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Molecular dimension and interaction parameters of polyacrylamide in water–dimethylsulphoxide mixtures: effect of temperature

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Abstract

The intrinsic viscosities $[\eta]$ of polyacrylamides having different molecular sizes are measured at 30–50°C temperature in various mixtures of water (good solvent) and dimethylsulphoxide (DMSO, poor solvent). The observed result and the Huggins constant values show a significant variation of cosolvency as a function of solvent composition (φ) and temperature. The nature of plots of $[\eta]$ vs. φ_{DMSO} indicates relative importance of entropy factors over energetic factors in determining molecular configuration at high temperature. The unperturbed dimensions (K_θ) of the polymer are determined by various methods, which agree well with each other and exhibit a minimum at $\varphi = 0.5$. The temperature coefficients of the unperturbed dimension (K') gives both positive and negative values depending on the solvent composition, which indicates the variation of compactness and the presence of low and high energy configurations as a function of solvent composition. Molecular extension factor (α_n) and the chain rigidity (σ) values are evaluated and the influence of temperature is discussed. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polyacrylamide; Cosolvency; Huggins constant; Unperturbed dimension; Molecular extension parameter; Chain rigidity

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1. Introduction

The dependence of the intrinsic viscosity of a polymer on polymer–solvent interaction as distinguished from the structural features affecting the chain configuration has been discussed [1–3]. The aqueous solutions of polyacrylamide (PAM) were suspected to contain fibrous aggregates of high molecular weight polymers. High value of excluded volume exponent, as was observed in some cases, once thought to be the result of great expansion of polyacrylamide in aqueous solution [4,5]. This arose doubts on the applicability of the method of extrapolation of the viscosity data in determining unperturbed dimension of the polymer in water. Further study, however, confirmed the high value of the exponent of molecular weight dependence of the radius of gyration was not due to a great expansion of the macromolecular coil in water and it is now believed that determination of the unperturbed dimension by extrapolating viscosity data in good solvents is possible [4]. Although some studies on the solution viscosity properties of acrylamide in water are available in the literature, similar studies in other solvents or cosolvent systems are surprisingly little [4–10]. Present paper describes the result of our investigation on unperturbed dimensions, interaction parameters and related aspects of unhydrolysed polyacrylamide in water–dimethylsulphoxide (water–DMSO) mixtures. While DMSO is a poor solvent for PAM, water–DMSO mixture acts as a cosolvent in certain proportions. Recently we have reported a technique by which the molecular weight of the PAM in aqueous solution was controlled by trapping the initiator components in the interlayer space of

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montmorillonite [11–13]. This method has been adopted selectivity to prepare polymers of varying molecular weights for the present study.

2. Experimental

2.1. Polymerization

PAM was synthesized from acrylamide monomer (AM) by solution polymerization technique. The crude monomer (acrylamide, Fluka AG) was purified by recrystallization from methanol and dried in vacuum oven at 45°C overnight. The polymerization technique of AM initiated by ferric-montmorillonite (FeM)–thiourea (TU) redox system has been discussed in a recent paper [12]. To obtain high molecular weight polymers for the present study, a similar technique has been adopted using 0.4 M monomer and 0.04 thiourea in aqueous suspension of 0.50% FeM (w/v) in the temperature range between 70°C and 50°C. Low molecular weight polymers were obtained via polymerization of AM monomers initiated by 1.5×10^{-3} M $FeCl_3$ and 0.04M TU redox system at 50°C in absence of montmorillonite. The molecular weights (determined from intrinsic viscosity measurements in water at 30°C) of the polymers used in the present study are listed in Table 1.

Methanol (Merck) and DMSO (Merck) were purified by fractional distillation following usual procedure before use.

2.2. Viscosity measurements

The intrinsic viscosities $[\eta]$ of the polymer in aqueous solutions were determined by an Ubbelohde viscometer, placed at appropriate temperature in a thermostat, measuring specific viscosities (η_{sp}) and using the Huggin's equation for extrapolation:

$$\eta_{sp}/C = [\eta] + K[\eta]^2 C, \tag{1}$$

where C is the concentration of the polymer solution. Molecular weights of the polymer were calculated from the intrinsic viscosity data [12]. The $[\eta]$ values of the polymer in various water–DMSO compositions (prepared by volume) were also measured in a similar way.

