low molar mass and large dispersity of the 10 500-dalton dextran may thus combine to distort ensemble averaging of the diffusion coefficient for this polymer. However, at higher concentrations in the dilute regime the averaging process would be aided by greater polymer–polymer proximity, and the fact that the higher concentration data extrapolate to D_0 and k_f values consistent with those of the higher molar mass dextrans reinforces this view.

The apparent molar mass independence of the friction coefficient k_f values is surprising. Of the theories that account for the value of k_f,[21-23] all predict a significant mass dependence. The only molar mass independent term in the theoretical expressions for k_f is the polymer specific volume, and this is an order of magnitude smaller than the observed k_f plateau.

However, the dextran k_f values are unique only in that the mass independence persists up to $M_w \simeq 5 \times 10^5$ daltons. Both King et al.[24] and ourselves[2] have observed a plateau in k_f values for polystyrenes of low M. In our own study of polystyrene in CCl_4 we found that the Yamakawa theory[21] gave an excellent description of the data for $M > 20\,000$ daltons but below this molar mass, the k_f values were constant at $\simeq 10^{-2}$ m^3 kg^{-1}, in contradiction with theory.

Acknowledgment. We thank Dr. Alex Mackay and Professor Robert Molday for valuable advice. The dextran diffusion measurements were performed in the laboratory of Professor Myer Bloom and we are indebted to him for his interest and support.

Registry No. Dextran, 9004-54-0.

References and Notes

(1) Callaghan, P. T.; Pinder, D. N. *Macromolecules* **1980**, *13*, 1085.
(2) Callaghan, P. T.; Pinder, D. N. *Macromolecules* **1981**, *14*, 1334.
(3) Hervet, H.; Léger, L.; Rondelez, F. *Phys. Rev. Lett.* **1979**, *42*, 1681.
(4) de Gennes, P.-G. *Macromolecules* **1976**, *9*, 587.
(5) de Gennes, P.-G. *Macromolecules* **1976**, *9*, 595.
(6) Cotton, J. P.; Decker, D.; Farnoux, B.; Jannink, G.; Ober, R.; Picot, C. *Phys. Rev. Lett.* **1974**, *32*, 1170.
(7) Kirkwood, J. G.; Riseman, J. *J. Chem. Phys.* **1948**, *16*, 565.
(8) Weill, G.; des Cloizeaux, J. *J. Phys. (Paris)* **1979**, *40*, 99.
(9) Callaghan, P. T.; Trotter, C. M.; Jolley, K. W. *J. Magn. Reson.* **1980**, *37*, 247.
(10) Mills, R. *J. Phys. Chem.* **1973**, *77*, 687.
(11) Stejskal, E. O.; Tanner, J. E. *J. Chem. Phys.* **1965**, *42*, 288.
(12) Pasika, W. M.; Cragg, L. H. *Can. J. Chem.* **1963**, *41*, 293.
(13) Luz, Z.; Gill, D.; Meiboom, S. *J. Chem. Phys.* **1959**, *30*, 1540.
(14) Some account of T_2 variations should be considered in weighting spin echoes as suggested. In fact, T_2 is molar mass independent for polymers in the semidilute and dilute regimes (Heatley, F. *Prog. NMR Spectrosc.* **1979**, *13*, 47). Indeed we observe no obvious variation in polymer proton T_2 values over the range of molar masses used in this work.
(15) Van Cleve, J. W.; Schaefer, W. C.; Rist, C. E. *J. Am. Chem. Soc.* **1956**, *78*, 4435.
(16) Larm, O.; Lindberg, B.; Svenson, S. *Carbohydr. Res.* **1971**, *20*, 39.
(17) de Gennes, P.-G. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca (NY) and London, 1979.
(18) Brown, W.; Stilbs, P.; Johnsen, R. M. *J. Polym. Sci., Polym Phys. Ed.*, submitted.
(19) Callaghan, P. T.; Pinder, D. N. *Polym. Bull.* **1981**, *5*, 305.
(20) Laurent, T. C.; Sundelöf, L. O.; Wik, K. V.; Wärmegård, B. *Eur. J. Biochem.* **1976**, *68*, 95.
(21) Yamakawa, H. *J. Chem. Phys.* **1962**, *36*, 2995.
(22) Pyun, C. W.; Fixman, M. J. *J. Chem. Phys.* **1964**, *41*, 937.
(23) Imai, S. *J. Chem. Phys.* **1969**, *50*, 2116.
(24) King, T. A.; Knox, A.; McAdam, J. D. *Polymer* **1973**, *14*, 293.

