Articles

Probe Diffusion Measurements of Polystyrene Latex Particles in Polyelectrolyte Solutions of Varying Ionic Strength

Kristen E. Bremmell[†] **and Dave E. Dunstan***[,‡]

Particulate Fluids Processing Centre and Cooperative Research Centre for Bioproducts, Department of Chemical Engineering, The University of Melbourne, Parkville, VIC 3010, Australia

Received January 10, 2001; Revised Manuscript Received November 6, 2001

ABSTRACT: The diffusion of polystyrene latex particles in solutions of a poly(acrylic acid-*co*-acrylamide) polyelectrolyte as a function of both polyelectrolyte concentration and solution ionic strength has been investigated using dynamic light scattering. Two apparent diffusion coefficients were measured for the latex probe particles in the polyelectrolyte solutions. Designated as D_{fast} and D_{slow}, the fast diffusional mode increases to a maximum as a function of polyelectrolyte concentration, with the maximum increasing in magnitude as the ionic strength increases. D_{slow} decreases as a function of polyelectrolyte concentration in low ionic strength solutions. However, D_{slow} shows a slight increase with polyelectrolyte concentration in the higher ionic strength solutions. The results are discussed with reference to calculated correlation lengths for the polyelectrolyte solutions and are compared with the data obtained from polymer solutions measured using dynamic light scattering where similar trends have been observed. The latex spheres appear to probe the single chain motion, cooperative diffusion, and the macroscopic diffusional motions, self-diffusion, of the polyelectrolyte molecules.

Introduction

The diffusion of probe particles in polymer and polyelectrolyte solutions and in gels has been measured by a number of workers using dynamic light scattering. Probe diffusion has been investigated in order to examine the dynamics of macromolecules in solution.[1−6] Probe diffusion has been used to investigate both the solution or gel microviscosity and chain dynamics. A theoretical interpretation of these results has been undertaken, and models of the behavior of gel systems and polymer solutions have been developed. The complex rheological behavior demonstrated by these systems include shear thinning, significant normal stresses, and elastic and extensional viscosities.[7] It is the complex viscoelastic behavior exhibited by these systems which has drawn us to undertaking the measurements reported here. Diffusing probe measurements enable the microstructure of solutions and gels to be investigated.

One issue of particular interest has been the variation of the apparent translational diffusion coefficient of probe particles as a function of their environment, for example, the type and molecular weight of the polymer.[8]

To interpret diffusion coefficients of spherical particles in liquids, the Stokes−Einstein relationship is used:

$$D = \frac{k_{\mathrm{B}}T}{6\pi\eta R_{\mathrm{h}}} \tag{1}$$

where D is the diffusion coefficient of the particles in solution, k_{B} is Boltzmann's constant, T is absolute temperature, η is the solution viscosity, and R_{h} is the hydrodynamic radius of the particle. It is assumed in this relationship that the radius of the probe is much greater than any solvent molecule. A significant number of studies have reported the Stokes−Einstein equation to fail for particles in high molecular weight polymer solutions where the polymer dimensions in solution are similar to the probe particle size.[3] This paper by Won et al. contains a comprehensive summary of relevant work. There exist numerous probe studies reported in the literature for uncharged systems of polymers and particles.[4,8,9] Much of these data have been empirically shown to follow a stretched exponential behavior[10] of the form

$$D/D_0 = \exp[-ac^{\nu}M^{\gamma}R^{\delta}] \tag{2}$$

where D_0 is the probes diffusion in solvent, c and M are the polymer concentration and molecular weight, respectively, R is the probe radius, and a, ν, γ, δ are fitting parameters. However, studies involving polyelectrolytes have often been observed to not follow this behavior.[11,12]

We have previously reported results for the diffusion of hematite particles in a high molecular weight sodium polyacrylate polymer[13] and for latex particle diffusion in a 30% charged anionic polyelectrolyte.[14]

In this study the diffusion of latex particles in AP30 solutions (a 3 million molecular weight, 30% charged anionic copolymer) as a function of concentration has been investigated in solutions of increasing ionic strength. The effect of ionic strength and thus the importance of electrostatic interactions and chain extension on the

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[†] Particulate Fluids Processing Centre.
[‡] Cooperative Research Centre for Bioproducts.
* Corresponding author: e-mail davided@unimelb.edu.au.

