vs. polymer concentration for TBA-PAMS (F_1) in organic media with and without TBA-Br.

Results

The average dn/dc values at 436 nm for the Na-PAMS fractions in aqueous solutions are plotted as a function of ionic strength, C_s (mol/L), in Figure 1. Table I summarizes the data for light-scattering measurements and polydispersity indices, $\overline{M}_w/\overline{M}_n$ (estimated from AEC chromatograms), where $\overline{M}_n$ is the number-average molecular weight, for Na-PAMS in aqueous NaCl solutions. Values of the second virial coefficient, as shown in this table, indicate that the polymer chains still remain expanded in 5 N NaCl. These results are similar to those found for another sulfonated polymer, sodium poly(3-methacryloyloxypropane-1-sulfonate) (Na-PMOS), previously studied here.[29] Table II summarizes light-scattering data for TBA-PAMS fractions in 1,2-dichloroethane and acetone containing various amounts of tetrabutylammonium

Table I
Light-Scattering Data for Na-PAMS in Aqueous NaCl Solutions

				Solvent, C_s (N NaCl) =					
Fraction	$\overline{M}_w \times 10^{-6}$	$\overline{M}_w/\overline{M}_n$		0.01	0.05	0.1	0.5	1.0	5.0
F_1	0.86_7	1.3	$A_2 \times 10^4$ [a]	19	7.2	5.2	2.8	2.2	1.8
			$\langle s^2\rangle_z^{1/2}$ [b]		52_0	58_0	43_0	35_0	38_0
F_2	0.54_8	1.3	$A_2 \times 10^4$ [a]	21	8.4	5.6	3.2	2.5	2.2
			$\langle s^2\rangle_z^{1/2}$ [b]		41_0	38_0	35_0	32_0	35_0
F_3	0.41_2	1.5	$A_2 \times 10^4$ [a]	27	9.2	6.5	3.7	2.4	2.3
			$\langle s^2\rangle_z^{1/2}$ [b]		36_0	42_0	32_0	28_0	27_0
F_4	0.22_4	1.4	$A_2 \times 10^4$ [a]	34	11	7.9	4.3	3.3	2.9
			$\langle s^2\rangle_z^{1/2}$ [b]		27_0	29_0	22_0	26_0	27_0
F_5	0.14_0	1.6	$A_2 \times 10^4$ [a]		13		4.8		
			$\langle s^2\rangle_z^{1/2}$ [b]		21_5		15_5		

[a] mol cm^3/g^2. [b] Å.

Table II
Light-Scattering Data for TBA-PAMS in Organic Solvents

			Solvent		
Fraction	$\overline{M}_w \times 10^{-6}$		$C_2H_4Cl_2$ + 0.001 N TBA-Br	Acetone + 0.02 N TBA-Br	Acetone + 0.1 N TBA-Br
F_1	1.7_0	$A_2 \times 10^4$ [a]	0.71	0.18	0.11
		$\langle s^2\rangle_z^{1/2}$ [b]	40_0	36_0	35_0
F_2	1.0_7	$A_2 \times 10^4$ [a]	0.96	0.34	0.24
		$\langle s^2\rangle_z^{1/2}$ [b]	32_5	30_5	28_0
F_3	0.80_6	$A_2 \times 10^4$ [a]	0.97	0.65	0.29
		$\langle s^2\rangle_z^{1/2}$ [b]	25_5	22_5	19_0
F_4	0.43_8	$A_2 \times 10^4$ [a]	1.1	0.67	0.28
		$\langle s^2\rangle_z^{1/2}$ [b]	19_0	19_0	19_0

[a] mol cm^3/g^2. [b] Å.