Quasi-Elastic Light Scattering by Polyelectrolyte Solutions without Added Salt

Rudolf S. Koene and Michel Mandel*

Department of Physical and Macromolecular Chemistry, Gorlaeus Laboratories, University of Leiden, 2300 RA Leiden, The Netherlands. *Received July 23, 1982*

ABSTRACT: Quasi-elastic light scattering experiments as a function of macromolecular concentration have been performed on aqueous solutions of sodium poly(styrenesulfonates) in the semidilute regime. Two different molar masses were investigated ($M_w = 6.5 \times 10^5$ and 12×10^5 g mol^{-1}). An effective diffusion coefficient was obtained from the dependence on the scattering angle of the first cumulant of the scattered light intensity autocorrelation function. For both samples of NaPSS three concentration regions could be observed. At very low concentrations, close to the critical concentration, D_{eff} was found to be practically concentration independent but with a lower value for the higher molar mass. It probably corresponds to D of a freely diffusing macromolecule. At higher concentrations D_{eff} was still molar mass dependent but decreased with increasing concentrations to very small values. An interpretation based on a reptation model has been tentatively proposed for the diffusion mechanism in that concentration range. When a certain concentration is reached, roughly corresponding to conditions where the correlation length in the solution is of the same order of magnitude as the (electrostatic part of the) persistence length of the macromolecular chain, a fast diffusion mechanism appears at the same time as the slow diffusion mode becomes nearly undetectable. The former seems to be characterized by a molar mass independent D_{eff}, but it has not yet been possible to establish whether or not D_{eff} in this concentration region increases with concentration. The exact nature of this probably cooperative diffusion mechanism could not be established.

Introduction

Polyelectrolyte solutions without added low molar mass electrolyte are quoted to belong to the category of physical systems the behavior of which is most difficult to understand. It has been widely accepted that a highly charged polyelectrolyte chain in such a solution and at very high dilution will be nearly fully stretched due to the strong electrostatic repulsion of the like charges along the macromolecular chain, which are only weakly screened. Under these conditions the polyelectrolyte can be represented as a rigid uniformily charged rod as has been used by Katchalsky[1] in his cell-model theory for salt-free polyelectrolyte solutions. This theory can fairly well explain the thermodynamic and some transport properties observed with such solutions at low concentrations. It is not suitable, however, to describe the concentration dependence

0024-9297/83/2216-0973$01.50/0

of the characeristic physical quantities of these solutions at higher concentrations or to predict how the average dimensions of the polyion will change with concentration because of deviations from the fully stretched conformation. The same remarks apply to other theories that neglect such deviations and are expected to be applicable only in the limit of infinite dilution.

A few years ago de Gennes et al.[2] used scaling concepts to take into account concentration dependencies in polyelectrolyte systems without added low molar mass electrolyte. They distinguished three concentration regimes with different polyion behavior for polyelectrolytes with a flexible backbone if uncharged. At the lowest concentrations (dilute regime; $c \ll c_G^*$, where c is the concentration in monomolecules per unit volume) the polyelectrolyte chains are on the average widely separated and fully stretched and the average dimensions are proportional to the degree of polymerization. Above c_G^* the fully stretched chain cannot orient freely any more and the electrostatic interaction between the polyions may lead to a tridimensional lattice. Detection of such a still very dilute lattice is difficult, however. Most experimental investigations seem to have been carried out at much higher concentrations, $c \gg c_G^*$, where considerable overlap between the chains in the solutions should occur, leading to a transient network with a characteristic length ξ, as is the case for flexible, neutral polymers. Chainlengths smaller than ξ (which decreases with concentration as $c^{-1/2}$) may be considered fully stretched, but over contour distances larger than ξ all electrostatic interactions are screened off by other chains so that the polyelectrolyte may be pictured as an ideal chain of segments with a length ξ. This leads to average dimensions that should decrease with concentration as $c^{-1/4}$ for $c \gg c^*$.

More recently Odijk[3] has reconsidered this scaling approach to polyelectrolyte solutions without added low molar mass electrolyte. He introduced explicitly a concentration-dependent flexibility of the polyelectrolyte chain through the persistence length of a wormlike model and counterion screening of the charges on the macromolecule. For the former an expression obtained by extrapolation of the equation for the persistence length in the presence of an excess of salt[4] to the case of no salt was used, and for the latter Debye–Hückel screening by uncondensed counterions only was considered. This leads to an expression for the persistence length L_t that decreases with concentration as c^{-1}. A critical concentration c^* is introduced where $L_t \simeq l$, with l being the contour length of the polyelectrolyte. Three different regimes are now considered for $c > c^*$. For $c^* < c < c^{**}$ the tridimensional lattice is deformed but retains some anisotropy; this is the regime where $L_t \gg \xi$. Above c^{**} (defined as the concentration where the lattice melts) the system is in an isotropic phase with $L_t \ll \xi$, and the macromolecular chain may be viewed as an ideal chain of "blobs" with average dimension ξ, each blob being treated as a wormlike chain with fully exerted excluded-volume effect. In the former regime $\xi \sim c^{-1/2}$ and $R \sim c^{-1/2}$ and in the latter we should have $\xi \sim c^{-3/8}$ and $R \sim c^{-5/16}$ or $\xi \sim c^{-5/8}$ and $R \sim c^{-3/16}$ for the case where $L_t \simeq L_e(c^{-1})$ or $L_t \simeq L_p$, respectively. Here the total persistence length L_t is split up in an intrinsic part, L_p (which would characterize the chain in the absence of charge interactions), and an electrostatic part, L_e, the latter having a decreasing contribution with increasing c according to a c^{-1} law.

Some evidence has been found for Odijk's theory from NMR relaxation measurements by Leyte and co-workers,[5] from sedimentation experiments by Roots and Nyström,[6] and from quasi-elastic light-scattering experiments by Grüner and Lehman.[7] The behavior of polyelectrolytes in salt-free aqueous solutions is, however, not yet well established, and its interpretation, especially above c^*, is not satisfactory.

