Unperturbed dimensions of poly(2-acrylamido-2-methyl propane sulfonamide)

Shaban R. Gooda and Malcolm B. Huglin*
Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, UK
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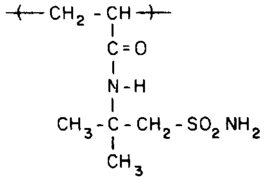
Poly(2-acrylamido-2-methyl propane sulfonamide) (PASAM) is a new, neutral polymer which is soluble in water and formamide. Fundamental parameters obtained previously by light scattering, osmometry and viscometry in these good solvents have been analysed by extrapolation procedures to yield the unperturbed dimensions $(\langle r^2\rangle_0/M_w)^{1/2}$, steric factor σ and characteristic ratio C_∞. θ-Conditions were established as water/dioxane (81.5/18.5 v/v) at 298 K and verified by osmometry and viscometry. There was good accord between the values of $(\langle r^2\rangle_0/M_w)^{1/2}$, σ and C_∞ thereby obtained directly and those derived indirectly, the mean values being 8.73×10^{-9} cm g$^{1/2}$ mol$^{1/2}$, 4.07 and 32 respectively. The temperature coefficient of the unperturbed dimensions was -5.5×10^{-4} K^{-1}. The high rigidity of the PASAM chain is discussed.

(Keywords: poly(2-acrylamido-2-methyl propane sulfonamide); unperturbed dimensions; θ-conditions; intrinsic viscosity; chain rigidity)

INTRODUCTION

In a previous report[1] we showed that dissolution of the polyelectrolyte poly(2-acrylamido-2-methyl propane sulfonic acid) (PAMS) in formamide is accompanied by partial amidation of the sulfonic acid moieties to amide groups. After prolonged dissolution at elevated temperature this process is virtually complete, thereby yielding a new polymer, poly(2-acrylamido-2-methyl propane sulfonamide) (PASAM), which has the following repeating unit:



PASAM is not a polyelectrolyte and is soluble only in water and formamide; moreover in binary mixtures formamide is selectively adsorbed over a considerable portion of the composition range[2]. In a short communication[3] data were presented on the weight average molar masses M_w and mean square radii of gyration $\langle S^2\rangle$ (both by light scattering in formamide), the number average molar masses M_n (via osmometry in water) and the intrinsic viscosities $[\eta]$ (in water) for nine fractions, F1–F9, of PASAM. The values of $\langle S^2\rangle_z^{1/2}$ ranged from 48.2 to 115 nm and the values of M_n ranged from 0.261×10^6 to 0.884×10^6 g mol^{-1}, the mean polydispersity index being 1.43. Although the Mark–Houwink (M–H) exponent was typical for a flexible coil in a good solvent, the exponent of M_w in its dependence on $\langle S^2\rangle$ was more indicative of considerable chain stiffness[3].

The present investigation is directed mainly to examining further the question of chain stiffness in this new polymer. To this end, the data reported on PASAM in good solvents are analysed to obtain the unperturbed dimensions (UD) indirectly, and θ-conditions are established in order to obtain the UD directly and thereby chain rigidity parameters.

EXPERIMENTAL

Materials

The monomer 2-acrylamido-2-methyl propane sulfonic acid (AMS) was obtained from Sigma Chemical Co. Its polymerization has been described elsewhere[1,3]. Isothermal fractionation of the resultant PAMS ($M_w = 0.851 \times 10^6$ g mol^{-1}) was carried out at 298 K. Progressive addition of propan-2-ol as a non-solvent to PAMS solution in 3.0 M aqueous $CaCl_2 \cdot 6H_2O$ at a concentration of 12×10^{-3} kg dm^{-3} produced 12 fractions. The second of these was very large and was refractionated to give a final total of 14 fractions. The overall recovery amounted to 95.6% of the initial weight of the polymer. Since the last fraction proved difficult to isolate by addition of propan-2-ol, it was obtained by freeze drying. Because of the presence of calcium chloride in the fractionation medium, all the fractions were dialysed against water for 4 days. They were dried finally *in vacuo* at 318 K for 3 days and weighed. From $[\eta]$ in water nine fractions were selected, converted to PASAM and characterized as indicated in the Introduction. The water used was deionized and bidistilled. 1,4-Dioxane (GPR) was obtained from BDH Ltd, Poole, UK.

