Dynamics of Polyelectrolyte Solutions by Neutron Spin Echo: Molecular Weight Dependence

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ABSTRACT: Neutron spin echo measurements have been carried out on polyelectrolyte solutions without added salts for a wide range of molecular weight at a fixed polymer concentration. From the data it is deduced that the transition from the dilute to the semidilute region occurs at a critical molecular weight, based on the wavevector-dependent effective diffusion coefficient $D_{\text{eff}}(Q)$ derived by Hayter et al. Q is the magnitude of the neutron scattering vector. This critical molecular weight agrees very well with the dilute-semidilute crossover line in the phase diagram of polyelectrolyte solution previously proposed by some of the authors. The Q dependence of $D_{\text{eff}}(Q)$ obtained in the semidilute (isotropic) region is compared with the theoretical predictions.

Introduction

Extensive studies have been carried out on the structure of polyelectrolyte solution using scattering techniques: neutron,[1-3] X-ray,[4,5] and light.[6,7] This structure depends on many factors, such as the polymer concentration, molecular weight, concentration of added salts, charge density on a polymer chain, etc. In order to separate the factors responsible for this complicated structure, some of the authors proposed a phase diagram[5] as functions of the degree of polymerization and the polymer concentration for vinyl polyelectrolyte aqueous solution without added salts at ambient temperature, based on scaling theory[8,9] and calculations of the persistence length by Le Bret,[10] as confirmed by small-angle neutron scattering.[2] This phase diagram is reproduced in Figure 1. It is classified into semidilute and dilute regions by a concentration C^*_S or C^*_R, which represents the crossover for the radius of gyration S or the end-to-end distance R of a polymer chain, respectively. The semidilute region is further separated by C^*_{b} and C^*_{m} into three regimes, termed lattice, transition, and isotropic. Here, C^*_{b} is a concentration at which the persistence length is equal to the contour length and C^*_{m} is a critical concentration where the lattice melts completely. The dilute region is also distinguished into order and disorder regimes. The crossover C^*_κ between two regimes is estimated as a concentration where the electrostatic screening length κ^{-1} is equal to half a distance between two neighbor polyion centers. The dilute-semidilute crossover line C^*_S has been confirmed by small-angle X-ray scattering.[5] It is now interesting to confirm this phase diagram by dynamical measurements and alternatively to interpret these dynamic results in terms of the phase diagram.

Dynamics of polyelectrolyte solutions have been already studied by scattering techniques; neutron spin echo[11,12] and photon correlation spectroscopy.[6,7] Hayter et al.[11] have theoretically derived the dependence of the effective diffusion coefficient $D_{\text{eff}}(Q)$ on the wavevector, Q. This Q dependence is related to the polyion concentration fluctuation and has been confirmed qualitatively by the neutron spin echo measurements. The dynamics of ionomer solutions[13] was also discussed by using the theoretical approach.

In the present work, a neutron spin echo study is reported of polyelectrolyte solutions without added salts as a function of molecular weight at a fixed polymer concentration. According to the phase diagram, the molecular weight range investigated covers both the dilute (order) and semidilute (isotropic) regions at the concentration employed in this experiment (see Figure 1). The variation with molecular weight of the dilute-semidilute transition is discussed in terms of the Q-dependent effective diffusion coefficient $D_{\text{eff}}(Q)$, and the Q dependence of $D_{\text{eff}}(Q)$ is compared with the theory.

Experimental Section

The samples are sodium polystyrenesulfonates (PSSNa) for GPC standards of Pressure Chemical Co. The weight-average degrees of polymerization (DP) are 9, 36, 87, 481, and 5790 and the polydispersity, characterized by the ratio $\bar{M}_{\text{w}}/\bar{M}_{\text{n}}$ of the weight- and number-average molecular weight, is 1.1 except for the sample with DP = 9 and $\bar{M}_{\text{w}}/\bar{M}_{\text{n}} = 1.2$. The polyelectrolyte was purified by deionization with anion- and cation-exchange resins (Amberlite IR120B and IRA400, respectively) and the resulting poly(hydrogen styrenesulfate) was neutralized with sodium hydroxide and then lyophilized. The concentration of the PSSNa aqueous solution used for the scattering experiment was 75.7 g/L or 0.37 monomer mol/L. The solvent was pure heavy water D_2O and the temperature of the solution was controlled at 300 K.