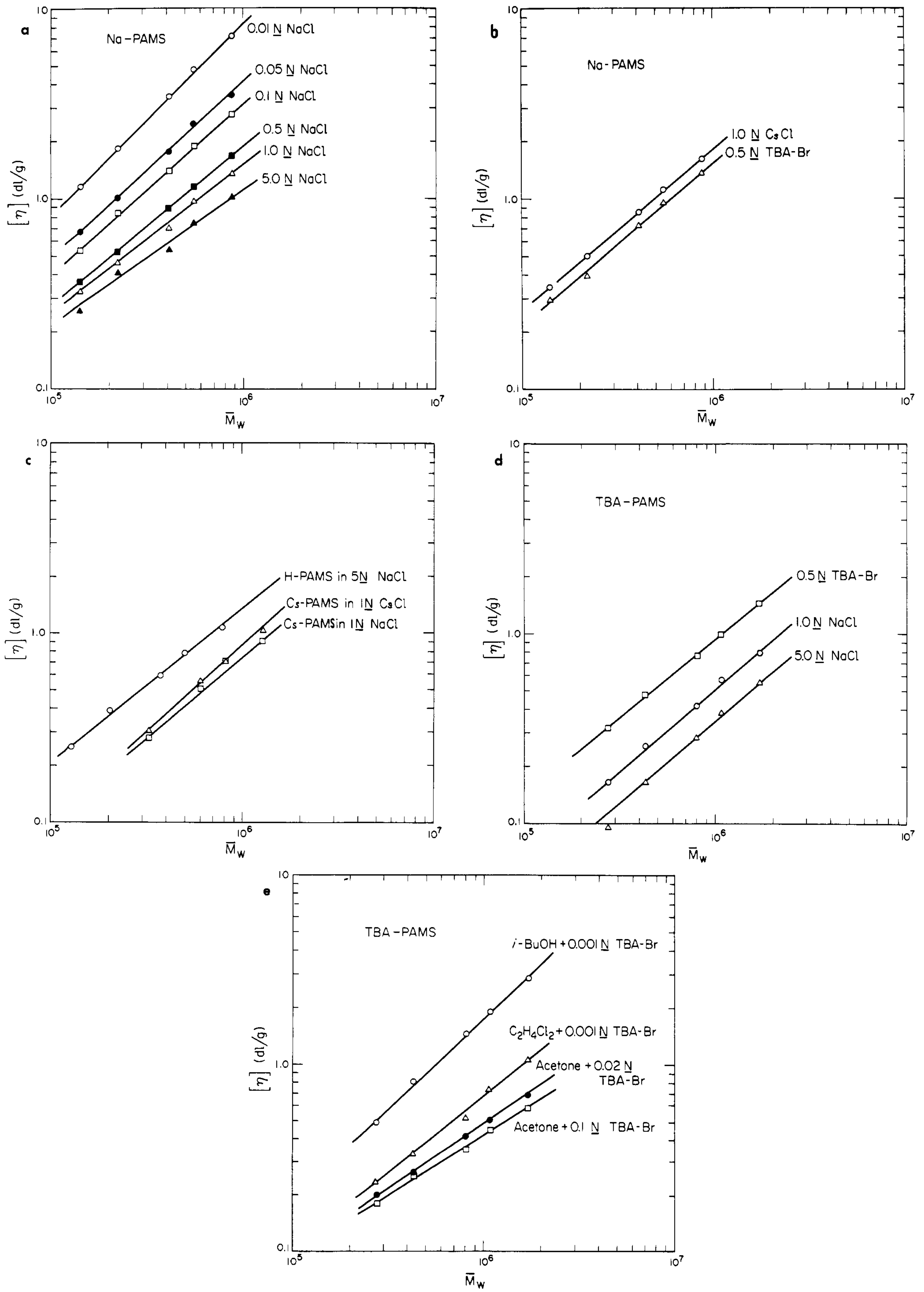


Figure 3. Double logarithmic plots of $[\eta]$ vs. $\bar{M}_w$: (a) Na–PAMS in aq NaCl; (b) Na–PAMS in 1.0 N CsCl and 0.5 N TBA–Br; (c) H–PAMS in 5 N NaCl and Cs–PAMS in 1 N CsCl and 1 N NaCl; (d) TBA–PAMS in 0.5 N TBA–Br, 1 and 5 N NaCl; (e) TBA–PAMS in organic media.

Table III
The Mark-Houwink Parameters for PAMS Polymers in Various Solvent Media

Polymer	Solvent	$K \times 10^5$	ν
Na-PAMS	0.01 N NaCl	0.83	1.00
	0.05 N NaCl	1.09	0.93
	0.1 N NaCl	1.64	0.88
	0.5 N NaCl	1.95	0.83
	1.0 N NaCl	3.60	0.77
	5.0 N NaCl	5.31	0.72
	0.5 N TBA-Br	1.06	0.86
	1.0 N CsCl	1.45	0.85
H-PAMS	5.0 N NaCl	2.11	0.80
Cs-PAMS	1.0 N CsCl	0.30	0.91
	1.0 N NaCl	0.51	0.86
TBA-PAMS	1.0 N NaCl	0.36	0.86
	5.0 N NaCl	0.27	0.85
	0.5 N TBA-Br	1.09	0.82
	i-BuOH + 0.001 N TBA-Br	0.31	0.96
	$C_2H_4Cl_2$ + 0.001 N TBA-Br	0.68	0.82
	Acetone + 0.02 N TBA-Br	1.21	0.70
	Acetone + 0.1 N TBA-Br	6.04	0.64

