Unperturbed dimensions of polyacrylamide in salt-water–methanol mixtures

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The unperturbed dimensions of polyacrylamide are determined by light scattering measurements, in methanol–water solutions and correspond to: $R_{G\theta}=0.39\pm0.01\ M^{0.5}$. This result is compared to that obtained from viscosity measurements in aqueous solution, through Stockmayer–Fixmann method. A possible explanation based upon the recent blob theory of polymers is proposed for the observed differences.

In a recent paper[1], we studied by light scattering and viscosimetry, the conformation of unhydrolysed polyacrylamide in aqueous solution, focusing our attention on the problem of the excluded volume exponent, ν, of the molecular weight dependence of the radius of gyration R_G ($R_G \propto M^\nu$). We obtained a value of ν (0.64) significantly different from the value 0.6 predicted for a polymer in good solvent by Flory's theory and confirmed by the recent renormalization calculation[2]. This high value of ν should lead, from the well known Fox–Flory relation[3] to an exponent (0.92) in the intrinsic viscosity dependence which completely disagrees with the experimental one (0.75).

On the basis of these first results it was difficult to understand such a behaviour. The value of ν suggested a great expansion of polyacrylamide in aqueous solution. If this is the case, the unperturbed dimensions cannot be determined by the extrapolation of the viscosity measurements at $M\to0$. This method (ex.: Stockmayer–Fixmann[4]) is only significant for low values of α. Therefore, to understand the conformational properties of polyacrylamide in aqueous solution, it was necessary to carry out direct measurements of their unperturbed dimensions.

EXPERIMENTAL

Samples

The polymer studied is a polyacrylamide sample of Calgon which is purified, analysed and fractionated. All details about the preparation and characterization of the different fractions are reported elsewhere[1]. The molecular weights and polydispersity indices of the samples used for this work are given in *Table 1*.

Research of a θ solvent

Reported in *Table 2*, are the results of solubility tests of polyacrylamide in different solvents, as a function of their solubility parameters[5]; it shows the difficulty in finding a unique θ solvent for this polymer in the explored temperature range ($0^\circ < T < 60^\circ$C). We, therefore chose a ternary solvent, salt–methanol–water, used for the fractionation of polyacrylamide[1].

Firstly, the θ composition of the solvents mixture were determined by turbidity measurements, with a Jobin and Yvon colorimeter. At constant temperature, we compared the results obtained either by addition of methanol in aqueous solution of polymer, or by addition of water in a diphasic polymer–methanol mixture. The two methods do not lead to the same result.

Figure 1 shows that the process is only reversible with salt present. Without salt, the precipitation kinetics are very low and it is not possible to determine the solubility limit.

T_p and c_p, temperature and volume fraction of methanol at the precipitation point, are linear functions of the reciprocal molecular weight of the polymer, the θ conditions corresponding to $M\to\infty$. We obtained the following relations:

$$\text{at } T=20^\circ\text{C} \qquad c_p=0.4+2.6\times10^6\frac{1}{M} \qquad (1)$$

and

$$\text{at } c_p=0.41 \qquad T_p=21.5-1.4\times10^6\frac{1}{M}\,^\circ\text{C} \qquad (2)$$

Table 1 Molecular weights and polydispersity indices of the fractions of polyacrylamide

	F_{2a}	F_{2b}	F_{22}	F_{23}
M_w	8.2×10^6	6.1×10^6	2.9×10^6	9.2×10^5
$\frac{M_w}{M_n}$	1.15	1.2	1.40	1.35

Table 2 Solubility tests of polyacrylamide in different solvents as a function of their solubility parameter δ

water	23.4	solvent
formamide	19.2	solvent
hydrazine	18.1	solvent
methylformamide	16.1	non-solvent
ethylene glycol	14.6	solvent
methanol	14.5	non-solvent
dimethylformamide	12.1	non-solvent
diethyleneglycol	12.1	non-solvent

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therefore we used the mixture containing 41% methanol. The θ temperature is more precisely determined by light scattering experiments.

