Polyelectrolyte Aggregates in Solutions of Sodium Poly(styrenesulfonate)

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Dynamic and static light-scattering experiments in combination with light microscopy have been performed on solutions of the highly charged polyelectrolyte sodium poly(styrenesulfonate) at low ionic strength. A double-exponential correlation function was found, and the reciprocal normalized scattering intensity shows a strong angular dependence, indicating the existence of polyelectrolyte aggregates. Light microscopy shows directly the existence of these aggregates. The dimensions of these aggregates increase with increasing polyelectrolyte concentration and increasing molar mass.

Introduction

Dynamic light-scattering experiments on polyelectrolytes with no added salt or low concentrations of added salt show a double-exponential correlation function. A double-exponential correlation function is interpreted as the existence of two modes: a fast mode and a slow mode. In 1978 Lin et al.[1] reported this behavior in their study on the highly charged polyelectrolyte poly(L-lysine). At fixed polyelectrolyte concentrations they varied the ionic strength. As the ionic strength was lowered two modes appeared; the region with one mode was called the ordinary phase, and the region with two modes was called the extraordinary phase. During the last decade, many investigators reported the existence of a double-exponential correlation function in their dynamic light-scattering studies on polyelectrolytes.[2−14] Two modes were found in dilute solutions and also in more concentrated solutions. The fast mode is often interpreted as a coupled diffusion of polyions and counterions. It seems that the general interpretation in terms of the existence of polyelectrolyte aggregates/domains can give a satisfactory explanation for the slow mode.

In this work we will show the existence of polyelectrolyte aggregates in solutions of sodium poly(styrenesulfonate). Three molar masses, 77.4, 168, and 350 kg/mol, with narrow molar mass distributions at one fixed added salt (NaCl) concentration of 0.01 M were used. Dynamic and static light-scattering experiments in combination with light microscopy were performed on several semidilute/concentrated NaPSS solutions.

Experimental Section

Sodium poly(styrenesulfonate) with molar masses of 77.4, 168, and 350 kg/mol were purchased from Viscotek Benelux. The M_w/M_n ratio of the polyelectrolytes was smaller than 1.2. Nondialyzed samples contain a certain amount of sodium sulfate and purification is necessary. In the purification procedure 1 g of NaPSS is dissolved in 0.2 M HCl (Baker Chemical Co.). This solution is dialyzed in a Visking seamless cellulose tubing against water, which was purified by a Milli-Q system. The dialysis bag was purified by heating in a solution of sodium bicarbonate (Merck), EDTA (Merck), and Millipore water, followed by extensive rinsing with Millipore water. The water surrounding the dialysis tube is refreshed several times, until the electric conductivity of this water equals the conductivity

of pure water (the conductivity was always smaller than 1 μS/cm). Subsequently the dialyzed solution is converted to the sodium salt of PSS by potentiometric titration with 0.1 M NaOH (Titrisol), and the solution is stored freeze dried. Ultrapure salt solutions with a concentration of 0.01 M were prepared by dissolving NaCl (Merck) in Millipore water. NaPSS solutions were prepared by dissolving the freeze-dried NaPSS in a salt solution. All samples were filtered through a Millipore DV 0.65 μm pore size filter, prior to the light-scattering experiment. After the light-scattering experiment the concentrations of the samples were determined spectrophotometrically at a wavelength of 261.5 nm, using an extinction coefficient of 1.92 $\pm$ 0.03 L g^{-1} cm^{-1}. The extinction coefficient was determined using the freeze-dried NaPSS. Infrared absorbance measurements were employed to determine the water content of the freeze-dried NaPSS, and the extinction coefficient was corrected accordingly.

Light Scattering. Dynamic light-scattering measurements on the NaPSS solutions were performed using an ALV goniometer (ALV, Langen, Germany), an ALV-5000 fast correlator, and a photomultiplier. The light source was an argon-ion laser (Spectra Physics model 2020-03), operating at a wavelength of 514.5 nm in the light-stabilized mode. The filtered NaPSS solutions go directly into a cylindrical quartz cuvette with an outer diameter of 2 cm. Before and during each measurement the solution was thermostated at a temperature of 25 °C. Before each experiment the filtration setup and the quartz cuvette were cleaned with 0.1 M NaOH and extensively flushed with Millipore water. To check if the filtration setup and the cuvette were clean, Millipore water was filtered in a cuvette. After this water was thermostated the intensity autocorrelation function was measured. If this autocorrelation function did not show any decay time in the multiple τ mode, the filtration setup and the cuvette were considered clean, and the NaPSS solution was filtered, after an appropiate rinse of the filter with the 0.01 M NaCl solvent.