Table 1
Molecular weights of polyacrylamides

Polyacrylamides types	$[\eta]^a$	$M_v \times 10^{-5}$
High molecular weight (HM)	369	12.55
Medium molecular weight (MM)	260	8.44
Low molecular weight (LM)	64	1.33

[a] Intrinsic viscosity ($ml\,g^{-1}$) in aqueous medium.

3. Results and discussion

Nature of the interaction between the liquids governs the solubility of a polymer in a binary liquid mixture. The changes in the molecular dimensions of the polymers in these systems are manifested in the varied molecular extension parameters (α_n) and the unperturbed dimensions due to the interaction with two component liquid [14,15]. Viscosities of pure water–DMSO mixtures show positive deviations from ideality which suggests that there is association of the liquids through hydrogen bonding. The intrinsic viscosity, $[\eta]$, vs. composition plot exhibits a maximum which decreases with increase in temperature [16]. The fact that the maximum in the viscosity isotherm decreases with increasing temperature suggests that any association complex formed between water and DMSO is thermally labile and could only be expected to exist in a completely undissociated state at low temperature. The viscosity behaviour of a solvent mixture is also related to the excess thermodynamic properties of the mixture. When a change in excess Gibb's free energy, ΔG_{12}^E, is positive a positive deviation of $[\eta]$ is observed while when $\Delta G_{12}^E$is negative a negative deviation of $[\eta]$ is observed. Calculation of ΔG_{12}^E values as a function of composition of the present solvent mixtures indicates a non-linear variation which passes through a maximum. These values are, however, low at high temperature. The changes in $[\eta]$ of various molecular weight fractions of PAM at 30°C and in different compositions of water–DMSO mixtures are shown in Fig. 1. The result is just opposite to that observed in pure solvent mixtures. With increasing DMSO (poor solvent) concentration, the intrinsic viscosity decreases probably due to contraction of the dimensions of the polymer coil as well as for the degree of intermolecular agglomeration. The negative deviation of $[\eta]$ as a function of the composition of associated binary solvent system like water–DMSO, can be explained easily because in such a medium the polymer cannot find a free volume and it is contracted. However, at high value of φ_{DMSO} (φ being the relative volume composition in the mixture) the $[\eta]$ value tends to increase again for preferential solvation of the polymer. It is found that for all the molecular weight fractions, the intrinsic viscosity attains the minimum near φ_{DMSO} value between 0.6 and 0.7 indicating energetically most unfavourable solvent composition for the polymers. The lowest value of $[\eta]$ around $\varphi_{DMSO} = 0.6$–0.7 indicates the maximum degree of intermolecular aggregation of the polymers at this solvent composition due to highest co-non-solvency effect. Similar nature of the variation of $[\eta]$ on solvent composition is also observed at 40°C temperature (Fig. 2). Such changes of the $[\eta]$ value as a function of solvent composition clearly indicates the flexibility of the PAM molecules in the present solvent systems. On the other hand, at 50°C temperature the nature of the curves is

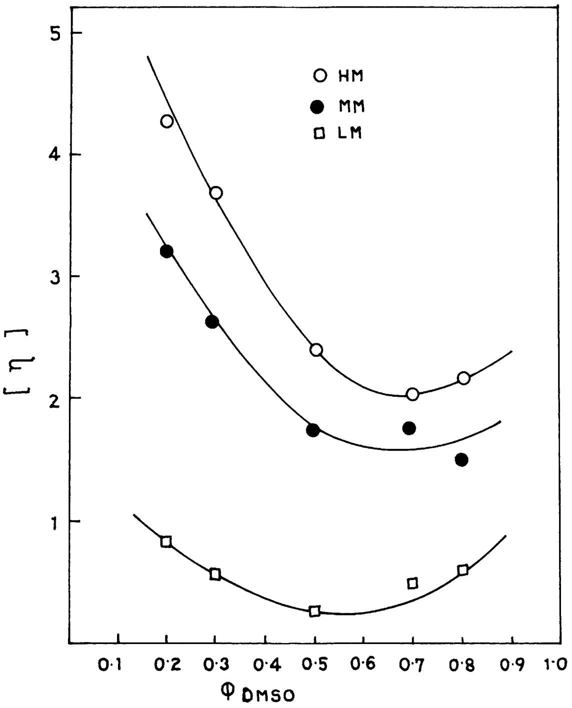

Fig. 1. Plot of intrinsic viscosity of PAM fractions at 30°C vs. volume fraction of DMSO.