Light scattering measurements

For our light scattering measurements, we used a laser diffusometer, realized in our Laboratory. Schematized in *Figure 2*, this apparatus follows the Wippler-Scheibling principle. It is equipped with:

(1) a gas laser He–Ne (SORO, $2M_w$) which provides a light beam linearly polarized ($\lambda = 6320$ Å). Millaud and Strazielle[6] have shown that the decrease of the scattered intensity (proportional to $1/\lambda^4$) is largely compensated for by the high value of the flux of the laser beam intensity.

(2) a photomultiplier (PM) which receives the scattered light reflected by a prism

(3) a stepping motor obeying a given program drives the PM, while the measurement cell does not move.

Therefore, we obtain the scattered intensity curve as a function of the scattering angle ($30° < \theta < 150°$).

The vertical nature of the polarization plane of the incident beam must be adjusted accurately. In this case, for a reference benzene we should obtain an angular dependence which depends only on the diffusing volume variation; the quantity $I_\theta \sin_\theta / I_{\theta=90°\mathrm{C}}$ should remain near to unity as it is shown in *Table 3*, for a reference benzene.

Benzene Rayleigh ratio at λ = 6320 Å. The fundamental relation of the light scattering in the case of a vertically polarized incident beam and for isotropic molecules is written:

$$K_v\left(\frac{\mathrm{d}n}{\mathrm{d}c}\right)^2 I_B\frac{c}{\Delta I\alpha} = P^{-1}(\theta)\left(\frac{1}{\langle M\rangle_w} + 2A_2c + \ldots\right) \qquad (3)$$

with M_w = average weight molecular weight; c = polymer concentration; A_2 = 2nd viriel coefficient of the osmotic pressure; $(\mathrm{d}n/\mathrm{d}c)$ = refractive index increment; $\alpha = \sin\theta$ diffusing volume correction; $P^{-1}(\theta)$ = angular dependance of the scattered intensity; I_B = scattered intensity at $\theta = 90°$C by benzene; ΔI = excess of scattered intensity between polymer solution and solvent

$$K_v = \frac{n_x^2\,4\pi^2}{R_{Bv}N_A\lambda^4} \quad \text{and} \quad R_{Bv} = R_B\frac{2}{1+\rho_n} \qquad (4)$$

ρ_n = depolarization factor of benzene for unpolarized light.

The R_B value must be known for the reference benzene. This parameter, as a function of the wavelength, is deduced from the following relation derived from the density fluctuations theory:

$$R_B = \frac{2\pi^2 kT\beta}{\lambda^4}\left(\mathrm{d}n\frac{\delta n}{\delta d}\right)^2\frac{6+6\rho_n}{6-7\rho_n} \qquad (5)$$

d = benzene density; K = Boltzmann constant (1.38 $\times 10^{-16}$ erg/K); β = compressibility coefficient of benzene (9.67×10^{-4} cm^2 dyne); $6+6\rho_n/6-7\rho_n$ = Cabannes factor.

The term $(\mathrm{d}n[\delta n/\delta d])$ can be expressed as a function of n from some semi empirical relations between n and d ($f(n) = \mathrm{d}\cdot$constant) and can be calculated taking into account the variation of n with λ_0. In *Table 4*, we compare the Carr and Zimm[7] experimental values ($\lambda = 4320$ and 5460 Å) with those obtained using different functions $f(n)$. The expressions which are in the best agreement with experimental results, are Lorentz Lorenz and Eykman ones: then we can evaluate an order of magnitude of R_B and K at 6320 Å, taking into account the discrepancies between theoretical and experimental values at the two other wave-lengths:

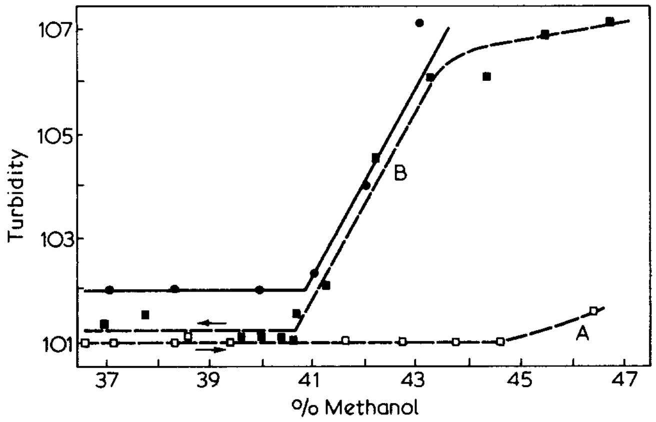

Figure 1 Research of the θ point by turbidity (——) in salt presence; (– – – –) without salt (A), methanol addition in aqueous solution; (B), water addition in diphasic polymer–methanol mixture