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*To whom correspondence should be addressed

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Procedures

For the binary solvent system, dioxane (nonsolvent)/water (solvent), the method of Cornet and Ballegooijen[4] was employed to determine the θ-conditions for PASAM at 298 K according to experimental procedures adopted previously[5]. A wide range of volume fractions of polymer ($\phi_p = 1.0 \times 10^{-2}$ to 13.5×10^{-4}) was used. The values of ϕ_p were calculated via the density of polymer (1.443 kg dm^{-3}) measured previously[3] and the densities of dioxane and water. The intrinsic viscosities $[\eta]$ of PASAM in water (over the interval 283–343 K) as well as in the binary θ-solvent (at 298 K) were measured in an Ubbelohde viscometer, data being treated according to the standard Huggins equation[6].

As a check for shear-rate dependence, a run was made on the highest molecular weight fraction (F1) of PASAM in the binary θ-solvent; results showed that no significant correction was necessary for this factor. Moreover, correction for kinetic energy was verified to be negligible. The refractive index of pure PASAM (n_2) at 589 nm was measured on an Abbé '60' refractometer (Bellingham and Stanley Ltd). Film was obtained by slow evaporation at 333 K from an aqueous solution placed on the prism. Validity of θ-composition was confirmed by osmometry, using an Osmomat 090 membrane osmometer (Gonotec, GmbH, Berlin, Germany). A regenerated cellulose membrane (cut-off <20000) purchased from Schliecher and Schull, Germany, was fixed in the osmometer after conditioning it in the water/dioxane mixed solvent of different compositions, namely 100/0, 95/5, 90/10, 85/15 and 81.5/18.5 (v/v) for 24 h each at room temperature prior to use. Both solvent and solutions were clarified by filtration through 0.2 μm poly(tetrafluoroethylene) membrane filters (Gelman Sciences) prior to use.

RESULTS AND DISCUSSION

Molecular weight distribution

It was shown previously[1] that no degradation occurred during conversion of PAMS to PASAM. The molecular weights of repeating units are also the same. Hence in *Figure 1*, which relates to PAMS, the molecular weights of the fractions are actually those measured by light scattering after their conversion to PASAM. The weights and hence weight fractions $W(M)$ in conjunction with the values of M_w were used to calculate the cumulative distribution $C(M)$ according to a procedure given by Schulz[7,8]. The differential distribution curve was obtained by graphical differentiation; the curve (*Figure 1*) was unimodal, having a maximum at a value of $M_w \approx 0.83 \times 10^6$ g mol^{-1}, i.e. slightly less than that measured for the unfractionated PASAM sample[3].

Refractive index of PASAM (n_2)

The calculation of n_2 was not possible due to the absence of entries for the sulfonamide group among tabulated group refractivity contributions[9,10]. However, the measured value of n_2 at 589 nm was 1.562. The data given before[3] for the values of specific refractive index increments (at 633 nm), the partial specific volume for PASAM in water as well as in formamide, and refractive indices at 633 nm (n_o) of these solvents (water and formamide) were employed to determine n_2 at 633 nm by calculations via the Gladstone–Dale (G–D), Lorenz–Lorentz (L–L) and Eykman (EYK) expressions, which are formulated elsewhere[11]. The results are given in *Table 1* where the average value of n_2 is seen to be 1.560 at $\lambda_o = 633$ nm, i.e. rather smaller than the experimental value at the slightly lower wavelength.