Following our quasi-elastic light-scattering experiments on aqueous poly(styrenesulfonate) solutions in the presence of NaCl[8-10] for which scaling relations as proposed by Odijk[3] have been tested, we wish to present and discuss here some quasi-elastic light-scattering results obtained with the same polyelectrolyte in salt-free aqueous solutions at concentrations in the semidilute regime above c^*.

Experimental Section

Sodium poly(styrenesulfonate) (NaPSS) samples of molar mass $M_w = 6.5 \times 10^5$ g mol^{-1} and $M_w = 12 \times 10^5$ g mol^{-1} have been purchased from Pressure Chemical Co. (Pittsburgh). They have been prepared by sulfonation of well-defined monodisperse polystyrene and are claimed to be fairly homodisperse ($M_w/M_n < 1.1$).

Solutions were prepared with filtered, deionized, and sterilized water obtained from a Millipore water purification unit. Concentrations were determined spectrophotometrically at 261 nm always after the light-scattering experiments for which the solutions had to be thoroughly filtered over Millipore filters (diameter 0.22 μm). Even after multiple filtration some solutions were still not dust free so that the recording of the correlation function was difficult (with a Malvern 4300 photocorrelation spectrometer incorporating the Malvern digital correlator Type K 7023/2 cm 96, with argon ion laser operating at 514.5 nm as described previously[8]). Further complications arose from the fact that the salt-free polyelectrolyte solutions have a rather low scattering intensity as compared to systems of analogous polyion concentrations but in the presence of low molar mass electrolyte. As a consequence the recording of the scattered light intensity autocorrelation function at 25 °C took a much longer time (15 min as compared to approximately 1 min) with a resulting lower signal-to-noise ratio (of the order of 5%). This influence unfavorably the standard deviations of the parameters obtained from an analysis of the correlation function.

Although the experimentally obtained correlation functions could be fitted to a single exponential with floating base line with a rather small standard deviation of the experimental points with respect to the fitted curve (of the order of a few tenths of a percent), the individual deviations showed a "structural" behavior and the quality factor of the fit was generally not good ($Q < 0.5$). Therefore the data analysis was performed with an exponential cumulant expression and floating base line

$$Y(t) = A + B\exp(-K_1 t + K_2 t^2 - K_3 t^3) \qquad (1)$$

by using a nonlinear least-squares technique with the Gauss–Newton algorithm as before.[8] The first cumulant, K_1, may be related to an effective diffusion coefficient if it is linearly dependent on $\sin^2(\theta/2)$, where θ is the scattering angle.

Due to the experimental difficulties mentioned above the standard deviation in K_1 was about 5%. In all cases considered the contribution of the second and third cumulant was small as compared to that of the first cumulant and, within experimental error, *independent of the concentration*. This is in agreement with the observation that the deviations of $Y(t)$ from a single exponential function are very small in absolute value although they appear to be a significant and systematic. None of the observed correlation functions could be fitted by a biexponential function. Only in a few cases was it possible to measure two separate parts of the correlation function but on two different time scales (see below).

No measurements could be performed in the dilute regime. The concentrations investigated were all above c^* as defined by Odijk[3]

$$C^*\ (\mathrm{g\ L^{-1}}) \simeq (16\pi Q A l)^{-1}(10^3 M_m/N_{Av}) \qquad (2)$$

Here l is the contour length of the macromolecular chain, which in the present case is given approximately by

$$l \simeq (2.5 \times 10^{-8})(M/M_m)\ \mathrm{cm} \qquad (3)$$

Table I
Effective Diffusion Coefficients of Polystyrenesulfonate Ion in Water[a]

C, g L^{-1}	$D_{\text{eff}}^{\text{slow}} \times 10^8$, cm^2 s^{-1}	$D_{\text{eff}}^{\text{fast}} \times 10^7$, cm^2 s^{-1}
0.08	5.6 ± 0.2	
0.12	5.6 ± 0.2	
0.33	3.00 ± 0.07	
0.93	1.40 ± 0.07	
1.52	1.40 ± 0.07	
2.40	1.10 ± 0.07	
3.60	0.38 ± 0.02	3.00 ± 0.15
4.20		3.54 ± 0.2
7.50		3.6 ± 0.2
8.50		3.7 ± 0.2

[a] $M_{\text{w}} = 6.5 \times 10^8$, 25 °C, $C^* \simeq 0.05$ g L^{-1}.

where M and M_{m} are the molar mass of the macromolecule and of the monomeric unit, repectively, $Q \equiv q^2/\epsilon k_{\text{B}}T$ is the Bjerrum length (q is the elementary charge and ϵ is the relative permittivity of water), $A \equiv l/Z$ is the contour distance between two successive charges along the macromolecular chain, which bears Z of them in total ($A \simeq 2.5 \times 10^{-8}$ cm in the present case), and N_{Av} is Avogadro's constant. Note that (2) follows from the assumption that only noncondensed counterions, as defined by the simple condensation approach determine κ^{-1}, the Debye screening length, in salt-free polyelectrolyte solutions where the polyions are characterized by $A < Q$.

$$\kappa^2 \simeq 4\pi Q c_{\text{nc}} \simeq 4\pi Q c(A/Q) = 4\pi A c \qquad (4)$$