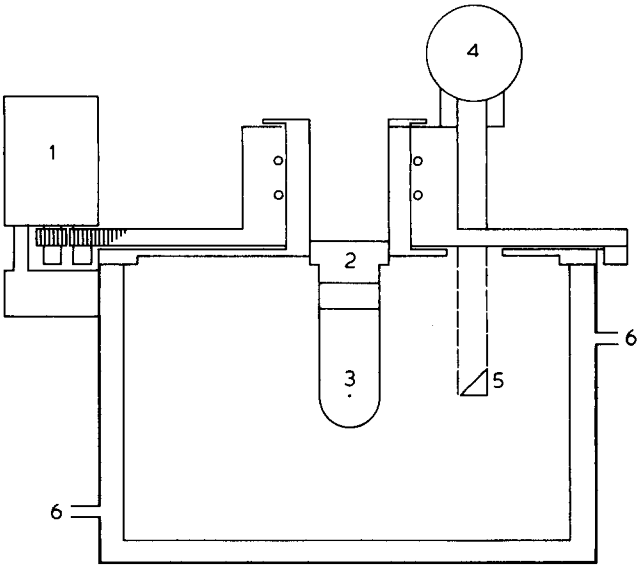

Figure 2 Shema of the diffusometer (1) stepping motor, (2) cell, (3) laser beam, (4) photomultiplier, (5) prism, (6) thermostatation

Table 3 Variation of the quantity $I_\theta \sin\theta / I_{\theta=90°\mathrm{C}}$ as a function of θ for the laser diffusometer with a reference benzene

30	37.5	45	60	75	90	105	120	135	142.5	150
1.007	1.002	1.005	1.002	1.005	1	1.004	0.994	1.000	1.000	1.002

Table 4 Comparison between the experimental and calculated values of R_B

λ_0 Å	n	(25) ρ_n	R_B 10^6 exp Carr–Zimm	R_B 10^6 Lorentz–Lorenz $f(n)=\frac{n^2-1}{n^2+2}$	R_B 10^6 Maxwell $f(n)=n^2-1$	R_B 10^6 Dale–Gladstone $f(n)=n-1$	R_B 10^6 Eykmann $f(n)=\frac{n^2-1}{n+0.4}$
4358	1.521	0.42	48.65	54	26.1	38.1	43.5
5461	1.503	0.41	16.3	19.1	9.46	13.6	15.5
6320	1.495	0.405*	–	9.96	5.00	7.18	8.17

