Chain Self-Diffusion in Aqueous Salt-Free Solutions of Sodium Poly(styrenesulfonate)

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ABSTRACT: Self-diffusion coefficients of polyelectrolyte chains in aqueous semidilute salt-free solutions of sodium poly(styrenesulfonate) have been determined at room temperature as a function of the concentration and the molar mass by use of pulsed field gradient NMR. Self-diffusion coefficients were found to be inversely proportional to the molar mass for degrees of polymerization up to about 1000. The result is discussed in terms of a polymer melt analogy amounting to local friction and ineffectiveness of entanglements. The observation of molar mass independent crossover behavior of D_s as a function of the concentration is in line with this interpretation. Comparison with results from literature leads to the conclusion that this crossover is a general feature of low-salt polyelectrolyte solutions. It is tentatively identified with the Odijk c^{**} crossover where the chain persistence length equals the transient network mesh size.

Introduction

In this paper a study of chain self-diffusion of linear highly charged polyelectrolytes in salt-free solutions is presented. Polyelectrolyte solutions show complex behavior due to the coupling of electrolyte and polymeric properties.[1] The effect of the electrostatic interactions is most manifest in salt-free solutions in which the Coulomb interaction is hardly screened. For instance, the increased local stiffness of the polyelectrolyte backbone combined with the long range of the segment interaction gives rise to local features typical for colloidal systems of overlapping charged rodlike particles.[2] Within this context the peak in the structure function is mentioned, the position of which scales inversely with the square root of the polymer concentration.[3]

Few general concepts concerning the solution behavior of single charged polymers have been developed so far. The most important concepts are the concept of charge renormalization on the surface of the polyelectrolyte backbone by condensation of counterions[4,5] and the concept of an increased persistence length due to interactions between charges on the chain backbone.[6,7] Odijk and Houwaart[8] discuss the validity of separating the electrostatic interactions between charged segments into a short-range part, giving rise to increased local stiffness, and a long-range part, responsible for the excluded volume effect. This analysis justifies the use of a wormlike equivalent chain model for modeling the static properties of polyelectrolyte chains in solution. The equivalent chain model allows the use of concepts developed in the field of neutral polymer physics. Depending on the magnitude of the effective volume fraction, different models from neutral polymer physics may apply. In the case of low effective volume fractions, for instance in solutions with excess added salt, scaling concepts[9] as developed for single chain properties and semidilute solutions may be applied to solutions of equivalent chains.[10] In this way the concept of a correlation length characterizing a transient network of entangled polyelectrolyte chains is introduced in the description of polyelectrolyte solutions. At high effective volume fractions it is expected that mean field like approaches as developed for concentrated polymer solutions and polymer melts can give useful results. As far as dynamic properties are concerned, the concept of an effective volume fraction does not address the full problem since the equivalent chain is not impermeable for the solvent. Both scaling and mean field approaches for the description of the chain self-diffusion coefficient D_s will be discussed in this paper.

For the description of the dynamic properties so far mainly phenomenological descriptions have emerged from experimental studies. Polyelectrolyte solutions without added salt show features like bimodal decay behavior of the time dependent scattered light intensity correlation function,[3] an anomalous concentration dependence of the viscosity,[11,12] and dielectric relaxation behavior characterized by many different regimes.[13] As dynamic theories for solutions of neutral polymers all give expressions for a relatively simple property like the chain self-diffusion coefficient D_s,[9,14] study of the polyelectrolyte chain self-diffusion coefficient should contribute a test of the applicability of these theories to polyelectrolytes. A few experimental studies on polyelectrolyte chain self-diffusion have already appeared.[15,16,17] Kielman[15] studied chain self-diffusion in aqueous solutions of polyphosphates by use of pulsed field gradient NMR for several molecular weights at a relatively high concentration of 1 monoM. Kim et al.[16] investigated chain self-diffusion of poly(*N*-ethyl-2-vinylpyridinium bromide) in salt-free solution by use of forced Rayleigh scattering. Their result of an increase of the chain translation diffusion coefficient with increasing molecular weight at high concentration seems, however, in conflict with physical intuition. At low concentrations, D_s is found to be only moderately dependent on concentration. Zero and Ware[17] studied the mobility of poly-L-lysine in salt-free solution. By use of fluorescence photobleaching recovery they found that D_s *increases* with increasing concentration. Unfortunately the diffusion coefficient was determined in only a small concentration regime (1 to 3 g/L) and for only one molecular weight (90 kg/mol).

In order to investigate the chain self-diffusion behavior in polymeric systems in which strong Coulomb interactions are present, *salt-free* solutions of the linear strong polyelectrolyte sodium poly(styrenesulfonate) (NaPSS) were studied. The NMR pulsed field gradient technique was used to determine the chain self-diffusion coefficient D_s.

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In this experimental technique no concentration gradients nor chemical labels are used and the calculation of D_s from the data is almost model free.[20a] The technique has been applied successfully to the study of chain self-diffusion in solutions of neutral polymers.[18] Chain self-diffusion coefficients have been determined for six molecular weights of NaPSS ($\bar{M}_w$ is 16 000–354 000 g/mol) in a range of concentrations in the semidilute regime (c_p is 0.02–0.5 monoM). Preliminary results of the present work have already been published.[19]

In the second section, the experimental setup, data handling, and sample preparation are described. In the third section, results are presented for the chain self-diffusion coefficient of sodium poly(styrenesulfonate) in water without added salt as a function of concentration for six molecular weights. In the fourth section, relevant experimental results on the same system, obtained with other experimental techniques, are described. In the Discussion section, where a specific equivalent chain model is applied, a semidilute description and a melt-like description for the salt-free polyelectrolyte system are considered. The latter description is an example of a model accounting for the observed locality of friction and an isotropic effective medium as reflected in the observed molar mass dependence of D_s. Subsequently, it is argued that this model may account for a molar mass independent crossover as observed in the concentration dependence of D_s and other dynamic quantities. In the last section a summary of results and conclusions are given.