Unperturbed dimensions in good solvent

From the values[3] of $[\eta]$ in water and of M_w, the UD were derived via six different extrapolation procedures, namely those of Stockmayer–Fixman[12] (S–F), Cowie[13] (CO), Dondos–Benoit[14] (D–B), Kurata–Stockmayer[15] (K–S), Inagaki–Suzuki–Kurata[16] (I–S–K) and Berry[17] (BE). The relevant plots yielded values of K_θ from which $(\langle r^2\rangle_o/M_w)^{1/2}$ was calculated via equation (1), in which a value of 2.5×10^{23} mol^{-1} was taken for the Flory constant Φ_o:

$$K_\theta = \Phi_o(\langle r^2\rangle_o/M_w)^{3/2} \qquad (1)$$

An example of these plots (S–F) is shown in *Figure 2a*. The values of K_θ and $(\langle r^2\rangle_o/M_w)^{1/2}$ listed in *Table 2* indicate that all these extrapolation procedures involving $[\eta]$ and M_w afforded good accord among the derived UD, the mean value being 8.77×10^{-9} cm g$^{-1/2}$ mol$^{1/2}$. Although three additional extrapolation plots were examined, namely Flory–Fox[18], Ueda–Kajitani[19] and Bohdanecký[20], details are omitted here, because they yielded some scatter as well as widely discordant values of K_θ (and hence UD), which were all considerably smaller than those presented in *Table 2*.

On the basis of the values of M_w and the weight average mean square radii of gyration $\langle S^2\rangle_w$ measured in

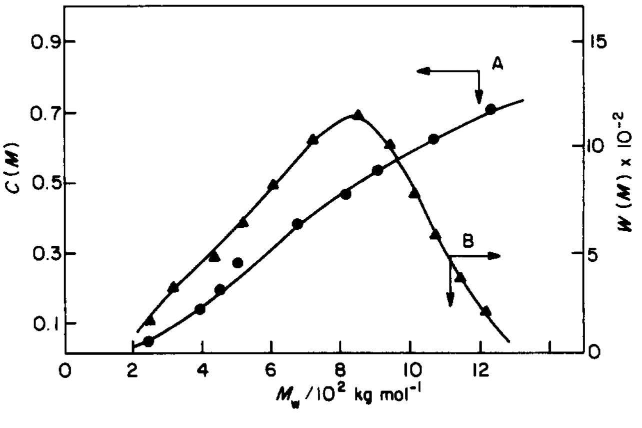

Figure 1 Integral (●, curve A) and differential (▲, curve B) molecular weight distribution of PAMS sample used in the main fractionation process

Table 1 Refractive indices (n_2) of PASAM at 298 K and 633 nm obtained via different relationships[11]

Solvent	λ_0 (nm)	dn/dc (dm^3 kg^{-1})	n_0	n_2 G–D	n_2 L–L	n_2 EYK	Average n_2
Water	633	0.157	1.3323	1.5601	1.5596	1.5594	1.560
Formamide	633	0.082	1.4433	1.5621	1.5585	1.5583	1.560

formamide, three more extrapolation procedures were also employed. For this purpose the directly measured values of $\langle S^2\rangle_z$ were converted[21] to $\langle S^2\rangle_w$.

The relevant equations for the plots were derived on the basis of the theories for the excluded-volume parameter Z as a function of the chain expansion factor α due to Kurata, Stockmayer and Roig[22] (K–S–R), Stockmayer's modification[23] of the expression of Flory[24] (FLO) and Fixman[25] (FIX). The forms of these extrapolation plots are as follows, in which $\langle S^2\rangle$ is in units of cm^2 and the long range interaction parameter B is in units of cm^3 g^{-2} mol^2:

K–S–R:

$$\langle S^2\rangle_w/M_w = \langle S^2\rangle_{ow}/M_w + 0.0286Bg(\alpha)M_w/(\langle S^2\rangle_w)^{1/2} \qquad (2)$$

where $g(\alpha) = 8\alpha^3/(1+3\alpha^2)^{3/2}$

FLO:

$$\langle S^2\rangle_w/M_w = \langle S^2\rangle_{ow}/M_w + 0.056B(\langle S^2\rangle_{ow}/M_w)M_w^2/(\langle S^2\rangle_w^{3/2}) \qquad (3)$$