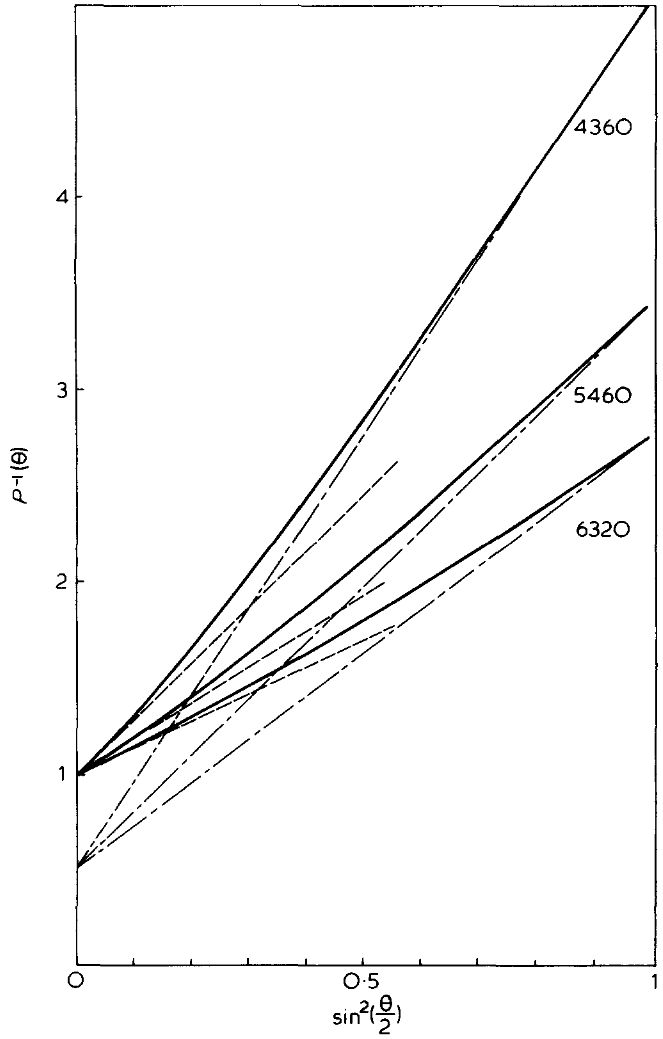

Figure 3 Variation of the P^{-1} (θ) function *versus* $\sin^2(\theta/2)$ at the different wave lengths (——); (— — — —) $\theta\rightarrow 0$ asymptot; (— · — · —) $\theta\rightarrow 180°$ asymptot

$$8.08\times10^{-6}<R_B<8.33\times10^{-6}$$

$$0.572>K>0.555$$

$$0.803>K_v>0.779 \qquad (1)$$

We have found an experimental verification of these values measuring the molecular weights of two standard samples being $M_w=300\,000$ and $M_w=157\,000$. We obtained $K_v=0.784$ and 0.796 respectively, slightly different from the Millaud and Strazielle experimental values[6] (≈ 0.770), and well situated inside the theoretical range (1).

Advantages and disadvantages of a $\lambda=6320$ Å light beam. The radius of the gyration (R_G) and the polydispersity index (IP) can be theoretically determined from the development of the $P^{-1}(\theta)$ function for $\theta\rightarrow 0$ and 180°C. In the case of a theta solvent:

$-\theta\rightarrow 0$

$$P^{-1}(\theta)_{\theta\rightarrow 0}=1+\langle R_G^2\rangle_z\frac{q^2}{3}+\ldots \qquad (6)$$

$\langle R_G^2\rangle_z^{1/2}$ is the radius of gyration of a molecule, the molecular weight of which is the z-average, q being the scattering wave vector.

$-\theta\rightarrow 180°$

$$P^{-1}(\theta)_{\theta\rightarrow 180°}=\frac{IP}{2}(1+\langle R_G^2\rangle_n q^2+\ldots) \qquad (7)$$

In this case, $\langle R_G^2\rangle_n^{1/2}$ corresponds to the number average molecular weight of the polymer.

According to the wavelength, the angle ranges in which these asymptotic behaviours can be applied are translated and extended. To simplify, we have represented *Figure 3*, $P^{-1}(\theta)$ as a function of $\sin^2(\theta/2)$ in the case of a monodisperse system ($M_w=9\times10^6$ $R_G=1900$ Å) for 3 different wavelengths:

(1) $\theta\rightarrow 0$, the more extended range in which the function is confounded with its asymptot, the higher the wavelength is. Therefore, we can expect a better determination of $\langle R_G^2\rangle_z^{1/2}$ with $\lambda=6320$ Å than with lower wavelengths

(2) $\theta\rightarrow 180°$, the asymptotic range is sufficiently important only for the lowest wavelength ($\lambda=4360$).

The informations expected from the study of this asymptotic behaviour (IP in the polydisperse system and the excluded volume exponent in good solvent[7]) cannot be obtained with too high a wavelength.