Neutron scattering measurements were carried out with the spin echo spectrometer IN11[14] at the Institut Laue-Langevin, Grenoble. This spectrometer allows measurement of changes in the energy of neutrons scattered by a sample by changing and keeping track of the neutron beam polarization nonparallel to the magnetic guide field. The resultant neutron beam polarization when normalized against a pure elastic scattering such as from glassy polystyrene is directly proportional to the cosine Fourier transform of the coherent scattering law $S_{\text{coh}}(Q,\omega)$, i.e., the intermediate scattering law, or the time correlation function $I_{\text{coh}}(t,Q)$ is measured directly. The measurements were made at scattering angles 2θ of 4°, 6°, 10°, 12°, and 14° (14° only for the sample with DP = 481), corresponding to the magnitude of the scattering vector Q = 0.057, 0.085, 0.114, 0.142, and 0.198 Å^{-1}, respectively. Q is defined by $(4\pi/\lambda)\sin\theta$ where λ is the incident wavelength. The time range obtained by changing the magnetic guide field was 0.43-9.69 ns. Resolution measurements were performed by using a solid solution of deuteriated glassy polystyrene in normal polystyrene at the scattering angles 4°, 8°, and 12°. The incident wavelength was 7.71 Å with a spread $\Delta\lambda/\lambda$ of 24.6%.

Results and Discussion

Time correlation functions observed for the sample with DP = 5790 are shown in Figure 2 at Q = 0.057, 0.114, 0.142, and 0.171 Å^{-1}. The correlation functions can be described

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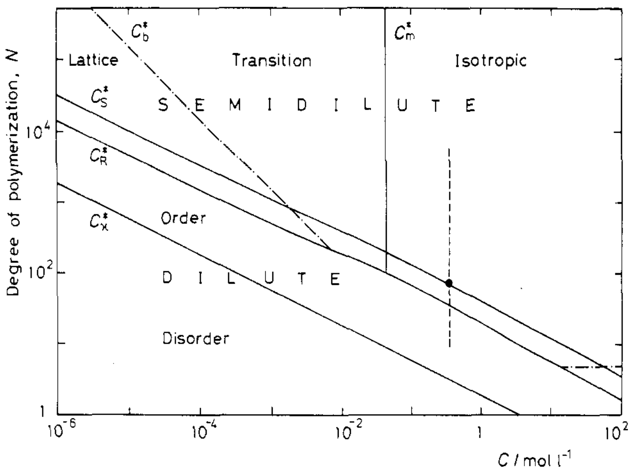

Figure 1. Phase diagram for vinyl polyelectrolyte solutions as functions of the degree of polymerization N and the polymer concentration C at ambient temperature. The crossover lines are briefly explained in the text. For more detail, see ref 5. Molecular weight range covered in the experiment is indicated by a dashed line. Critical molecular weight M^* for the dilute–semidilute transition determined in this work is marked by a closed circle (●).

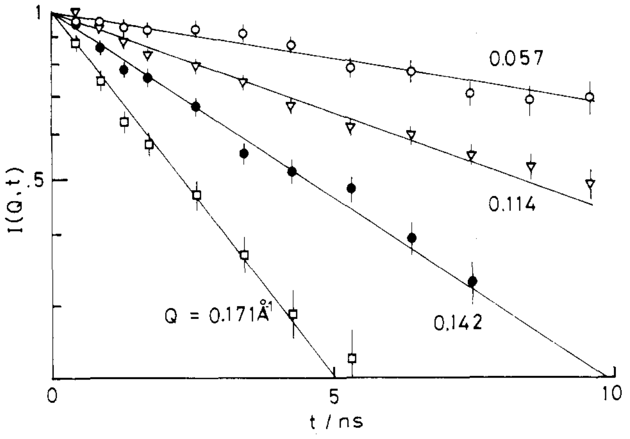

Figure 2. Correlation functions for the sample PSSNa with DP = 5790 at various Q values. Solid lines are the best fit of a single-exponential function $\exp(-t/\tau(Q))$.

