Dynamic Light Scattering Study of Linear Polyelectrolyte Diffusion in Gels

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ABSTRACT: Dynamic light scattering (DLS) was used to study diffusion of linear sodium poly(styrenesulfonate) (NaPSS), with molecular weights ranging from 35 000 to 1 200 000, in poly(acrylamide) (PA) gels made by copolymerizing acrylamide and *N,N'*-methylenebis(acrylamide) (BIS) in aqueous solvents of high and low ionic strengths. Laplace inversion of the correlation functions shows that for the gels swollen in solvents with a high effective ionic strength two distinct, well-separated bands appear in distributions of diffusion coefficients, corresponding to the collective diffusion mode of the gel, D_g, and the tracer diffusion of the probe polymer, D_p. The scaling laws $D_p \sim M_p^{-2}$ and $D_p \sim M_p^{-2.1}$, where M_p is the molecular weight of probe NaPSS polymer, were found for 11 and 18 wt % gels, respectively. These results are close to the reptation prediction for the self-diffusion of neutral flexible polymers in gels. The dependence of D_p and D_g on the concentration of the gel, c_g, was also measured, and scaling relationships were observed with $D_p \sim c_g^{-2.5}$ and $D_g \sim c_g^{0.67}$. The dependence of D_p on the concentration of the probe polymer c_p did not obey a power law but showed behavior similar to that predicted by random phase approximation theory for semidilute solutions of polymer mixtures. In the case of gels swollen in deionized water, three different bands were observed where the slowest one was on the long time measurement limit.

Introduction

In recent years several dynamic light scattering studies on the diffusion of neutral polymer chains in swollen gels have been reported.[1–4] The problem of polymer chain diffusion in gels is both of fundamental and applied interest. From a fundamental viewpoint, gels provide a means to investigate polymer diffusion in random porous media and the effect of obstacles on polymer diffusion. In this respect, it is important to investigate the scaling laws for the dependence of diffusion constant on probe molecular weight, and on the gel and probe concentrations. The DLS measurements give exponents for the dependence of diffusion constant on molecular weight of the probe polymer ranging from 2 (consistent with the reptation prediction[1–3]) to 3 (consistent with the idea of entropic traps[4]). The other scaling laws have not been systematically examined. In particular, the dependence of the diffusion constant with increasing probe polymer concentration may provide a means to investigate how the diffusion constant varies from the tracer-diffusion to the mutual diffusion limit. Another variable is the nature of the polymer, linear versus branched and neutral versus polyelectrolytic. In spite of the obvious technological importance of the polyelectrolyte diffusion in gels, there have been no DLS studies of the diffusion of charged polymers in gels.

The structure and dynamics of polyelectrolyte solutions have been extensively studied in recent years,[5–20] yet many questions remain unanswered. The transport of polyelectrolytes in gels is of particular relevance to many biological processes. In particular, the technique of gel electrophoresis used for characterizing and purifying DNA and proteins involves the diffusion of charged polyelectrolytes in a gel under the influence of an external electric field.[21–27] Despite its technological importance, the molecular mechanisms governing this process are still not theoretically understood and the present approach is based on empirically finding the molecular weight by using a calibration with molecular weight standards (biopolymers with very well-defined molecular weights). An understanding of the whole process may lead to improvements in the resolution of molecular weight determination by gel electrophoresis. Measurements of electrophoretic mobilities of NaPSS in gels[23–25] show deviation from the reptation model prediction, particularly in the case of weak gels. On the other hand Guo and Chen[27] found that the mobilities for a range of proteins in SDS–gel electrophoresis scaled with the molecular weight of the protein according to the reptation prediction.

Our goal, in this paper, is to extend the DLS studies of polymer diffusion in gels to examine the case of a polyelectrolyte, and to also determine the dependence of the diffusion constant on the concentrations of the gel and the probe polymer. For this we consider the diffusion of linear sodium poly(styrenesulfonate) (NaPSS) in poly(acrylamide) (PA) gels prepared under the same conditions as used in gel electrophoresis. Here we study the diffusion without any external electric field applied. We have previously studied[1–3] the tracer diffusion of linear polymer chains in methyl methacrylate (MMA) gels as a function of their molecular weight, and we confirmed scaling predictions of the reptation theory in the case of high molecular weight probe polymers.[3] Due to problems of incompatibility in the MMA system we were not able to scan a big range of gel concentrations. In the work described in this paper, using PA gel with bis(acrylamide) (BIS) as a cross-linker and NaPSS as a probe polymer, it has been possible to span a greater range of the gel and probe concentrations. This is partly due to a higher value of copolymerization reactivity of BIS which lowers the critical gel threshold to, e.g., c_g = 2.5 wt % for cross-link content f_c = 2.7 wt % of c_g.

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Moreover, NaPSS probes and PA gels are more compatible than polystyrene probes and MMA gels, and this prevents phase separation even at very high gel concentrations. Therefore, we were able to study additional scaling relationships relating diffusion coefficients of the probe polymer and the gel mode to the concentration of the gel and of the probe polymer.

