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Quasi Elastic Light Scattering Study on Solutions of Linear Flexible Polyelectrolytes at Low Ionic Strengths

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ABSTRACT: Dynamic light scattering measurements have been performed on aqueous solutions of linear poly(ethyleneimine), poly(2-vinylpyridine), and sodium poly(styrenesulfonate), all flexible polyelectrolytes, at several polymer concentrations above the overlap concentration c^* and over a wide NaCl concentration range. A change in the shape of the intensity correlation functions (ICFs) of the scattered light from a monomodal to a bimodal decay is observed with an increase of the polyelectrolyte concentration and a decrease of the NaCl concentration. The decay rates of the monomodal ICFs and the fast decay rates of the bimodal ICFS are related and can be explained by the cooperative diffusion in a transient polyelectrolyte network. The slow mode of the bimodal decay can be removed by filtration, disappears for some solutions spontaneously after a given time, and, for solutions of linear poly(ethyleneimine), exhibits hysteresis depending on the way the NaCl concentration has been established. It is concluded that the slow mode is related to clusters of polyelectrolyte chains which are apparently formed in solutions with a high polyelectrolyte concentration and low concentrations of added NaCl.

Introduction

Despite extensive studies in the last 2 decades the dynamic light scattering behavior of flexible polyelectrolytes in aqueous solutions is not yet fully understood. In particular, for polyelectrolyte solutions where the concentration of the added low molar mass salt is smaller than the equivalent polyelectrolyte concentration, the interpretation of the observed bimodal shape of the intensity correlation functions is still controversial.

For polyelectrolyte solutions containing an abundant amount of salt the intensity correlation functions (ICFs) are of the monomodal type and their interpretation is less complicated.[1] The apparent cooperative diffusion coefficients (D_{app}) determined from these correlation functions are discussed in analogy to those observed in solutions of uncharged macromolecules for which at least two different concentration regimes are distinguished.[2] In the *dilute* regime, in which the polyelectrolyte coils are well separated and behave like more or less independent entities, the cooperative diffusion coefficient depends on the size of the individual coils. In the *semidilute* regime the polyelectrolyte concentration is such that the polyelectrolyte chains interpenetrate to form a transient physical network and the cooperative diffusion coefficient depends on the mesh size of this network. This leads to predictions concerning the dependence of D_{app} on the chain length, polyelectrolyte concentration, and ionic strength of the solution which are different for the two regimes.[3] Experimental evidence for these differences has been given, *i.e.*, by Koene *et al.*[4-6] for solutions of sodium poly(styrenesulfonate) (NaPSS) and by Smits *et al.*[7] for solutions of linear poly(ethyleneimine) chloride (LPEI).

The interpretation of dynamic light scattering data of polyelectrolyte solutions in which the salt concentration is smaller than the equivalent polyelectrolyte concentration is less simple. The interpretation becomes particularly complicated when, with a decreasing concentration of added salt, the intensity correlation functions of polyelectrolyte solutions are no longer of the monomodal type but display a bimodal behavior with two characteristic decay rates differing by at least two orders of magnitude termed fast and slow. Although the first observation concerning the influence of decreasing ionic strength on the correlation rate of polyelectrolyte solutions as reported by Lin *et al.*[8] for aqueous solutions of poly(L-lysine) only mentioned a change of a fast into a slow decay rate (described in terms of an *ordinary–extraordinary phase transition*), later on it has been shown that the correlation functions become bimodal indeed, with both a slow and a fast decay rate as shown for rodlike and flexible polyelectrolyte molecules such as DNA[9,10] and NaPSS.[11,12] Analogously for the polyelectrolyte concentration dependence of the ICFs Koene and Mandel[13] first reported for NaPSS solutions without added salt a rapidly decreasing decay rate of the intensity correlation function with an increasing polyelectrolyte concentration, followed at higher NaPSS concentrations by the appearance of a faster decay rate instead. Subsequently it has been demonstrated for NaPSS[12] and for quaternized poly(2-vinylpyridine)[14] that for polyelectrolyte solutions without added salt the intensity correlation functions are monomodal at very low polyelectrolyte concentrations and bimodal at the higher ones.

