

Light Scattering on Semidilute Polyelectrolyte Solutions: Molar Mass and Polyelectrolyte Concentration Dependence

J. J. Tanahatoe and M. E. Kuil*

Leiden Institute of Chemistry, Gorlaeus Laboratories, Section Physical and Macromolecular Chemistry, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands

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Dynamic and static light scattering experiments on solutions of the flexible highly charged polyelectrolyte sodium poly(styrenesulfonate) have been performed in the semidilute concentration regime. Over a very wide polyelectrolyte concentration range double-exponential correlation functions were found. At the lowest polyelectrolyte concentrations the correlation functions became single exponential. Apparent fast and slow diffusion coefficients were determined for three molar masses at a fixed added salt concentration of 0.01 M. The fast diffusion coefficient is both molar mass and polyelectrolyte concentration dependent at the lowest concentrations and becomes molar mass independent at semidilute concentrations. At even higher polyelectrolyte concentration the apparent fast diffusion coefficient is independent of both the molar mass and polyelectrolyte concentration. In the semidilute regime the fast diffusion coefficient follows the power law $D_f \propto c^{0.72}$, close to the theoretical prediction of Odijk's scaling theory for a transient polyelectrolyte network. The apparent slow diffusion coefficient decreases with increasing molar mass and increasing polyelectrolyte concentration. The reciprocal normalized scattering intensity shows a strong angular dependence. The slow mode is interpreted as aggregates or domains that form in semidilute and concentrated solutions. The dimensions of these aggregates decrease with decreasing polyelectrolyte concentration and decreasing molar mass. The existence of aggregates and the change in their dimensions are directly seen with conventional light microscopy. The general trend of the apparent diffusion coefficients of NaPSS in 0.01 M NaCl resembles earlier data on NaPSS without added salt.

Introduction

Polyelectrolytes with no added salt or low concentrations of added salt show a characteristic behavior that is not yet fully understood. Mostly an apparent double-exponential correlation function is measured with dynamic light scattering. A double-exponential correlation function is interpreted as consisting of two modes: a fast mode and a slow mode. Already 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. On lowering the ionic strength two modes appear, and they called the regime in which one mode was detected the ordinary phase and the regime in which two modes were detected the extraordinary phase. At semidilute or concentrated polyelectrolyte concentrations of sodium poly(styrenesulfonate) with no added salt^{2,3} or at low concentrations of added salt,^{4,5} only one mode was reported. Remarkably, in the frequently cited paper of Grüner et al.² it was reported that "most of the data were conveniently fitted by the sum of two exponentials" while only one diffusive mode was given. In the semidilute concentration regime they found that the cooperative diffusion coefficient scales as $c^{1/2}$, which was predicted by the polyelectrolyte theory of Odijk.⁶ Koene et al.^{4,5} tested the scaling theory of Odijk⁶ for polyelectrolytes with added salt and performed also some measurements on NaPSS without added salt.³ At low polyelectrolyte concentrations they reported a slow mode and at high concentrations a fast mode. The simultaneous existence of two modes was not reported, in contrast to the results of Drifford and Dalbiez⁷ and later by Sedláč et al.⁸

During the past decade several investigators reported the existence of a double-exponential correlation function in their

dynamic light scattering studies on polyelectrolytes.^{7–17} A lively discussion^{18–20} on the origin of the slow mode appeared in the literature. It was possible to make the slow mode disappear if an appropriate filter was used in the preparation procedure of the polyelectrolyte solution.^{15,21}

The fast mode is often interpreted as a coupled diffusion of polyions and counterions. The interpretation and cause of existence of the slow mode are not yet clear. It seems that the interpretation in terms of the existence of polyelectrolyte aggregates or domains can give a satisfactory explanation for the slow mode.