Experimental Methods

Technique. The chain translation diffusion coefficients have been measured using the pulsed field gradient NMR technique.[20]

The measurements reported here have been performed with a home-built spectrometer equipped with a 2.1-T electromagnet (Bruker). Field gradients were generated in a quadrupole coil with a home-built current pulse generator, capable of generating well-defined rectangular field gradient pulses with a maximum amplitude of 400 $G{\cdot}cm^{-1}$. During all measurements the temperature was maintained at 298 ± 0.2 K. Diffusion coefficients were determined from decay curves of 90–180 and 90–90–90 proton spin echoes monitored at resonance using quadrature detection. Spin echo amplitudes were monitored as a function of the gradient current with a constant gradient pulse width and pulse interval. Pulse widths were in the range 3–7 ms. The echo shape was determined by a linear background gradient of 1 $G{\cdot}cm^{-1}$. It is noted that the effect of residual gradients in the spin echo experiment[20c,d] was minimized by adjustment of the second gradient pulse. The adjustments were generally quite small with typical values on the order of 0.1 μs. This method has been described in the literature[20c] and was applied in the case of 90–180 pulse sequences. Most of the experiments, however, were performed using the stimulated echo sequence[20b] in which during some period of time the magnetization is stored along to the main field. In this case no adjustments of the pulse widths were applied. Minor systematic deviations of the spin echo amplitudes due to residual fields were corrected afterward using the glycerol decay curve as a standard. These corrections amounted to only a few percent of the value of the diffusion coefficient. The phase of the spin echo as a function of the applied current in the gradient coil changed as a consequence of residual gradients and was adjusted during the experiment. Calibration of the coil factor was performed on water and dry glycerol diffusion ($D_s = 2.15 \times 10^{-12}$ m²/s).

System. The system consists of carefully purified sharp fractions of sodium poly(styrene sulfonate) dissolved in water (Millipore quality; conductivity typically less than 10^{-6} Ω^{-1}) without added salt. For most molecular weights, concentrations are in the range 0.02–0.5 monoM. It may be remarked that in solutions *without* added salt the concentration of salt not originating from the polyelectrolyte chains is about 10^{-5} M as can be estimated from measurements of the pH. Clearly this salt concentration is too low to be of influence in the concentration range of interest for this study. The fractions were obtained from Pfannenschmidt, Hamburg, and were manufactured at Pressure Chemical Company, Pittsburgh. Degrees of polymerization were 87 ($\bar{M}_w$ = 16 kg/mol), 166 ($\bar{M}_w$ = 31 kg/mol), 355 ($\bar{M}_w$ = 65 kg/mol), 481 ($\bar{M}_w$ = 88 kg/mol), 967 ($\bar{M}_w$ = 177 kg/mol), and 1934 ($\bar{M}_w$ = 354 kg/mol). (Molecular weights always denote the weight of the parent PSS chain.) In the text the fractions are denoted by PSS16, PSS31, PSS65, PSS88, PSS177, and PSS354, respectively. In the purification procedure 1 g of solid NaPSS is dissolved in 75 mL of water (Millipore quality). This solution is first dialyzed in Visking seamless cellulose tubing in a nitrogen atmosphere at 4 °C against 0.2 M HCl to remove metal ions and thereafter against pure water. The pH of the dialyzed solution is brought to a value of 7.5 with 0.1 M NaOH to ensure that the solution contains only the sodium salt of PSS. This solution is dialyzed against pure water until the electric conductivity in the solution surrounding the dialysis tube equals the conductivity of the pure water used. The pH is checked and if necessary adjusted by adding 0.1 M NaOH to a value of 7.5. The solution then is freeze-dried. The water content of the solid, purified NaPSS is determined by use of IR spectroscopy in D_2O. Solution concentrations are determined by weight. The degree of sulfonation was checked by use of sodium atomic absorption spectroscopy and was always found to be 100 ± 1%.

As far as polydispersity is concerned, a gel permeation chromatography analysis performed in our laboratory showed $\bar{M}_w/\bar{M}_n$ ratios to be 1.2 or smaller for all molecular weights except for the lowest (16 kg/mol, $\bar{M}_w/\bar{M}_n$ = 1.25) and the highest (354 kg/mol, $\bar{M}_w/\bar{M}_n$ = 1.5).

Data Handling. Checks have been performed on possible time dependence of the decay coefficients as determined from the echo amplitude curves. Diffusion coefficients were found to be in a range of approximately 5×10^{-11} to 5×10^{-13} (m²/s). With an effective diffusion time of 55 ms, this amounts to root mean square displacements of the chains in the range of 2 μm down to 0.2 μm. No time dependence was detected for effective diffusion times ranging from 12 to 150 ms, indicating that the decay coefficients can be identified with the chain self-diffusion coefficients. Samples measured approximately $^1/_2$ h respectively 3 days after preparation gave identical results indicating that the NaPSS solutions have been measured in equilibrium. Furthermore, significant changes in sample response after storage at −18 °C for more than 1 year could not be detected.

Chain self-diffusion coefficients are obtained from monoexponential fits of the echo attenuation curves. A typical result for fractions with $\bar{M}_w/\bar{M}_n \leq 1.2$ is shown in Figure 1a. The reported diffusion coefficients typically have standard deviations on the order of 5% in this case. For concentrations lower than 0.05 monoM, errors are estimated to be on the order of 10% due to a lower signal to noise ratio of the echo amplitudes. It is noted that, as a consequence of improved data handling, diffusion coefficients in the very low concentration regime differ somewhat from preliminary results already published.[19]

For larger $\bar{M}_w/\bar{M}_n$ ratios the echo attenuation curves are not properly represented by a monoexponential decay. This can be seen in Figure 1b for the case of fractions of PSS354. Treatment of polydispersity effects is in general not trivial. First, the distribution of chain lengths is in general reflected in the relaxation of the respective contributions to the magnetization of chains of different length. Similarly, a distribution of chain self-diffusion coefficients will exist. The functional form of these distributions and the associated weighted averages of the quantities can, however, only be given in the case of very dilute solutions. As soon as interchain interactions become important, the single-chain responses will depend on the molecular weight distribution of the chains that constitute the surrounding matrix.[21] Decay constants in the case of PSS354 were determined for every concentration from equivalent initial parts of the respective attenuation curves. As there is no unique way for the determination of the decay constants, the accuracy in this case is estimated to be approximately 15%. Even so, the data in Figure 3e show rather more scatter than expected. As no satisfactory explanation has yet been found, the results for this fraction are shown for illustration purposes only. Until truly sharp fractions of high molecular weights are available, the study will be limited