Experimental Methods

Sample Preparation. For the preparation of acrylamide (PA) gels we have used the method described in the Sigma Chemical Co. electrophoresis kit. A solution (solution C in the Sigma recipe) of acrylamide (AA) and bis(acrylamide) (BIS) at concentrations $C_{AA} = 0.22$ g/mL and $C_{BIS} = 6.1 \times 10^{-3}$ g/mL was prepared separately and used within 2 weeks from the day of preparation. The second solution (solution A in the Sigma recipe) contains TEMED, which serves as a catalyst, and a phosphate buffer (0.053 M $Na_2HPO_4 \cdot 2H_2O$ + 0.0044 M KH_2PO_4) with pH equal to 8.0. For the samples prepared in deionized water, only TEMED was used in this solution. The third solution is one containing ammonium persulfate (solution J in the Sigma catalog) which serves as initiator and is made just before sample preparation. This solution was de-aired for a few minutes by bubbling with nitrogen. The probe polymer NaPSS was dissolved in water. Solutions A, C, and J and in some cases NaCl and water with dissolved NaPSS were mixed together in appropriate amounts and slowly filtered through a 0.22 μm filter into clean measuring cells. It takes approximately 20 min for samples to start to gel. The samples were kept for more than 1 h thermostated at 40 °C in order to complete the polymerization and to ensure reproducible conditions for polymerization of all samples.

Two sets of samples containing NaPSS probe molecules with the total monomer concentrations $c_g = 11$ and 18 wt % were prepared with the same cross-link content $f_c = 2.7$ wt % of c_g.

Apparatus. Dynamic light scattering (DLS) measurements were made with an argon ion laser (power at the sample ≤ 200 mW) and a variable-angle goniometer using a 264 channel BI 2030 autocorrelator. The samples were thermostated in a refractive index matching liquid at 40 °C. Most of the measurements were done at a scattering angle of 90°, except in the case when angular dependence was measured.

Extended correlation functions were measured in two different ways: (i) multisampling time (MST), on a Brookhaven Instruments correlator, which involved splitting the available 264 real-time channels into four separate groups of channels, each with different sampling times, covering effectively more than 4 orders in delay times; (ii) composite multisampling time (CMST), on the same Brookhaven Instruments correlator, by measuring two different multisampling correlation functions with overlapping measuring time ranges and then setting up from them a composite correlation function which can cover up to 7 orders in delay time (the two correlation functions were overlapped for 33 identical delay times in this procedure).

The correlation functions obtained in these measurements extend to very long times (maximum delay times extending from 1 to 100 s) and thus the duration of the experiment ranges between 4 and 30 h. Figure 1a shows typical composite correlation functions obtained by matching two multisampling time correlation functions for three identical PA gels containing linear NaPSS chains of different molecular weights, as indicated. In all cases two distinct dynamic contributions to the correlation function are clearly visible, the faster corresponding to a collective gel mode and the slower to the probe diffusion. We can also see from Figure 1a that the baseline is well-defined in the case of PA gels swollen in solvents with high ionic strengths. The measured baselines obtained by using delayed channels agreed with the calculated baselines based on the total number of counts within 0.2%. It is only in the case of gels swollen in deionized water (low ionic strength) that baselines were not well-defined since the slowest dynamic process was on the long time measurement limit of the correlator used.

Data Analysis. The composite and multisampling time autocorrelation functions were analyzed by an inverse Laplace transform using two methods of constrained regularization, CONTIN[28] and REPES,[29] in order to obtain a distribution $A(D)$ of diffusion constants. We also tried an alternative method involving a subtraction of the gel mode contribution to the correlation function as obtained from primary CONTIN analysis. The modified correlation function thus obtained was then again analyzed with CONTIN, by a single exponential fit and by the cumulant method. In this manner we could minimize the effect of the dominant gel mode on the probe diffusion data.

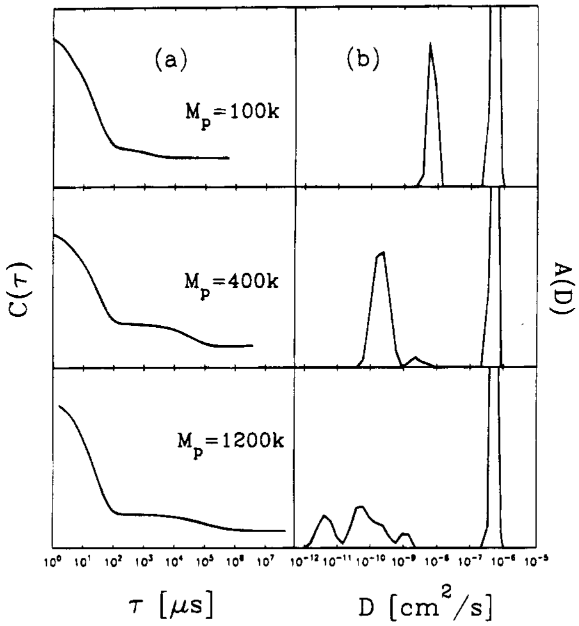

Figure 1. (a) Correlation functions $C(\tau)$ obtained from PA gels (c_g = 11 wt %, f_c = 2.7 wt %) with three different molecular weights of NaPSS probes, as indicated on the graph. (b) Semilogarithmic plots showing diffusion constant distributions $A(D)$ that are obtained from CONTIN analysis of the composite correlation functions shown in Figure 1a.