In this work apparent diffusion coefficients of NaPSS were obtained in aqueous solutions for three molar masses, 77.4, 168, and 350 kg/mol, with narrow molar mass distributions. The added salt (NaCl) concentration was fixed at 0.01 M, and the polyelectrolyte concentration was varied over a very wide range. The polyelectrolyte concentration and molar mass dependence of the fast and slow diffusion coefficient are extensively studied and compared with earlier investigations. The scattering intensity as a function of the polyelectrolyte concentration and the scattering angle is also investigated. Conventional light microscopy experiments were performed to study possible aggregates.

Experimental Section

Sodium poly(styrenesulfonate) with different molar masses were purchased from Viscotek Benelux. The molar masses were 77.4, 168, and 350 kg/mol. 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

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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 $1 \mu\text{S}/\text{cm}$.) 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 $1.92 \pm 0.03 \text{ L g}^{-1} \text{ cm}^{-1}$. 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 whether the filtration setup and the cuvette were clean, Millipore water was filtered in a cuvette. After thermostating this water, the intensity autocorrelation function was measured. If this autocorrelation function does not show any decay time in the multiple tau mode, the filtration setup and the cuvette are considered clean, and the NaPSS solution was filtered after an appropriate 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 for almost all polyelectrolyte concentrations. Only for the lowest polyelectrolyte concentrations are the correlation functions single-exponential. A double-exponential correlation function shows two well-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. All correlation functions were analyzed with the CONTIN program to obtain the distribution function of decay rates $A(\Gamma)$ defined as

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

$g^{(1)}(\tau)$ 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. It appears that the fast decay rate Γ_f depends linearly on q^2 , with q the magnitude of the scattering vector defined as $q = (4\pi n_s/\lambda_0)$

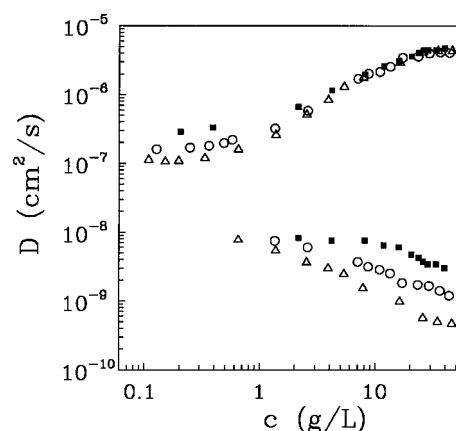


Figure 1. Apparent diffusion coefficient as a function of the NaPSS concentration for three molar masses: (■) $M_w = 77.4 \text{ kg/mol}$, (○) $M_w = 168 \text{ kg/mol}$, and (△) $M_w = 350 \text{ kg/mol}$. The ionic strength is 0.01 M NaCl. The temperature is 25 °C.

$\sin(\theta/2)$, 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 $q^2 = 0$.

Light Microscopy. A Leica DMR microscope was applied to perform conventional light microscopy experiments on the NaPSS solutions. A CCD camera was used to view the light microscopy images. Images were digitalized with a Quantimet 500+ image processing and analysis system. The images shown in Figures 6–8 are directly recorded CCD images; no resolution enhancements were performed. In fact, the images contain some structures that are due to the optical system used and appear on all images. The microscopy images were recorded at room temperature ($\approx 21 \text{ °C}$).

Results

In this study we have performed dynamic light scattering experiments on the flexible highly charged polyelectrolyte sodium poly(styrenesulfonate) over a very wide polyelectrolyte concentration range, from about 0.1 to 45 g/L. Three molar masses, 77.4, 168, and 350 kg/mol, with narrow molar mass distributions were used in an aqueous solution with an added NaCl concentration of 0.01 M. From the highest polyelectrolyte concentration down to about 1 g/L the measured correlation functions are double-exponential. Only at the lowest polyelectrolyte concentrations are the correlation functions single-exponential.