S–FLO–FIX:

$$\langle S^2\rangle_w/M_w = \langle S^2\rangle_{ow}/M_w + 0.0229B(\langle S^2\rangle_{ow}/M_w)^{-1/2}M_w^{1/2} \qquad (4)$$

All these plots should afford $\langle S^2\rangle_{ow}/M_w$ as the intercept, from which the values of $\langle r^2\rangle_o/M_w$ (and hence the UD) may be obtained via the multiplicative factor[26] of 6. However, the plot according to equation (3) yielded considerable scatter and hence it was not possible to derive a reliable value for the intercept. The plot according to equation (2) is an iterative procedure, which involves calculation of α [and hence $g(\alpha)$] after $\langle S^2\rangle_{ow}/M_w$ has been obtained. In principle, the procedure is repeated until no change is obtained in $\langle S^2\rangle_{ow}/M_w$ after successive plots involving new values of $g(\alpha)$. In practice, two iterations were sufficient. The derived values of $(\langle S^2\rangle_{ow}/M_w)$ and hence $(\langle r^2\rangle_o/M_w)^{1/2}$ obtained from plots via equations (2) and (4) are listed in *Table 2*, where it is seen that there is good accord, the mean value of $(\langle r^2\rangle_o/M_w)^{1/2}$ being 8.67×10^{-9} cm g$^{-1/2}$ mol$^{1/2}$, which is very close to that obtained from plots involving $[\eta]$ and M_w. An example of these plots (FIX) involving $\langle S^2\rangle_w$ and M_w is shown in *Figure 2b*. Additional extrapolation procedures[27–30] based on utilizing the values of M_w and the second virial coefficient A_2 were examined. Details are omitted here because of the big scatter yielded. The reason may lie in the fact that PASAM solutions are unusual in the respect[3] that A_2 is almost independent of M_w.

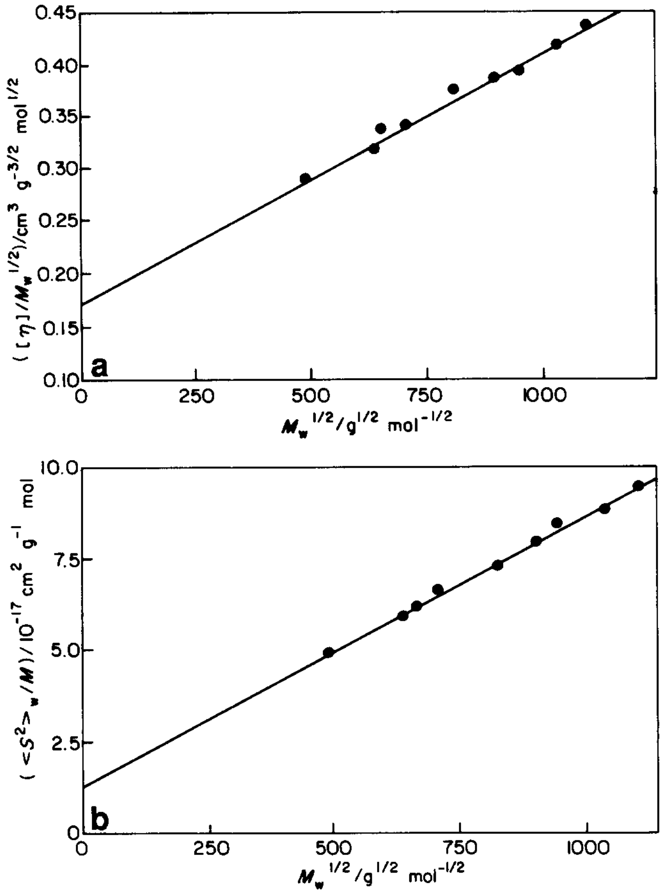

Figure 2 (a) Stockmayer–Fixman plot for PASAM in water at 298 K; (b) Fixman plot for the determination of $\langle S^2\rangle_{ow}/M_w$ of PASAM in formamide at 298 K

