polymer communications

Dynamic dimensions in the polyacrylamide–water system

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(Received 12 November 1979)

A careful study of polyacrylamide in aqueous solutions[1], performed with well-characterized fractions, has revealed the following exponents of the radius of gyration, R_G and intrinsic viscosity $[\eta]$ –molecular weight power laws:

$$R_G = 0.0749\,M^{0.64} \qquad (1)$$

$$[\eta] = 9.33 \times 10^{-3} M^{0.75} \qquad (2)$$

The exponents of these laws present two peculiarities. First, the value of 0.64 is significantly higher than the expected classical one $\nu = 0.60$ and has been cross-checked by the analysis of the asymptotical behaviour of the scattering curve $S(q)$, in the case of very high molecular weight samples.

Secondly, the relation between the two exponents $\nu = 0.64$ and $a = 0.75$ does not fit the classical Flory–Fox relation[2]:

$$[\eta] = \phi 6^{3/2}\ R_G^3/M$$

which leads to

$$a = 3\nu - 1$$

Indeed, one would expect $a = 0.8$ for $\nu = 0.6$ and $a = 0.92$ if we take $\nu = 0.64$. In fact, in spite of its common use, this relation is seldom verified by experiments. Many attempts[3] have been made in order to explain its failure and have led to the introduction of a distinction between the static and dynamic dimensions R_G and R_D of a polymer chain: one has to write for the intrinsic viscosity:

$$[\eta] \propto \frac{R_G^2 R_D}{M} \qquad (3)$$

and the translational diffusion coefficient D and sedimentation coefficient S must be expressed as:

$$D \propto \frac{1}{R_D} \neq \frac{1}{R_G} \qquad (4)$$

$$S \propto \frac{M}{R_D} \qquad (5)$$

Several experimental studies have shown that the exponents ν_G and ν_D in the power laws for R_G and R_D are indeed different[4].

Recently, Weill and Des Cloizeaux[5] have suggested that this discrepancy can be due to a crossover effect between Gaussian and excluded volume statistics, occurring at a critical number of segments N_c (ref. 6). Their theory predicts that ν_G increases rapidly from 0.5 at $N/N_c \leqslant 1$ to 0.60 at $N/N_c \sim 6$ while ν_D increases rather slowly and reaches its asymptotic value 0.60 at much higher values of $N/N_c > 100$. Therefore, in an intermediate range of molecular weight depending on the value of N_c characteristic of the polymer solvent system, one must observe a difference between the effective values $\nu_D < \nu_G$.

Such a theory, if it does not explain the high value of $\nu = 0.64$ (a point which is considered in a separate paper[7]), should at least give an interpretation of the relation between ν_G and a, since from equation (3):

$$a = 2\nu_G + \nu_D - 1$$

Measurements of S and D have therefore been performed in order to obtain ν_D. Simultaneously it is possible to check the value of ν_G from purely hydrodynamic experiments. It has already been shown in one case[8] where the values of $[\eta]$ and D were known on individual fractions that a log–log plot of the product $[\eta]DM$, proportional to R_G^2 (see equations (3) and (4)), *versus* M can provide an accurate value of ν_G (ref. 8). The same holds for the product $[\eta]S$.

Experimental

Samples. A commercial polyacrylamide sample from CALGON was carefully purified, analysed and fractionated. All details concerning the preparation and characterization of the different fractions are reported elsewhere[1]. The weight-average molecular weights measured by light scattering, and the polydispersity indices determined from gel chromatography are given in *Table 1*.

Sedimentation coefficient S *and translational diffusion coefficient* D *measurements.* A SPINCO Model E Analytical Ultracentrifuge was used for both S and D measurements.

Sedimentation coefficient. In all experiments the rotor speed was 45 000 rpm. Photographs of the Schlieren pattern were taken every 8 min and analysed with a Nikon Model 6C profile projector. The apparent sedimentation coefficient S_{app} was determined for each concentration from the usual linear log r *versus* t plot, (r being the distance of the peak of the Schlieren pattern measured from the centre of the rotation and t the time), using least square analysis. Dilution effects due to the cell shape and hydrostatic pressure effects

0032–3861/80/030247–03$02.00

Table 1

	M_w (10^{-6}) (ref. 1)	S_w (10^{12})	D_w (10^8)	$M(S/D)_{exp}$ (10^{-6})	$M(S/D)_{cal}$ (10^{-6})	M_w/M_n (ref. 1)	$[\eta]$ (cm^3 g^{-1}) (ref. 1)
F_2a	8.2	2.04	2.57	7.0	–	1.15	–
F_1a	6.7	2.24	2.75	6.2	6.4	1.2	1258
F_2b	6.1	2.00	–	–	–	1.2	1071
F_{13}	2.9	1.82	–	–	–	1.4	
F_2c	2.56	1.29	5.01	2.26	2.11	1.3	–
F_{23}	0.92	0.71	8.31	0.75	0.78	1.35	263.0
F_{24}	0.32	0.45	–	–	–	1.2	120.2
1AP	0.13	0.34	23.24	0.10	0.097	1.4	52.5