by a single exponential function normalized to unity at $t = 0$ for all the samples. A correlation time $\tau(Q)$ was obtained by fitting a curve with a function $\exp(-t/\tau(Q))$ at each Q. The solid lines in Figure 2 show the results of these curve fits. It should be noted that Nallet et al.[12] performed similar experiments and fitted the correlation functions with an unnormalized exponential function $A \exp(-t/\tau(Q))$, assuming fast relaxation modes. This function was also tried here but it was found that the contribution of the fast relaxation modes is not significant in this case, i.e., $A \simeq 1$. In this report, therefore, only the results of the curve fit with $\exp(-t/\tau(Q))$ are reported. Other types of functions such as cumulant expansions were not employed because of the poor statistics of the measurements.

The Q-dependent effective diffusion coefficient $D_{\mathrm{eff}}(Q)$ is defined[11] by

$$D_{\mathrm{eff}}(Q) = \tau^{-1}(Q)/Q^2 \qquad (1)$$

If the diffusion systems can be described by a simple diffusion theory where interactions between the diffusion components are ignored; $D_{\mathrm{eff}}(Q)$ is independent of Q. The inverse effective diffusion coefficients $D_{\mathrm{eff}}^{-1}(Q)$ observed are shown in Figure 3 as a function of Q where the polyion–polyion static structure factors $S(Q)$ measured by IN11

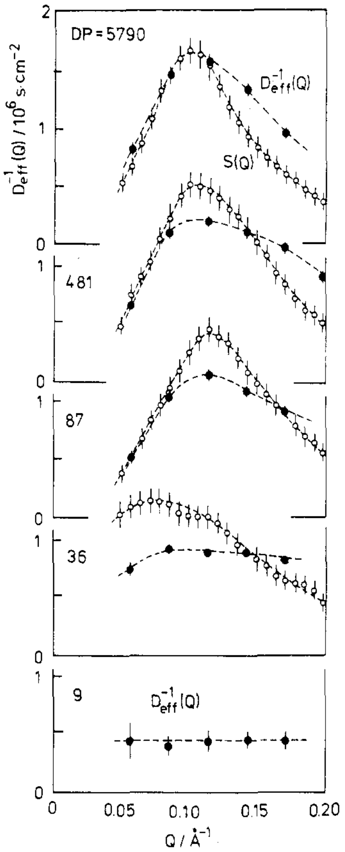

Figure 3. Inverse of the effective diffusion coefficient $D_{\mathrm{eff}}^{-1}(Q)$ (●) and the polyion–polyion static structure factor $S(Q)$ (○) for PSSNa samples. Dashed lines are drawn by eye.

are also plotted except for the sample with DP = 9. $D_{\mathrm{eff}}^{-1}(Q)$ for the high molecular weight samples (DP ≥ 87) shows a broad peak at $Q_m \simeq 0.11$ Å^{-1} which is almost at the same position as that of the static structure factor $S(Q)$. This broad peak strongly supports that the electrostatic interactions between the polyion segments are repulsive. On the other hand, $D_{\mathrm{eff}}^{-1}(Q)$ for the low molecular weight samples (DP ≤ 36) is almost independent of Q, especially for DP = 9. This fact may suggest that the diffusion for the low molecular weight samples can be described by a simple diffusion theory and the effects of the electrostatic interactions are negligible for the diffusion. According to the phase diagram, the low and high molecular weight samples belong to the dilute and semidilute regions, respectively. It is expected that the change of the Q dependence of $D_{\mathrm{eff}}^{-1}(Q)$ with molecular weight suggests the transition from the dilute region to the semidilute region with increasing the molecular weight.