Here the concentration of noncondensed counterions, c_{nc}, is related to the concentration of monomeric units, c, assuming thus that every monomeric unit bears one elementary charge. Within the framework of the same approximations Odijk's prediction for c^{**} is given by

$$C^{**}\ (\text{g L}^{-1}) \simeq (100\pi Q^2 A)^{-1}(10^3 M_{\text{m}}/N_{\text{Av}}) \qquad (5)$$

For $M_{\text{w}} = 6.5 \times 10^5$ g mol^{-1} and $M_{\text{w}} = 12 \times 10^5$ g mol^{-1} the values of C^* according to (2) are 0.05 g L^{-1} and 0.03 g L^{-1}, respectively; $C^{**} \simeq 9$ g L^{-1} for both cases according to (5). It was impossible, however, to perform accurate measurements above C^{**} as the scattered intensity was too weak.

In general the first cumulants, K_1, obtained from fitting the correlation functions for a given solution were found to depend linearly on $\sin^2(\theta/2)$ at low scattering angles only ($\theta < 60°$). This corresponds to what has been observed with polyelectrolyte–salt solutions at very low concentrations.[8] Probably at the higher scattering angles a contribution from intramolecular relaxation also influences the relaxation rate of the correlation function that is measured. Therefore an effective difusion coefficient D_{eff} was derived from the slope of K_1 vs. q^2, where the length q of the scattering vector $\mathbf{q}$ at a given wavelength in vacuo, λ_{v}, of the incident radiation and a given refraction index of the solution, n, is given by $q = 4\pi n \lambda_{\text{v}}^{-1} \sin(\theta/2)$.

Results and Discussion

The values of the effective diffusion coefficients as determined from the light-scattering intensity correlation function as discussed above are collected in Tables I and II. For each molar mass three distinct concentration dependences can be seen. At the lowest concentrations the diffusion coefficient seems to be concentration independent; then with increasing concentration it decreases to very low values as compared to the D_{eff} measured in the same concentration range but in the presence of NaCl.[8] This suggests that the relaxation velocity in this concentration region is not determined by a cooperative diffusion mechanism as is the case for neutral polymers and polyelectrolyte–salt systems where for $c > c^*$ the effective difusion coefficient *increases* with concentration and is proportional to ξ^{-1}. If the same mechanism were responsible for the relaxation of the correlation function observed here with aqueous polyelectrolyte solutions, than D_{eff} should increase with concentration as $C^{1/2}$ in the region $C^* < C < C^{**}$. Another argument supporting the view that in this regime the correlation length ξ is not the length scale that determines the value of D_{eff} can be found in the fact that D_{eff} is not molar mass independent contrary to ξ. In fact, although the values for D_{eff} of the two samples studied seem to converge with increasing concentrations,D_{eff} of the higher molar mass remains always smaller.

Table II
Effective Diffusion Coefficients of Polystyrenesulfonate Ion in Water[a]

C, g L^{-1}	$D_{\text{eff}}^{\text{slow}} \times 10^8$, cm^2 s^{-1}	$D_{\text{eff}}^{\text{fast}} \times 10^7$, cm^2 s^{-1}
0.09	2.4 ± 0.1	
0.24	2.4 ± 0.1	
0.51	1.2 ± 0.1	
1.23	1.10 ± 0.05	
2.13	0.54 ± 0.03	
6.73		3.3 ± 0.2
8.80		3.5 ± 0.2

[a] $M_{\text{w}} = 12 \times 10^5$ g mol^{-1}, 25 °C, $C^* \simeq 0.03$ g L^{-1}.

The larger C is, the more difficult it is to determine the very low values of D_{eff} (which corresponds to the effective diffusion coefficient of what we shall call the "slow mode" diffusion) as the amplitude of the correlation function, on the time scale where the corresponding mode can be observed, becomes smaller and smaller. Although for concentrations approaching C^{**} the slow mode is still detectable, it is impossible to make accurate determinations of D_{eff}. Therefore in Tables I and II no values of D_{eff} for $C > 4$ g L^{-1} have been given. At the same time when the slow mode becomes less detectable a new mode with a much larger relaxation rate (a "fast mode") is developing and can be detected but on a much shorter time scale. A reliable analysis of this part of the correlation function was only possible, however, for those concentrations where the contribution of the slow mode has a very small amplitude and cannot be fitted accurately to (1). This is the reason why in Tables I and II no broad concentration range is reported where the diffusion coefficient corresponding to the slow mode and that of the fast mode has been determined simultaneously. We think, however, that such a concentration range with contributions of both modes may exist.

In fact, in a recent paper Grüner and Lehman[7] using quasi-elastic light scattering have found for aqueous solutions of NaPSS of a lower molar mass ($M = 10^5$ g mol^{-1}) that in a concentration range 0.1–5 g L^{-1} the effective diffusion coefficient increases with concentration from $D_{\text{eff}} \simeq 5 \times 10^{-8}$ cm^2 s^{-1} to a value of 5×10^{-7} cm^2 s^{-1}. This seems to be in contradiction with our results. But it could well be that what they have observed would correpond to our fast mode although in a concentration range where we have been largely unable to detect it because of its small amplitude. Neither is it yet clear why Grüner and Lehman only found the fast mode and do not mention a slow mode corresponding to the one we could definitely identify with our NaPSS samples of somewhat higher molar mass. They do mention, however, that their experimental correlation functions could be fitted by a sum of two exponentials, the deviations from a single exponential being largest at the low concentrations. This is perhaps an indication for the occurrence of a slow mode. As only the mean relaxation rate (in the form of the first cumulant) is given in their paper without any indication of the order of magnitude of the two separate effective diffusion coefficients, this remains purely speculative. It is interesting finally to note that for their NaPSS solutions D_{eff} becomes practically concentration independent at the highest and the lowest concentrations investigated.