Laplace inverse of the correlation functions shown in Figure 1a gives the diffusion constant distributions shown in Figure 1b. We can see that there are two distinct modes separated by several decades in delay times. A comparison of the diffusion constant distribution obtained from the composite correlation function with those obtained from the multisampling correlation function has shown that composite correlation functions improve the resolution of the analysis but do not affect the peak positions.[1,2]

Results and Discussion

Predictions of the Reptation Model. The predictions of the reptation model for the tracer diffusion of a linear polymer chain inside a gel depend on relative values of the molecular weights of the probe (M_p) and parameters that characterize the gel such as the molecular weight of the chain between cross-links, M_x, and the molecular weight between entanglements if the system was not cross-linked, M_e. Three different dynamic regimes can be obtained:[30]

(1) **free draining** in the case when $M_p < M_e$ and $M_p < M_x$, with a diffusion coefficient of the form

$$D_t = D_o M_p^{-1} \tag{1}$$

(2) **simple reptation** when $M_p > M_e$ and $M_x > M_e$ with

$$D_t = D_o M_e M_p^{-2} \tag{2}$$

(3) **strangulation** when $M_e > M_x$ and $M_p > M_x$ with

$$D_t = D_o M_x M_p^{-2} \tag{3}$$

Table 1. Characteristics of the PA Gel Matrices

c_g (g/mL)	f_c (g/g)	ξ_H (nm)	M_e	M_x
0.11	0.027	4.1	1680	2780
0.18	0.027	2.9	840	2780

Since the two main parameters of the gel network which determine the mechanism of diffusion of a linear polymer probe in a gel are M_x and M_e, we estimate both of them for the gels involved in this experiment. The M_x value is usually evaluated from swelling measurements preferably in nonpolar organic solvents by using the Flory–Rehner equation.[31] In the particular case of PAA gels swollen in aqueous solvents this approach could not be applied because acrylamide groups can hydrolyze. Even a small amount of hydrolysis can substantially modify the swelling equilibrium and, consequently, the value of M_x. Assuming that the copolymerization would be fully random and the reaction goes to completion, we estimate $M_x = 2780$ independent of the overall gel concentration. Since the reactivity of bis(acrylamide) is lower than that of acrylamide, the estimated value of 2780 represents a lower bound. The M_e value was roughly estimated from the hydrodynamic correlation length, ξ_h, using the relation $\xi_h = 0.1M_e^{0.5}$ valid for unperturbed dimensions of PA macromolecules.[32] ξ_h is a measure of the distance between entanglements and was obtained from DLS measurements by calculating from the gel mode diffusion constant, D_g; $\xi_h = kT/6\pi\eta D_g$ (where η is the solvent viscosity, T the absolute temperature). The characteristics of gel networks are shown in Table 1.

By comparing the molecular weights of the probes used with the values of M_x and M_e in Table 1, we conclude that $M_p > M_e$ and $M_x > M_e$ and thus we are in the simple reptation regime (2). For this case the tracer diffusivity scales as[33]

$$D_t \sim M_p^{-2}\xi^{5/3} \sim M_p^{-2}c_g^{-1.25} \quad \text{(Rouse friction)} \quad (4)$$

$$D_t \sim M_p^{-2}\xi^{7/3} \sim M_p^{-2}c_g^{-1.75} \quad \text{(Stokes friction)} \quad (5)$$

for a good solvent and as

$$D_t \sim M_p^{-2}\xi^{2} \sim M_p^{-2}c_g^{-2} \quad \text{(Rouse friction)} \quad (6)$$

$$D_t \sim M_p^{-2}\xi^{3} \sim M_p^{-2}c_g^{-3} \quad \text{(Stokes friction)} \quad (7)$$

for a Θ-solvent.

Here Rouse and Stokes friction refer to two different types of friction that can be assumed for the friction of the blob. Rouse-like friction of the blob is proportional to the number of monomers in the blob, while Stokes-like friction is proportional to the size of the blob.

Another scaling relationship that is of interest in this work is the scaling of the cooperative gel mode diffusion constant, D_g, with the concentration of the gel, c_g, i.e.

$$D_g \sim 1/\xi(c) \sim c_g^{\nu/(3\nu-1)} \quad (8)$$

which for a good solvent ($\nu = 0.6$) becomes

$$D_g \sim 1/\xi(c) \sim c_g^{0.75} \quad (9)$$

Results of Diffusion Measurements in Pure NaPSS Solution. As is well-known from earlier studies,[5-20] the diffusion of polyelectrolytes in an aqueous solution depends on the ionic strength, μ. In order to assess the effect of the ionic strength on the diffusion we have measured the diffusion constant distribution for solutions of NaPSS ($M_{\text{NaPSS}} = 400\text{k}$) in the same solvents as used in the studies with gels. These solvents are (i) deionized water ($\mu \approx 0$), (ii) water with 0.05 M NaCl ($\mu \approx 0.05$), and (iii) phosphate buffer with pH 8.0 ($\mu \approx 0.16$).