Figure 1 shows the apparent diffusion coefficient of three molar masses at a fixed ionic strength of 0.01 M as a function of the polyelectrolyte concentration. In the polyelectrolyte concentration range from 0.1 to about 1 g/L the measured correlation functions were single-exponential, yielding one diffusion coefficient. In this dilute concentration regime the apparent diffusion coefficient is strongly dependent on the molar mass. When the molar mass decreases, the apparent diffusion coefficient increases. For polyelectrolyte concentrations larger than 1 g/L the correlation functions were double-exponential, yielding two apparent diffusion coefficients, a fast and a slow diffusion coefficient. When the polyelectrolyte concentration increases, the fast diffusion coefficient also increases and becomes independent of the molar mass. For polyelectrolyte concentrations larger than about 20 g/L the fast diffusion coefficient does not increase any more with increasing poly-

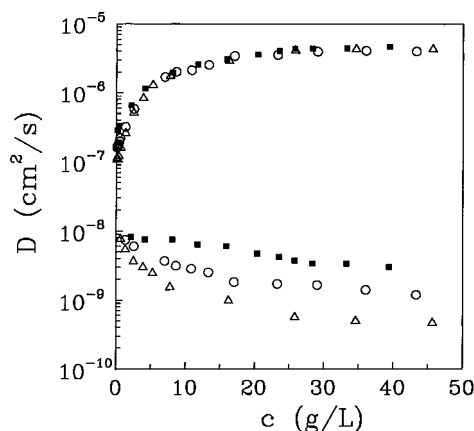


Figure 2. Apparent diffusion coefficient as a function of the NaPSS concentration for three molar masses. Symbols and conditions are the same as in Figure 1.

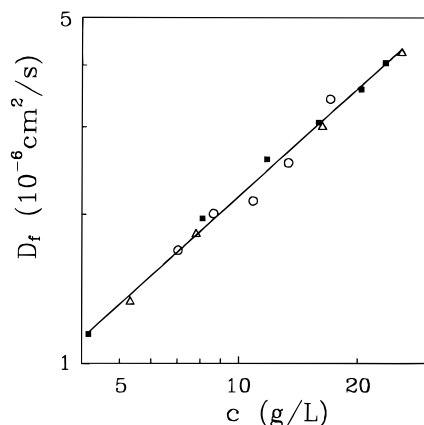


Figure 3. Fast diffusion coefficient as a function of the NaPSS concentration for three molar masses. Symbols and conditions are the same as in Figure 1. The drawn line is the linear least-squares best fit of all displayed data. Detail of Figure 1.

electrolyte concentration; see Figure 2. The experimental data in Figure 2 are the same as in Figure 1. For a clear representation of the apparent diffusion coefficients at high polyelectrolyte concentrations a linear x axis is taken in Figure 2. A maximum value of about $4 \times 10^{-6} \text{ cm}^2/\text{s}$ for the fast diffusion coefficient is reached. In this regime the fast diffusion coefficient remains also molar mass independent. In the polyelectrolyte concentration range from 5 to about 20 g/L the fast diffusion coefficient can be described by the power law $D_f \propto c^{0.72 \pm 0.02}$. The experimental data from which this power law has been derived are displayed in Figure 3. The experimental power law is derived using the fast diffusion coefficients of all three molar masses.

The slow mode appears when the polyelectrolyte concentration is larger than about 1 g/L. Figure 1 shows that the slow diffusion coefficient decreases with increasing polyelectrolyte concentration. The slow diffusion coefficient depends on the molar mass, as can be seen in Figures 1 and 2. In the slow mode regime and when the polyelectrolyte concentration is larger than about 8 g/L, the slow diffusion coefficient is inversely proportional to the molar mass for fixed polyelectrolyte concentrations. For polyelectrolyte concentrations of 8, 16, and 27 g/L, we find for the power law exponent m in $D_s \propto M_w^{-m}$ 1.04, 1.19, and 1.17, respectively.