Static light-scattering experiments were performed with the same experimental setup. Scattering intensities were normalized with toluene as a standard. The scattering intensity of the solvent has been subtracted from all reported scattering intensities.

Analysis of the Dynamic Light-Scattering Data. The correlation functions measured in this investigation are double exponential. Double-exponential correlation functions show two separated modes: a fast mode and a slow mode, characterized by a fast decay rate Γ_f and a slow decay rate Γ_s, respectively.

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TABLE 1: Slow and Fast Diffusion Coefficients of NaPSS for Different Molar Masses and Polyelectrolyte Concentrations at $c_s = 0.01$ M

c (g/L)	D_s (10^{-9} cm²/s)	D_f (10^{-6} cm²/s)
	$M_w = 77.4$ kg/mol	
33.3	3.4 ± 0.3	4.4 ± 0.2
23.5	4.2 ± 0.7	4.0 ± 0.2
11.8	6.4 ± 0.8	2.6 ± 0.1
	$M_w = 77.4$ kg/mol	
15.9	6.0 ± 0.9	3.1 ± 0.2
	$M_w = 168$ kg/mol	
17.0	1.8 ± 0.3	3.4 ± 0.2
	$M_w = 350$ kg/mol	
16.3	1.0 ± 0.1	3.0 ± 0.1

The correlation functions were analyzed with the CONTIN program to obtain the distribution function of decay rates $A(\Gamma)$ defined as

$$g^{(1)}(\tau) = \int_0^\infty A(\Gamma) \exp(-\Gamma\tau) \, d\Gamma \qquad (1)$$

$g^{(1)}(\tau)$ is the normalized electric field autocorrelation function. From the moments of the distribution function the decay rates were obtained. All samples were measured over the angular range from 30° up to 150° with 10° increments.

Light Microscopy. Light microscopy experiments were performed with a Leica DMR microscope. Light microscopy images were viewed with a CCD camera. Images were digitalized with a Quantimet 500+ image-processing and analysis system. The images shown in Figures 2–4 are directly recorded CCD images; no software resolution enhancements were performed. In fact the images contain some structures (5) that are due to the optical system used and appear on all images.

Results and Discussion

In this study six samples of the flexible highly charged polyelectrolyte sodium poly(styrenesulfonate) were prepared; see Table 1 for concentrations and molar masses. The added salt concentration was 0.01 M. The dynamic light-scattering experiments show a double-exponential correlation function for all samples studied. A double-exponential correlation function is interpreted as the existence of two modes: a fast and a slow mode. It appears that the fast decay rate Γ_f depends linearly on q^2, with q the magnitude of the scattering vector defined as $q = (4\pi n_s/\lambda_0) \sin(\theta/2)$, n_s is the refractive index of the solvent, λ_0 is the wavelength of the incident light in vacuo, and θ is the scattering angle. From the linear least-squares best fit of Γ_f versus q^2 the apparent fast diffusion coefficient D_f was obtained. The slow decay rate Γ_s deviates from a linear dependence on q^2. The apparent slow diffusion coefficient was obtained by extrapolating the linear least-squares best fit of Γ_s/q^2 versus q^2 to $q^2 = 0$. Values for the slow and fast diffusion coefficients are collected in Table 1. In this work we only focus on the slow mode. In Figure 1 the reciprocal normalized scattering intensity of NaPSS with a molar mass of 77.4 kg/mol is depicted for three different polyelectrolyte concentrations. From the slope of $I(0)/I(\theta)$ versus $\sin^2(\theta/2)$ an apparent radius of gyration $R_{g,app}$ can be derived using the expression for the particle structure factor for isolated particles:

$$\frac{I(0)}{I(\theta)} \cong 1 + \frac{1}{3}(R_{g,app}^2)q^2 \quad q \to 0 \qquad (2)$$

The angular dependence of the reciprocal normalized scattering intensity is very strong, suggesting the existence of light
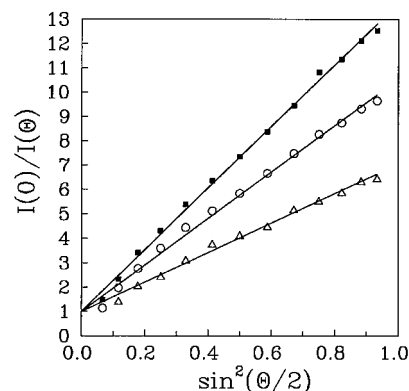
Figure 1. Reciprocal normalized scattering intensity as a function of $\sin^2(\theta/2)$ for three different NaPSS concentrations: (■) $c = 33.3$ g/L, (○) $c = 23.5$ g/L, and (△) $c = 11.8$ g/L. Drawn lines are linear least-squares best fits. $M_w = 77.4$ kg/mol, $c_s = 0.01$ M.