RESULTS

As a consequence of the preferential adsorption phenomena it is generally difficult to extrapolate the light scattering laws established for binary mixtures to the cases of ternary and quaternary mixtures[8,9]. The fluctuation theory, shows that the measured molecular weight has an apparent value and is related to the true molecular weight by the relation:

$$M_{\text{app}}=M\left[1+\lambda'\left(\frac{dn}{d\varphi_1}\Big/\frac{dn}{dc}\right)\right]^2 \qquad (8)$$

λ' = preferential adsorption coefficient; $dn/d\varphi_1$ = index increment of the solvent 2 with respects of its volume fraction φ_1.

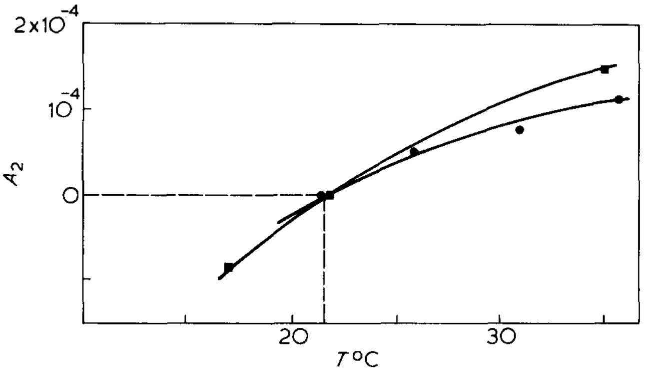

Figure 4 Variation of A_2 as a function of temperature. For F_{2a} (●) and F_{2b} (■) fractions of polyacrylamide in salt–methanol–water mixture

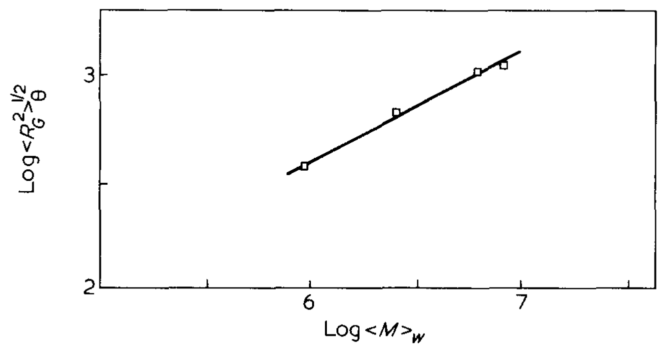

Figure 5 Log plot of $R_{G\theta}$ is a function of M_w for polyacrylamides at the θ point

Similarly the measured second virial coefficient is apparent

$$A_{2\mathrm{app}}=A_2\frac{M}{M_{\mathrm{app}}} \qquad (9)$$

Yamakawa[9] have demonstrated that the θ point does not coincide with the point of $A_{2\mathrm{app}}=0$, which complicates the determination of unperturbed dimensions.

However, it appears from the relation (8) that these difficulties vanish if the term $\mathrm{d}n/\mathrm{d}\varphi_1$ tends to 0; then, all the classical light scattering relations, established for binary mixtures become valid. For our system, starting from the variation of the refractive index with the volume fraction of methanol[5], one can evaluate the ratio M_{app}/M equal to 0.9 which is of the same order of magnitude as the incertitude of the light scattering measurements. The experimental ratios between the molecular weights measured in the ternary and binary solvents are never significantly lower than 0.9. Therefore, at the theta point, we should simultaneously observe $A_2=0$ and $R_G \alpha M^{0.5}$. *Figures 4* and *5* show that it is verified for our system at $T=21$°C. The first represents the variation of A_2 *versus* temperature for two different samples. In the second, we have reported the variation of log R_G *versus* log M, which is linear with a slope equal to 0.5, following the relation

$$\langle R_G^2\rangle_\theta^{1/2}=(0.39\pm0.01)\langle M_w\rangle^{0.5} \qquad (10)$$