We will first consider the molecular weight dependence of the effective diffusion coefficient $D_{\mathrm{eff}}(Q)$ in order to clarify the transition with molecular weight. In Figure 4, $D_{\mathrm{eff}}(Q)$ is plotted as a function of the degree of polymerization DP at $Q = 0.114$ Å^{-1} which is almost equal to the peak position Q_m. For the high molecular weight samples $D_{\mathrm{eff}}(Q)$ is almost independent of DP, while $D_{\mathrm{eff}}(Q)$ increases rapidly with decreasing DP for the low molecular weight samples. In order to describe the molecular weight dependence of $D_{\mathrm{eff}}(Q)$ in the low molecular weight region, we calculated the diffusion coefficient using Perrin's formula[15] for translational diffusion of a prolate ellipsoid which would describe the polyion fully extended due to the electrostatic repulsive forces between charged groups on the backbone. The lengths of the long and short axes of the prolate ellipsoid used in the calculation are 2.5 × DP Å and 16.6 Å, respectively. The latter value is a diameter

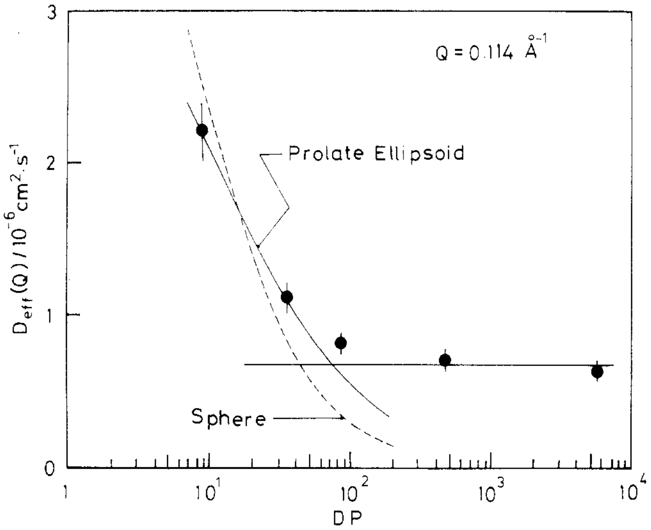

Figure 4. Dependence of the effective diffusion coefficient $D_{\mathrm{eff}}(Q)$ on the degree of polymerization at $Q = 0.114$ Å^{-1}. Solid and dashed lines are calculated for a prolate ellipsoid by using Perrin's formula and for a sphere having the same radius of gyration as the prolate ellipsoid, respectively.

of PSSNa determined by small-angle X-ray scattering.[16] The electrostatic interactions between polyions and polyions, polyions and counterions, and counterions and counterions were neglected because $D_{\mathrm{eff}}(Q)$ of the low molecular weight samples is independent of Q. The results are shown in Figure 4 where the diffusion coefficient of a sphere having the same radius of gyration as the prolate ellipsoid is also indicated as comparison. The diffusion coefficient of the prolate ellipsoid shows very good agreement with the experimental values of $D_{\mathrm{eff}}(Q)$ for the low molecular weight samples. It is noteworthy that effects of the electrostatic interactions are not significant for the diffusion in the low molecular weight range but they are effective for the static structure factor $S(Q)$ which shows a broad peak even for DP = 9 as revealed by small-angle X-ray scattering.[5] As for the high molecular weight samples, it is natural to consider the molecular weight dependence is negligibly weak as the experimental results suggest. The diffusive behavior is determined by the segmental motions and not by the diffusion of the center of mass, because the diffusion of the center of mass is highly suppressed by the entanglements. We estimated the effective diffusion coefficient $D_{\mathrm{eff}}(Q)$ in the molecular weight independent region at $Q = 0.114$ Å^{-1} by averaging $D_{\mathrm{eff}}(Q)$'s of the samples with DP = 481 and 5790. Based on the molecular weight dependence of $D_{\mathrm{eff}}(Q)$ in the above two regions, we can determine the critical molecular weight M^* marking a transition from the dilute region to the semidilute region at fixed concentration ($C = 75.7$ g/L). This critical molecular weight M^* agrees very well with the dilute–semidilute crossover line (C^*_S) in the phase diagram of polyelectrolyte solutions, which is indicated by a closed circle in Figure 1.