θ-Composition in binary solvent

The volume fraction of the non-solvent (dioxane) ϕ_{ns} *versus* log ϕ_p (where ϕ_p is the volume fraction of polymer) displayed good linearity for the binary solvent system, PASAM/dioxane/water, as shown in *Figure 3*. Extrapolation to pure polymer, i.e. to log $\phi_p = 0$, yielded the θ-composition as dioxane/water, 18.5/81.5 (v/v), at 298 K.

Intrinsic viscosity under θ-conditions

The intrinsic viscosities of the polymer fractions were measured at 298 K in the binary θ-solvent (see *Table 3*).

Table 2 Unperturbed dimensions (UD) of PASAM derived from extrapolation procedures and directly in the binary θ-solvent at 298 K

Plot	E/D[a]	Relevant parameters	Solvent	K_θ (cm^3 g$^{-3/2}$ mol$^{1/2}$)	$(\langle S^2\rangle_{ow}/M_w)\times10^{17}$ (cm^2 g^{-1} mol)	$(\langle r^2\rangle_{ow}/M_w)^{1/2}\times10^9$ (cm g$^{-1/2}$ mol$^{1/2}$)
S–F	E	$[\eta]$, M_w	Water	0.170	–	8.79
CO	E	$[\eta]$, M_w	Water	0.178	–	8.92
K–S	E	$[\eta]$, M_w	Water	0.173	–	8.84
I–S–K	E	$[\eta]$, M_w	Water	0.164	–	8.68
D–B	E	$[\eta]$, M_w	Water	0.160	–	8.61
BE	E	$[\eta]$ M_w	Water	0.174	–	8.86
K–S–R	E	$\langle S^2\rangle_w$, M_w	Formamide	–	1.21	8.52
FIX	E	$\langle S^2\rangle_w$, M_w	Formamide	–	1.30	8.83
M–H	D	$[\eta]$, M_w	θ-solvent	0.172	–	8.82

[a] E, UD obtained by extrapolation procedures; D, UD obtained by direct method

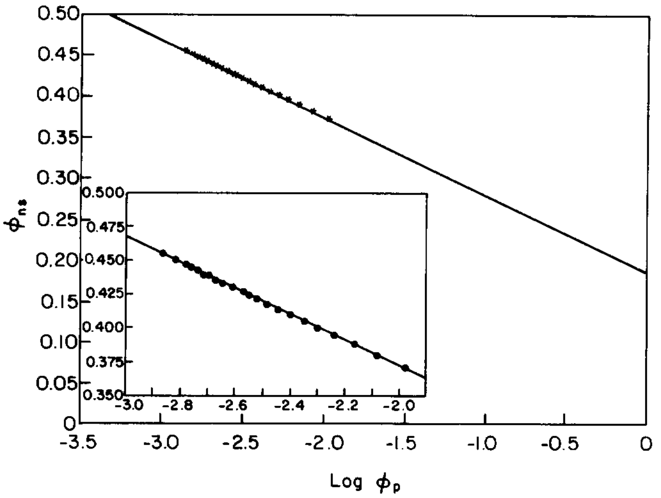

Figure 3 Determination of θ-composition at 298 K according to method of Cornet and Ballegooijen[4] (ϕ_p and ϕ_{ns} are volume fractions of polymer and non-solvent, respectively)

Table 3 Viscometric data for PASAM under θ-conditions

Fraction	M_w (kg mol^{-1})	$[\eta]_\theta$ (dm^3 kg^{-1})
F1	1225	192
F2	1075	179
F3	905	165
F4	815	155
F5	680	144
F6	505	123
F7	445	115
F8	409	110
F9	245	85.5

The exponent '*a*' of the Mark–Houwink (M–H) equation was confirmed to be 0.50 and the value of the M–H constant K ($=K_\theta$) is given in *Table 2.*