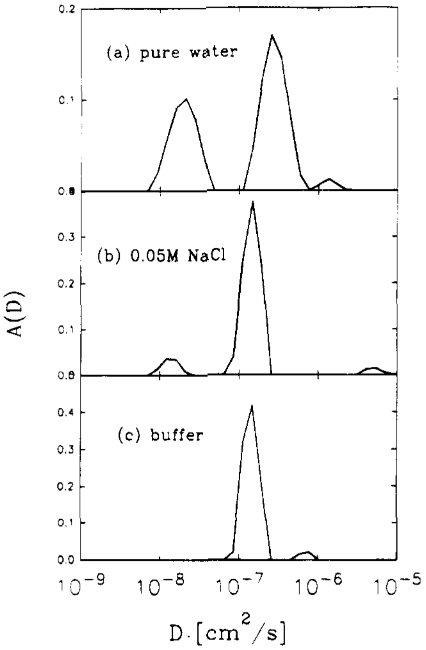

Figure 2. Laplace inversion of the correlation functions obtained for the measurements on the NaPSS solution ($c_{\text{NaPSS}} = 8 \times 10^{-4}$ g/mL) in (a) pure (deionized) water, (b) water with 0.05 M NaCl salt added, and (c) phosphate buffer, pH 8.0.

The ionic strength is a parameter directly related to the screening of electrostatic interactions in polyelectrolyte solutions and consequently influences the stiffness of polyelectrolyte chains due to a repulsion among charges along the chain. If we adopt the theory of Odijk[6,7] and Skolnik and Fixman[8] for the electrostatic persistence length, the effect of the ionic strength on the stiffness of polyelectrolyte macromolecules can be expressed in terms of the total persistence length, $L_t = L_p + L_e$, where L_p and L_e are the polymer and electrostatic persistence lengths, respectively. In the case of NaPSS dissolved in deionized water the screening of electrostatic interactions is governed by counterions only and generally $L_e \gg L_p$ in dilute solutions. The polyelectrolyte molecules are stiff with a rodlike conformation. For dilute solutions of NaPSS in aqueous solvents, using Odijk's theory[7] and assuming that counterion condensation occurs in NaPSS, we obtain $L_e \approx 1.3$ and 0.42 nm for aqueous solutions with 0.05 M NaCl and phosphate buffer solutions, respectively. Comparing these L_e values with L_p = 1–5 nm published for NaPSS[11] aqueous solutions we conclude that $L_p \approx L_e$ in aqueous solutions of NaPSS with 0.05 M NaCl and $L_p > L_e$ in phosphate buffer solutions of NaPSS. Thus the electrostatic repulsion effects play only a minor role in buffer solutions and the dynamic behavior of NaPSS chains can be described as any other neutral flexible chains with the total persistence length close to L_p.

The distributions of diffusion constants for NaPSS solutions in these three solutions are shown in Figure 2. Characteristic slow and fast modes are observed in the case of the diffusion in deionized water (system with very low ionic strength). The values for the slow and the fast mode diffusion constants are consistent with the values obtained in previous studies[9,10] under similar conditions. However, the slow diffusion constants differ by approximately one decade from the values obtained

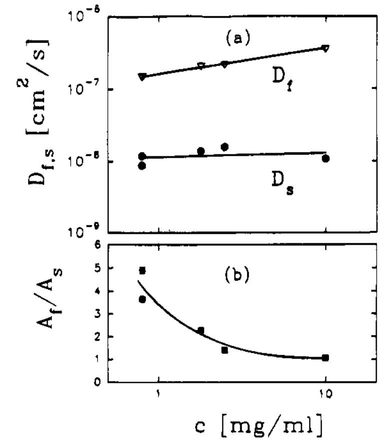

Figure 3. (a) log–log plot of the fast (D_f) and slow (D_s) diffusion mode versus the concentration of NaPSS, c, for NaPSS solution in deionized water. (b) Semilog plot of the ratio of the intensities of the fast and the slow mode, A_f/A_s, vs the concentration of NaPSS, c.

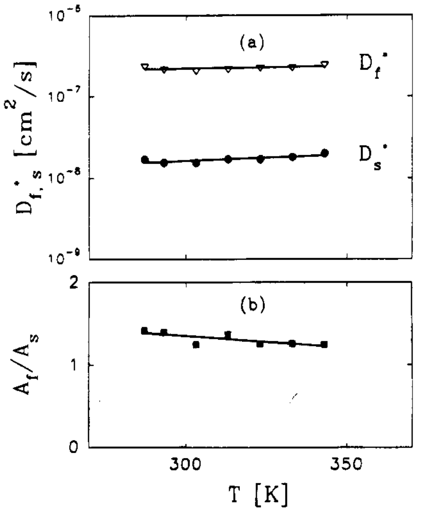

Figure 4. (a) Dependence of the corrected diffusion constant of the slow (D_s^*) and the fast (D_f^*) mode on the absolute temperature, T. The diffusion constant is corrected for the dependence of the viscosity of water on temperature; $D^*_{f,s} = D_{f,s}(\eta_T 293/\eta_{293}T)$, where η_T is the solvent viscosity at temperature T. The factor $\eta_{293}/293$ is used to normalize the viscosity and temperature scales. (b) Dependence of the relative ratio of the fast and slow mode, A_f/A_s, on temperature, T.