In the case of our solutions it remains very difficult to establish the concentration dependence of D_{eff} for the fast mode although there seems to be a trend for D_{eff} to increase with C. The rather large standard deviations on these values do not allow us to reach a definite conclusion in that respect. Our results seem to indicate that D_{eff} corresponding to the fast mode is molar mass independent, in contrast to what is found for the diffusion coefficient of the slow mode. This could indicate that in the fast mode we deal with a cooperative diffusion mechanism. The order of magnitude of D_{eff} for this mode would support this conclusion. But an eventual concentration independence of D_{eff} around C^{**}, as also suggested by the results of Grüner and Lehman,[7] would make the interpretation within the framework of the scaling approach as proposed by Odijk very difficult.

The appearance of both a slow and a fast mode in quasi-elastic light-scattering correlation functions in solutions of charged macromolecules is not uncommon and has been reported several time although mostly for different systems than those studied here. Schurr et al.[11] have found a fast and a slow mode using solutions of high molar mass DNA in 0.02 M salt at semidilute concentrations. They have attributed this to a coupling between translational diffusion and internal relaxation. Jamieson and Presley[12] have found similar effects as described here with partially hydrolyzed polyacrylamide in aqueous solutions. At 0.5 M NaCl only a fast mode could be detected. Unfortunately in both papers the concentration dependence of the diffusion coefficients corresponding to the two modes has not been studied.

Recently Mathiez et al.[13-15] have reported a fast and an extremely slow mode in the correlation function of poly(A) even in 0.1 M NaCl. The fast mode could be explained with the blob model while the slow mode ($D_{\mathrm{eff}} \simeq 10^{-9}$ cm^2 s^{-1} and decreasing with increasing concentration) was attributed to structural properties of the solution. Strikingly the slow mode was found to disappear after a few weeks.

We have checked if such structural effects can be detected in our solutions. Therefore we have measured the light-scattering intensity correlation function of several systems and repeated the measurements on the same solutions after a few weeks. No significant change in the correlation function and in the fit parameters could be found. Thus it seems unlikely that the slow mode observed with our NaPSS solutions in water should be associated with structural properties as suggested in the case of poly(A). It is also important to note that in aqueous solutions of NaPSS in the presence of NaCl down to concentrations of 0.01 M a concentration-independent D_{eff} of low value has been found only in the dilute regime and that in the semidilute regime only a fast mode with a D_{eff} increasing with concentration of the macromolecule could be detected.

Very recently Fulmer et al.[16] have reported quasi-elastic light-scattering results on short DNA fragments (approximately 500 Å long) at a single concentration in the semidilute regime. For ionic strengths lower than 0.01 M a fast mode ($D_{\mathrm{eff}} \simeq 10^{-6}$ cm^2 s^{-1}) together with a slow mode ($D_{\mathrm{eff}} \simeq 10^{-9}$ cm^2 s^{-1}) was found. Upon increase of the ionic strength by addition of low molar mass electrolyte the slow mode disappeared. Here again no concentration dependence was studied.

It is rather obvious that in the case of NaPSS solutions investigated here no satisfying explanation is available yet for the slow mode observed at the lower concentration where D_{eff} is molar mass dependent and is either constant or decreasing with C. The latter observation rule out that the slow mode may be attributed to a cooperative diffusion as observed in the case of NaPSS solutions in the presence of low molar mass salt.[8,9]

In order to interpret the results obtained it may be useful to consider separately the concentration-independent D_{eff} and the slow mode characterized by a D_{eff} that decreases with increasing concentration. For the former we tend to believe that it corresponds to the free diffusion as expected below c^*; for the latter we propose a reptation-like mode.

For the free diffusion mechanism, assuming in such a case the macromolecule, which is highly charged and is in a sufficiently diluted system, to be rodlike, D_{eff} can be estimated wiith the help of Perrin's expression for the translational diffusion constant of an elongated ellipsoid.[17] If p represents the ratio of the length of the longer axis, l, to the diameter, d, of the ellipsoid we have

$$D = \frac{k_{\mathrm{B}}T}{3\pi\eta d}\,\frac{\ln\,[p + (p^2 - 1)^{1/2}]}{(p^2 - 1)^{1/2}} \tag{6}$$