Unperturbed dimensions in θ-solvent

The UD are defined as $(\langle r^2\rangle_o/M_w)^{1/2}$, where $\langle r^2\rangle_o$ is the unperturbed mean square end-to-end distance. Under θ-conditions the constant K and the exponent '*a*' of the M–H equation are K_θ and 0.50, respectively:

$$[\eta]_\theta = K_\theta M_w^{0.5} \tag{5}$$

The directly obtained value of K_θ and that of the UD calculated via equation (1) are listed in *Table 2*, from which the value of 8.83×10^{-9} cm g$^{-1/2}$ mol$^{1/2}$ for $(\langle r^2\rangle_o/M_w)^{1/2}$ lies in good accord with the average yielded from extrapolation plots involving $[\eta]$ in the single solvent (water). The validity of the θ-composition was examined by membrane osmometry at 298 K. Measurements were made on sample F9 and the plot, shown in *Figure 4*, verifies that $A_2 = 0$.

Temperature coefficient of the unperturbed dimensions

For sample F4, the values of $[\eta]$ were measured in water at eight temperatures within the interval 283–343 K. The plot of ln $[\eta]$ *versus* temperature (T) is linear and has a slope of -8.21×10^{-4} K^{-1}. The slope can be expressed in the form of equation (7), which follows directly from equation (6) in which α is the viscometric expansion factor[31]:

$$[\eta] = K_\theta M_w^{1/2}\alpha^3 \tag{6}$$

$$\mathrm{d}\ln[\eta]/\mathrm{d}T = 3/2\,\mathrm{d}\ln\langle r^2\rangle_o/\mathrm{d}T + 3\mathrm{d}\ln\alpha/\mathrm{d}T \tag{7}$$

In water, the system is far from θ-conditions (in the vicinity of which α changes markedly). Hence the constant value of the left-hand-side of equation (7) may be equated to $(3/2)\mathrm{d}\ln\langle r^2\rangle_o/\mathrm{d}T$. The value of $(2/3)\mathrm{d}\ln[\eta]/\mathrm{d}T$ is thus the temperature coefficient of the UD in water, namely

$$\mathrm{d}\ln\langle r^2\rangle_o/\mathrm{d}T = -5.473 \times 10^{-4}\,\mathrm{K}^{-1}$$

An alternative route for evaluation of this coefficient is via the procedure of Bohdanecký[32], whose analysis predicts linearity in a plot of $(P/Q)\mathrm{d}\ln[\eta]/\mathrm{d}T$ *versus* $(1/Q)$ and a slope equal to $\mathrm{d}\ln\langle r^2\rangle_o/\mathrm{d}T$. The quantities P and Q are functions of α which are defined elsewhere[32]. The values of α were obtained from equation (8) in which $[\eta]_\theta$ is the intrinsic viscosity measured in the binary θ-solvent:

$$\alpha = ([\eta]/[\eta]_\theta)^{1/3} \tag{8}$$

The Bohdanecký plot was found to be linear and yielded a small value of $\mathrm{d}\ln\langle r^2\rangle_o/\mathrm{d}T = -5.50 \times 10^{-4}\,\mathrm{K}^{-1}$ which is practically the same as that obtained from the plot of ln$[\eta]$ *versus* T.

Chain rigidity

The structural parameters of PASAM, namely the steric factor σ and the characteristic ratio C_∞, were calculated in the usual manner[33] from the following equations:

$$\sigma = [\langle r^2\rangle_{ow}/M_w]^{1/2}/[\langle r^2\rangle_{of}/M_w]^{1/2} \tag{9}$$

$$[\langle r^2\rangle_{of}/M_w]^{1/2} = [\langle r^2\rangle_{of}/N]^{1/2}[1/M_o]^{1/2} \tag{10}$$