10.1021/ma010051w CCC: $22.00

probe–polyelectrolyte behavior are reported. The effect of the collapse of the polyelectrolyte chain on the apparent diffusion of the probe particles is quantified. The results are discussed in terms of the correlation length of the polyelectrolyte solution and the effective Debye length.

Experimental Section

Poly(styrene sulfate) lattices of 0.2 μm diameter (Interfacial Dynamics Corp. (IDC)) were used without further purification. A surface charge density of -0.8 μC/cm^2 was obtained from conductiometric titration by IDC. Sizes obtained from light scattering were 200 ± 5 nm diameter, in agreement with the electron microscope sizes quoted by the manufacturer.

The polyelectrolyte used was Separan AP30 obtained from Dow Chemical Co. with a weight-average molecular weight of 3.1×10^6 with a polydispersity of 1.07 as measured using GPC/MALLS. AP30 has a 30% degree of ionization and is therefore an anionic polyelectrolyte at pH values greater than 6.8. For these experiments the pH of solutions was adjusted to 10.5. At this pH the polyelectrolyte is fully dissociated while the latex also carries a negative charge. All solutions were filtered with a 0.1 μm filter to remove any dust for the light scattering measurements. Polyelectrolyte solutions were transferred to the measuring cell, and an aliquot of tracer particles was added. An appropriate volume of latex particles was added so as to ensure no multiple scattering or particle–particle interactions would occur.

Dynamic light scattering measurements were performed using a Malvern 4700 apparatus with a 10 mW Ar$^+$ ion laser at 488 nm. Unless stated otherwise, analysis was performed at an angle of 90° and a temperature of 25 °C. The dilute particle concentration in the samples ensures that multiple scattering and particle–particle interactions are negligible in this system. The particle concentration was adjusted so that the scattering from the particles dominated that from the polymer by several orders of magnitude. The time autocorrelation functions were analyzed by an inverse Laplace transform algorithm, CONTIN,[15] to obtain a distribution of relaxation times related to the diffusion coefficient, D, by

$$\Gamma = Dq^2 \tag{3}$$

where q is the magnitude of the scattering vector, described by the following equation:

$$q = \frac{4\pi n}{\lambda} \sin \frac{\theta}{2} \tag{4}$$

Here, n is the refractive index of the solvent, λ is the wavelength of laser light, and θ is the scattering angle. It should be noted that the CONTIN analysis yielded two relaxation times with random residuals less than 10^{-3} over the time ranges measured

Results and Discussion

The diffusion coefficients of latex particles in AP30 solution measured using dynamic light scattering show a range of behaviors that depend on the polyacrylate concentration and the ionic strength of the solution. The observations of this work are in qualitative agreement to those measured previously using latex spheres in aqueous AP30 solutions[14] and of particulate hematite particles in a high molecular weight sodium polyacrylate flocculant.[13] Two apparent diffusion coefficients are measured with the faster mode showing a maximum with added polyelectrolyte concentration. At finite polyelectrolyte concentrations the apparent fast diffusion is more rapid than in the solvent. Other researchers have also observed positive deviations from Stokes–Einstein behavior in both aqueous and nonaqueous polymer solutions.[9,16,17] We have also observed two apparent diffusion coefficients above a critical polyelectrolyte concentration where the intensity autocorrelation function displays a bimodal decay. The CONTIN analysis yielded an apparent fast and slow mode for the relaxation times that were interpreted, as described by eq 3, as diffusion coefficients referred to as D_{fast} and D_{slow}.