The scattering intensity as a function of the polyelectrolyte concentration is displayed in Figure 4. The molar mass is 168 kg/mol and the scattering angle is 90° . Scattering intensities were normalized with toluene as a standard, and the intensity

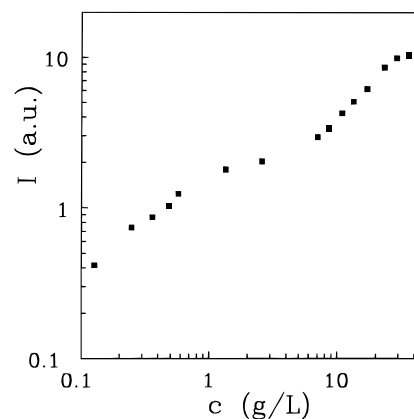


Figure 4. Scattering intensity at an angle of 90° as a function of the NaPSS concentration. $M_w = 168 \text{ kg/mol}$, $c_s = 0.01 \text{ M NaCl}$. The temperature is 25°C .

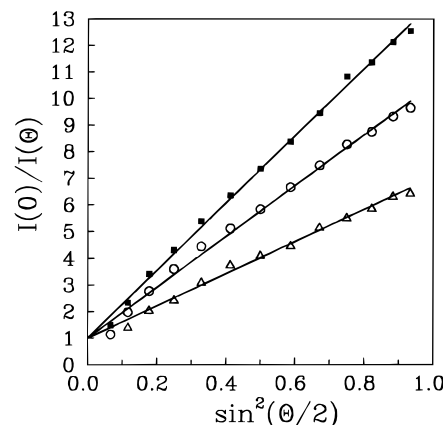


Figure 5. Reciprocal normalized scattering intensity as a function of $\sin^2(\theta/2)$ for three different NaPSS concentrations: (■) $c = 33.3 \text{ g/L}$, (○) $c = 23.5 \text{ g/L}$, and (△) $c = 11.8 \text{ g/L}$. Drawn lines are linear least-squares best fits. $M_w = 77.4 \text{ kg/mol}$, $c_s = 0.01 \text{ M}$.

of the solvent was subtracted. Figure 4 shows a discontinuity at a polyelectrolyte concentration of about 1 g/L. If we compare Figures 4 and 1, we see that for polyelectrolyte concentrations smaller than 1 g/L the slow mode is absent. Apparently, this concentration is a transition concentration. Figure 4 shows a second discontinuity at a polyelectrolyte concentration of about 7 g/L. The slow diffusion coefficient in Figure 1 shows also a discontinuity at this concentration. At decreasing polyelectrolyte concentration from below 7 g/L the increase of the slow diffusion coefficient becomes smaller. This is clearly seen for the molar mass of 77.4 kg/mol, although the transition concentration is somewhat larger than 7 g/L, indicating that this transition concentration may depend on the molar mass. This same conclusion can also be reached for the first transition concentration.

In Figure 5 the reciprocal normalized scattering intensity of NaPSS with a molar mass of 77.4 kg/mol is depicted for three different polyelectrolyte concentrations in the slow mode regime. From the slope of $I(0)/I(\theta)$ versus $\sin^2(\theta/2)$ an apparent radius of gyration $R_{g,\text{app}}$ can be derived using the expression for the particle structure factor for isolated particles:

$$\frac{I(0)}{I(\theta)} \approx 1 + \frac{1}{3}(R_{g,\text{app}}^2)q^2 \quad q \rightarrow 0 \quad (2)$$

For the polyelectrolyte concentrations in Figure 5, $c = 33.3$, 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 concentra-