by Sedlak et al.[20] In general, these measurements are very sensitive to the purity of the water used and differences could arise from the fact that Sedlak et al.[20] were deionizing their samples within the light scattering cell so that any residual salt present in commercially available NaPSS samples would not affect their results. Nevertheless, qualitatively our results agree with theirs in the sense that two modes were observed in the case with low ionic strength but we did not observe significant dependence of the slow mode diffusion constant on concentration (Figure 3a). In addition to the diffusion data, we have estimated the ratio between the amplitudes of the fast and slow modes (see Figure 3b). It is obvious that as the polymer concentration lowers, the slow mode disappears. In Figure 4 we see that both the slow and fast diffusion modes show no dependence on the temperature except for the usual dependence of solvent viscosity on temperature.

In the case of high ionic strength solution, the distribution of diffusion constants becomes much simpler. As can be seen from Figure 2, in system ii there are traces of the slow mode but the fast mode dominates. For system iii only the fast mode is observed and the value of the diffusion constant corresponds to the value for a neutral chain with the same molecular weight in a good solvent. This suggests that the gel samples containing NaPSS probes and prepared in the buffer or in water containing excess salt (NaCl) would follow simple reptation predictions.

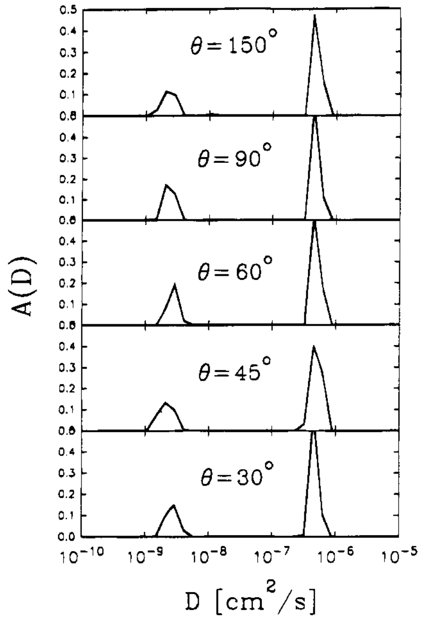

Figure 5. Semilog plot of the distributions of the diffusion constant, $A(D)$, for the case of NaPSS with M_p = 100k for five different scattering angles, as indicated.

Results of Tracer Diffusion Measurements in a Gel. *Diffusion in a PA Gel Swollen in Solvents with High Ionic Strengths.* Figure 1a shows typical autocorrelation functions obtained from PA gels swollen with pH 8.0 phosphate buffer of high ionic strength ($\mu \approx 0.16$) and containing NaPSS probe of three different molecular weights. The corresponding distributions of the diffusion constant, $A(D)$, obtained by Laplace inversion of these correlation functions in Figure 1a are shown in Figure 1b. It is noticeable that only two separate bands are observed. The faster process corresponds to the cooperative gel mode since it is observed in a pure gel without probe, while the slower mode is related to the tracer diffusion of NaPSS probes since it is dependent on the molecular weight of the NaPSS. As shown in Figure 5, for the case of the NaPSS probe polymer with M_p = 100k, both dynamic modes are diffusive since the positions of the maxima in $A(D)$ bands do not shift with the scattering angle. The dynamic mode due to diffusion of sol into the gel, observed in weak MMA gels,[1-3] was not observed because the PA gels used are far from the gel point and therefore the sol concentration is negligible.

Using the first moments of the probe diffusion peaks, we have estimated diffusion constants of the probe, D_p, which are plotted vs the weight-averaged molecular weight of the probe polymer, M_p, in Figure 6a,b for 18 and 11 wt % PA gels, respectively. The least squares fit to data obtained for the case when NaCl salt is added to water gives us the scaling relationships $D_p \sim M_p^{-2.1\pm0.1}$ and $D_p \sim M_p^{-2.0\pm0.1}$ for 18 and 11 wt % gels, respectively, which is consistent with prediction of the reptation model. Concentrations of the NaPSS used in these samples were kept below the overlap concentration. Our results for this exponent differ from those of Rotstein and Lodge[4] who obtained higher exponents (−3) at very high concentrations of the gel (c_g = 24 wt % of PVME gel). In the experiment with PA gels, the M_p-exponent

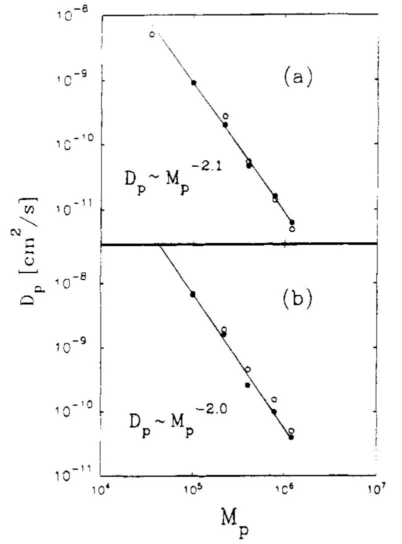

Figure 6. (a) log–log plot of the probe diffusion constant of NaPSS probes, D_p, in 18 wt % PA gel *versus* the molecular weight, M_p, of NaPSS. Filled circles represent values obtained for the system with 0.1 M NaCl added to pH 8.0 phosphate buffer and hollow circles represent the system which contained buffer only. The lines are the least squares fit to data for the system containing NaCl. It follows the scaling prediction $D_p \sim M_p^{-2.1}$. (b) Same as Figure 6a except that the gel concentration in this case was 11 wt %. The line representing the least squares fit to data for the system containing NaCl gives scaling $D_p \sim M_p^{-2.0}$.