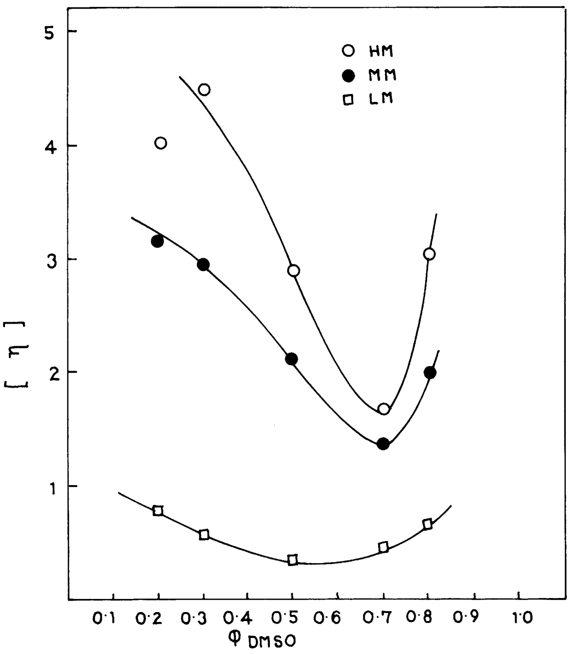

Fig. 2. Plot of intrinsic viscosity of PAM fractions at 40°C vs. volume fraction of DMSO.

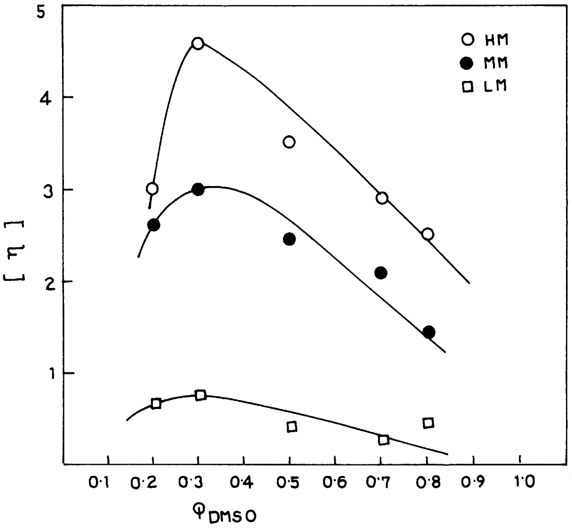

Fig. 3. Plot of intrinsic viscosity of PAM fractions at 50°C vs. volume fraction of DMSO.

changed dramatically (Fig. 3). Instead of giving a minimum with the variation of solution composition, the $[\eta]$ reaches a maximum near $\varphi_{\mathrm{DMSO}} = 0.3$, for all the polymer fractions. The maximum intrinsic viscosities for all polymer fractions at this solvent composition indicate preferential solvation of the polymers due to most powerful cosolvent effect [17]. The effect of temperature upon $[\eta]$ should depend strongly on the nature of the solvent. At high temperature (50°C), the association between the solvents is decreased and a different behaviour of $[\eta]$ as a function of solvent composition is observed. In a binary solvent composition where co-solvency factor is poorer, an increase of temperature should increase the relative importance of entropy factors over energetic factors, and results in an uncurling of the molecule [18]. The uncurled configurations will be favoured due to long chain molecule being surrounded by solvated hull which tends to prevent polymer–polymer contracts. In such a solvent, a temperature increase should result in an increase of $[\eta]$. On the other hand, at higher cosolvency condition, the energetic weighting factors favour the more extended configuration; here an increase in temperature should diminish the $[\eta]$ value. As a result $[\eta]$ vs. φ_{DMSO} plots pass through maxima at high temperature (50°C) for all the polymer studied under the present investigation (Fig. 3). The cosolvency and the intermolecular interaction of polymers are also manifested in the Huggins constant values when the composition of the solvent system were varied. Plots of Huggins constant as a function of solvent composition are shown in Figs. 4–6. The Huggins constant (K) are calculated from the least square slopes of Eq. (1). It is observed that there is a maximum at solvent composition $\varphi_{\mathrm{DMSO}} = 0.7$ for