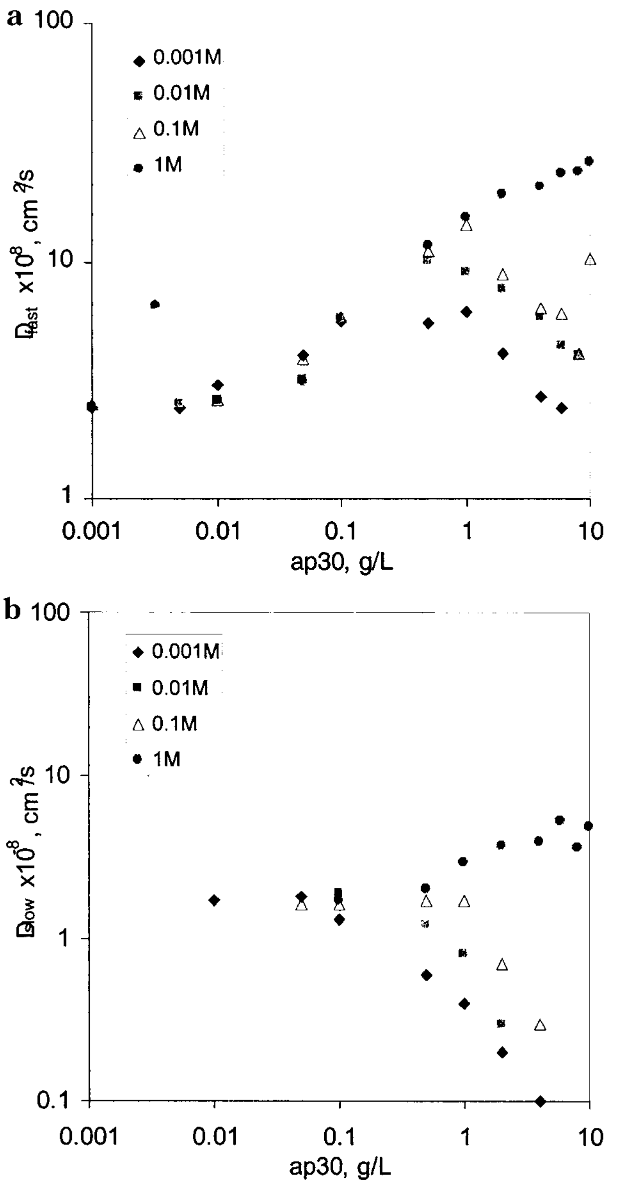

Figure 1. (a) Fast diffusion coefficient for latex particles in AP30 solutions as a function of concentration. Solution ionic strength increases from 1 mM to 1 M NaNO$_3$. (b) Slow diffusion coefficient for latex particles in AP30 solutions as a function of concentration. Solution ionic strength increases from 1 mM to 1 M NaNO$_3$.

The apparent diffusion coefficients of latex particles in AP30 solutions are shown in Figure 1a,b for NaNO$_3$ concentrations from 10^{-3} to 1 M. In general, the intensity autocorrelation functions of the latex particles yield two apparent diffusion coefficients at polyacrylate concentrations greater than 0.05 g/L for all solutions studied. The fast mode, D_{fast}, increases to a maximum value and then at higher concentrations of polyacrylate is seen to decrease. As the ionic strength is increased, the maximum value of D_{fast} increases from 6.2×10^{-8} cm^2/s at 0.001 M NaNO$_3$ to 26.1×10^{-8} cm^2/s in 1 M NaNO$_3$ solution, as illustrated in Figure 2 where the

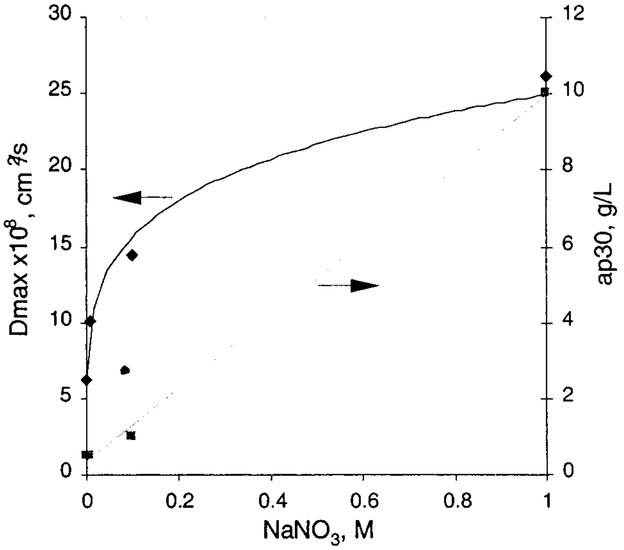

Figure 2. Maximum in the fast diffusion coefficient as a function of $NaNO_3$ concentration and the AP30 concentration where this occurs. Both parameters increase with ionic strength. D_{max} is represented by the diamond symbols and the AP30 concentration by the square symbols.

