Dilute Solution Properties of a New Water-Soluble Polymer

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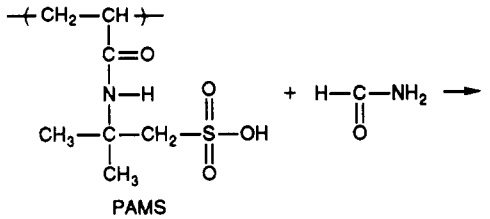
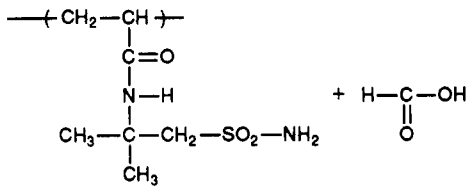
Received December 2, 1991
Revised Manuscript Received April 15, 1992

Introduction

Poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMS) is soluble in water and is a strong polyelectrolyte. Screening of the ionic charges so as to afford normal viscometric behavior requires the inclusion in the water of a very high concentration (4.5 M) of NaCl.[1] We have noted[2] that PAMS also dissolves in formamide. However, during the dissolution there is simultaneous reaction, viz., amidation of the sulfonic acid groups to the corresponding sulfonamide to an extent dependent on the time and temperature of dissolution. Hence in general the products are copolymers exhibiting different levels of polyelectrolyte character, but after a considerable time of dissolution the amidation is >99.5% complete, the PAMS being converted to poly(2-acrylamido-2-methylpropanesulfonamide) (PASAM).



PAMS



PASAM

PASAM is a neutral water-soluble polymer. As far as we are aware, there have been no previous reports on its preparation other than our recent one.[2] In the present paper attention is focused on some fundamental dilute solution properties of this new polymer. Fractionation and measurements were conducted at 298 K.

Experimental Section

Materials. The monomer, 2-acrylamido-2-methylpropanesulfonic acid (AMS) (Sigma Chemical Co.), ammonium persulfate, 1,4-dioxane (GPR grade), propan-2-ol, and $CaCl_2 \cdot 6H_2O$ were used as received. All water used was deionized and doubly distilled. Spectrophotometric grade formamide was dried, vacuum distilled, and stored over zeolite 5A.

Measurements. Any residual acidic content of the PASAM fractions was assessed as before[2] by titration and via pH measurements. Intrinsic viscosities $[\eta]$ of PASAM in water were measured in an Ubbelohde viscometer; kinetic energy corrections were shown to be negligible. At $\lambda_0 = 633$ nm specific refractive index increments (dn/dc) were measured on a modified Brice-Phoenix differential refractometer[3,4] calibrated with aqueous KCl,[3] and light scattering measurements on all PASAM fractions were made on a modified[4] Sofica light scattering photometer calibrated with benzene.[5] Partial specific volumes ($\bar{v}_2$) of PASAM in solution were obtained according to previous[6] procedures. Number-average molar masses M_n for PASAM fractions in water at 298 K were measured in an Osmomat 090 membrane osmometer (Gonotec, Berlin, Germany) containing a cellulose acetate membrane (Schleicher & Schull, Germany).

Preparation of PAMS. Polymerization of AMS in aqueous solution at 323 K initiated by ammonium persulfate was effected as before,[2] except for the present reaction time of 30 min. The mode of isolation of the PAMS obtained to 68% conversion has also been described.[2] For this unfractionated PAMS, the weight-average molar mass, M_w, was 0.851×10^6 g mol^{-1} from light scattering in 4.5 M aqueous NaCl.[2] After full conversion to its sulfonamide form, i.e., PASAM, the value of M_n was 0.261×10^6 g mol^{-1}. Because the molar masses of the repeating units are nearly identical in the sulfonic acid and sulfonamide forms (207 and 206 g mol^{-1}, respectively), the values of M_w and M_n may be taken to relate to both PAMS and PASAM.

Fractionation of PAMS. A solution of PAMS in 3.0 M aqueous $CaCl_2 \cdot 6H_2O$ was fractionated by progressive additions of propan-2-ol as a nonsolvent to give 14 fractions. The last fraction proved difficult to obtain by addition of propan-2-ol and was isolated by freeze-drying. Because of calcium chloride in the fractionation medium, all the fractions were dialyzed against water for 4 days. They were dried finally in vacuo at 318 K for 3 days and weighed.