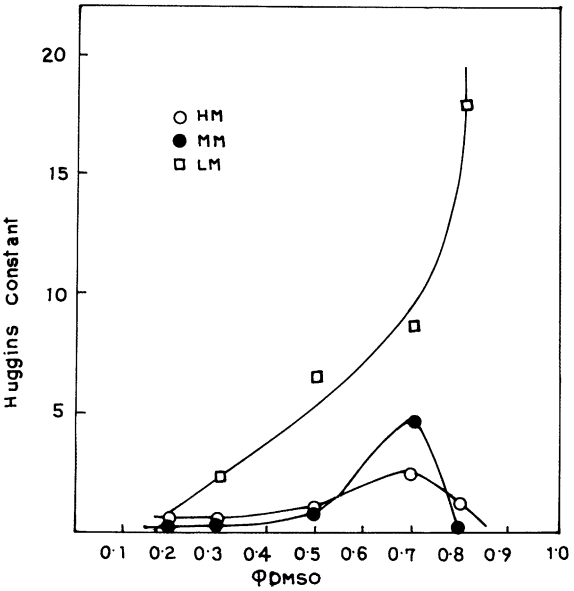

Fig. 4. Plot of Huggins constant of PAM fractions at 30°C vs. volume fraction of DMSO.

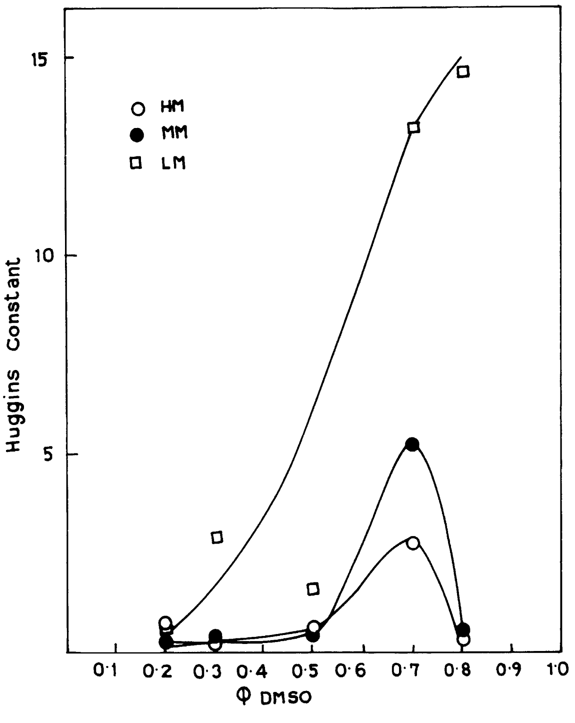

Fig. 5. Plot of Huggins constant of PAM fractions at 40°C vs. volume fraction of DMSO.

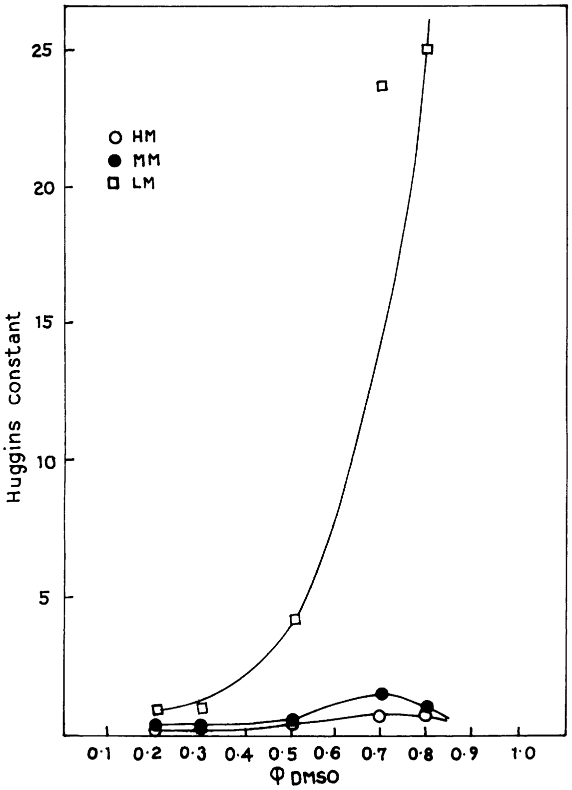

Fig. 6. Plot of Huggins constant of PAM fractions at 50°C vs. volume fraction of DMSO.

medium and high molecular weight polymers. This shows that cosolvent effect is apparent above φ value of 0.7. However, at 50°C temperature, although a maximum is obtained at $\varphi_{\text{DMSO}} \sim 0.7$, the small value of K indicate better cosolvency at this temperature for MM and HM samples. For LM fraction, very high values of K indicate strong aggregation of polymer molecules at all the temperatures studied. Fig. 7 shows a plot of Huggins constant against log M_v for three different solvent compositions (up to $\varphi_{\text{DMSO}} = 0.5$). All the curves show a decrease in the Huggins constant value with the increase in molecular weight indicating higher tendency of intermolecular aggregation for smaller fractions of the polymers in poor cosolvent conditions.