maximum in D_{fast} is plotted as a function of $NaNO_3$ concentration. At an $NaNO_3$ concentration of 1 M the diffusion coefficient did not reach a maximum over the AP30 concentration range measured. Sample preparation was problematic at higher polyacrylate concentrations. Also shown in Figure 2 is the AP30 concentration where the maximum occurred as a function of the salt concentration. This is seen to increase by a factor of 10 as the ionic strength is increased.

The slow mode, D_{slow}, generally decreases as the polyelectrolyte concentration is increased (Figure 1b). However, in the highest ionic strength solution measured (1 M $NaNO_3$) the diffusion coefficient exhibits an increase over the polyelectrolyte concentrations measured. D_{slow} in 0.1 M salt solutions shows a maximum value before decreasing for AP30 solutions greater than 1 g/L.

Angular Dependence. True Brownian diffusion requires that the relaxation time is independent of the length scale of the measurement as is described by eq 3. Therefore, the nature of the system can be investigated further by considering the diffusive properties as a function of the scattering vector squared, q^2. The apparent latex particle diffusion as a function of q^2 is reported in Figure 3a−d for solutions of ionic strength from 0.001 to 1 M $NaNO_3$ concentration. The measurement angle was varied from 30° to 150° with a resulting q^2 range from 0.886 to 3.31×10^{-2} nm^{-2}. In solutions of low AP30 concentration (0.01 g/L), the latex particle diffusion is independent of q^2 for all salt concentrations investigated. The motion of the particles therefore appears to be purely diffusional. The latex diffusion coefficient is also independent of the solution ionic strength with a value of 2.2×10^{-8} cm^2/s for all salt concentrations measured. This value is consistent with the hydrodynamic radius using the Stokes−Einstein equation (eq 1).

At intermediate AP30 concentrations (0.5−1 g/L) the diffusion is dependent on q^2, where it is seen to increase with q^2 over the entire range. In solutions of polyelectrolyte concentration greater than those at D_{max} (4−8 g/L), Figure 3a−d shows the diffusion of probes to increase rapidly to high values when q^2 is large and the length scale probed is the smallest. The data for concentrated polyacrylate solutions cross over the data of intermediate concentrations for high q^2 values. This may be attributed to the constrained diffusion of the probe particles at higher polyelectrolyte concentrations where the particles show restricted "cagelike" motion in the polyelectrolyte solution.

In high ionic strength solutions (greater than 0.1 M $NaNO_3$), both the fast and slow diffusional modes observed in concentrated polyelectrolyte solutions are dependent on the scattering vector. Thus, the behavior is not purely diffusional, suggesting that the probes are coupled to polyelectrolyte motion in solutions of high salt. The relative magnitudes of the relaxation times change in a complex manner with salt, polyelectrolyte, and scattering vector. The relative magnitude of the rapid component, D_{fast}, increased with polyelectrolyte concentration and decreased with salt at fixed polyelectrolyte concentration. The relative magnitude of the rapid component also increased with increasing q.

Correlation Length. In semidilute solutions of macromolecules, the correlation length is used to characterize the solution behavior. At concentrations greater than the critical overlap concentration, C^*, the polymer system forms a network of transient entanglements characterized by a mesh size referred to as the correlation length (ξ). For polyelectrolytes, $\xi \sim C^{-0.5}$.[18] In Figure 4 the fast diffusion coefficient is plotted as a function of the correlation length ($\xi \sim C^{-0.5}$) for the four ionic strength solutions under investigation. As the correlation length decreases, the diffusion coefficient increases to a maximum for $NaNO_3$ solutions of 0.1 M or less concentration. The measured apparent diffusion coefficients continue to increase for the 1 M $NaNO_3$ solution over the measured range.