$$C_\infty = (K_\theta/\Phi_o)^{2/3}(M_o/2L^2) \tag{11}$$

where $\langle r^2\rangle_{of}$ is the unperturbed mean square end-to-end distance for a freely rotating chain, N is the degree of polymerization, M_o is the molecular weight of the monomer unit and L is the backbone bond length ($L = 0.154$ nm). For vinyl polymers[34], the value of $(\langle r^2\rangle_{of}/N)^{1/2} = 3.08 \times 10^{-8}$ cm. Hence from equation (10) it follows that $(\langle r^2\rangle_{of}/M_w)^{1/2}$ for PASAM = 2.14×19^{-9} cm g$^{-1/2}$ mol$^{1/2}$. Employing the mean of all values for the UD, namely 8.73×10^{-9} cm g$^{-1/2}$ mol$^{1/2}$, a value of 4.07 was obtained for σ.

Cowie[35] has stated that the range of values normally found for σ is about 1.5–2.5. However, higher values of

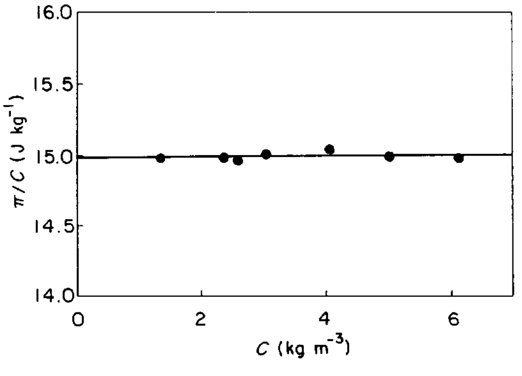

Figure 4 Membrane osmometry data for PASAM (F9) in the binary θ-solvent at 298 K

σ (3.4–3.95) have been reported for poly(alkyl-phenyl methacrylates)[36–39] and poly(hexadecyl methacrylate)[34]. Similar high values for σ were reported for the long chain alkyl and dialkyl esters of poly(itaconic acid)[40–43] in which the hindrance to free rotation increases slowly and monotonously with increasing length of the side chain, i.e. $\sigma = 3.58–4.00$.

The mean value of $K_\theta = 0.172\ \mathrm{cm}^3\ \mathrm{g}^{-3/2}\ \mathrm{mol}^{1/2}$, in conjunction with equation (11), gives a high value of 32 for C_∞. The high values reported for σ, referred to above, naturally give rise to large values of C_∞, namely 24.5–31.3. Charge effects may exert a great influence on chain rigidity. Thus, quite high values for C_∞ ($C_\infty = 12–23$) are reported[44] for the strong polyelectrolyte PAMS and its salts. Anionic charge repulsion does indeed occur in PAMS and its partially amidated form. However, absence of polyelectrolyte behaviour has been confirmed[1] by viscosity for the present PASAM wherein the content of residual SO_3H groups is only about 2 per 1000 units. In formamide, protonation of the chain and subsequent cationic charge repulsion does not seem possible.

The relatively high rigidity of PASAM is indicative of considerable chain stiffness and may be attributed to the specific dipolar interactions in the polymer molecule which lead to the intra-group and intra-chain association. Chain stiffness is also indicated by the high exponent found[3] in the relation $\langle S^2 \rangle_\mathrm{w} \propto M_\mathrm{w}^{1.31}$.

Related discussion[41] on systems exhibiting high chain rigidity parameters has involved the length of the side groups and repulsion between methyl groups. However, these are unlikely to be the main contributory factors for the large value of C_∞ found here (e.g. PASAM is an acrylate and does not contain an α-methyl group). We have noted recently[2] that the value of about 1200 MPa for the cohesive energy density of PASAM is greatly in excess of the value for all other polymers. In this connection it may be noted that the only two solvents for the polymer, water and formamide, possess the highest solubility parameters and dielectric constants of all common liquids. PASAM is clearly very polar and the presence of the amide and sulfonamide groups within the side chain allows ample facility for intra-chain and inter-chain hydrogen bonding, with resultant restrictions to the flexibility of the carbon–carbon main chain.

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