Synthesis of New Polymer, PASAM. The general procedure indicated previously[2] for the amidation of PAMS was applied similarly to all of the 14 fractions and to the main unfractionated PAMS. However, as the aim was to attain high conversion of sulfonic acid to sulfonamide groups in the present work, dissolution in formamide was conducted at moderately high temperature (323 K) and for long periods (5 days), followed by precipitation in 1,4-dioxane, washing, and drying. Since some of the fractions of PASAM did not differ much in intrinsic viscosity (in water), only 9 of them were used in characterization studies, for which they are identified as F1, F2, ..., F9.

Θ-Conditions. Θ-conditions for PASAM were established by the method of Cornet and Ballegooijen,[7] using water and 1,4-dioxane as solvent and nonsolvent, respectively. Volume fractions of polymer were calculated taking $1/\bar{v}_2$ as the density of polymer.

Results and Discussion

Composition of Polymer. Acid–base titration[2] of aqueous solutions of the modified polymer and the fractions showed that the conversions of SO_3H to SO_2NH_2 groups were in the range 99.6–99.9%. The polymers may thus be regarded fundamentally as PASAM containing a mole fraction of ca. 0.002 of AMS units.

Properties of Polymer. PASAM was found to be soluble in water, formamide, and mixtures of these two liquids over the whole range of composition. Values of 0.693 and 0.692 dm^3 kg^{-1} were obtained for $\bar{v}_2$ of PASAM in water and formamide, respectively, and the values of dn/dc were 0.157 and 0.082 dm^3 kg^{-1} in water and formamide, respectively.

Θ-Conditions. At 298 K the turbidimetric method afforded the mixture water/1,4-dioxane (81.5/18.5 v/v) as Θ-solvent.

Intrinsic Viscosity. Of the two possible solvents, water was selected for viscometry merely as a matter of convenience, viz., lower flow time of water than of formamide. The values of $[\eta]$ in water are listed in Table I. For the fraction of highest molecular weight (F1), use of a variable rate of the shear viscometer verified that there was no necessity for applying any shear dependence corrections. The Huggins viscosity slope constant k' did not display any variation with molar mass. The average value of 0.25 and the overall range of $k' = 0.23$–0.32 are typical for unbranched polymers in very good solvent media. For F5 in formamide and water the values of $[\eta]$ were 498 and 316 dm^3 kg^{-1}, respectively, thus indicating that formamide is the better solvent thermodynamically. Intrinsic viscosities $[\eta]_\Theta$ measured under Θ-conditions

0024-9297/92/2225-4215$03.00/0

Table I
Parameters from Viscosity and Osmometry in Water and Light Scattering in Formamide for PASAM Solutions at 298 K

		light scattering in formamide			osmometry in water		
fraction	$[\eta]$/(dm^3 kg^{-1}) in water	M_w/(10^6 g mol^{-1})	$\langle S^2\rangle_z^{1/2}$/nm	A_2/(10^{-4} m^3 kg^{-2} mol)	M_n/(10^6 g mol^{-1})	A_2/(10^{-4} m^3 kg^{-2} mol)	M_v/(10^6 g mol^{-1})
F1	480	1.22	115	21.3	0.884	12.2	1.19
F2	455	1.07	110	21.6	0.753	13.3	1.04
F3	401	0.905	95.1	23.3	0.729	14.0	0.883
F4	368	0.815	92.6	23.5	0.627	15.6	0.794
F5	316	0.680	73.3	22.6	0.539	13.9	0.664
F6	255	0.505	66.7	24.3	0.344	19.6	0.488
F7	243	0.445	61.0	25.7	0.295	20.6	0.428
F8	217	0.409	56.8	24.8	0.234	16.5	0.389
F9	147	0.245	48.2	30.6	0.159	14.1	0.235
F[a]	424	0.851	104	22.6	0.261	9.8	0.788

[a] F is the main unfractionated PASAM sample.

yielded values ranging from 192 dm^3 kg^{-1} for F1 to 85.5 dm^3 kg^{-1} for F9.