The diffusion coefficients of polyelectrolyte solutions have been previously observed to increase with increasing concentration and to decrease as the ionic strength is increased.[2,19−21] At concentrations above the critical overlap concentration, C^*, where a transient network of overlapping chains characterizes the semidilute concentration regime, a scaling approach implies that the effective diffusion coefficient derived from the correlation function corresponds to the cooperative motion of the blobs and should be independent of molecular weight and increase with concentration according to a power law with an exponent close to 0.75.[22,23]

$$D_{app} \propto \zeta^{-1} C^{-3/4} \tag{5}$$

where ζ is the Debye length and C is the concentration of polyelectrolyte.

In the semidilute regime and at constant molecular weight and concentration, the absolute value of the diffusion coefficient is observed to decrease with increasing salt concentration.[21] This is consistent with the fact that the correlation length of the transient network in the semidilute polyelectrolyte regime increases with the ionic strength. In the current experiments this behavior is seen for the diffusion coefficients of the polyelectrolyte solutions. However, diffusion of the probe particles in these solutions did not follow this trend. D_{fast} values and the slope of D_{fast} increase similarly for all salt solutions investigated. The maximum in D_{fast} increases as a function of the salt as shown in Figure 2.

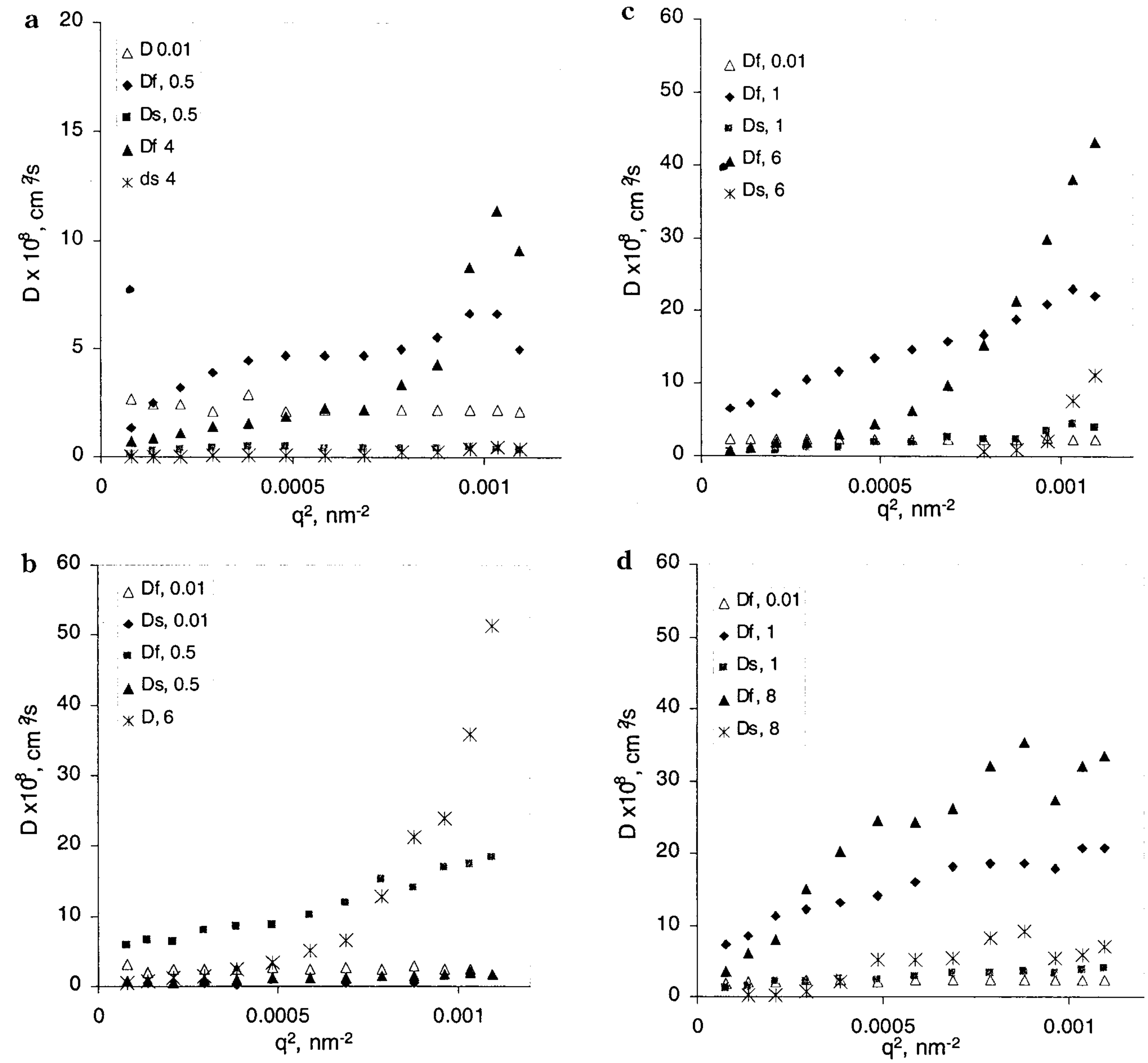

Figure 3. (a) Diffusion coefficient as a function of the scattering vector squared, q^2, for latex particles in AP30 of 0.001 M $NaNO_3$ solutions. The inset in the figure shows the symbols used for the fast and slow diffusion coefficients at the different AP30 concentrations. (b) Diffusion coefficient as a function of q^2 for latex particles in AP30 prepared in 0.01 M $NaNO_3$ solutions. The inset shows the symbols used for the different fast and slow diffusion coefficients at the respective AP30 concentrations. (c) Diffusion coefficient as a function of q^2 for latex particles in AP30 of 0.1 M $NaNO_3$ solutions. The inset shows the symbols used for the different fast and slow diffusion coefficients at the respective AP30 concentrations. (d) Diffusion coefficient as a function of q^2 for latex particles in AP30 of 1 M $NaNO_3$ solutions. The inset shows the symbols used for the different fast and slow diffusion coefficients at the respective AP30 concentrations.