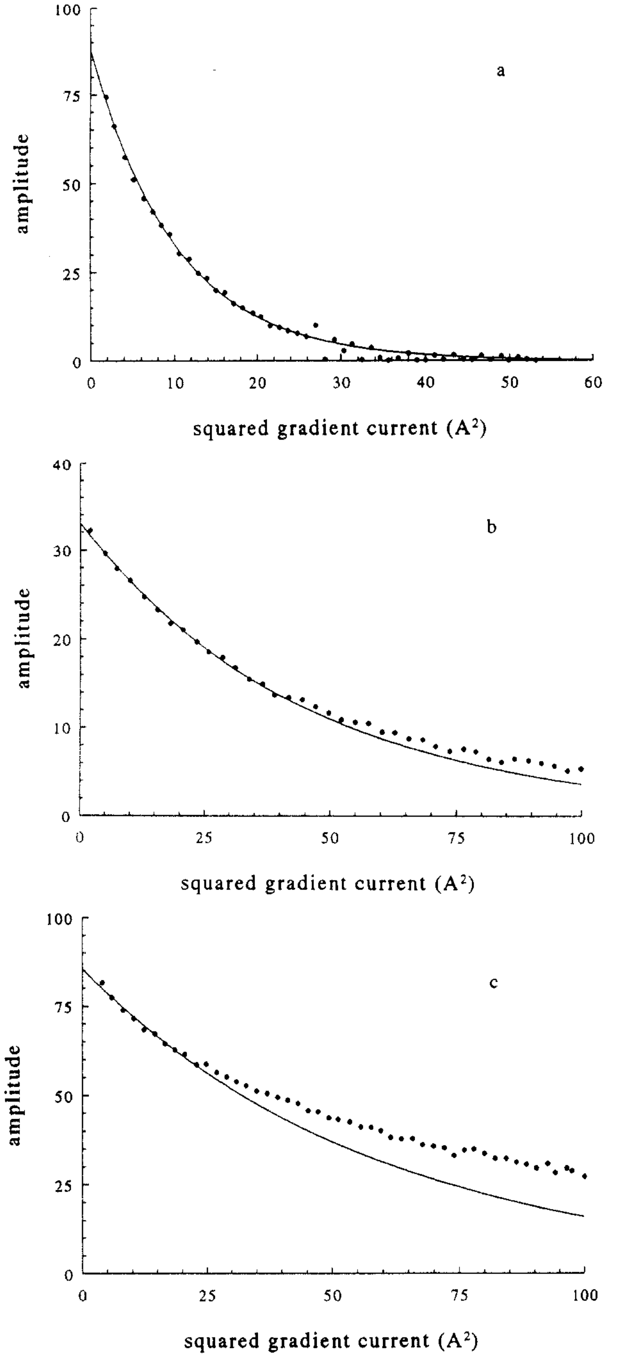

Figure 1. Pulsed field gradient NMR echo attenuation plots of NaPSS in water: (a) PSS177; (b) PSS354; (c) fraction with dp = 5761 ($\bar{M}_w = 1.06 \times 10^6$ g/mol). Solid lines are exponential fits to the initial decay.

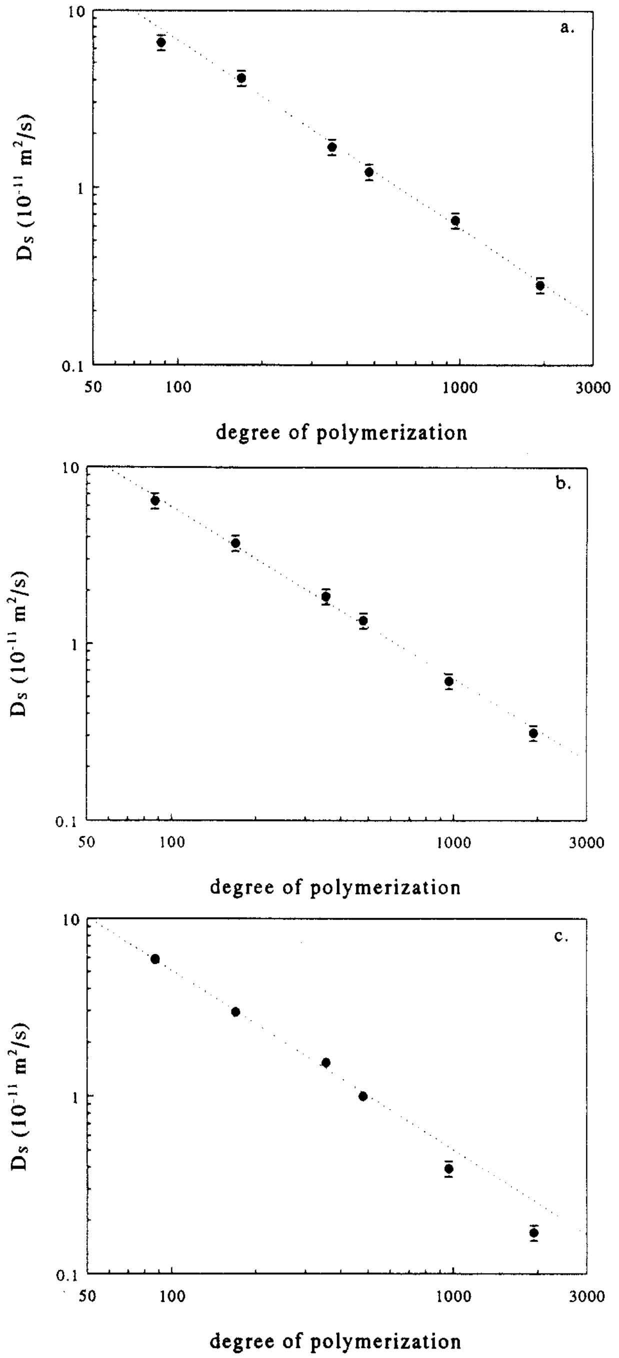

Figure 2. Self-diffusion coefficients as a function of the degree of polymerization, logarithmically plotted; NaPSS in water, no added salt: (a) $c_p = 2.0 \times 10^{-2}$ monoM; (b) $c_p = 4.8 \times 10^{-2}$ monoM; (c) c_p = 0.247 monoM.

to the range up to 177 000. This point is even more clearly illustrated by results obtained on fractions of molecular weights 690 000 and 1.06×10^6 g/mol. A gel permetion chromatography analysis of these samples showed severe polydispersity ($\bar{M}_w/\bar{M}_n \simeq 3.5$) of these fractions. In Figure 1c a typical echo attenuation plot with exponential fit for $\bar{M}_w = 1.06 \times 10^6$ g/mol is given. The results for these fractions will not be discussed in this report.

Results

Molar Mass Dependence of the Chain Self-Diffusion. In Figure 2a–c the self-diffusion coefficients are given as a function of the degree of polymerization for three representative concentrations. The dotted lines represent fits to the data which are, as can be seen from the figures, fairly well described by a power law:

$$D_s \simeq M^{-\alpha} \qquad (1)$$

Table I. Self-Diffusion Coefficients of NaPSS in Water: PSS16[a]

c_p (g/kg)	c_p (monoM)	D_s (10^{-11} m²/s)	c_p (g/kg)	c_p (monoM)	D_s (10^{-11} m²/s)
386.3	1.88	1.18	33.0	0.160	6.10
234.9	1.14	2.85	20.2	0.098	6.66
164.5	0.799	3.69	15.6	0.075	6.50
128.7	0.625	4.27	9.91	0.048	6.40
100.0	0.485	4.50	7.20	0.035	6.70
71.3	0.346	5.37	4.20	0.020	6.50
52.2	0.253	5.60			

[a] No added salt.