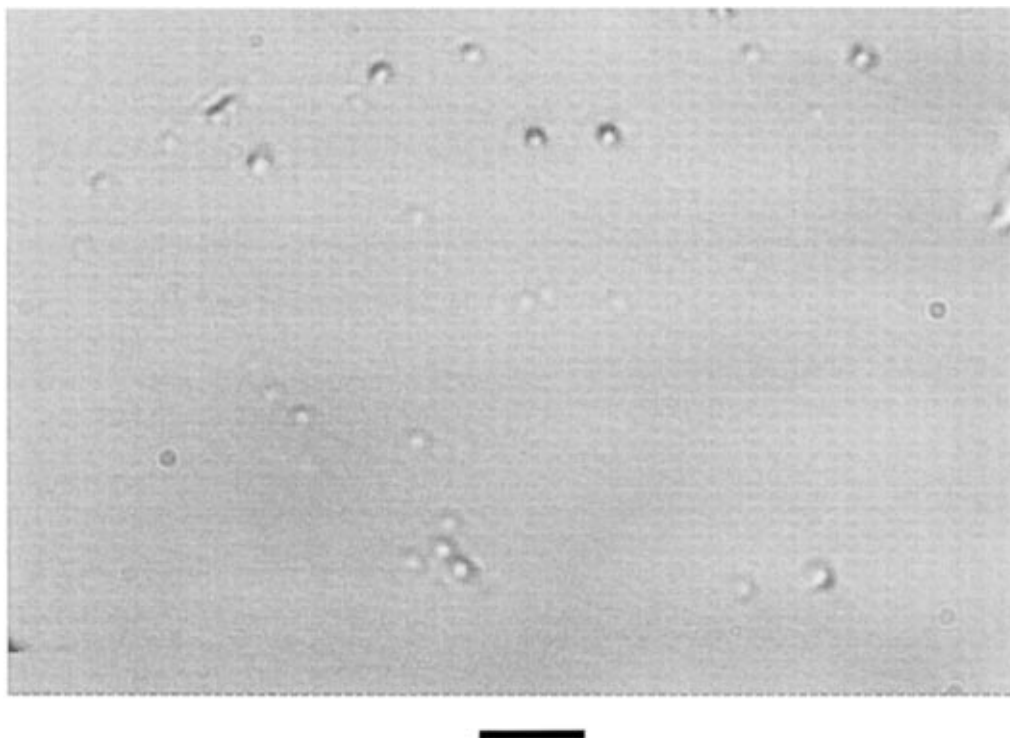


Figure 6. Light microscopy picture of a NaPSS solution with a polyelectrolyte concentration of 16.3 g/L at 21 °C. $M_w = 350$ kg/mol, $c_s = 0.01$ M. The bar represents a length of 10 μm .