3.1. Unperturbed dimension

The unperturbed dimension of a polymer chain is important in understanding the physical properties of the polymer both in solution as well as in the solid state. It is the dimension of the polymer chain where the volume exclusion due to long range segmental interaction is nullified by its interaction with a definite solvent (θ solvent) [19]. The unperturbed dimension (K_θ) is the end-to-end dimension of polymer chain under θ conditions and can be determined from the intrinsic viscosity measurement at this condition.

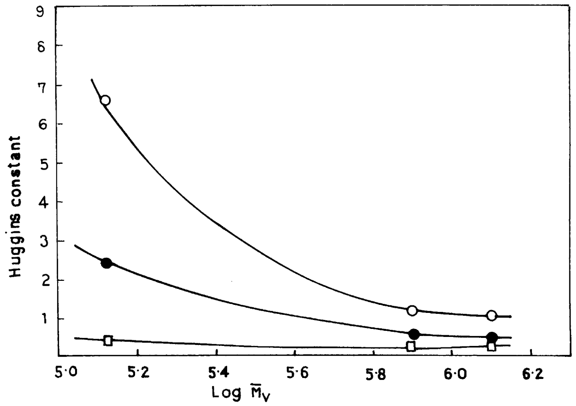

Fig. 7. Plot of Huggins constant vs. log (molecular weight) at different solvent compositions at 30°C: (○) $\varphi_{\mathrm{DMSO}} = 0.5$, (●) 0.3, (□) 0.2.

$$[\eta]_\theta = \phi_0(\bar{r}_0^2/M)^{2/3}M^{1/2} = K_\theta M^{1/2} \tag{2}$$

where ϕ_0 is the Flory's universal constant (2.5×10^{23} mol^{-1}), M stands for molecular weight and $\bar{r}_0^2$ is the mean square unperturbed dimension. However, in the present study, the Burchard–Stockmayer–Fixman equation (3) has been used for deriving K_θ of PAM in various water–DMSO mixtures under non θ-conditions [20,21]. The K_θ values obtained by plotting $[\eta]/M^{1/2}$ against $M^{1/2}$ from Eq. (3) in different cosolvent compositions

$$[\eta]/M^{1/2} = K_\theta + 0.51B\phi_0 M^{1/2} \tag{3}$$

(B being the polymer–solvent interaction free energy parameter) are compared with those obtained from other methods of measurement, viz., Kurta–Stockmayer (KS) [22,23], Fox–Flory (FF) [3], Berry (Be) [24], Tanaka (T) [25] and Bohdanecky (Bo) [26] methods. The results are summarized in Table 2. The values obtained by different methods agree well with each other except in a few composition conditions of the solvent. From the Table 2, it is apparent that at $\varphi_{\mathrm{DMSO}} = 0.5$ i.e., at the same volume ratio of water and DMSO in the mixture, strong attraction of two solvents, causes the polymers to have the lowest value of unperturbed chain. This observation is independent of the method of measurement with certain exceptions. Effect of temperature is rather interesting. With an increase in temperature, $\bar{r}_0^2$ and hence K_θ, is decreased due to greater freedom to rotation around the skeletal bonds [19]. Such a temperature dependence of unperturbed dimension can be attributed not only to the change in flexibility of macromolecular chains but also to the specific polymer–solvent interaction [27]. The effect may also be correlated to the cohesive energy density of the polymer and the solvent [28].