The values corresponding to the different figures are tabulated in Tables I–VI. The molecular weight dependencies have been summarized in Table VII. All exponents α have values of 1.0 ± 0.05. As will be discussed below,

Table II. Self-Diffusion Coefficients of NaPSS in Water: PSS31[a]

c_p		D_s	c_p		D_s
(g/kg)	(monoM)	(10^{-11} m^2/s)	(g/kg)	(monoM)	(10^{-11} m^2/s)
83.2	0.404	2.37	33.1	0.161	3.20
74.2	0.360	2.46	22.6	0.110	3.51
67.4	0.327	2.59	14.5	0.070	3.65
58.4	0.284	2.80	10.01	0.049	3.70
51.6	0.247	2.95	7.41	0.036	3.8
41.5	0.202	3.05	4.51	0.22	4.1

[a] No added salt.

Table III. Self-Diffusion Coefficients of NaPSS in Water: PSS65[a]

c_p		D_s	c_p		D_s
(g/kg)	(monoM)	(10^{-11} m^2/s)	(g/kg)	(monoM)	(10^{-11} m^2/s)
51.7	0.251	1.54	9.90	0.048	1.85
33.8	0.164	1.66	7.41	0.036	1.85
22.7	0.110	1.72	4.26	0.021	1.68
15.3	0.074	1.77			

[a] No added salt.

Table IV. Self-Diffusion Coefficients of NaPSS in Water: PSS88[a]

c_p		D_s	c_p		D_s
(g/kg)	(monoM)	(10^{-11} m^2/s)	(g/kg)	(monoM)	(10^{-11} m^2/s)
95.9	0.466	6.3	33.7	0.163	11.4
86.7	0.421	6.8	22.7	0.110	12.4
77.1	0.374	7.1	15.2	0.074	12.8
67.7	0.329	7.8	10.0	0.049	13.5
58.1	0.282	8.4	7.14	0.035	13.4
51.5	0.250	9.8	4.26	0.022	12.2
49.5	0.240	8.6	2.81	0.014	10.7

[a] No added salt.

Table V. Self-Diffusion Coefficients of NaPSS in Water: PSS177[a]

c_p		D_s	c_p		D_s
(g/kg)	(monoM)	(10^{-12} m^2/s)	(g/kg)	(monoM)	(10^{-12} m^2/s)
117.2	0.455	2.9	20.0	0.097	5.6
102.2	0.397	3.1	15.0	0.073	5.6
90.0	0.350	3.4	14.8	0.058	5.9
79.2	0.307	3.5	9.97	0.048	6.1
60.7	0.236	3.9	9.61	0.037	6.4
48.0	0.233	4.3	7.46	0.029	6.5
44.6	0.173	4.6	7.20	0.035	6.3
36.7	0.143	4.9	5.49	0.021	6.3
30.9	0.120	5.0	4.07	0.019	6.5
30.2	0.146	5.1	3.35	0.013	5.8
25.7	0.100	5.3	1.98	0.096	6.4
21.6	0.084	5.4			

[a] No added salt.

the fractions PSS16 show slightly different behavior as a function of the polymer concentration. The noted deviations do not show up completely in the scaling behavior as a function of the molar mass.

In view of the remarks made in Experimental Methods, it is noted that the apparent conformance of diffusion coefficients for the fractions PSS354 with the $\alpha = 1$ power law behavior may be fortuitous. As stated before, this fraction is used for illustration only and is not used in the determination of α.

Concentration Dependence of the Chain Translation Diffusion Coefficient. The self-diffusion coefficients D_s for several molecular weights are shown as a function of the monomeric concentration in Figure 3a–e. The data are represented logarithmically. It is noted that the concentration scale for $\bar{M}_w = 16\,000$ is different.

Table VI. Self-Diffusion Coefficients of NaPSS in Water: PSS354[a]

c_p		D_s	c_p		D_s
(g/kg)	(monoM)	(10^{-12} m^2/s)	(g/kg)	(monoM)	(10^{-12} m^2/s)
96.1	0.466	0.87	32.7	0.159	2.1
85.8	0.417	0.9	32.6	0.158	1.5
75.1	0.364	1.1	23.3	0.113	1.9
66.9	0.325	1.7	23.2	0.113	2.5
60.0	0.291	1.3	15.4	0.075	2.6
51.7	0.251	1.4	15.4	0.075	2.2
51.3	0.249	1.5	10.1	0.049	2.5
44.5	0.216	1.5	10.0	0.049	2.8
41.3	0.201	1.4	7.46	0.036	3.0
39.2	0.190	1.8	7.26	0.035	2.9
32.9	0.160	1.6	4.67	0.023	3.0

[a] No added salt.

Table VII. Exponents from Power Law Fits of D_s vs Degree of Polymerization (dp): $D_s \simeq \mathrm{dp}^{-\alpha}$

c_p (monoM)	α	fit range (dp)
2.0×10^{-2}	1.03 (0.06)	169–967
3.5×10^{-2}	1.03 (0.03)	169–967
4.8×10^{-2}	0.96 (0.04)	169–967
7.3×10^{-2}	1.00 (0.03)	87–967
0.106	1.00 (0.03)	87–967
0.160	1.04 (0.06)	87–967

Several interesting features appear from the figures. For all degrees of polymerization, the chain self-diffusion coefficient of NaPSS in salt-free semidilute solutions is only a weak function of the concentration in the range studied. An increase of the monomer concentration c_p by an order of magnitude in the range 0.05–0.5 monoM causes the self-diffusion coefficient to decrease by only a factor of about 1.5. Although the behavior of neutral polymers in semidilute solution varies widely, the concentration dependence is generally stronger.[18,22] Unfortunately, due to experimental limitations, the concentration regime for c_p smaller than about 0.03 monoM is not accessible to the NMR pulsed field gradient technique available to us at present.

The data may be interpreted as showing the presence of a crossover between a regime where D_s hardly varies with c_p to a regime where D_s decreases appreciably with the concentration. The onset for the decrease is somewhere between 0.05 and 0.15 monoM and appears to be *independent* of the molar mass within experimental accuracy. It is noted that an increase of the chain self-diffusion coefficient with concentration has been observed in a small concentration range by Zero and Ware for poly-L-lysine in salt-free aqueous solutions.[17] In the case of the fractions PSS88 and PSS177, our data do not exclude a maximum value of D_s at low concentration, but experimental accuracy is limited in this region. Further indications for the existence of a crossover regime will be discussed in the subsequent sections.