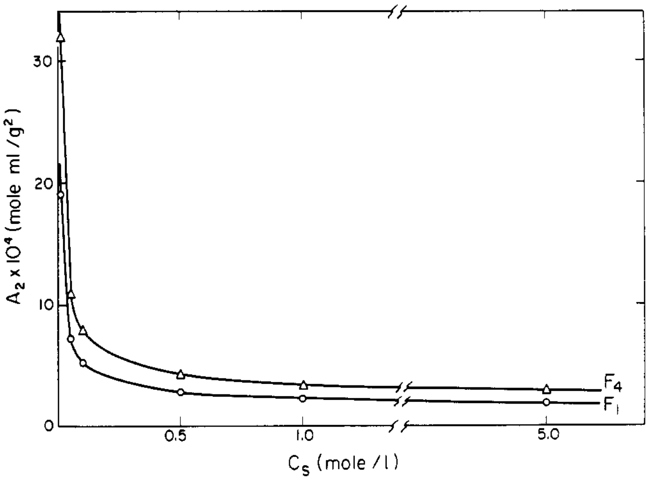


Figure 4. A_2 vs. C_s for fractions F_1 and F_4 of Na-PAMS in aqueous NaCl solutions.

bromide (TBA-Br). This supporting electrolyte was added in order to suppress polyelectrolyte charge repulsion upon dilution as discussed below.

Figure 2 shows the plots of the reduced viscosity, η_{sp}/C_p (where η_{sp} is the specific viscosity), as a function of polymer concentration, C_p, for TBA-PAMS in various organic media. A distinct polyelectrolyte behavior (i.e., a concave-upward curvature in the plot of η_{sp}/C_p vs. C_p) was demonstrated for this polymer in acetone, $C_2H_4Cl_2$, and isobutanol solutions. This behavior disappeared, however, upon the addition of tetrabutylammonium bromide (TBA-Br) as shown in this figure.

The intrinsic-viscosity data for the various forms of this polymer as a function of ionic strength and counterion are plotted against $\overline{M}_w$ on a double logarithmic scale in Figure 3a-d. Similar data for TBA-PAMS in organic media are presented in Figure 3e. The straight lines drawn through the data points were estimated from persistence length calculations to be discussed in part 2. The Mark-Houwink constants K and ν, as defined by

$$[\eta] = K\overline{M}_w^{\nu} \quad (1)$$

according to these straight lines, are shown in Table III. The large values for ν are consistent with the large values of A_2 shown in Table I. The smaller values of ν for the acetone solutions also agree with the smaller A_2 values shown in Table II.