where η represents the viscosity of the solvent. Using for the viscosity 0.01 P and for l the contour length as given by (3) and estimating $d \simeq 10^{-7}$ cm (the expression for D being rather insensitive to the exact value of d as long as $p^2 \gg 1$ and $D \sim \ln\,(2p)/l$) we obtain a translational diffusion coefficient at 25 °C according to (6) of 4×10^{-8} and 2×10^{-8} cm^2 s^{-1} for $M_{\mathrm{w}} = 6.5 \times 10^5$ and $M_{\mathrm{w}} = 10^5$ g mol^{-1}, respectively. These values can be compared to D_{eff} as found experimentally at the lowest concentrations for both NaPSS samples. The agreement is rather satisfactory. The question of why free diffusion should be observed at all above c^* remains. This critical concentration is defined by Odijk[3] by the condition $l \simeq L_{\mathrm{e}}$, where L_{e} is the contribution arising through short-range electrostatic interactions to the total persistence length, $L_{\mathrm{t}} = L_{\mathrm{p}} + L_{\mathrm{e}}$, and L_{p} is its intrinsic part. In the case of polyelectrolytes in the presence of an excess of low molar electrolyte, Odijk derived an expression for L_{e} given by[4]

$$L_{\mathrm{e}} = (Q/4\kappa^2A^2)\mathrm{f}(A) \tag{7}$$

where $\mathrm{f}(A)$ is a correction factor to include strong interaction between polyion and counterions, which may lead to an increase of the effective value of A. For polyelectrolytes in the absence of low molar mass electrolyte, Odijk has proposed to use the same expression for L_{e} with κ^2 defined by (4). This implies the additional assumption that simple condensation theory can be used for estimating both the concentration of the counterions determining κ^2 and the effective value of A; i.e., $c_{\mathrm{nc}} = c(A/Q)$ in (4) and $\mathrm{f}(A) = A^2/Q^2$ in (7) if $Q/A > 1$ as is the case for the polyelectrolytes investigated here, and leads to the value $L_{\mathrm{e}} \simeq (16\pi AQc)^{-1}$ as used in Odijk's paper to derive the estimate for c^*. It cannot be excluded that in this way the value of L_{e} is somewhat underestimated. In the opposite case where the "effective charge" effects are neglected altogether (as was done originally by Odijk[18] in his derivation of L_{e} and also, independently, by Skolnick and Fixman[19]) $L_{\mathrm{e}} \simeq (16A^2c)^{-1}$ and would lead to a larger value for c^* given the condition $l \simeq L_{\mathrm{e}}$. It is at present not yet possible to decide where the transition from the dilute to the semidilute regime really lies.

On the other hand at the lower end the semidilute regime cannot be characterized, according to Odijk's treatment, with the help of a bloblike approach. It should rather be described as a deformed tridimensional lattice where the polyions are still more or less rigid and their interactions do not lead to entanglements. Here L_e ($\gg\xi$) is the characteristic length scale although with increasing concentration L_e it will approach ξ. Under those conditions a reptation-like mode may be thought to be responsible for the low values of D_{eff} observed and their molar mass and concentration dependence.

Reptation is a wormlike motion that will occur if a given chain has to move within constrains arising from the presence of other chains as, e.g., through a network or in a concentrated solution.[20] Edwards[21] has compared this situation to the case where a chain is trapped in a flexible tube formed by its surrounding. However, during the progress of the chain, the tube will be continuously modified: the chain will be leaving some parts of the tube, thereby creating new ones. A characteristic quantity in the reptation model is the terminal time, τ_t, defined as the average time required for a complete renewal of the tube. In such a model the translational diffusion coefficient of the reptating chain is given by[22]

$$D_{\text{rep}} \simeq \langle R^2 \rangle / \tau_t \tag{8}$$

where $\langle R^2 \rangle$ is the mean-square distance over which the chain has moved in time τ_t. It is assumed here that after one time interval, τ_t, all memory of the original conformation of the reptating chain has been lost. Because the tubes are contorted, $\langle R^2 \rangle$ will be of the order of the mean-square dimensions of the macromolecule in the constrained system.

In the situation above c^* where we still have that l is of the same order as $L_e \simeq L_t \gg \xi$ we would expect intramolecular excluded volume effects to be negligible and L_e to be the characteristic length determining the terminal time of the tube. Generalizing the expression for τ_t proposed by de Gennes[22] for the blob model, we could use

$$\tau_t \simeq (l/L_e)^3 \tau_L \sim cl^3/k_B T \tag{9}$$

Here τ_L is the relaxation time associated with rodlike parts of the chain with lengths L_e for which we have assumed

$$\tau_L \sim \eta L_e^{\,3}/k_B T \tag{10}$$

In view of the condition $l \simeq L_e$ the mean-square end-to-end distance of the macromolecules, treated as a wormlike chain, would be given by[23]

$$\langle R^2 \rangle \simeq 2lL_e[1 - (L_e/l)(1 - e^{-l/L_e})] \tag{11}$$

if $L_t \simeq L_e$. Substitution of (9) and (11) into (8) leads to the following expression for D_{rep}

$$D_{\text{rep}} \sim \frac{2k_B T L_e[(1 - (L_e/l))(1 - e^{-l/L_e})]}{\eta l^2} \tag{12}$$

Values of D_{rep} have been estimated for the two molar masses of NaPSS investigated by use of the two extreme possibiliites for L_e, e.g., L_e calculated according to (7) with either the condensation approach or with neglect of "effective charge" effects. These values are collected in Table III and should be compared to the values of D_{eff} corresponding to the slow mode inasfar as it is concentration dependent.