For the lowest molar mass fraction PSS16 we were able to determine D_s up to a concentration of about 2 monoM, and somewhat different behavior can be seen. The crossover to steeper concentration dependence is shifted to higher concentrations. Taking into account that the Kuhn segment length may be on the order of the chain contour length for these shorter chains, an analysis in which the chains are treated as rodlike particles may be of interest. Such an analysis yields that the rigid rod overlap concentration, $C^* \equiv 1/L^3$,[14] is 0.013 monoM. As a result of a remaining degree of flexibility, the effective overlap concentration may, however, be increased. It is instructive to estimate the self-diffusion coefficient in an infinitely diluted system assuming the particle to be rodlike. It is

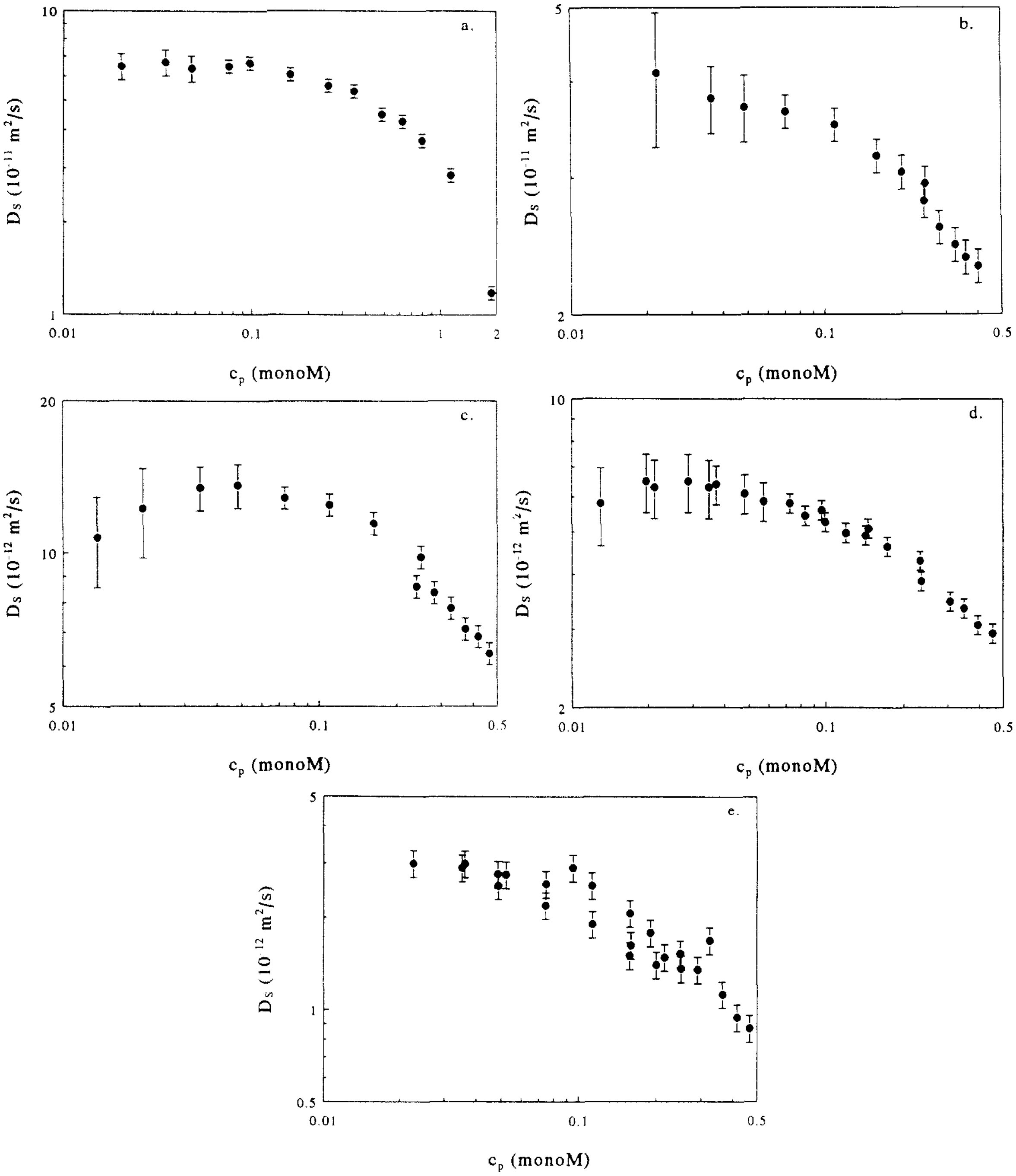

Figure 3. Self-diffusion coefficients as a function of the polymer concentration c_p, logarithmically plotted; NaPSS in water, no added salt; (a) PSS16; (b) PSS31; (c) PSS88; (d) PSS177; (e) PSS354.

also assumed that the influence of the ionic shell around the rod and the microscopic nature of the object can be disregarded. Though the influence of the ionic shell is not known exactly for a charged rod, it accounts for only a minor effect in the case of a single charged sphere.[23] The relation for the self-diffusion coefficient of the rod[24a] is then given by

$$D_s = \frac{k_B T}{3\pi\eta_s L}[\ln(L/d) + \gamma] \qquad (2)$$

where k_B is Boltzmann's constant, T is the temperature, η_s is the solvent viscosity, the chain contour length L = 217.5 Å, the chain bare diameter d = 8 Å, and where γ is a corresponding correction for the L/d ratio, $\gamma \approx 0.34$.[24b] This yields $D_s = 8.0 \times 10^{-11}$ m^2/s. The value obtained in this way is not very different from the measured diffusion coefficient ($D_s = 6.0 \times 10^{-11}$ m^2/s) at low concentrations. It should of course not be concluded from these results that salt-free solutions of the fraction PSS16 are dilute below $c_p \approx 0.15$ monoM. Evidence for the *nondilute* character of the system comes from viscosity measurements which show that NaPSS chains with dp = 87 still strongly interact at concentrations lower than 0.1 monoM.[12]

Transition Behavior As Seen in the NMR Signal. Clearly, any significant change in chain dynamics should be visible in the relaxation of the polymer protons. Unfortunately, measuring the relaxation rates is at least as time consuming as a diffusion experiment, and analysis of the relaxation is sufficiently complicated to be the subject of separate research. Still, it is possible, without going into the details of the relaxation, to observe a change in the relaxation as a byproduct of the diffusion measurements. Spin echo amplitudes have been determined in this experiment by varying the amplitude of the magnetic field gradient, the timing being kept constant.