We will now consider the Q dependence of $D_{\mathrm{eff}}(Q)$ in the isotropic regime without added salts. This has been theoretically predicted by Hayter et al.[11] According to the theory, $D_{\mathrm{eff}}(Q)$ is expressed as

$$D_{\mathrm{eff}}(Q) = k_B T \frac{\mu(Q)}{S(Q)} \tag{2}$$

where k_B is Boltzmann's constant, $\mu(Q)$ is a Q-dependent mobility which is a correlation function of the mass flux integrated with time t in Q space, and $k_B T S^{-1}(Q)$ measures the strength of the restoring forces for a wavevector fluctuation. The expression in eq 2 is very general and not restricted to polyelectrolytes. In the case of polyelectrolytes, taking into account the rigidity usually expressed by a long persistence length L_p, $\mu(Q)$ varies with Q^{-1} in the range $Q > L_p^{-1}$. As for the static structure factor $S(Q)$, the correlation hole concept[9] and the rigid rod picture of a polyelectrolyte chain predict that $S(Q)$ increases as $S(Q) \sim Q$ for $Q < Q_m$ and decreases as $S(Q) \sim Q^{-1}$, $Q > Q_m$. Consequently, the Q dependence of the effective diffusion coefficient $D_{\mathrm{eff}}(Q)$ in the semidilute (isotropic) region is given by

$$\begin{aligned} D_{\mathrm{eff}}(Q) &\sim Q^{-2} \qquad (L_p^{-1} < Q < Q_m) \\ &\sim \text{const} \qquad (Q > Q_m) \end{aligned} \tag{3}$$

It is remarkable in this theory that the diffusion of polyelectrolytes is dominated by rigidity effects and not by backflow effects as for neutral flexible polymers.

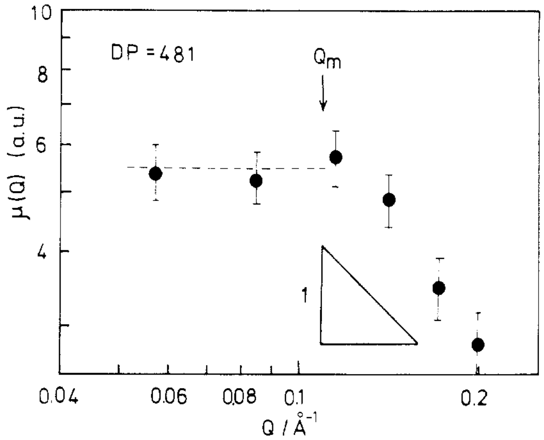

Figure 5. Mobility $\mu(Q)$ for the PSSNa sample with DP = 481. Triangle shows the slope of the theoretical prediction.

As mentioned before, the main features of the theory have been confirmed for polyelectrolyte solutions by neutron spin echo measurements.[11,12] Our present results show some disagreement with the theory in both the Q ranges $Q < Q_m$ and $Q > Q_m$. As shown in Figure 3, the Q dependence of $D_{\mathrm{eff}}^{-1}(Q)$ is almost the same as for $S(Q)$ in the region $Q < Q_m$, though the theory predicts a steep Q dependence of $D_{\mathrm{eff}}^{-1}(Q)$ compared with $S(Q)$. If eq 2 holds, this indicates that the mobility $\mu(Q)$ is independent of Q for $Q < Q_m$. We therefore evaluated the Q dependence of $\mu(Q)$ from the observed $S(Q)$ and $D_{\mathrm{eff}}(Q)$, defining $\mu(Q) \propto S(Q)D_{\mathrm{eff}}(Q)$. The result is shown in Figure 5 in the double-logarithmic form for the sample with DP = 481. It is clearly seen that $\mu(Q)$ is constant for $Q < Q_m$ and begins to decrease at Q_m. A similar result has been reported by Nallet et al.[12] In the region $Q > Q_m$, the theory predicts that $D_{\mathrm{eff}}^{-1}(Q) \sim$ constant. However, the observed $D_{\mathrm{eff}}^{-1}(Q)$ decreases with Q although the Q dependence is weak compared with that of $S(Q)$. It is impossible to judge from Figure 5 whether the observed Q dependence of $\mu(Q)$ can be described by the theoretical prediction $\mu(Q) \sim Q^{-1}$ for $Q > Q_m$. At the present stage, therefore, it is not clear whether the reason for the disagreement between the data and eq 3 arises from the contribution of $S(Q)$ or of $\mu(Q)$.