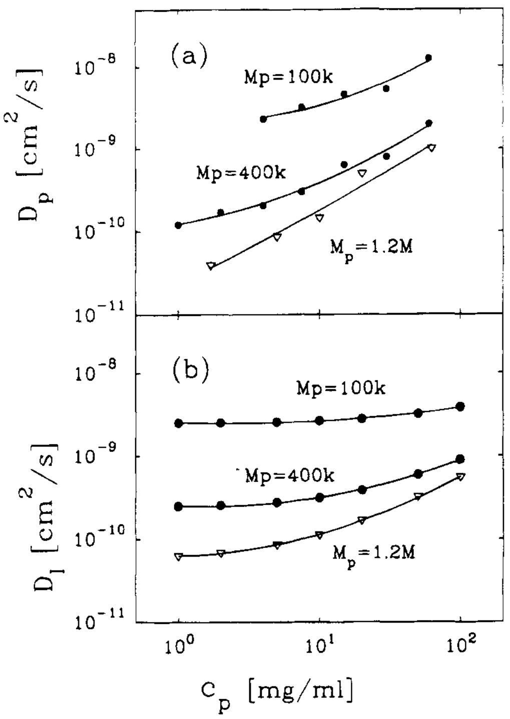

Figure 7. (a) Dependence of the NaPSS probe diffusion constant on the concentration of the probe plotted as D_p vs c_p. Molecular weights of NaPSS: 100k, 400k, and 1.2M. (b) log–log plot of D_I vs c_p where D_I designates the interdiffusion coefficient, as predicted by random phase approximation theory for the interdiffusion mode of the same molecular weights as in (a). Data designated with open triangles are rescaled with a factor of 2 for both graphs (twice lower). This is done for better visibility of the data.

values are independent within the experimental error of gel concentration as we go from 11 to 18 wt % of the gel. On the other hand, we observe that the probe diffusion bands in $A(D)$ distributions broaden with the increasing value of M_p (see Figure 1b), as was also observed in our previous work with polystyrene probes diffusing inside the MMA gel.[3] This broadening cannot be due to the polydispersity of the probe polymers. It is possible that this broadening reflects the effects of inhomogeneities in the structure of the gel. In previous studies of the diffusion of latex particles in PAA gels, we had observed that the gels have regions with large pores as well as regions of tightly clustered cross-links. In such a heterogeneous system tracer-diffusion dynamics is quite complex, ranging from a Stokes–Einstein type of diffusion in large pores to reptation and slower processes in regions with a higher cross-link content. The typical scattering volume in our DLS experiments, of the order of 10^{-3} mm^3, is large enough to sample the microscopic spatial variation of gel cross-linking density. Although it is difficult to estimate a width, because the CONTIN fitting procedure tends to resolve the broad region into multiple peaks, qualitatively the results obtained here are similar to those seen in PMMA gels,[3] with the slowest diffusion constants representing a scaling exponent of −3, which is consistent with the measurements of Rotstein and Lodge.[4] It is also possible that with these very slow diffusion processes DLS does not measure the true long-time limit of the diffusion constant and this may account for some of the discrepancies seen in different studies.

Hoagland et al.[23–25] observed the reptation prediction for the M_p dependence of the electrophoretic mobility (exponent −1) of NaPSS probes in PA gels only in the case of well-defined gels and low electric fields. In the case of weak gels serious deviations from the reptation prediction were observed. Strong electric fields can lead to weakened molecular weight dependences, because high fields affect both the conformation of the probe polymer and the gel structure, as has been shown in the recent birefringence studies of gels with applied electric fields.[34] On the other hand, an exponent larger than −1 was found for high molecular weight probes even in weak electric fields for gels which were sufficiently dilute.[23] This effect was not observed in our diffusion experiments even with the weak gels.