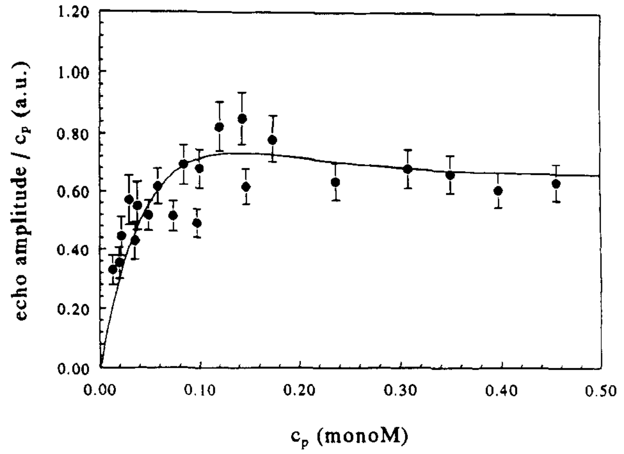

Figure 4. NMR echo amplitudes at zero current divided by the concentration vs c_p; NaPSS in water, no added salt for the fraction PSS177. The solid line is drawn as an aid for the eye.

This implies that the contribution of magnetic relaxation processes to the amplitude of the spin echoes is identical for all applied gradient currents and need not be taken into account in the determination of the self-diffusion coefficient. By using equivalent timing schemes for different concentrations, the effect of magnetic relaxation on the spin echo amplitude at a given gradient current can be examined as a function of concentration. In Figure 4 the amplitudes at zero current, normalized on the polymer concentration, as obtained from diffusion measurements on the fractions PSS177 are represented as a function of the concentration. Due to the use of stimulated echoes, in this experiment the spin echo amplitudes are determined by both transverse and longitudinal relaxation rates of the chain protons. The relaxation is due to reorientational motion of the phenyl groups and the methylene groups. In particular the relaxation of the methylene group will be sensitive to local motion of the polyelectrolyte backbone. Slowing down of the local reorientational motion will increase the transverse relaxation rate. The results shown in Figure 4 constitute further indication for the existence of a transition regime.

Comparison with Other Experiments

In this section, results obtained by other experimental techniques will be compared with the NMR pulsed field gradient results. Such a comparison is useful because one expects to find similar features in other dynamic properties. Emphasis will be placed on crossover behavior, motivated by the observed indication for a crossover in the concentration dependence of D_s.

It is noted that in static properties no transition behavior has been detected. The osmotic pressure of salt-free solutions increases monotonously in the transition region for the dynamic properties.[1,25] Also, the concentration dependence of the position of the peak in the structure function as found in both light and neutron scattering experiments[3] does not show transition behavior. Below, we describe results from experiments on dynamic properties of salt-free polyelectrolyte solutions.

Shear Viscosity. Typical results for the viscosity of polyelectrolyte solutions under low-salt conditions can be found in a paper by Cohen et al.,[12] who studied aqueous solutions of NaPSS. At very low polyelectrolyte concentration, $c_p \approx 10^{-5}$ monoM, these authors find a molecular weight independent maximum in the reduced specific viscosity. This maximum, which had been found before in several other low-salt polyelectrolyte systems,[11] is most probably due to the influence of background ionic strength. Cohen et al. refer to the possible existence of a second transition concentration c^{**} at which the viscosities for different added salt concentrations coincide. Strictly speaking, it is not necessary to introduce a critical concentration to explain the behavior as seen by these authors. As soon as the polyelectrolyte concentration exceeds the salt concentration by about an order of magnitude, it is of course always expected that the viscosities for different salt concentrations coincide. In a forthcoming paper[26] it will be shown, however, that a molecular weight independent transition in the viscous behavior at fixed low-salt concentration does exist. This transition coincides with the transition in the chain self-diffusion behavior.

Dynamic Light Scattering. Many experiments on polyelectrolyte solutions have been performed by use of dynamic light scattering techniques. So far no quantitative explanation for the observed behavior has been given. The book by Schmitz[3] provides a recent extensive review of work in this field.

Generally, the time dependent intensity correlation function as measured in salt-free systems is characterized by a bimodal decay pattern.[27-29] A study by Sedlak and Amis on salt-free solutions of NaPSS[28,29] shows a concentration independent and molecular weight independent fast cooperative diffusion constant at concentrations higher than about 1×10^{-3} monoM (0.2 g/L). At lower concentrations the cooperative diffusion coefficient decreases with decreasing concentration. The onset of this decline occurs at too low a concentration to be identified with the transition found for the chain self-diffusion coefficient. Rather similar behavior was seen by Förster et al.[27] in light scattering experiments on quaternized poly(2-vinylpyridine). These authors normalized dynamic light scattering data for several salt concentrations on the ratio of the polyelectrolyte concentration and the (background) salt concentration. In this way the transition is identified with the onset of the influence of background ionic strength. The slow mode generally has a nondiffusive character and shows rather similar behavior for different polyelectrolytes. At very high molecular weights a transition in the slow mode as a function of concentration in salt-free aqueous solutions of NaPSS is found at about 0.05 monoM.[29] The physical significance of the slow mode as far as low salt solution properties are concerned is, however, under scrutiny.[30]

It can be concluded that the transition behavior as observed in the chain self-diffusion coefficient is not clearly reflected in the cooperative diffusion behavior.

Sedimentation. The sedimentation coefficient of NaPSS in salt-free solution has been determined by Roots and Nyström[31] as a function of concentration for molecular weight 1.06×10^6 g/mol. The sedimentation coefficient was found to be constant for concentrations between about 0.01 and 0.03 monoM. At higher concentrations the sedimentation coefficient decreases as $c_p^{-0.45}$. It is noted that the transition in the sedimentation behavior agrees well with the transition in chain self-diffusion behavior. Furthermore, the exponent of 0.45 for the friction coefficient as determined from the sedimentation coefficient is within experimental error equal to the one that may be derived from the self-diffusion coefficient in the same concentration range. It would be interesting to know if similar concentration dependence of the sedimentation coefficient exists for different molecular weights. Data are, however, not available at present.