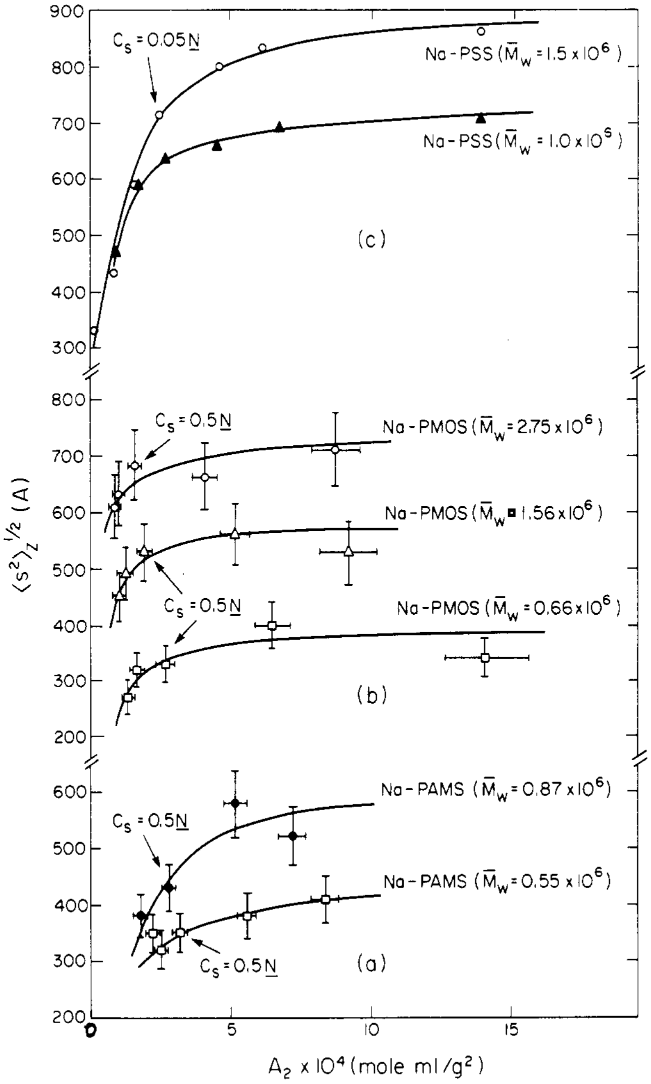


Figure 5. $\langle s^2 \rangle_z^{1/2}$ vs. A_2 for (a) Na-PAMS, (b) Na-PMOS, and (c) Na-PSS in aqueous NaCl solutions.

Discussion

As in other polyelectrolyte-salt systems, the values of A_2, a measure of total excluded volume effect, for the present polymer are large at low ionic strength,[26] indicating a large excluded volume effect partly due to strong charge repulsion within the polymer chain. This interaction should ultimately diminish if enough counterions are present to screen the charges on the polymer. The plots of A_2 vs. C_s for two fractions of Na-PAMS in aqueous NaCl solutions are shown in Figure 4. The second virial coefficient drops sharply with an increase in ionic strength at low C_s, levels off at about C_s = 0.5 N, and would eventually approach zero at infinite ionic strength.

This behavior is consistent with changes in coil dimensions. The radius of gyration for polyions also decreases with an increase in ionic strength or a decrease in A_2. These data are plotted in Figure 5a-c for this polymer (Na-PAMS) and two other sulfonated polymers, sodium poly(3-methacryloyloxypropane-1-sulfonate) (Na-PMOS)[29] and sodium poly(styrenesulfonate) (Na-PSS).[26] One common feature observed from these plots is that the polymer coils are expanded at low

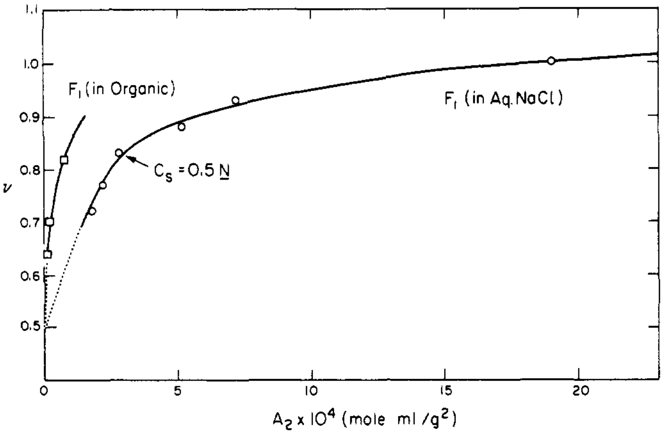


Figure 6. The Mark–Houwink exponent ν vs. A_2 for TBA–PAMS (F_1) in aqueous and organic media.

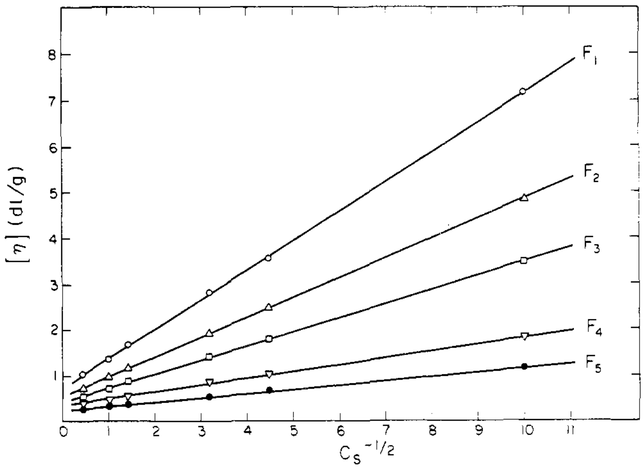


Figure 8. $[\eta]$ vs. $C_s^{-1/2}$ for Na–PAMS in aqueous NaCl solutions.