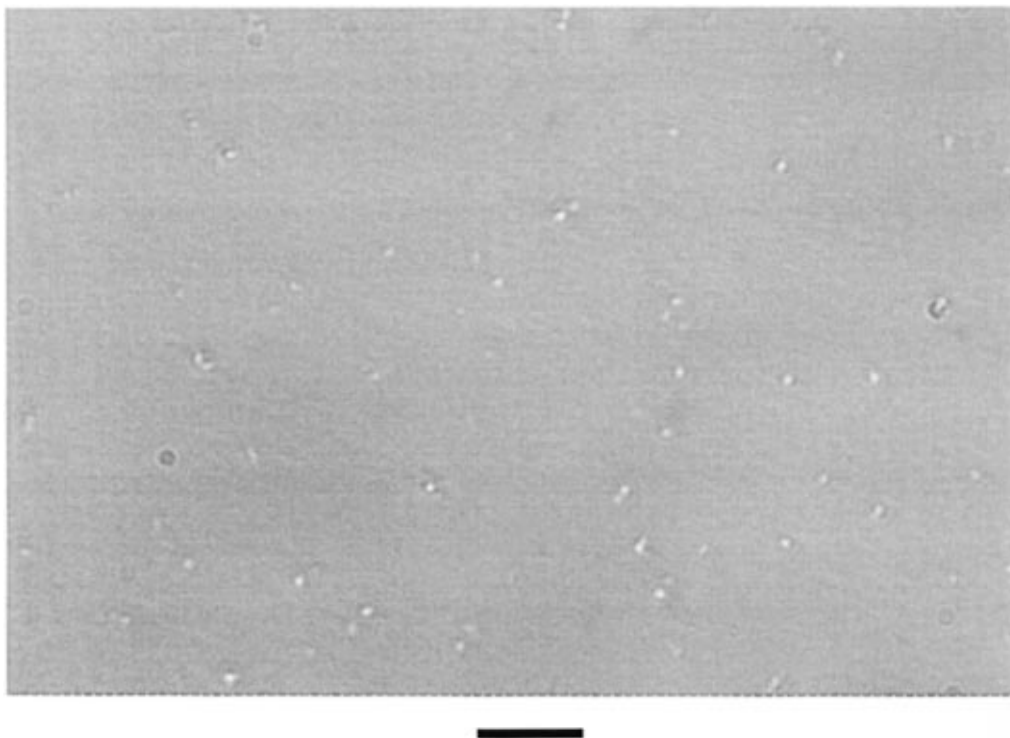


Figure 7. Light microscopy picture of a NaPSS solution with a polyelectrolyte concentration of 11.8 g/L at 21 °C. $M_w = 77.4$ kg/mol, $c_s = 0.01$ M. The bar represents a length of 10 μm .

tion. For fixed polyelectrolyte concentration the apparent radius of gyration increases with increasing molar mass. For example, 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. We are aware that eq 2 is only valid for isolated particles. Here it is applied to show relative changes.

Figures 6–8 show light microscopy images of some NaPSS solutions. The magnification factor was always 630. Figure 6

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 image shows structures with a diameter of about 750 nm. Figure 7 shows the obtained image for a molar mass of 77.4 kg/mol, a polyelectrolyte concentration of 11.8 g/L, and an added salt concentration of 0.01 M. Again structures are seen, but now they are noticeably smaller. A rough estimate leads to a diameter of about 400 nm. Figure 8 shows a light microscopy image of the same sample as shown

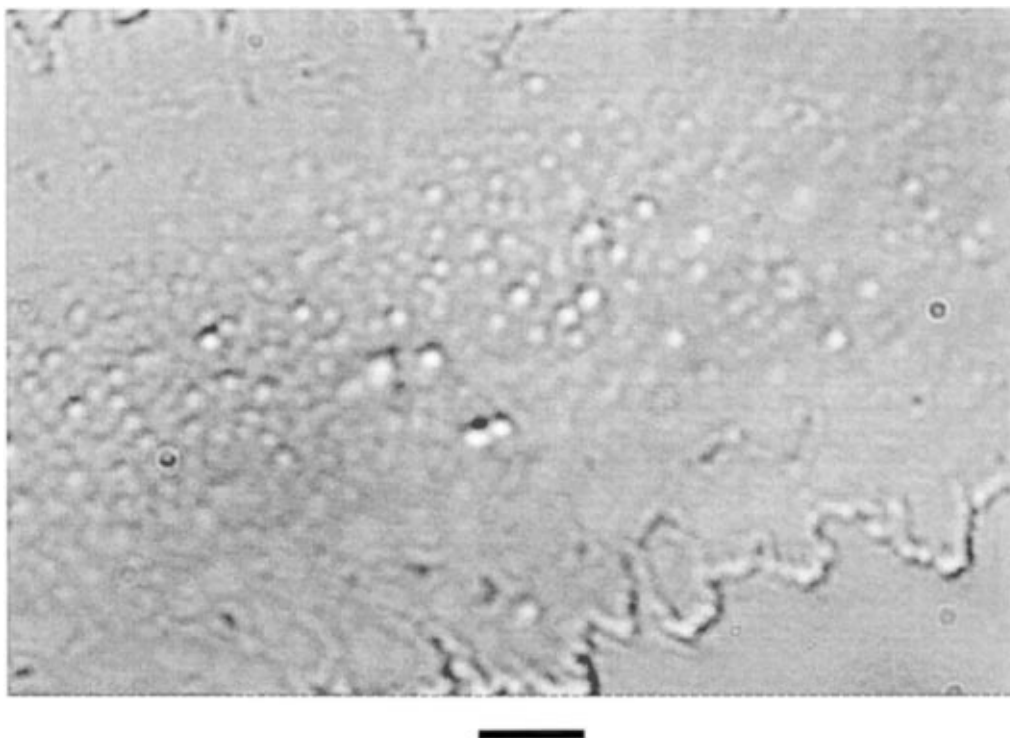


Figure 8. Light microscopy picture of a NaPSS solution with a polyelectrolyte concentration of 16.3 g/L at 21 °C. $M_w = 350$ kg/mol, $c_s = 0.01$ M. The image was taken 1.5 h after putting a solution droplet on the slide. The bar represents a length of 10 μ m.

in Figure 6. The difference with Figure 6 is that the image was taken about 1.5 h after putting a solution droplet on the slide. It is seen that the structures have become larger and that they approach each other more closely.