NMR Relaxation. Nuclear magnetic relaxation experiments on salt-free aqueous solutions of neutralized poly(acrylic acid) (PAA) have been performed by van Rijn et al.[32] The transverse relaxation rate of deuterons on the backbone of methylene deuterated PAA was found to increase strongly upon diluting below a concentration of about 0.1 monoM. The relaxation behavior was analyzed in terms of the influence of an increasing persistence length on the anisotropic rotational diffusion of chain segments.[33] It is noted that the crossing of chain persistence length and correlation length of the transient network is assumed to be responsible for the observed increase of the transverse relaxation rate of polymer backbone nuclei in *neutral* polymer solutions.[34,35]

The relaxation of quadrupolar counterions in salt-free aqueous solutions of NaPSS was found to show a transition at a concentration of about 0.1 monoM.[36,37] Relating the counterion relaxation to the segmental mobility of the polyelectrolyte, the increase of the persistence length upon diluting is taken to be responsible for this relaxation behavior. Levij et al.[36] tentatively explained the transition in terms of reduced segmental mobility due to crossing of a characteristic length of the chain and the correlation length of a semidilute network.[10]

Electric Birefringence. In the relaxation of the electric birefringence of salt-free aqueous solutions of NaPSS for several molecular weights, four different concentration ranges can be recognized, as has been found by Krämer and Hoffmann.[13] A transition concentration c_2^* was found which is in the range 5×10^{-3} to 0.02 monoM but is molecular weight dependent and is not visible at all for the lowest molecular weight ($\bar{M}_w$ = 100 kg/mol). The results have been analyzed by Cates.[38] This author concluded that the observed behavior of the Kerr effect favors a (qualitative) description using the Odijk model[10] instead of the model due to Witten and Pincus.[39] In the latter model it is assumed that the chain persistence length is renormalized by interchain interactions.

Discussion

The exponent α = 1.0 (±0.05), typical for free draining, as found in this study (see Table VII), is not usually found in the semidilute regime of neutral polymers.[18] Furthermore, since the polyelectrolyte chains are strongly coupled, the rather weak concentration dependence of D_s is striking. In the discussion of these observations, it will be assumed that the description of long time scale properties of polyelectrolytes should reflect features of neutral polymer behavior. The underlying idea is based on the concept of an equivalent chain model in which the influence of the screened electrostatic interaction potential is cast into two effective parameters. The first is the Kuhn segment length, which depends on the ionic strength. The second is an effective diameter on the order of the Debye screening length to represent the effect of the ionic atmosphere surrounding the chain. As a consequence of the fact that both the Kuhn segment length and the segment diameter depend on ionic strength, the excluded volume parameter is also ionic strength dependent. The validity of this approach in terms of a separation of short- and long-range contributions to the interaction between charges has been discussed by Odijk and Houwaart.[8] The equivalent chain model has been applied by Odijk to derive scaling relations for the static properties of polyelectrolyte solutions with and without added salt.[10]

As far as the dynamic properties of the polyelectrolyte chain are concerned, care has to be taken in applying this model. Due to the large difference between the time scales for the relaxation of deformations of the ionic atmosphere and large-scale deformations of the chain conformation, the validity of the equivalent chain model is probably retained as far as direct interactions between segments are concerned. In the case of the hydrodynamic interactions, however, it is important to note that at the ionic strengths of interest for this study the distance from the surface of shear to the chain backbone is much smaller than the Debye length.[23,40] This implies that the effective volume fraction relevant for hydrodynamic interactions is much smaller than the volume fraction of equivalent chains. The latter is about 25% while the first is on the order of the bare volume fraction, which does not exceed 0.5% in this experiment.

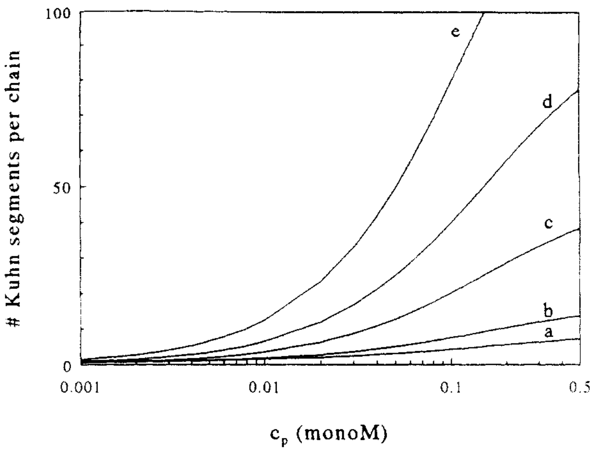

Figure 5. Number of Kuhn segments per chain as a function of the polymer concentration c_p for various molecular weights, according to the Odijk, Skolnick, Fixman model; NaPSS in water, no added salt: (a) PSS16; (b) PSS31; (c) PSS88; (d) PSS177; (e) PSS354.

In the following the application of two models for the description of neutral polymer dynamics on systems in which the polyelectrolyte chains have been replaced by equivalent chains is discussed. In the first model it is assumed that the solution of equivalent chains is semidilute and shows universal behavior on the scale of the correlation length of a dynamic network. Semidilute dynamic scaling theory[9,10] may then be applied. In the second model the solution is regarded as a dense system. Meltlike properties are expected which can be described by mean field theory.

Semidilute Description. In the semidilute description of the solution of equivalent chains, the existence of a transient entangled network is assumed. When the system is assumed to show universal behavior on the scale of the correlation length, which equals the mesh size of the transient network, scaling arguments can be applied.[9,10] As far as chain self-diffusion is concerned, scaling arguments yield an inverse square dependence on molecular weight, $D_s \simeq M^{-2}$. This dependence follows from the assumption of reptative motion of long blob chains.[9] To account for the observed molecular weight dependence of the self-diffusion coefficient, only a description in terms of a renormalized solution of *short* blob chains yields $D_s \sim M^{-1}$.[41] Universal behavior on the scale of the correlation length is expected, however, only if the number of statistical segments between contact points is sufficiently large. An estimate of the number of Kuhn segments per chain as a function of the polymer concentration c_p in salt-free solution is given in Figure 5 for various molecular weights. Calculation of the Kuhn segment is based on the Odijk,[6] Skolnick, Fixman[7] model corrected for small values of κL.[6] As can be seen from this figure, the number of Kuhn segments for the fraction PSS177 is about 80 at 0.5 monoM and 40 at 0.1 monoM. Taking into account that the number of Kuhn segments is even (much) smaller for the other molar masses, which show, however, the same behavior, the assumption of universal behavior of chain segments between contact points may not be tenable in salt-free solutions. In addition it is remarked that the model for the persistence length due to le Bret[42] predicts even larger persistence lengths.

Furthermore, an underlying basic assumption of the semidilute scaling theory is that all interactions between segments can be cast into a single effective interaction parameter. This amounts to neglecting the actual physical volume of the segments. Since, as was mentioned before, volume fractions of the equivalent chains are higher than 25% in salt-free solutions, higher body interactions may not be negligible.

If it is assumed that the screening lengths for the hydrodynamic interaction and excluded volume interaction have similar scaling properties,[10] similar reasoning applies to the scaling properties of dynamic quantities. In a different paper[43] the combined results of self-diffusion and solution viscosity will be discussed. It will be shown that the concept of a semidilute transient network of entangled polyelectrolyte chains indeed cannot explain the observed dynamic behavior of salt-free solutions of polyelectrolytes.