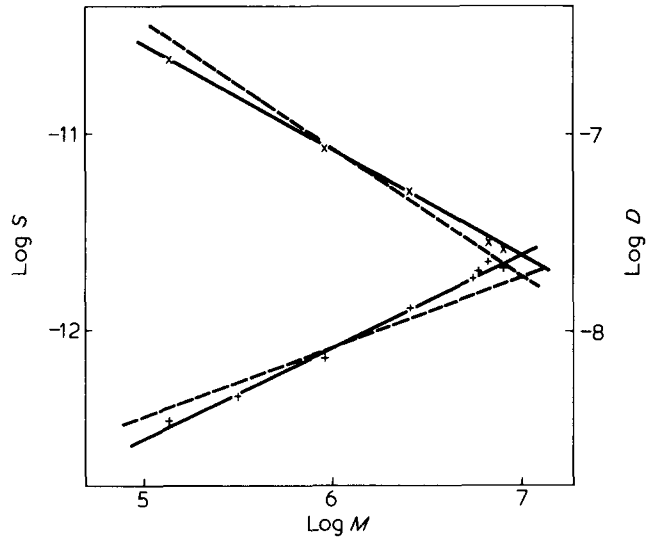

Figure 1 Log–log plot of *S* and *D versus M.* ———, straight line given by least square analysis; – – – –, straight line with slope 0.6

can sometimes lead to a time dependence of S_{app}, but the good linearity of our curves $\log r = f(t)$ allows us to neglect these effects.

The concentrations of our solutions ranged between 10^{-4} and 10^{-3} g cm^{-3} and the sedimentation coefficient S was determined by extrapolation at $c = 0$ of the straight line $1/S_{app} = f(c)$. For a polymolecular sample, we obtained S_w, the weight average value of S.

Translation diffusion coefficient. A synthetic boundary cell and a low rotor speed (22 000 rpm) was used in order to obtain the sedimentation equilibrium conditions. D was calculated using the surface method:

$$D \propto \frac{(\Delta c)^2}{\left(\dfrac{\partial c}{\partial r}\right)^2_{max} t}$$

$(\partial c/\partial r)_{max}$, the maximum value of the gradient, is proportional to the maximum height H_{max} of the curve of concentration (or index of refraction) gradient. Δc, the concentration difference between the two cell compartments, is proportional to the surface A_t, limited by the curve. t, the diffusion time = $t_m - t_0$.

In practice:

$$D \propto \left(\frac{A_t}{H_{max}}\right)^2 \frac{1}{(t_m - t_0)} \tag{6}$$

A_t is determined either by planimetry or by summation of elementary surfaces, the two methods being in good agreement. t_0, the real zero time for the beginning of the diffusion process, corresponds to the value of t_m, (time measured from the beginning of the experiment) for which $(A_t/H_{max})^2 = 0$.

Corrections related to dilution effects and to the displacement with respect to the force field are not necessary since we have verified that the distance of H_{max} from the meniscus does not vary during our experiments.

The value of D calculated from equation (6) depends on time and we have to extrapolate at $t_m - t_0 = 0$, neglecting the first points which correspond to a situation where the sedimentation equilibrium is not reached.

The measurement was carried out on only one solution of each sample, but the concentrations (10^{-4} g cm^{-3} for higher molecular weight and $\sim 10^{-3}$ g cm^{-3} for the lower) are chosen so that we could neglect the concentration effects on friction coefficient F, which are known from previous sedimentation studies.

Results

Our experimental results are reported in *Table 1* and the log–log plots of S and D *versus* M are shown in *Figure 1*.

The power laws determined by least square analysis are:

$$D = 1.24 \times 10^{-4} M_w^{-0.53 \pm 0.01} \text{ cm}^2 \text{ s}^{-1} \tag{7}$$

$$S = 1.07 \times 10^{-15} M_w^{0.48 \pm 0.01} \text{ Svedberg} \tag{8}$$

One can obtain a comparison for these results from the Svedberg relation:

$$M = \frac{1 - \bar{v}_{sp} d_1}{RT} \frac{S}{D} = C \frac{S}{D} \tag{9}$$

where $\bar{v}_{sp}$ is the partial specific volume of the polymer (0.708 cm^3 g^{-1} for polyacrylamide in aqueous solutions[1]) and d_1 the solvent density. The values of M designated by $M(S/D)_{exp}$ thus obtained are reported in *Table 1*. They are normally lower than the weight average M_w measured by light scattering, since they correspond to:

$$M\left(\frac{S}{D}\right) \sim \frac{\int_0^\infty Mf(M)M^{0.48} \mathrm{d}M}{\int_0^\infty Mf(M)M^{-0.53} \mathrm{d}M} \tag{10}$$