This law defines the unperturbed regime of polyacrylamide and allows us to determine the variation of the expansion coefficient of polyacrylamide in aqueous solution[1]

$$\alpha=0.19\ M^{0.14} \qquad (11)$$

the calculation of α, for $M_w\approx10^7$, gives a value of 1.8 which is not very high. For comparison, the α value of the polystyrene of the same molecular weight in benzene solution is 2.10 which is significantly higher. Thus, we can conclude that the high value of the exponent (0.64) of the molecular weight dependence of the radius of gyration is not related to a great expansion of the macromolecular coil. The determination of the unperturbed dimensions by extrapolation of viscosity measurements in good solvents, at $M\rightarrow0$ should be possible and works of Okada[10] and Yamaguchi[11] provide such determinations. *Figure 6* shows a disagreement between the extrapolated and experimental values. In the following discussion, we should like to show that this discrepancy could be explained by the theoretical approach used to interpret our other results[13–16]. As pointed out in a previous paper[1], no alternative approach is likely to explain all our experimental results.

DISCUSSION

The methods of the Stockmayer–Fixmann type are based upon the perturbation theory which implies that the expansion coefficient α, for its low values, can be developed as

$$\alpha^x \propto 1+az \qquad (12)$$

where z is the excluded volume parameter

$$z=\left(\frac{3}{2b^2M_s^3}\right)^{3/2}\beta M^{1/2} \qquad (13)$$

b = length of the elementar segment; M_s = molecular weight of the elementar segment; $\beta=(1\text{-}\exp\,(W(r)/kT))\mathrm{d}r$ binary cluster integral; $W(r)$ = interaction potential between two segments at distance r.

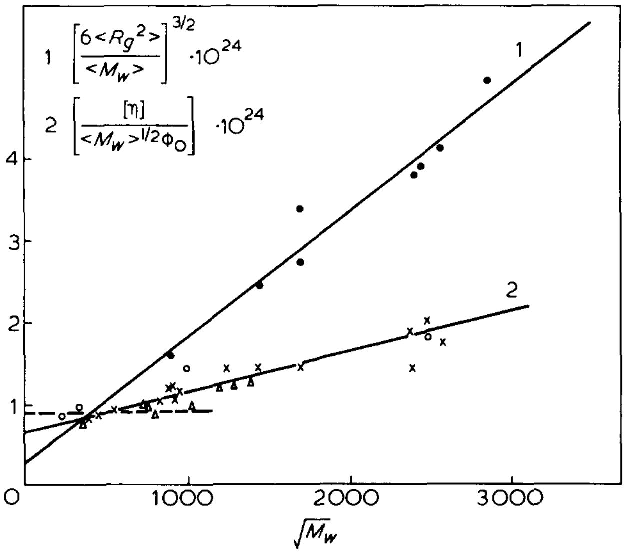

Figure 6 Determination of the unperturbed dimensions of polyacrylamide from light scattering (●) and viscosity measurements (x) in 0.1 M NaCl aqueous solution. (△) and (○) viscosity data of Yamaguchi *et al.*[11] and Sholtan[17]; (——) straight line determined by least squares analysis; (— — —) value of A^3 as determined from relation (2)

Table 5 Unperturbed dimensions of some vinyl polymers[5] for comparison with the polyacrylamide behaviour. V_θ values determined from viscosity measurements in θ solvent. V values determined from viscosity measurements in good solvent (extrapolation at $M \rightarrow 0$). R_θ values determined from light scattering measurements in θ solvent

	A' 10^{11} (cm)	Method
Polyvinylacetate	6537	V
Poly(vinyl alcohol)	6301	V
Poly 4 bromostyrene	6695	V_θ
Polymethylstyrene	7512	V
Polystyrene	7036	V_θ
"	7045	V_G
"	8600	R_θ
"	6869	R_θ
Polyvinylpyridine	7205	V
Polyacrylamide	6968	V
"	7836	R_θ

The most used relation with $x=3$ has been established by Stockmayer–Fixmann[4]; for the viscosity they have obtained

$$[\eta]/M^{1/2}\varphi_0 = A^3 + K_1 M^{1/2} \tag{14}$$

A relation of the same type can be proposed from the radius of gyration measurements

$$\left(\frac{6R_G^2}{M}\right)^{3/2} = A^3 + K_2 M^{1/2} \tag{15}$$

with

$$A^3 = \left(\frac{6\langle R_G\rangle_\theta^2}{M}\right)^{3/2}$$

In these perturbations theories, the expansion is assumed to be uniform along the chain. But, as pointed out by the more recent theories[2], a chemical distance corresponding to a number N_c of elements, is required for the development of an excluded volume statistic. Thus:

(1) for $M < M_c$, the chain obeys the Gaussian statistic with $R_G \propto M^{0.5}$

(2) for $M > M_c$ $R_G \propto (M/M_c)^\nu$, with a variable value of ν which attains for $M \approx 6M$ its asymptotical value[12], 0.6. This point of view leads us to propose a development of α of the type:

$$\alpha^3 \propto 1 + a\left(\frac{M}{M'_c} - 1\right)^{1/2}$$

M'_c being $6.M_c$[13–15] which transforms the relations (14) and (15) into:

$$[\eta]/M^{1/2}\varphi_0 = A^3 + K'_1\left(\frac{M}{M'_c} - 1\right)^{1/2} \tag{16}$$

and

$$\left(\frac{6R_G^2}{M}\right)^{3/2} = A^3 + K'_2\left(\frac{M}{M'_c} - 1\right)^{1/2} \tag{17}$$

It is then clear that, in the classical Stockmayer–Fixmann representation, one must extrapolate $[\eta]/M^{1/2}\varphi_0$ to $M = M'_c$ and not to $M = 0$, in order to obtain the A^3 values. The curves $[\eta]/M^{1/2}\varphi_0 = f(M^{1/2})$ and $(6R_G^2/M)^{3/2} = f(M^{1/2})$ should cross at $M = M'_c$. One can understand that the validity of the Stockmayer–Fixmann method depends on the value of N_c which is a characteristic of the considered system polymer–solvent. For low values of N_c, the method can be rather good but for its high values, it provides underestimated values of A.

In the case of polyacrylamide in 0.1 m NaCl water, we have obtained, from previous experimental results[1], the curves of *Figure 6*. For viscosity measurements, there is good agreement between our results and those obtained by other authors[11,17]. The two straight lines, determined by least squares analysis do not cross for $M = 0$ but for $M'_c = 143\,000$. Also this cross point corresponds to a value of A^3 equal to 0.83×10^{-24} Å^3, which is in good agreement with the experimental value obtained from relation (10): 0.87×10^{-24} Å^3. These values are significantly different to the extrapolation values at $M \rightarrow 0$, 0.65×10^{-24} for viscosity, and 0.25×10^{-24} for radius gyration measurements.

Under a critical molecular weight equal to 140 000, the polyacrylamide in aqueous solution remains constant. Such a value of M'_c can also be found, from the comparison between the molecular weight dependences of R_G in water solution and $R_{G\theta}$ in θ solvent (relations (10) and (11)). R_G becomes equal to $R_{G\theta}$ for a molecular weight, $M'_c \sim 130\,000$, agreeing with our last determination. For comparison, the same treatment was applied to the case of polystyrene in benzene and cyclohexane following the experimental relation[16]

$$R_{G(\text{benzene})} = 0.145\ M^{0.6} \tag{18}$$

$$R_{\theta(\text{cyclohexane } 34^\circ\text{C})} = 0.347\ M^{0.5} \tag{19}$$

leads to a value of $M'_c = 6160$ for this polymer in benzene, much lower than the value found for polyacrylamide in aqueous solution.

To compare the unperturbed dimensions of polyacrylamide with those directly measured of other vinyl polymers in organic solvents, we have reported the values of the A' parameter in *Table 5* defined as:

$$A' = (6\langle R_G^2\rangle_\theta/N)^{1/2}$$

N = polymerization degree.

It appears that the polyacrylamide has the same order of magnitude of local rigidity as the other vinyl polymers.

CONCLUSION

In θ conditions the polyacrylamide presents an unusual behaviour of vinyl without particular rigidity of the polymer. In aqueous solution, the expansion coefficient is not very high despite the value of the excluded volume exponent. This apparent contradiction is explained elsewhere[16] from hypothesis of the recent blob theory. The same approach seems likely to explain the discrepancies between the values of the unperturbed dimensions as measured in a theta solvent and as determined by extrapolation method.

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