Meltlike Description. The argument of a high effective volume fraction of the solution of equivalent chains can be used to make a comparison between low-salt polyelectrolyte solutions with dense strongly coupled systems of neutral polymers like polymer melts. A similar argument was put forward by Victor.[44] Mean field like arguments similar to those applied in the case of a low molecular weight polymer melt then lead to a description of the dynamics in terms of a mode model.[14] In this model only local interactions between segments (connectivity) are accounted for. As a consequence, the total chain friction is proportional to the chain length, $\zeta_{\mathrm{tot}} \approx \zeta_{\mathrm{l}} L$. The expression for the chain self-diffusion coefficient reads

$$D_{\mathrm{s}} = \frac{k_{\mathrm{B}}T}{\zeta_{\mathrm{tot}}} = \frac{k_{\mathrm{B}}T}{\zeta_{\mathrm{l}}L} \tag{3}$$

The factor ζ_{l}, which has the dimension of a viscosity, denotes the friction per unit of length. As can be seen from eq 3, the melt analogy leads to the molar mass dependence of D_{s} as observed experimentally. The concentration dependence of D_{s} is contained in the factor ζ_{l}. It is concluded from the experimentally observed concentration dependence of D_{s} that the friction factor varies only slightly with concentration for c_{p} smaller than about 0.1 monoM. At higher concentrations the friction factor increases considerably with the concentration.

It is remarked that chain conformations are Gaussian in a melt, a feature expected to be observable in neutron scattering experiments.

Locality of Friction. Equation 3 was given within the context of the naive melt analogy but actually expresses the general case of an (effectively) freely drained polymeric object in a system without topological constraints. The relation in principle applies to both flexible and semiflexible polyelectrolytes. Low-salt polyelectrolyte solutions are then characterized by (i) (strong) screening of the (electro)hydrodynamic interactions along the polyelectrolyte backbone causing the friction of the polyelectrolyte chain to be proportional to the chain length and (ii) an effective medium constituted by the polyelectrolyte chains which is isotropic on the relevant time scale for chain self-diffusion; that is, entanglements are not effective (entanglements may, however, be effective for very long chains). The factor ζ_{l} may be interpreted as an intensive property of the effective medium.

The following three points are noted.

(1) The melt analogy as discussed above is an example of a model accounting for an (isotropic) effective medium and local friction. It is noted again, however, that the distance from the surface of shear to the chain backbone and the effective radius of the chain in general do not coincide.[23,40] The system is effectively dense as far as direct (Coulomb) interactions between segments are concerned but probably not for hydrodynamic interactions, the effective volume fraction being much smaller in that case. The screening mechanism of the excluded volume effect therefore may be similar to the screening mechanism in neutral polymer melts.[14] A clear picture of the microscopic features underlying the effective screening of (electro)hydrodynamic interactions is, however, lacking.

(2) The observed molecular weight independence of the crossover in the concentration dependence of the friction is in accordance with the assumption of ζ_{l} being an intensive property of the effective medium. It is expected that the degree of flexibility of chains between contact points is an important factor to determine the intrinsic properties of the effective medium. The concentration at which the two length scales become equal is assumed to be observable as a transition concentration for the dynamic properties. The notion of a transition concentration at which the persistence length and the average distance between contact points cross has been introduced by Odijk.[10] This transition concentration is denoted by c^{**}. Tentatively the observed transition in the chain self-diffusion coefficient is identified with c^{**}.

(3) A crossover regime must exist in which the dynamic properties as a function of added salt change from (effectively) freely drained under low-salt conditions to nondrained under excess added salt conditions. The latter behavior is expected to be reminiscent of behavior observed in semidilute solutions of neutral polymers.

Concluding Remarks Concerning c^{**}. At this point it is useful to digress on two different models for the solution structure of polyelectrolytes under low-salt conditions. The treatment by Odijk[10] focuses on the semidilute character of the system and corresponding scaling properties. Basic length scales in this analysis are the mesh size of a semidilute transient network and the persistence length of the polyelectrolyte chain. Depending on which length scale dominates, two different semidilute regimes can be distinguished with corresponding scaling laws. At the transition concentration, c^{**}, between these two regimes, the mesh size equals the persistence length. At high concentrations the chain is flexible on the scale of the mesh size, which now is identical to the correlation length of the semidilute solution. In the description of de Gennes et al.[45] of the semidilute regime, the existence of an anisotropic regime of semiflexible polyions is discussed. The melting point of this latticelike structure happens to coincide with the Odijk c^{**}. It is important to note that no lattice structure is supposed in the Odijk model on the scale of *chains*. The isotropic phase of de Gennes et al. in which the correlation length is of the same order as the local chain stiffness may then qualitatively be identified with the region just above c^{**} in the Odijk model. Though no arguments are given in favor of the use of semidilute (dynamic) scaling theory, the notion of the crossing of an intrinsic chain length scale, the persistence length, and an intrinsic solution length scale, the distance between contact points, is important.

Summary and Conclusions

The main result for the behavior of the chain self-diffusion coefficient in salt-free semidilute solutions of

NaPSS is a molar mass dependence of D_s characterized by a free draining exponent for the whole measured concentration regime. The result implies that the chain friction is locally determined. Furthermore, the effective medium constituted by the chains is isotropic on the time scale of chain self-diffusion; entanglements are not effective for the global dynamics. The result has been discussed in terms of a specific equivalent chain model. The long-range Coulomb interaction tends to give the system a concentrated character as far as the static properties are concerned. As a consequence, the solution of equivalent chains is probably to be compared with a neutral polymer melt as far as static properties are concerned. The analogy is less straightforward for the dynamic behavior since the distance from the surface of shear to the chain backbone is much smaller than the Debye screening length. The microscopic mechanism causing the effective screening of (electro)hydrodynamic interactions is not known. This situation is, however, not very different from neutral polymer melts where free draining behavior is observed but not fully understood. It is important to note that the locality of friction in the polyelectrolyte system is valid in principle on all length scales.

Features as observed in the concentration dependence of the chain self-diffusion coefficient are reflected in crossover behavior of other dynamic properties of low-salt polyelectrolyte solutions like shear viscosity, sedimentation, NMR relaxation, and the Kerr effect. It was argued that the transition behavior of the local friction is due to the crossing of the chain persistence length and the average distance between contact points of different chains.

Finally it should be mentioned that it is important that both the M_w and the concentration ranges should be extended. The molecular weight range obviously depends on the availability of sufficiently narrow fractions. Recently, new equipment has become available to us, with which lower concentrations should become accessible. Work in this direction has presently been started.

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