Since concentrations of NaPSS probe polymers used in our study were very close to the overlap concentration, the question arises as to whether the experiment measures the tracer diffusion or the interdiffusion (mutual)[35] of probe against gel. In order to address this, we have studied the dependence of D_p vs c_p for three different molecular weights of NaPSS: 100k, 400k, and 1.2M. The results are shown in Figure 7a, and it appears that the probe polymer concentration dependence cannot be represented by a power law, particularly for the sample with 100k and 400k NaPSS. The dynamic behavior of probe polymers (NaPSS) in a gel matrix (PA) can be at least qualitatively interpreted using a theory of quasi-elastic light scattering in mixtures of homopolymer in solution, based on the random phase approximation.[35–38] The main result of the theory is the prediction of the existence of two dynamic processes in DLS spectra, which are interpreted as cooperative and interdiffusion modes.[34] Modifying contrast factors of polymer components does not affect diffusion constants but only changes the relative amplitudes of these modes in DLS spectra. This theory can be adapted to the problem of the diffusion of linear polymer chains in chemically cross-linked gels using the idea of the so-called "c^*-theorem",[39] according to which an equilibrium gel can be treated as a semidilute solution of linear macromolecules having the same molecular weight as the chains between cross-links, M_x, at overlap (crossover) concentration c^*. Since the second virial coefficient of NaPSS ($A_2 = 2.47 \times 10^{-4}$ mol cm^3 g^{-2} for NaPSS of M_w = 320k in aqueous solutions with 0.5 M NaCl[40]) is comparable to that of PA polymers ($A_2 = 4.6 \times 10^{-4}$ mol cm^3 g^{-2} for PA with M_w = 390k[41]), we can assume that the thermodynamic quality of the solvent with high ionic strength is approximately the same for both polymers. Under this assumption the decay rates corresponding to the cooperative, Γ_C, and interdiffusion, Γ_I, mode are[42]

$$\Gamma_C = \Gamma_o(q)[A + 1/2(B)^{1/2}] \tag{10}$$

$$\Gamma_I = \Gamma_o(q)[A - 1/2(B)^{1/2}] \tag{11}$$

where

$$A = [z_p + (1/P_p) + (1/(yP_g))] \tag{12}$$

$$B = [z_p + (1/P_p) - (1/(yP_g))]^2 - 4xz_p[(1/P_p) - (1/(yP_g))] + 8x(1 - x)z_p^{\,2}(\chi/v) \tag{13}$$

$$z_p = 2A_2M_pc_t \tag{14}$$

Here c_t is the total concentration of polymers in g/cm^3, x is the fraction of the gel in the system, $y = N_g/N_p$, where N_g and N_p are the degrees of polymerization of the gel and probe polymer, P_g and P_p are the form factors of a coil of the gel and probe polymer respectively, Γ_o corresponds to the diffusion of a single chain in the mixture, and χ/v is the Flory interaction parameter between NaPSS and PA. In the calculation we have assumed that $P_g = P_p = 1$, $A_2 = 4.6 \times 10^{-4}$ mol cm^{-3} g^{-2}, and $\chi/v = 0$. The last assumption is based on our experience that the compatibility of NaPSS probes with PA gel matrices is very good. The calculated values of the interdiffusion coefficient $D_I = \Gamma/q^2$ are plotted as a function of the NaPPS concentration, c_p, for M_p = 100k, 400k, and 1.2M in Figure 7b. The Γ_o values were selected to match the experimental data at low concentrations for the probe polymer with M_p = 400k and to reflect the tracer-diffusion molecular weight dependence; $\Gamma_o \sim M_p^{-2}$. A comparison of Figure 7a,b reveals a similar concentration dependence of the calculated D_I and the experimentally measured diffusion coefficient D_p; D_I increases with increasing c_p and for different molecular weights the values of D_I approach each other at high NaPSS concentrations. Changes of D_I due to varying concentration are systematically smaller ($\approx 2\times$) than those observed experimentally. This is not surprising given the simplifying approximations used; the qualitative agreement between the calculated and experimental values is quite satisfactory. As D_p values at low c_p concentrations are only slightly c_p-dependent, measurements of D_p at low c_p are very close to the tracer-diffusion coefficients defined for infinite dilutions ($c_p = 0$).

In order to study the dependence of the dynamics on c_g we have scanned the range of concentrations from below the gelation threshold up to the maximal one that our experiments permitted, which is 18 wt % (above this concentration D_p is too slow to be measured by DLS). The dependence of both D_p and the cooperative gel mode D_g on the concentration of the gel, c_g, was measured, and power law dependences for both quantities were found: $D_g \sim c_g^{0.67}$ and $D_p \sim c_g^{-2.5}$ (see Figure 8) in relatively good agreement with the theoretical predictions.[39,43] The straight line represents the least squares fit only to points from samples above the gel threshold (designated with the line).

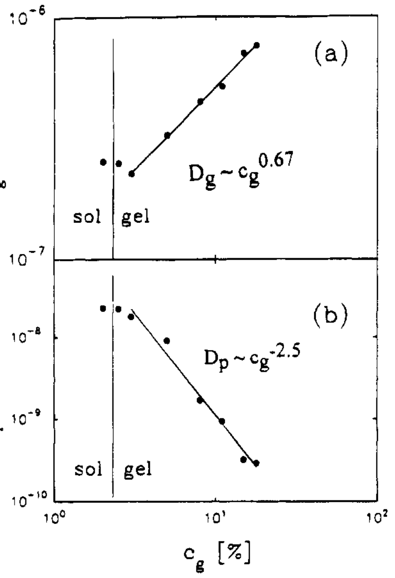

Figure 8. (a) log–log plot of the diffusion constant corresponding to a gel cooperative mode, D_g, vs concentration of the gel, c_g. The scaling relationship observed is $D_g \sim c_g^{0.67}$, whereas theoretically $D_g \sim c_g^{0.75}$. (b) log–log plot of the NaPSS probe diffusion constant, D_p, vs concentration of the gel, c_g. The straight line represents the least squares fit only to points which are above the gel threshold and follows scaling relationship $D_p \sim c_g^{-2.5}$.