Table 2
Unperturbed dimension of PAM in water + DMSO mixtures at different temperatures determined by different methods

Temperature (°C)	φ_{DMSO}	$K_\theta \times 10$ (cm^3 g$^{-3/2}$ mol$^{1/2}$)					
		BSF[a]	KS[b]	T[c]	Bo[d]	FF[e]	Be[f]
30	0.2	1.500	1.480	1.446	1.500	1.440	1.440
	0.3	1.125	1.115	0.910	1.120	1.114	1.123
	0.5	0.150	0.116	0.110	0.125	0.107	0.086
	0.7	0.650	0.649	0.490	0.375	0.196	0.225
	0.8	1.600	1.570	1.430	1.312	1.250	1.370
40	0.2	1.250	1.240	1.070	1.125	1.174	1.123
	0.3	0.950	0.960	0.954	0.968	0.960	0.945
	0.5	0.350	0.327	0.287	0.187	0.290	0.256
	0.7	0.500	0.465	0.435	0.312	0.164	0.100
	0.8	1.500	1.483	1.300	1.281	1.253	1.225
50	0.2	0.825	0.818	0.435	0.812	0.801	0.730
	0.3	0.200	0.125	0.110	0.125	0.098	0.095
	0.5	0.250	0.241	0.165	0.125	0.218	0.170
	0.7	0.925	0.925	0.807	0.688	0.512	0.484
	0.8	1.550	1.525	1.375	1.343	1.525	1.520

[a] Burchard–Stockmayer–Fixman.
[b] Kurata–Stockmayer.
[c] Tanaka.
[d] Bohdanecky.
[e] Fox–Flory.
[f] Berry.

3.2. Temperature coefficient of unperturbed dimension

K_θ is related to the statistical parameters $(\bar{r}_0^2)$ and the unperturbed mean square end-to-end distance by the Flory's equation (4)

$$K_\theta = \phi_0[\bar{r}_0^2/M_\omega]^{2/3} \tag{4}$$

On differentiating Eq. (4) with respect to T, the temperature coefficient of unperturbed dimension may be obtained

$$(\mathrm{d}\ln K_\theta/\mathrm{d}T) = 3/2[\{\mathrm{d}\ln(\bar{r}_0^2)\}/\mathrm{d}T] = K' \tag{5}$$

Here K', the temperature coefficient of K_θ, provides information regarding the configuration dependent properties of polymer chain and energies of bond conformations in the molecule [29]. In water–DMSO composition of 2:8, K' is found to be 0.046 deg^{-1} for acrylamide polymer (Table 3). The value of the temperature coefficient increases upto 3:7 mixture of the solvent, indicating again that the solvency power increases with the increase in temperature upto above solvent composition [30]. This further shows that the acrylamide polymer molecule expands more in the latter solvent composition and reveals the presence of low energy configuration in this solvent mixture at high temperature. On the other hand, at 5:5 and 7:3 compositions, the K' value is negative. The negative coefficient value indicates more compact structure and the existence of high energy configuration of the polymer in these compositions of the solvent [31]. However, at 8:2 composition, K' again assumes a positive value showing better cosolvency of the mixture.

Table 3
Temperature co-efficients (K') of unperturbed dimension at different DMSO compositions

φ_{DMSO}	K' (deg^{-1})
0.2	0.0460
0.3	0.0947
0.5	−0.0300
0.7	−0.0280
0.8	0.0320

3.3. Molecular extension factor (α_n)

The molecular extension factor (α_{n}) has been calculated from the relation [17]:

$$\alpha_{\mathrm{n}}^3 = [\eta]/K_\theta M_{\mathrm{v}}^{1/2} \tag{6}$$

using K_θ from the BSF plot. The actual end-to-end distance, $\alpha_{\mathrm{n}}K_\theta$, of polymer molecule is also computed, which are shown in Table 4. It is observed that at $\varphi_{\mathrm{DMSO}} = 0.5$, $\alpha_{\mathrm{n}}K_\theta$ attains the lowest value for all the molecular weight fractions of the polymer. However, α_{n} value is the highest at the above composition. The intermolecular interaction is probably responsible for the high value of α_{n} at $\varphi_{\mathrm{DMSO}} = 0.5$ because of the small value of the unperturbed dimension at this composition. The molecular weight dependency of α_{n} is also clear from the table; α_{n} increases with the increase in molecular weight of the polymer. As the molecular weight of the polymer increases, the number of segmental interactions of the polymer molecule with solvent molecule increases, resulting in a larger value of α_{n}.