scatterers with large dimensions. For the polyelectrolyte concentrations in Figure 1, $c = 33.3$, 23.5, and 11.8 g/L, apparent radii of gyration are 189, 164, and 131 nm respectively. This indicates that the apparent radius of gyration decreases with decreasing polyelectrolyte concentration. At a polyelectrolyte concentration of about 16 g/L, the apparent radii of gyration for the molar masses 77.4, 168, and 350 kg/mol are 140, 167, and 293 nm, respectively. This indicates that the apparent radius of gyration depends on the molar mass. The general interpretation for the apparent slow diffusion coefficient and the apparent radius of gyration is that they are caused by large polyelectrolyte aggregates/domains. We are aware that eq 2 is only valid for isolated particles. Here it is applied to show relative changes in the dimensions of the aggregates.

Some light microscopy experiments were performed on the NaPSS solutions. Figure 2 shows the obtained image for a molar mass of 350 kg/mol, a polyelectrolyte concentration of 16.3 g/L, and an added salt concentration of 0.01 M. The magnification factor was 630. Structures with a diameter of about 750 nm were directly seen. Most detected structures were immobile, but on every slide mobile structures were found. Despite of the difficulties in focusing on the mobile structures, it is our impression that the sizes of the mobile and immobile structures are about the same. From the apparent radius of gyration of 293 nm, an apparent diameter of about 600 nm is calculated. So, it is likely that the structures in Figure 2 are the polyelectrolyte aggregates. Figure 3 shows the obtained image for a molar mass of 77.4 kg/mol, polyelectrolyte