The exponent for c_g dependence of D_g was found to be 0.67, slightly lower than the theoretical value of 0.75.[44] Theoretical predictions for the c_g dependence of D_p vary significantly, and the range of valid exponents is relatively large (−1 to −3) (see eqs 4–7). In the case of a Θ-solvent this exponent should be −3, and in the case of a good solvent it is −1.75 for the Stokes type of friction (see eqs 4–7). The exponent obtained here, −2.5, falls within this range, but agreement should be termed only as relatively good. Since water is a good solvent for NaPSS, we would expect an exponent of about −1.75. However electrostatic effects due to the surrounding charges might affect the scaling within a blob. Also dragging of the counterions is more likely to produce a different type of friction. Rotstein and Lodge[4] have shown that if the relevant topological distance above which movement of the probe becomes constrained is determined by M_e estimated from the empirical c dependence of the plateau modulus G_N, then for Rouse-like friction $D_t \approx c^{-2-2.4}$. This is very close to the result that we have obtained.

Diffusion in a PA Gel Swollen in Solvents with Low Ionic Strengths. Figure 9 shows a typical correlation function obtained for the 11 wt % gel with NaPSS prepared in deionized water. It is clear that the experimental baseline was far beyond the measurement limit. If we use the calculated baseline and ignore extremely slow processes in the Laplace inversion, diffusion constants of the fast and middle modes have the same values as the diffusion constant for the equivalent sample in the high ionic strength solvent. The extremely slow dynamic process is probably due to the same mechanism which produces the slow mode in NaPSS solutions in deionized water. It appears that the gel further slows down this mode, since for the same NaPSS solutions in water the slow mode could be measured (Figure 2) whereas in the gels it is beyond the measuring range. The mechanism responsible for the slow mode in NaPSS solutions is a matter of

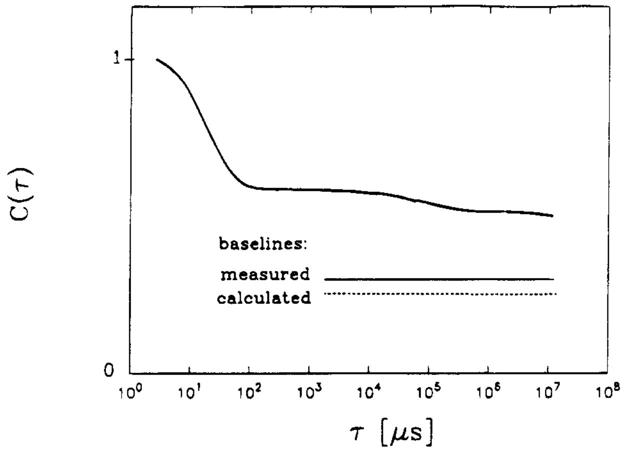

Figure 9. Typical correlation function obtained for the case of diffusion of NaPSS in a gel with low ionic strength water as a solvent. For almost all samples, differences between measured and calculated baselines were too big. Also the last data points never got close to a measured baseline.

considerable debate,[20] and many explanations have been proposed. Recently, Manning[45] has developed a theory based on counterion condensation in polyelectrolytes in which they obtain an attractive region. He attributes the slow mode seen in DLS experiments to the movement of large polymer clusters stabilized by electrostatic attractive forces. Our observations that (i) the slow mode is temperature independent and (ii) the slow mode is influenced by the friction of the medium becoming slower in the gel than in the aqueous solution are consistent with this suggestion of large multichain domains in polyelectrolyte solutions.

Conclusion

In conclusion, the observed exponent of −2 for the scaling of the tracer diffusion of NaPSS probes, D_p, on their molecular weight, M_p, is consistent with the reptation prediction. Broadening of the probe diffusion peak with increasing M_p was also observed, implying that probe diffusion in gels has a complex dynamics due to the presence of inhomogeneities in gel structure. The dependence of the collective gel mode diffusion constant, D_g, on the concentration of gel, c_g, was found to be $D_g \sim c_g^{0.67}$, consistent with the theoretical prediction of $D_g \sim c_g^{0.75}$. Furthermore, $D_p \sim c_g^{-2.5}$ with the exponent of −2.5 falling within the range of values predicted by the reptation model using different types of friction, although this range is relatively wide and cannot be used as a strict test of the reptation model.

Dependence of D_p on the concentration of the probe, c_p, reveals that it is not strictly power law. Comparison with the interdiffusion mode predictions for semidilute solutions of polymer mixtures, as calculated from random phase approximation theory, shows some similarities.

For the dynamics of polyelectrolyte in the case of low ionic strength three characteristic processes were observed. The slowest one could be described only qualitatively since it was on the measurement limit of the DLS apparatus used. However, the further slowing down of this mode in the gel as compared to the polymer solution and the temperature independence seen in the slow mode in NaPSS solutions are consistent with the presence of large multichain clusters stabilized by attractive electrostatic forces, arising from counterion condensation.

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