Discussion

The Fast Mode. At the smallest polyelectrolyte concentrations it was found that the apparent fast diffusion coefficient depends on the molar mass. This concentration regime represents the dilute regime. The separation between the dilute regime and the semidilute regime is indicated by the critical overlap concentration.⁶ According to the polyelectrolyte theory of Odijk,⁶ the polyelectrolyte chains will form entanglements above the overlap concentration leading to a transient network. The average distance between neighboring entanglements is called the correlation length. In semidilute solutions of polyelectrolytes it has been derived that the cooperative diffusion coefficient scales as $D_f \propto c^{0.75}$. Our experimentally determined power law exponent is 0.72 ± 0.02 , close to the theoretical value. Since the correlation length does not depend on the molar mass, the cooperative fast diffusion coefficient has to be molar mass independent. This is confirmed by our experiments.

Koene and Mandel⁴ performed similar experiments as we did and found a value of 0.66 ± 0.02 for the power law exponent. They have used high molar masses, 400, 650, and 1200 kg/mol. We have taken small molar masses with narrow molar mass distributions. It is likely that they did not observe two modes and that the slow mode contribution was included in a floating baseline used in their data analysis.

The Slow Mode. The slow mode in polyelectrolyte solutions without added salt or with low concentrations of added salt is a frequently reported phenomenon in dynamic light scattering studies. The general interpretation for the slow mode is that it is caused by large aggregates or domains of polyelectrolyte chains. Our measurements support this interpretation. At high polyelectrolyte concentrations the angular dependence of the

reciprocal normalized scattering intensity is very strong, suggesting the existence of light scatterers with size of the order of the wavelength of the light. The size of these structures depends on the molar mass and the polyelectrolyte concentration. With increasing molar mass the aggregates become larger. When the polyelectrolyte concentration increases, the dimensions of the aggregates also increase. Decreasing the polyelectrolyte concentration, the dimensions of the aggregates decrease, and if the polyelectrolyte concentration is sufficiently small, aggregates disappear. Our dynamic light scattering data displayed in Figure 1 support this interpretation.

Some investigators^{15,21} have discovered that the slow mode can be removed when the filtration of the polyelectrolyte solution is done with a filter with a small pore size. However, these experiments were performed at low polyelectrolyte concentrations. Our largest polyelectrolyte concentration with a molar mass of 350 kg/mol could not flow through a filter with a pore size of 0.1, 0.22, or 0.45 μ m, even when the air pressure used for the filtration was extremely high. Filtration with a filter with a pore size of 0.65 μ m works well. This filter has been used for all our NaPSS solutions, establishing the same experimental conditions for each solution. It must be noted that, based on the values for the apparent radius of gyration, solutions with lower concentrations may flow through a filter with a smaller pore size than 0.65 μ m. The preliminary experiment with different filters indicates that there are large structures in the NaPSS solution that can only flow through a filter with a sufficiently large pore size. It was suggested that the slow mode was caused by the preparation procedure of the polyelectrolyte solution. Our preliminary experiments with NaPSS solutions, which were not purified (the solid NaPSS from the manufacturer was directly dissolved in 0.01 M NaCl), show the fast and slow mode also. In fact, the general trend of the fast and slow diffusion coefficient in Figure 1 was found. This indicates that it is unlikely that the slow mode is caused by our purification procedure. Since we have seen that the dimensions of the aggregates vary by changing the molar mass or the polyelec-

trolyte concentration, it is likely that the aggregates are not solid particles. If solid particles are present, they would be permanently removed by filtration. This conclusion has also been reached by Sedláč, ¹³ who studied the filtration effect with two different filters, 0.1 and 0.2 μm pore size. His results show that filtration with a smaller pore size filter lead only to a smaller scattering intensity and a larger slow diffusion coefficient.