In polymer solutions the exponential decay of the autocorrelation is due to the translational diffusion of polymer in the solvent.[24] In concentrations greater than C^*, deviations from a single-exponential decay have been observed.[25−28] These workers found that diffusion due to the cooperative motion of the chains was the dominant relaxation mode. However, other viscoelastic modes give rise to a broad distribution of relaxation times becoming more pronounced as the solvent quality was decreased. Adam and Delsanti[26] modified de Gennes theory by including the relaxation of the transient gel and have obtained a q^2-dependent cooperative diffusion mode and a single q-independent viscoelastic relaxation mode in their calculations.

Our results show a similar behavior for the measured diffusion coefficients of the latex particles in the AP30 solutions where increased D_{fast} and two apparent modes are observed, suggesting that the particles are probing the polyelectrolyte fluctuations observed in previous scattering studies of macromolecular solutions.

At concentrations greater than 0.05 g/L two diffusion coefficients were interpreted for the latex probes in AP30 solutions. Observation of two apparent diffusion coefficients in macromolecular solutions has been observed previously. Brown and Rymden,[8] Mustafa and Russo,[16] and Streletzky and Phillies[29−32] have all reported two apparent diffusional modes for probe particles in hydroxypropylcellulose (HPC). They used multiexponential analysis and two different Laplace inversion methods to interpret the data for probes in HPC. The analysis methods used all revealed two relaxation modes interpreted from the autocorrelation functions.

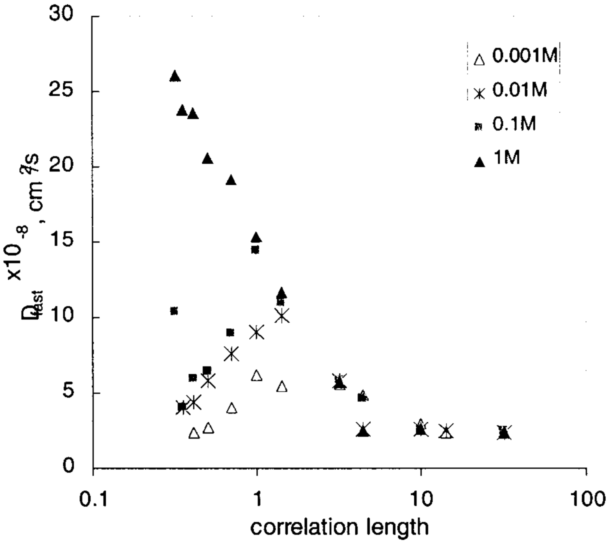

Figure 4. Fast diffusion coefficient, D_{fast}, as a function of the correlation length ($[AP30]^{-0.5}$). The correlation length has been calculated using the theory of de Gennes as discussed in the text. The inset shows the symbols used for the different $NaNO_3$ concentrations.