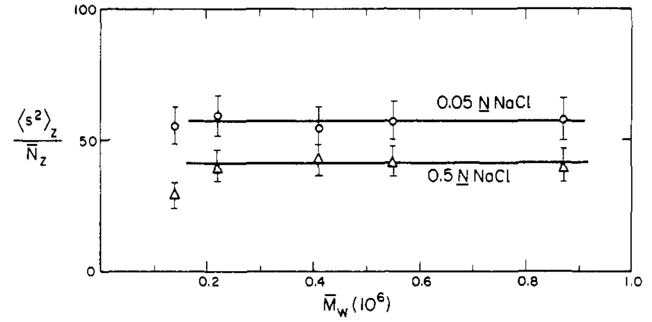


Figure 7. $\langle s^2\rangle_z/\overline{N}_z$ vs. $\overline{M}_w$ for Na–PAMS in 0.05 N and 0.5 N NaCl solutions.

C_s (i.e., high A_2) and collapse drastically with decreasing A_2 (i.e., high C_s). The onset of significant collapse of the coil is at C_s = 0.05 N for Na–PSS (Figure 5c) but is at a higher C_s (>0.5 N) for Na–PAMS and Na–PMOS (Figure 5a–b). The decreases in $\langle s^2\rangle_z^{1/2}$ (Figure 5a–c) and A_2 (Figure 4) at infinite ionic strength suggest that the polymers are inherently coillike as long as enough counterions are present in the coil domain.

The viscosity data also support this conclusion. Figure 6 shows plots of the Mark–Houwink exponent ν vs. A_2 for Na–PAMS (F_1) in aqueous NaCl solutions and for TBA–PAMS (F_1) in organic media. Although the values for ν, which is a measure of chain stiffness, are relatively large in the high-A_2 region (i.e., low C_s), they begin to decrease sharply at C_s = 0.5 N, in good agreement with the curves shown in Figure 5a. The data for TBA–PAMS in organic media, on the other hand, show slightly lower A_2 values for comparable ν values, indicating that the higher values for A_2 in aqueous systems are partly attributed to electrostatic interactions. Nevertheless, a theta condition (i.e., ν = 0.5 and A_2 = 0) is approachable in both media, as shown by the dotted portions of the curves in Figure 6.

The curves in Figures 4–6 discussed above show that a theta condition could be approached if enough supporting electrolyte could be added. Direct measurements of $\langle s^2\rangle_z^{1/2}$ and $[\eta]$ at the theta conditions are difficult for these systems, however. Extrapolation in Figure 5a is also difficult in view of the sharp decrease of $\langle s^2\rangle_z^{1/2}$ with A_2. Consequently, an alternative method to obtain the unperturbed dimensions is to employ viscosity–molecular weight extrapolation techniques. These results will be discussed in part 2.

The coillike behavior of the present polymer is further examined by the variation of $\langle s^2\rangle_z/\overline{N}_z$ with molecular weight, where $\overline{N}_z$ is the z-average degree of polymerization. By using the wormlike-coil model of Kratky–Porod,[30] Benoit and Doty[31] derived the following expression for the radius of gyration,

$$\langle s^2\rangle = q^2\left[\frac{x}{3} - 1 + \frac{2}{x^2}(1 - e^{-x})\right] \tag{2}$$

where q is the persistence length, $x = Nb/q$, b is the monomeric projection along the contour direction, and N is the degree of polymerization. In the limit of coillike behavior, eq 2 becomes

$$\lim_{x\to\infty} \frac{\langle s^2\rangle}{N} = \frac{bq}{3} \tag{3}$$

In order to use the observed $\langle s^2\rangle_z$ data, values of $\overline{N}_z$ were used to replace N in eq 3. The values of $\overline{N}_z$ are related to the polydispersity parameter h by

$$\frac{\overline{N}_n}{\overline{N}_w} = \frac{\overline{M}_n}{\overline{M}_w} = \frac{h}{h+1} \tag{4}$$