concentration of 11.8 g/L, and an added salt concentration of 0.01 M. The magnification factor was also 630. Again aggregates are seen, but now they are noticeably smaller. A rough estimate leads to a diameter of about 400 nm. The apparent radius of gyration of 140 nm corresponds to an apparent diameter of 280 nm. Within the resolution of the microscope the polyelectrolyte aggregates could be seen directly. We have shown direct evidence for the existence of polyelectrolyte aggregates. Also the change in dimensions of these aggregates is found when the sample parameters are varied. These findings agree qualitatively with the slow diffusion coefficients, since aggregates with large dimensions will move slower, leading to a smaller diffusion coefficient. An extensive investigation of the diffusion behavior of semidilute solutions of NaPSS is the subject of a separate publication. In Figure 4 a light microscopy image is shown of the same sample as shown in Figure 2. The magnification factor was also 630. The difference with Figure 2 is that the image in Figure 4 was taken about 1.5 h after putting a droplet on the slide. From this picture
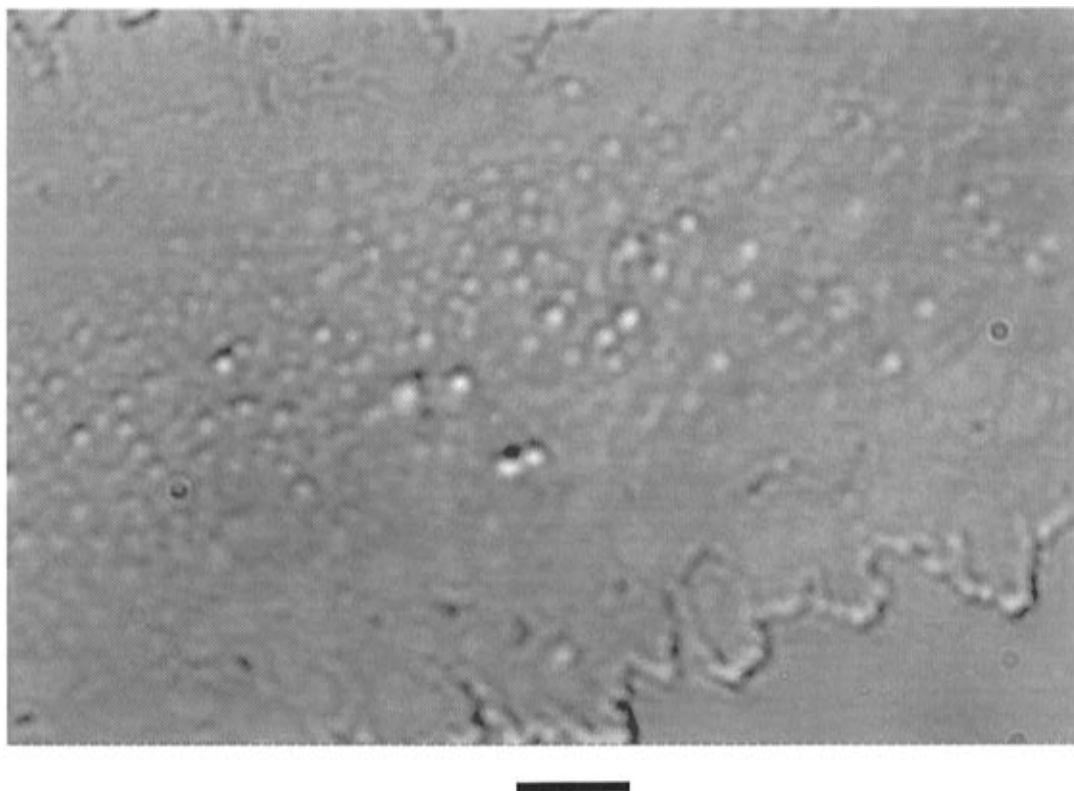
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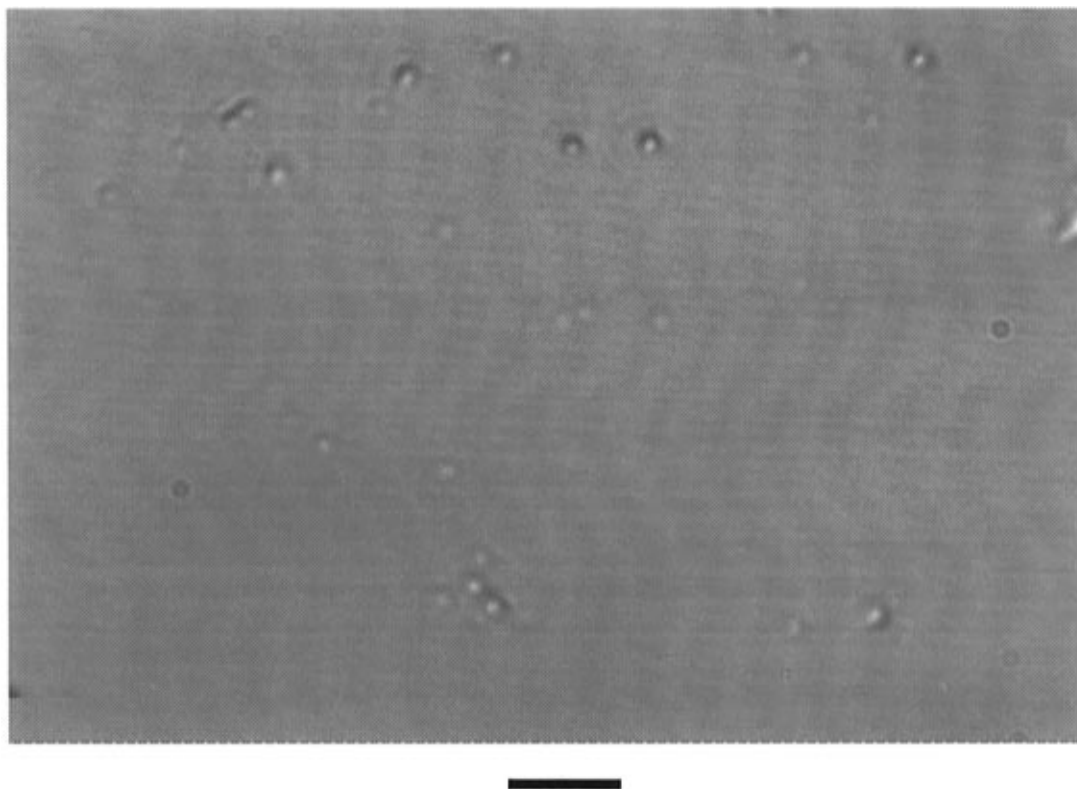
Figure 2. Light microscopy picture of a NaPSS solution with a polyelectrolyte concentration of 16.3 g/L. M_w = 350 kg/mol, c_s = 0.01 M. The bar represents a length of 10 μm.
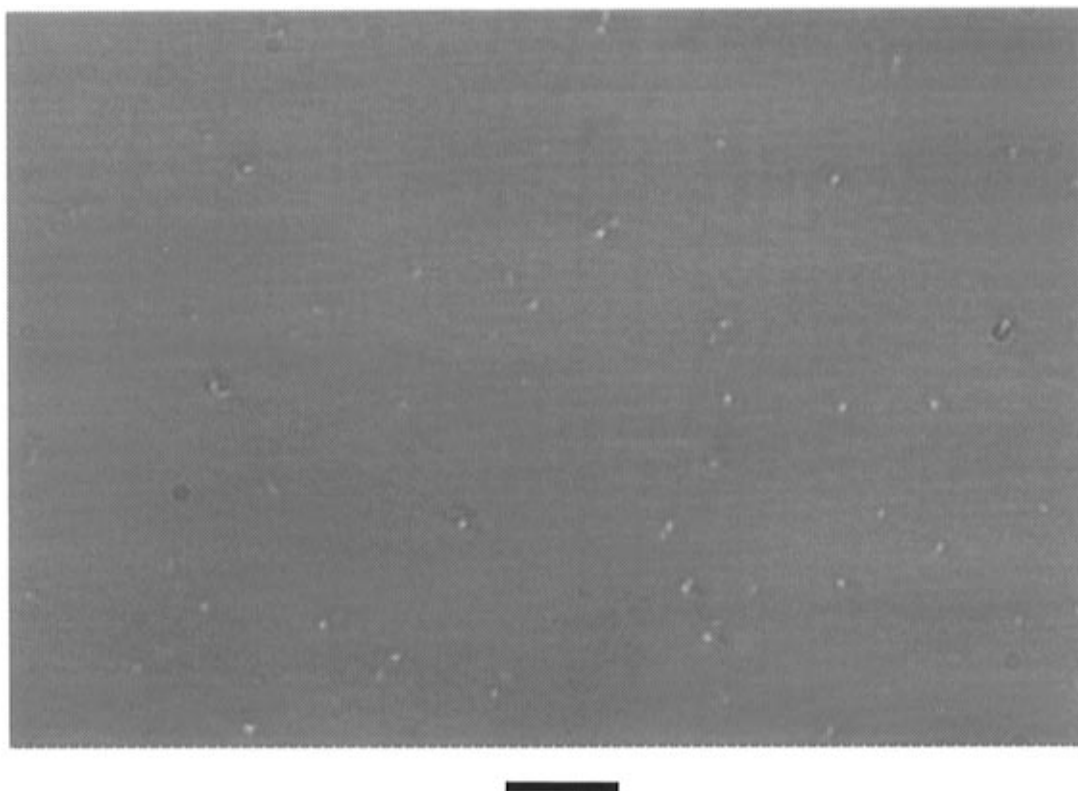
Figure 3. Light microscopy picture of a NaPSS solution with a polyelectrolyte concentration of 11.8 g/L. M_w = 77.4 kg/mol, c_s = 0.01 M. The bar represents a length of 10 μm.