Membrane Osmometry. Standard osmotic pressure plots were accurately linear and yielded the values of M_n and second viral coefficient A_2 listed in Table I. The values of A_2 for PASAM in water are large, but a regular decrease in A_2 with increase in molecular weight, which is the normal situation, is not observed clearly here. This may possibly indicate that the fractions do not coincide exactly in their chain structure.

Light Scattering. Despite the much higher value of dn/dc for PASAM in water than in formamide, the latter solvent was used for light scattering because it enabled clarification to be made more efficiently. The relevant portions of Zimm plots were linear down to the lowest angle used (30°). The values of the root-mean-square radius of gyration $(\langle S^2\rangle_z)^{1/2}$, M_w, and A_2 derived for all the fractions and the unfractionated PASAM are listed in Table I. The values of A_2 are extremely high and exceed the corresponding values in water (by osmometry), which confirms that formamide is the better solvent thermodynamically. The previous comments on the variation of A_2 with molecular weight apply here also. It may be noted that no regular variation of A_2 with molecular weight has been reported for other polymers.[8-12] The reason for this departure from the predicted theoretical interrelation[13] remains to be resolved satisfactorily.

Interrelation among Molecular Weight, Intrinsic Viscosity, and Dimensions. Analysis of the data in Table I yielded the following Mark–Houwink (M–H) relationships for PASAM in water:

$$[\eta]/(\mathrm{dm^3\ kg^{-1}}) = 8.12 \times 10^{-3} M_n^{0.810} \quad (1)$$

$$[\eta]/(\mathrm{dm^3\ kg^{-1}}) = 12.3 \times 10^{-3} M_w^{0.757} \quad (2)$$

Allowance for polydispersity followed by iteration[14,15] yields the M–H equation in terms of the viscosity-average molecular weight M_v:

$$[\eta]/(\mathrm{dm^3\ kg^{-1}}) = 11.8 \times 10^{-3} M_v^{0.762} \quad (3)$$

Under Θ-conditions the following relationship is obtained:

$$[\eta]/(\mathrm{dm^3\ kg^{-1}}) = 0.172 M_w^{0.50} \quad (4)$$

Hence the viscosity constant K_Θ has a value of 0.172 cm^3 g$^{-3/2}$ mol$^{1/2}$, when determined directly. Indirect determination via application of the Stockmayer–Fixman plot[16] to the data in water affords practically the same value. The unperturbed dimensions $(\langle r^2\rangle_{0w}/M_w)^{1/2}$, steric factor σ, and characteristic ratio C_∞[17] are thereby calculated to be 0.088 nm g$^{-1/2}$ mol$^{1/2}$, 4.0, and 32, respectively. In formamide the dimensions vary with molar mass according to eq 5 and, after allowance for polydispersity,[15] the dependence is given by eq 6:

$$\langle S^2\rangle_z/\mathrm{nm^2} = 4.56 \times 10^{-5} M_w^{1.38} \quad (5)$$

$$\langle S^2\rangle_w/\mathrm{nm^2} = 11.8 \times 10^{-5} M_w^{1.31} \quad (6)$$

Conclusions

Major features of the present work are as follows: (a) the M–H exponents (eqs 2 and 3) are typical for a flexible coil in a good solvent; (b) the very high values of σ and C_∞ are indicative of considerable chain stiffness [the only comparably high values are those for the long-chain alkyl and dialkyl esters of poly(itaconic acid)];[18-21] (c) chain stiffness is also indicated by the exponents of molar mass in eqs 5 and 6, which exceed the values of 1.0 and 1.2 expected under Θ-conditions and for a flexible coil in good solvent, respectively. In formamide protonation of the chain and subsequent cationic charge repulsion do not seem possible. Anionic charge repulsion does indeed occur in PAMS and its partially amidated form. However, absence of polyelectrolyte behavior has been confirmed[2] by viscosity for the present PASAM wherein the content of residual SO_3H groups is only ca. 2 per 1000 units. Hence the findings comprise both normal and abnormal behavior, the latter of which will require more detailed investigation to resolve.

Acknowledgment. Financial support (to S.R.G.) from the Egyptian Government is gratefully acknowledged.

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