and

$$\frac{\overline{N}_z}{\overline{N}_w} = \frac{h+2}{h+1} \tag{5}$$

for a Zimm–Schulz distribution.[32] Using these relations, the plots of $\langle s^2\rangle_z/\overline{N}_z$ vs. $\overline{M}_w$ are shown in Figure 7 for several fractions of Na–PAMS in 0.05 and 0.5 N NaCl. The nearly asymptotic behavior of these data for high molecular weight fractions suggests that this polymer approximately obeys eq 3 and is coillike in the range of the molecular weights studied. Since A_2 does not vanish, however, $\langle s^2\rangle_z/\overline{N}_z$ would be expected not to reach an asymptotic limit but to increase as some power of $\overline{N}_z$ less than 0.2. The error bars on the data in Figure 7 accommodate such behavior. Detailed calculations of the persistence length by using eq 3 as well as by using the recently modified equations by Yamakawa and co-workers[33,34] will be presented in part 2.

A linear relationship between intrinsic viscosity and $C_s^{-1/2}$ for a given molecular weight has been observed for most polyelectrolyte–salt systems as reported by Pals and Hermans,[35] Cox,[36] and Takahashi and Nagasawa.[18] Our data, shown in Figure 8, further substantiate these empirical findings. Unfortunately, none of the current published theories[37] were able to predict this relation. Although Fixman's equation[38] predicts the linear relationship between $[\eta]$ and $C_s^{-1/2}$, and one single straight line was indeed observed for the plot of $[\eta]/M^{1/2}$ vs. $(M/C_s)^{1/2}$ for the several fractions of the present system, the model used was somewhat questionable according to Nagasawa and co-workers.[37]

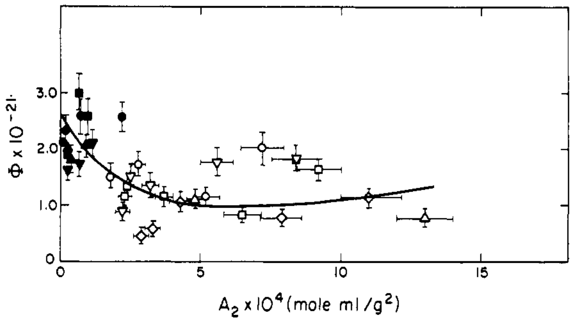


Figure 9. The viscosity constant Φ vs. A_2 for Na–PAMS in aqueous NaCl solutions and for TBA–PAMS in organic media.

A number of equations have been derived to describe the viscosity constant Φ defined as follows,[28]

$$\Phi = [\eta]M/6^{3/2}\langle s^2\rangle^{3/2} \qquad (6)$$

as a function of the excluded volume and hydrodynamic interaction parameters.[39] Because of the scatter of data points caused by experimental uncertainties, particularly for polyelectrolyte–salt systems, evaluation of these theories is rather difficult. Figure 9 shows the calculated Φ as a function of A_2 for Na–PAMS in aqueous NaCl solutions and TBA–PAMS in organic media. The values of Φ were calculated according to eq 6 using the measured $\overline{M}_w$ values and the estimated $\langle s^2\rangle_w$ values where

$$\langle s^2\rangle_w^{1/2} = \langle s^2\rangle_z^{1/2}\left(\frac{h+1}{h+2}\right)^{1/2} \qquad (7)$$

Comparable to previously published data, the values of Φ for TBA–PAMS in organic media (filled data points) fluctuate around 2.0–2.5 × 10^{21}. The values for the aqueous systems (unfilled data points) are smaller and decrease with an increase in excluded volume (i.e., A_2). Smaller values of Φ were also reported for Na–PSS[26] and K–PSS.[40] More accurate data for Φ and coil expansion, or studies on solvation of the polymer coils by other methods, are needed to assess the nature of draining property in polyelectrolyte–salt systems.

In conclusion, poly(2-acrylamido-2-methylpropanesulfonate) polymers, although highly expanded in good solvents or low ionic strength aqueous media, appear to be coillike if enough supporting electrolyte is added. A linear relationship was observed between $[\eta]$ and $C_s^{-1/2}$. The viscosity constant Φ was small and decreased with A_2.