it is seen that the aggregates have become larger and that they approach each other more closely. A possible explanation for this phenomenon is the evaporation of water, leading to a more concentrated NaPSS solution, and following the interpretation of Figure 1 the polyelectrolyte aggregates become larger.

Although it is not yet clear what the cause is for the formation of aggregates of flexible linear highly charged polyelectrolytes, a suggestion by Ise[15] has been put forward in the literature. Since polyions are particles with the same electric charge, which repel each other, it is quite remarkable that aggregates can be formed.

Figure 4. Light microscopy picture of a NaPSS solution with a polyelectrolyte concentration of 16.3 g/L. M_w = 350 kg/mol, c_s = 0.01 M. The image was taken 1.5 h after putting a solution droplet on the slide. The bar represents a length of 10 μm.

The formation of aggregates can only exist if there is a net attraction. Probably the interplay of the counterions and the added salt ions is important in the solution. According to Ise[15] there is an analogy between highly charged linear polyelectrolytes and highly charged latex spheres or colloids. He claims that the Derjaguin−Landau−Verwey−Overbeek (DLVO) potential fails for these systems since this potential only predicts electrostatic repulsion. However, the Sogami potential predicts besides an electrostatic repulsion also an electrostatic attraction due to the role of the counterions. Possibly, attractive interactions of nonelectrostatic origin play a role in the formation of aggregates of highly charged polyelectrolytes.[14]

Conclusions

The double-exponential correlation function, the strong angular dependence of the reciprocal normalized scattering intensity, and the direct image of a light microscope show the existence of large polyelectrolyte aggregates. The dimensions of these aggregates become larger with increasing polyelectrolyte concentration and increasing molar mass.

References and Notes

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