If we compare our measurements with those of Koene and Mandel, ⁴ a remarkable difference is seen: no slow mode is reported. Their experiments were also performed in an added salt concentration of 0.01 M. Our experiments were done with small molar masses, while they used high molar masses. Comparing our highest molar mass, $M_w = 350$ kg/mol, with their lowest molar mass, $M_w = 400$ kg/mol, the fast diffusion coefficients agree well, but no slow diffusion coefficients were reported. Since from our Figure 1 it is expected that the slow mode will start to be detectable at lower polyelectrolyte concentrations for higher molar masses, a slow mode must have been present in the NaPSS solutions of Koene and Mandel. ⁴

The explanation must be found in their experimental procedure. For a clear detection of our measured double-exponential correlation functions a time scale covering 4 decades is necessary. With the advent of modern multiple-tau correlators this observation can now be done in a reliable way, while Koene and Mandel have used a linear 96-channel Malvern correlator in their experiments. As already mentioned, it is likely that the slow mode contribution was included in a floating baseline used in their data analysis.

An extensive dynamic light scattering investigation on the dynamics of NaPSS without added salt as a function of the molar mass and polyelectrolyte concentration has been done by Sedláč and Amis. ^{11,12} The general trend of their experimental data agrees with our measurements. According to Sedláč, ¹⁴ the formation of aggregates is not caused by poor solvation of the polyelectrolyte chain in a polar solvent.

The light microscopy image in Figure 6 shows structures with a diameter of about 750 nm. Most detected structures were immobile, but on every slide mobile structures were found. Despite the difficulties of focusing on the mobile structures, it is our impression that the size of the mobile and immobile structures is 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 are the polyelectrolyte aggregates. Figure 7 shows structures with 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. Figures 6–8 have been reported before in a letter ²² and are included for completeness. In Figure 8 a light microscopy image is shown of the same sample as shown in Figure 6. The difference with Figure 6 is that the image was taken about 1.5 h after putting a solution droplet on the slide. It is seen that the aggregates 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 on the slide, and following the interpretation of Figure 5, the polyelectrolyte aggregates then become larger.

Although it is not clear at all what the mechanism is for the formation of aggregates, some suggestions have been tentatively put forward in the literature. Since polyions are particles with the same electric charge, it is quite remarkable that aggregates can be formed. The formation of aggregates can only appear 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, ²³ 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. ^{24,25}

Schmitz ²⁶ uses the term “temporal aggregates” and proposes the concept of attractive fluctuating dipolar interactions due to an asymmetric distribution of counterions around the polyelectrolyte chain.

Conclusions

In this work apparent diffusion coefficients of the flexible highly charged polyelectrolyte sodium poly(styrenesulfonate) were determined for three molar masses over a very wide concentration range at a fixed added salt concentration of 0.01 M. At dilute polyelectrolyte concentrations the apparent diffusion coefficient depends on the molar mass and on the polyelectrolyte concentration. At higher concentrations two modes were detected. The fast diffusion coefficient does not depend on the molar mass and follows the power law $D_f \propto c^{0.72}$, close to the theoretical power law derived by Odijk. For the highest concentrations the fast diffusion coefficient is independent of the concentration and molar mass.

The slow diffusion coefficient depends on the molar mass and on the polyelectrolyte concentration. The slow mode is interpreted as the existence of aggregates or domains of polyelectrolyte chains. From the angular dependence of the reciprocal normalized scattering intensity, the dimensions of these aggregates become smaller with decreasing polyelectrolyte concentration and decreasing molar mass. Conventional light microscopy images show directly the existence of aggregates and also show the change in aggregate dimensions when varying the polyelectrolyte parameters.

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