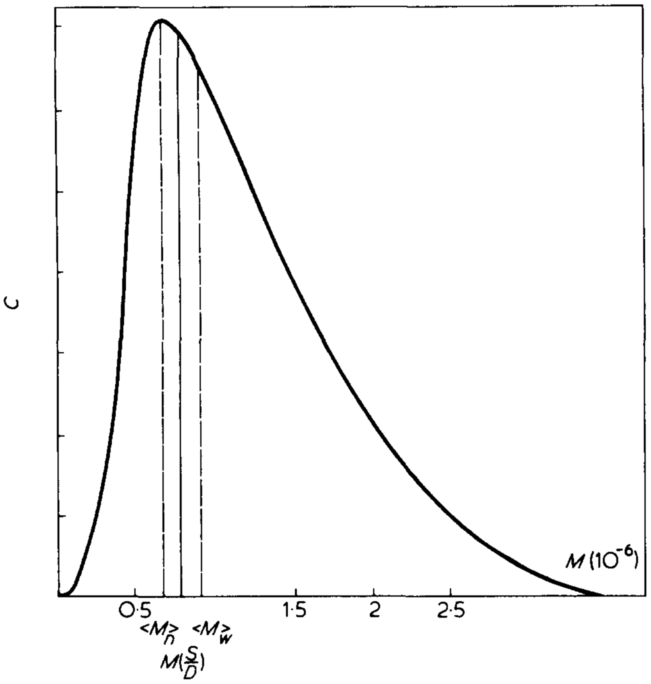

Figure 2 Weight distribution function of molecular weight of the F_{23} sample

From the weight distribution function $f(M)$, given by our previous g.p.c. experiments, we can calculate from equation (10) a value $M(S/D)_{cal}$. *Figure 2* shows, in the case of the f_{23} fraction, how the three averages M_w, $M(S/D)$ and M_n are situated with respect to the distribution function. The good agreement between the values $M(S/D)_{cal}$ and $M(S/D)_{exp}$ given in *Table 1* provides a confirmation of the validity of the power laws (7) and (8).

Discussion

Essentially, these results lead us to draw two conclusions. The dynamic exponent $\nu_D \sim (0.53\text{–}0.52)$ is much smaller than the static exponent $\nu_G = 0.64$. The Weill and Des Cloizeaux theory predicts this in the case of a poor solvent. The values of A_2 obtained in water solution[1] as well as the values of the expansion factor α obtained from a comparison of the dimensions with those in a θ solvent[9] indeed show that water is not a good solvent, and that in the range of molecular weight under study, N/N_c remains smaller than 5×10^2 (ref. 8).

The high value $\nu_G = 0.64$ is confirmed by the measurement of the dynamic quantities $[\eta]$, S and D. For the individual fractions for which all three quantities have been independently measured, the two equivalent products $[\eta]\,DM$ and $[\eta]\,CS$ (see equation 9) have been calculated. The log–log plot of these two products *versus* M (represented in *Figure 3*) gives, from least square analysis, a slope of $2\nu_G = 1.28$ in excellent agreement with the result of the direct measurements of the radius of gyration. Such a result substantiates simultaneeously the abnormally high value of ν_G found in direct experiments and the validity of the combination of dynamic quantities such as $[\eta]$, D and S to obtain ν_G. A direct combination of the power laws for $[\eta]$, S and D ($a = 2\nu_G + \nu_D - 1$, see equation (3)) would lead to a less satisfactory agreement. Using the values of ν_G and ν_D in equations (1), (7) and (8), one would get $a = 0.80 \pm 0.02$, or inversely, using the values of a and ν_D, one would get $\nu_G = 0.61 \pm 0.02$. This discrepancy calls attention to the difficulties of combining power laws obtained by a separate fitting of related quantities in a range of molecular weight where ν_D and eventually ν_G are only 'effective' indices[5].

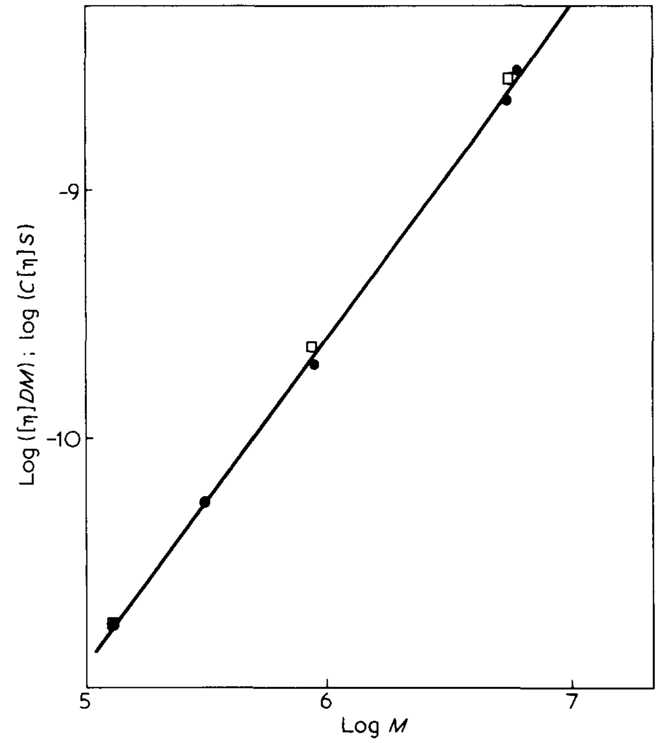

Figure 3 Log–log plot of the products ($C[\eta]\,S$), ●, and ($[\eta]\,DM$), □, *versus M*

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