Table III shows that D_{rep} at a given molar mass is a decreasing function of concentration C, and at a given concentration is a decreasing function of molar mass. Also striking is the fact that the order of magnitude of D_{rep} is comparable to that of D_{eff} in the slow mode, although the calculated values of D_{rep} seem to be systematically lower than the corresponding values for D_{eff} even if the highest value of L_e yielding also the largest value of D_{rep} is used.

Table III
Calculated Values of D_{rep} for NaPSS According to Eq 12 at 25 °C

C, g L^{-1}	$M_w = 6.5 \times 10^5$ g mol^{-1}		$M_w = 12 \times 10^5$ g mol^{-1}	
	$D_{\text{rep}}{}^a \times 10^8$, cm^2 s^{-1}	$D_{\text{rep}}{}^b \times 10^8$, cm^2 s^{-1}	$D_{\text{rep}}{}^a \times 10^8$, cm^2 s^{-1}	$D_{\text{rep}}{}^b \times 10^8$, cm^2 s^{-1}
0.33	1.3	2.6	(0.39)	(0.92)
(0.51)	0.86	2.0	0.26	0.65
0.93	0.50	1.3	(0.15)	(0.38)
(1.23)	0.38	0.98	0.11	0.30
1.52	0.31	0.82	(0.09)	(0.24)
(2.13)	(0.22)	0.60	0.06	0.18
2.40	0.20	0.54		
3.60	0.13	0.36		

[a] $L_e = (16\pi AQc)^{-1}$. [b] $L_e = (16\pi A^2 c)^{-1}$.

This quantitative discrepancy may, however, be due to a numerical factor in the expression of τ_t as given by (9). We may therefore conclude that, qualitatively at least, the reptation model could explain the slow mode in the light-scattering intensity correlation function observed in the first part of the semidilute concentration regime. Table III also shows that D_{rep} becomes very small with increasing polyelectrolyte concentration. This could explain why the slow mode can no longer be detected at concentrations approaching C^{**}; diffusion according to a reptation mode takes place then on a semimacroscopic time scale. On the other hand it is not completely to be excluded that somewhere in the region $c^* < c < c^{**}$ the physical conditions necessary for reptation break down. This could, for instance, be the case if the persistence length L_e reaches a value that is comparable to the correlation length ξ (representing the average distance between chains). This will occur for $1 < C < 9$ g L^{-1}, where the extreme values have again been estimated by using either the expression for L_e with the condensation approach or the value calculated with complete neglect of "effective charge" effects, respectively. At the same concentration there could be an onset of a cooperative diffusion, giving rise to the fast mode diffusion coefficient as already observed below c^{**}.

Conclusions

The diffusion coefficient of salt-free polyelectrolyte solutions and its dependence on macromolecular concentration cannot yet be fully understood within the framework of the scaling theory as proposed by Odijk,[3] contrary to what is the case for polyelectrolyte solutions containing low molar mass electrolyte. Of the three distinct concentration regions that can be observed, only that in the neighborhood of c^* lends itself to a simple interpretation. The concentration-independent diffusion coefficient can be attributed to a free diffusion mechanism of the practically fully stretched macromolecule. For the diffusion coefficient of the slow mode, which decreases with c, no simple and satisfactory explanation is available yet. We have tentatively proposed an interpretation based on a reptation model with rodlike parts of length L_e as the characteristic unit. This could explain at least qualitatively the decrease of $D_{\text{eff}}{}^{\text{slow}}$ with increasing concentration and molar mass. However the approach is rather crude, and more experimental and theoretical work will be needed to reach a better understanding of the diffusion mechanism in this concentration regime. The large values of $D_{\text{eff}}{}^{\text{fast}}$ observed when approaching c^{**} are probably related to a cooperative diffusion mechanism as the diffusion coefficients seem to be molar mass independent. It is not yet possible to ascertain whether or not this cooperative diffusion can be explained with the help of a blob model.

Our results confirm that various concentration regimes exist in aqueous solutions of charged macromolecules in the absence of low molar mass electrolyte and can be detected by quasi-elastic light-scattering experiments. Much more systematic investigations are needed, together with further theoretical work, for even the qualitative understanding of these systems.