Streletzky and Phillies reported the exact behavior to be dependent on the probe size with three different modes being used to describe the diffusion: (1) the slow diffusional mode of the large probe had characteristics of particle motion in a viscous medium; (2) the fast mode of the large probe and slow mode of the small probe had properties characteristic of probe motion coupled to internal chain dynamics; (3) the fast mode of the small probe has properties that can be attributed to the probe sampling local chain relaxations.

Streletzky and Phillies[29] proposed that the probe particles are influenced by the motions of the polymer chains that occur on different time scales. On long time scales, all polymer modes have decayed, and the solution behaves like a viscous fluid which the particles probe. On the intermediate time scale probe diffusion is coupled to the polymer chain relaxations. For the shortest time scale, local motions of single chains are significant, and the particles probe the local chain relaxations of individual chains.

Shibayama et al.[33] observed two modes of diffusion in their study of polystyrene particles in polymer solutions. The fast mode was assigned as a cooperative diffusion of polymer chains and the slow mode as the translational diffusion coefficient. The relaxation time of the probe particles in the polymer solutions was found to increase by a few orders of magnitude compared to that of water. Benmouna et al.[34] analyzed the experiments of Nemota et al.[35] and identified the observed modes in the bimodal relaxation as the cooperative and interdiffusion modes. These results are in agreement with those found in the work reported here.

In the present study the behavior of the diffusion coefficient as a function of AP30 concentration combined with the angular dependence analysis suggests that the probes are sensing the different modes of fluctuation of the polyelectrolyte. In low ionic strength solutions the angular dependence study suggests the slow mode is diffusive and therefore could be considered as a translational diffusional mode. At high ionic strengths the slow mode is dependent on the angle of measurement. The motion of the polyelectrolyte is altered as a result of the increase in ionic strength shielding the charges and influencing the polyion/solvent interaction. The fast mode is also dependent on the angle of measurement, the extent of which depends on the AP30 concentration. In intermediate concentrations the diffusion coefficient increases almost linearly with q^2. However, in solutions of high concentration, the diffusion coefficient increases only at large q values, where the length scale measured is the shortest. Here, the latex particles are probing the very short and rapid internal fluctuations which are hypothesized as arising from a coupling of the probe to the internal motions of the polyelectrolyte. In high AP30 and ionic strength solutions the fast mode increases with q^2 more uniformly. This suggests a change in the polymer/solvent interactions is occurring.

The collapse of the polyelectrolyte chains with increasing ionic strength would be expected to decrease the rigidity of the polyelectrolyte backbone and decrease the rapidity of the diffusional fluctuation. This has been observed by Mandel et al.,[19] who reported a decrease in the apparent diffusion with an increase in ionic strength. This is as expected in terms of the backbone rigidity. The data presented in this study show the opposite trend that is difficult to rationalize while indicating that the different polyelectrolyte/probe systems show trends that must be attributed to the specific chemistry of the system.

Conclusions

Dynamic light scattering has been used to probe the dynamics of an anionic polyelectrolyte solution as a function of polyion concentration and ionic strength. It is proposed that the diffusion of the probe particles is coupled to the relaxation modes of the polyelectrolyte. The slow mode may represent the diffusion of the particle as a result of translational diffusion through the polymer solution. The fast mode reflects the influence of internal macromolecular fluctuations that increase with polyelectrolyte concentration. The ionic strength has a strong influence on the probe behavior as a result of the electrostatic interactions involved between polyelectrolyte segments, between individual polyelectrolyte molecules and between the polyelectrolyte and particles.

Acknowledgment. The authors acknowledge financial support of the Particulate Fluids Processing Research Centre, an Australian Research Council Special Research Centre.

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MA010051W