Table 4
Molecular extension factor and coil dimensions of PAM at different temperatures in water + DMSO mixtures

Temperature (°C)	φ_{DMSO}	LM		MM		HM	
		α_{n}	$\alpha_{\mathrm{n}}K_\theta \times 10$	α_{n}	$\alpha_{\mathrm{n}}K_\theta \times 10$	α_{n}	$\alpha_{\mathrm{n}}K_\theta \times 10$
30	0.2	1.031	1.546	1.026	1.539	1.085	1.628
	0.3	1.053	1.185	1.192	1.340	1.176	1.323
	0.5	1.723	0.258	2.332	0.350	2.426	0.364
	0.7	1.330	0.865	1.640	1.070	1.720	1.117
	0.8	1.133	1.813	1.299	2.080	1.339	2.142
40	0.2	1.114	1.392	1.203	1.503	1.296	1.620
	0.3	1.091	1.036	1.170	1.112	1.169	1.110
	0.5	1.438	0.503	1.890	0.661	1.948	0.682
	0.7	1.470	0.735	1.858	0.929	2.000	1.001
	0.8	1.130	1.695	1.313	1.970	1.338	2.008
50	0.2	1.143	0.943	1.235	1.020	1.393	1.150
	0.3	1.580	0.316	2.250	0.450	2.347	0.470
	0.5	1.663	0.416	2.216	0.554	2.327	0.582
	0.7	1.293	1.196	1.522	1.408	1.650	1.526
	0.8	1.074	1.664	1.222	1.894	1.200	1.860

Table 5
Unperturbed dimension, steric factor (σ), characteristic ratio (C_α) as functions of φ_{DMSO} and temperature

Temperature (°C)	φ_{DMSO}	$[\langle r^2\rangle_0/M]^{1/2}\times 10^9$ ($\mathrm{cm\,g^{-1/2}\,mol^{1/2}}$)	C_α	σ^{a}
30	0.2	8.43	8.85	2.31
	0.3	7.66	7.30	2.10
	0.5	3.91	1.89	1.07
	0.7	6.38	5.05	1.75
	0.8	8.62	9.24	2.36
40	0.2	7.94	7.83	2.17
	0.3	7.24	6.52	1.98
	0.5	5.19	3.34	1.42
	0.7	5.85	4.24	1.60
	0.8	8.43	8.85	2.31
50	0.2	6.91	5.93	1.89
	0.3	4.31	2.30	1.62
	0.5	4.64	2.67	1.27
	0.7	7.18	6.40	1.97
	0.8	8.52	9.01	2.33

[a] Value of $[\langle r^2\rangle_0/M]^{1/2}$ has been taken as 3.65×10^{-9} $\mathrm{cm\,g^{-1/2}\,mol^{1/2}}$.

3.4. Chain rigidity

The structural parameters of PAM, viz., the steric factor σ and the characteristic ratio C_α; are also calculated in the usual manner from the following equations [30]

$$\sigma = [\langle r^2\rangle_0/M]^{1/2}_{0\mathrm{f}}/[\langle r^2\rangle_{0\mathrm{f}}/M]^{1/2} \tag{7}$$

$$[\langle r^2\rangle_{0\mathrm{f}}/M]^{1/2} = [\langle r^2\rangle_{0\mathrm{f}}/N]^{1/2}[1/M_0]^{1/2} \tag{8}$$

$$C_\alpha = (K_{\mathrm{q}}/\phi_0)^{2/3}(M_0/2L^2) \tag{9}$$

where $\langle r^2\rangle_{0\mathrm{f}}$ is the unperturbed mean square end-to-end distance for a freely rotating chain, N is the degree of polymerization, M_0 is the molecular weight of the monomer unit and L is the backbone bond length ($L = 0.154$ nm). For vinyl polymers the value of $(\langle r^2\rangle_{0\mathrm{f}}/N)^{1/2} = 3.08\times 10^{-8}$ cm [32]. The computed values of C_α, σ and $(\langle r^2\rangle_0/M)^{1/2}$ for PAM at different solvent compositions and temperatures are shown in Table 5. Cowie [32] observed that the range of values of σ normally encountered is about 1.5–2.5 [33]. In the present study also the value of σ falls within the above range and it decreases with ϕ_{DMSO} initially and, then increases giving rise to the lowest value at $\phi_{\mathrm{DMSO}} = 0.5$. This indicates the lowest rigidity of the polymer chain at this solvent composition and consequently, the molecules present a higher compacity expressed by the decrease of $[\eta]$.

Acknowledgement

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