References and Notes

(1) Katchalsky, A. *Pure Appl. Chem.* **1971**, *26*, 327.
(2) de Gennes, P. G.; Pincus, P.; Velasco, R.; Brochard, F. *J. Phys.* (*Orsay, Fr.*) **1976**, *37*, 1461.
(3) Odijk, T. *Macromolecules* **1979**, *12*, 688.
(4) Odijk, T. *Polymer* **1978**, *19*, 989.
(5) (a) Levij, M.; de Bleijser, J.; Leyte, J. C. *Chem. Phys. Lett.* **1981**, *83* 183. (b) *Ibid.* **1982**, *87*, 34.
(6) Roots, J.; Nyström, B. *Polymer* **1981**, *22*, 573.
(7) Grüner, H.; Lehman, F. *J. Phys. A: Math. Gen.* **1981**, *24*, L307.
(8) Koene, R.; Mandel, M. *Macromolecules* **1983**, *16*, 220.
(9) Koene, R.; Nicolai, T.; Mandel, M. *Macromolecules* **1983**, *16*, 227.
(10) Koene, R.; Nicolai, T.; Mandel, M. *Macromolecules* **1983**, *16*, 231.
(11) Lee, W. J.; Schmitz, K. S.; Lin, S. C.; Schurr, J. M. *Biopolymers* **1977**, *16*, 583.
(12) Jamieson, A. M.; Presley, C. T. *Macromolecules* **1973**, *6*, 358.
(13) Mathiez, P.; Mouttet, C.; Weisbuch, G. *Biopolymers* **1979**, *18*, 1465.
(14) Mathiez, P.; Mouttet, C.; Weisbuch, G. *J. Phys.* (*Orsay, Fr.*) **1980**, *41*, 519.
(15) Mathiez, P.; Mouttet, C.; Weisbuch, G. *Biopolymers* **1981**, *20*, 2381.
(16) Fulmer, A.; Benbasit, J.; Bloomfield, V. *Biopolymers* **1981**, *20*, 1147.
(17) (a) Perrin, F. *J. Phys. Radium* **1934**, *5*, 497. (b) *Ibid.* **1936**, *7*, 1.
(18) Odijk, T. *J. Polym. Sc., Polym. Phys. Ed.* **1977**, *15*, 477.
(19) Skolnick, J.; Fixman, M. *Macromolecules* **1977**, *10*, 944.
(20) de Gennes, P. G. *J. Chem. Phys.* **1971**, *55*, 572.
(21) Edwards, S. F.; Grant, J. W. *J. Phys. A: Math. Nucl. Gen.* **1973**, *6*, 1169, 1186.
(22) de Gennes, P. G. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, NY, 1979; Chapter 8.
(23) Kratky, O.; Porod, G. *Recl. Trav. Chim. Pays-Bas* **1949**, *68*, 1106.

Static Light Scattering from Aqueous Poly(ethylene oxide) Solutions in the Temperature Range 20–90 °C

William F. Polik[†] and Walther Burchard[*]

Institute of Macromolecular Chemistry, University of Freiburg, 7800 Freiburg im Breisgau, West Germany. *Received May 31, 1982*

ABSTRACT: Static light scattering from aqueous solutions of poly(ethylene oxide) has been recorded over the temperature range 20–90 °C and at eight different concentrations varying from 0.25% to 2% for a polymer of molecular weight 20 000. In spite of the low molecular weight, strong angular dependence of the scattering and a very high average particle weight M_w were found, indicating the presence of large aggregates of poly(ethylene oxide) in the aqueous solutions. The aggregation increases markedly upon heating; above 60 °C, however, a decrease in M_w occurs. At 40 °C minima and maxima in the angular distribution were observed that are characteristic of globular, fairly monodisperse structures. The dimensions of these globular particles were found to decrease with rising temperature, in contrast to the mean square radius of gyration $\langle S^2 \rangle_z$, which increases up to 70 °C. The second osmotic virial coefficient A_2 decreases with rising temperature as the system approaches its Θ temperature of 102 °C. Finally, the intrinsic viscosity in water is shown to be only slightly influenced by the presence of globular aggregates. These findings indicate the coexistence of high-density spherulites with low-density microgel aggregates and are discussed in terms of the hydrophobic interactions between the polymer and solvent.

Introduction

Poly(ethylene oxide) (PEO) is a simple polymer with rather remarkable properties.[1] It dissolves readily not only in a large number of organic solvents but also in water. Moreover, it exhibits both upper and lower critical solution temperature phenomena (UCST and LCST) in both *tert*-butyl acetate[2] and water.[2–4] However, these two systems are very different, for in the organic solvent the UCST lies well below the LCST but in the PEO–water system there is a closed miscibility loop, the UCST lying higher than the LCST. The former type of behavior is an example of the well-understood "free-volume" or "equation of state" effects discussed by Prigogine,[5] Patterson and Delmas,[6] and Flory and his co-workers.[7] Closed miscibility loops, however, are seen only in highly polar systems with strong orientation dependence of the molecular interactions.[8] Our interest in the solution behavior of PEO increased when we noticed that only a few light scattering measurements of PEO in water have been published.[2,9–14] The purpose of the present study was to measure the thermodynamic solution properties and, so far as possible, the conformational properties of the polymer in water as a function of temperature.

Experimental Section

Sample. Polywachs-20,000 from Chemische Werke Huls, Marl, Germany, was used. To remove possible traces of initiator the product was dissolved in benzene, filtered, precipitated with freshly distilled petroleum ether, and dried in a vacuum oven at 50 °C. Gel permeation chromatography (GPC) in *N*,*N*-dimethylacetamide, which was kindly performed by Peuscher and Eisenbach[15,16] in our institute, gave a molecular weight of $M_{\mathrm{GPC}} = 21\,400$ and a polydispersity of $M_w/M_n = 1.37$, while light scattering in acetonitrile gave a value of $M_w = 17\,000$, which agrees fairly well with the GPC values.[16]

Solution Preparation. A dilution series of eight concentrations ranging from 0.25% to 2% in increments of 0.25% was prepared at room temperature with freshly doubly distilled water. The solutions were centrifuged for optical clarification at 20 °C in a Spinco Model L ultracentrifuge at 40 000 rpm with a fixed angle Titan rotor. The upper two-thirds of a total of 25 mL were pipetted into cylindrical light scattering cells made of optical glass

---

[†] On leave from Dartmouth College (1981). Present address: Department of Chemistry, University of California, Berkeley, CA 94720.

0024-9297/83/2216-0978$01.50/0