References and Notes

(1) P. J. Flory, "Statistical Mechanics of Chain Molecules", Interscience, New York, N.Y., 1969.
(2) A. Katchalsky and S. Lifson, *J. Polym. Sci.*, **11**, 409 (1956).
(3) M. Kurata and W. H. Stockmayer, *Fortschr, Hochpolym.-Forsch.*, **3**, 196 (1963).
(4) M. Bohdanecky, *Polym. Lett.*, **3**, 201 (1965).
(5) P. Karagannidis and A. Dondos, *Makromol. Chem.*, **147**, 135 (1970).
(6) A. Dondos and H. Benoit, *Macromolecules*, **4**, 279 (1971).
(7) M. Tricot, G. Merteus, P. Collette, and V. Desreux, *Bull. Soc. R. Sci., Liege*, **43**, 502 (1974).
(8) A. Dondos and H. Benoit, *Eur. Polym. J.*, **4**, 561 (1968).
(9) A. Dondos and H. Benoit, *Polym. Lett.*, **7**, 335 (1969).
(10) A. Dondos, P. Rempp, and H. Benoit, *J. Polym. Sci., Part C*, **30**, 9 (1970).
(11) A. Dondos and H. Benoit, *Macromolecules*, **6**, 242 (1973).
(12) D. K. Sarkar and S. R. Palit, *J. Polym. Sci., Part C*, **30**, 69 (1970).
(13) M. Abe and H. Fujita, *J. Phys. Chem.*, **69**, 3263 (1965).
(14) S. V. Bereza, Ye. A. Bekturov, and S. R. Rafikov, *Vysokomol. Soedin., Ser. A*, **11**, 1681 (1969).
(15) Ye. A. Bekturov and R. Ye. Legkunets, *Vysokomol. Soedin., Ser. A*, **12**, 626 (1970).
(16) E. V. Frisman, M. A. Sibileva, N. T. K. Ngan, and T. N. Nekrasova, *Vysokomol. Soedin., Ser. A*, **10**, 1834 (1968).
(17) P. J. Flory and J. E. Osterheld, *J. Phys. Chem.*, **58**, 653 (1954).
(18) A. Takahashi and M. Nagasawa, *J. Am. Chem. Soc.*, **86**, 543 (1964).
(19) N. M. Wiederhorn and A. R. Brown, *J. Polym. Sci.*, **8**, 652 (1952).
(20) A. Silberberg, J. Elliassaf, and A. Katchalsky, *J. Polym. Sci.*, **23**, 253 (1957).
(21) T. N. Nekrasova, O. B. Ptitsyn, and M. S. Shikanova, *Vysokomol. Soedin., Ser. A*, **10**, 1530 (1968).
(22) J. S. Tan and S. P. Gasper, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 1785 (1974).
(23) H. Morawetz, *Isr. J. Chem.*, **11**, 173 (1973).
(24) H. Eisenberg and D. Woodside, *J. Chem. Phys.*, **36**, 1844 (1962).
(25) A. Raziel and H. Eisenberg, *Isr. J. Chem.*, **11**, 183 (1973).
(26) A. Takahashi, T. Kato, and M. Nagasawa, *J. Phys. Chem.*, **71**, 2001 (1967).
(27) A. L. Spatorico and G. L. Beyer, *J. Appl. Polym. Soc.*, **9**, 2933 (1975).
(28) P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, N.Y., 1953.
(29) J. S. Tan and S. P. Gasper, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 1705 (1975).
(30) O. Kratky and G. Porod, *Recl. Trav. Chim. Pays-Bas*, **68**, 1106 (1949).
(31) H. Benoit and P. Doty, *J. Phys. Chem.*, **57**, 958 (1953).
(32) B. H. Zimm, *J. Chem. Phys.*, **16**, 1099 (1948).
(33) H. Yamakawa and M. Fujii, *Macromolecules*, **7**, 128 (1974).
(34) H. Yamakawa and M. Fujii, *Macromolecules*, **7**, 649 (1974).
(35) D. T. F. Pals and J. J. Hermans, *Recl. Trav. Chim. Pays-Bas*, **71**, 433 (1952).
(36) R. A. Cox, *J. Polym. Sci.*, **47**, 441 (1960).
(37) I. Noda, T. Tsuge, and M. Nagasawa, *J. Phys. Chem.*, **74**, 710 (1970).
(38) M. Fixman, *J. Chem. Phys.*, **41**, 3772 (1964).
(39) See the review by H. Yamakawa, "Modern Theory of Polymer Solutions", Harper and Row, New York, N.Y., 1971.
(40) A. Raziel and H. Eisenberg, *Isr. J. Chem.*, **11**, 183 (1973).