The theory sheds light on substantial natures of the dynamics of polyelectrolyte in the isotropic region, but it is probably too rough to compare with the experimental results in detail, because the rodlike model used is very crude for the structure. For example, effects of the cross section of polyelectrolyte are not negligible in the present Q range, as we have shown by small-angle X-ray scattering.[4] The theory also neglected local fluctuation of the polyions (main chain and/or side chain) or the backflow effects. Further experimental and theoretical studies are necessary to clarify the detail of the problem.

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Registry No. PSSNa, 9080-79-9; neutron, 12586-31-1.

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Anisotropic Counterion Polarizations and Their Dynamics in Aqueous Polyelectrolytes As Studied by Frequency-Domain Electric Birefringence Relaxation Spectroscopy

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ABSTRACT: Dielectric properties of polyelectrolyte solutions in a semidilute regime at low ionic strength were studied by means of frequency-domain electric birefringence (FEB) relaxation spectroscopy. The observed FEB spectra showed simultaneously three relaxations, two of which were assigned to the low-frequency (LF) and high-frequency (HF) relaxations already found in the dielectric relaxation spectroscopy. The remaining one in the lowest frequency was the orientational (rotational) relaxation of the polyion with an extended conformation. The LF relaxation distinct from the rotational one indicated that it arose from the counterion motion along the polyion axis with a slower mobility than that in a free medium. The HF relaxation, on the other hand, showed the birefringence sign opposite to that of the LF relaxation and hence it was attributed to the counterion motion perpendicular to the polyion axis. Thus, the LF and HF relaxations of polyelectrolyte solutions are regarded as manifestations of anisotropic motions of bound counterions relative to the extended polyion in the directions parallel and perpendicular to the polyion axis, respectively.

Introduction

A linear polyelectrolyte solution (polyion–counterion system) has long been an attractive subject for many researchers because of its peculiar properties[1-3] such as a strong dependence of the conformation of highly charged polyions on the ionic environment and an anomalous dielectric behavior due to the counterions in the vicinity of the polyions.

The polyion conformation has been theoretically analyzed in terms of the electrical persistence length L_e (i.e., the contribution of electrostatic forces to the persistence length) of the polyion by using Debye–Hückel[4-6] and Poisson–Boltzmann[7,8] formulations. These analyses have revealed that if the ionic strength determined by the concentrations of added salts and counterions dissociated from polyions is sufficiently low, L_e can be large enough to lead the polyion to an extended conformation. In high ionic strength, on the contrary, as in the case with excess amount of added salts, L_e would be reduced to a much smaller value and the polyion would be of a coiled form just like uncharged flexible polymers in solution.

Under low ionic strength, the polyions with large L_e entangle with each other more easily than uncharged flexible polymers, and thus the polyelectrolyte solution becomes semidilute in a wide concentration range where the average distance ξ between polyions is smaller than L_e.[9] It is in this semidilute regime that the counterion condensation, i.e., an accumulation of counterions in the vicinity of a highly charged polyion, has been theoretically predicted.[1,2,10] Various equilibrium properties have been well explained by the condensation theories based on the two-phase model where the counterions are distributed either in the free or in the bound phase. The free counterions contribute to the conductivity (or the activity) while the bound ones to the dielectric properties since they are assumed to be bound but mobile (i.e., polarizable) in the potential produced by the polyion. Thus, the dielectric relaxation spectroscopy of the polyelectrolyte solutions in

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