The interpretation of the fast and the slow mode for the bimodal intensity correlation functions is not yet well established. A major difficulty arises from the absence of theoretical indications about how far the differentiation between two concentration regimes, valid at high ionic strengths, is maintained down to lower values before it breaks down into a much more complicated pattern involving different transition regimes.[3] The fast mode has been attributed to different origins such as to the coupled diffusion of polyions and counterions[15] or to cooperative fluctuations in a polyelectrolyte network[13,16] as for D_{app} in the semidilute regime of polyelectrolyte solutions containing an abundant amount of added salt. The latter attribution stems from the fact that the decay rate of the fast mode seems to be molar mass independent.

On the other hand, the origin of the slow mode, of which the decay rate is molar mass dependent, has been ascribed to a reptation mechanism,[13,17] to collective modes resulting from long-range electrostatic interactions,[18,19] or to polyelectrolyte clusters resulting either from the attraction between polyions[20] or from entanglements of the poly-

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electrolyte chains[14,15,21] as it was also postulated for uncharged macromolecules.[22]

Recent observations by Gosh *et al.*[23] seemed to indicate that the slow mode was determined by large clusters or parasitic particles in the solution. They found that it is possible to eliminate the slow mode in, *e.g.*, NaPSS and poly(L-lysine) solutions by filtration through filters with a small pore size of 0.1 or 0.05 μm (instead of the more customary 0.22-μm filters). Once the slow mode had disappeared after such a filtration, it did not reappear again in the correlation functions, at least not for several days. This observation was, however, different from that of Sedlak *et al.*,[24] who reported only a partially filtering out of the slow mode for NaPSS and poly(methacrylic acid) solutions with filters of the same pore sizes.

None of the interpretations given for the fast and slow mode can convincingly explain *all* the experimental observations. Therefore, we have started an investigation of the dynamic light scattering behavior of several polyelectrolytes with a low intrinsic persistence length. The ionic strength was varied in such a way that at the upper end the concentration of added salt exceeds the polyelectrolyte equivalent concentration but finally reaches values where the contribution of the polyelectrolyte counterions dominates the ionic strength. We have used LPEI and poly(2-vinylpyridine) (P2VP), both charged up 80% by HCl, and NaPSS at various concentrations. Varying NaCl concentrations c_s have been added with $2 \geq c_s \geq 10^{-4}$ mol/L. A smooth transition has been observed between the monomodal decay rate and the fast decay rate of the bimodal intensity correlation functions upon lowering the ionic strength. Various interesting observations could be made concerning the decay rate of the slow mode. In agreement with the results of Gosh *et al.*,[23] we found that the slow mode for systems at low ionic strengths fully disappears after filtration of the NaPSS and LPEI solutions through 0.1-μm filters. We have, however, detected other effects which seem to rule out as the origin of the slow mode the presence of parasitic scatterers, already existing in the polyelectrolyte solutions or originating from the dialysis bags, as suggested by Gosh *et al.*[23] Although no definite conclusions could be reached yet, we feel that the evidence from this study points to entanglements or loose aggregates of polyions, formed in the polyelectrolyte solutions at certain polyelectrolyte and concentrations of added salt, as being responsible for the appearance of the slow mode.

Experimental Section

Material. Two batches of LPEI·HCl, with the chemical formula

$$(\text{-}CH_2CH_2N^+H_2\text{-})_n + nCl^-$$

have been synthesized with the molar masses $M_w = (42.0 \pm 2.0) \times 10^3$ (520 monomeric units) and $M_w = (88.2 \pm 4.5) \times 10^3$ (1109 monomeric units), with the M_w/M_n ratios of 1.3. As described earlier[7] polymerization of 2-phenyl-2-oxazoline following the method of Tanaka *et al.*[25] has been used, with methyl trifluoromethanesulfonate as initiator. The backbone of the LPEI·HCl prepared by this method is nonbranched and contains no substituent groups. The charges on the LPEI are positioned directly on the backbone of the chain. This uncommon position of the charges results in partially nonscreenable interactions between the nearest and the next-nearest charged secondary amino groups at high NaCl concentrations, as is manifested in the potentiometric and viscosity data of LPEI.[26] The influence of these local nonscreenable interactions on the ionic strength dependence of the decay rates of the ICFs of the scattered light was, however, small for LPEI with a charge density of 80%.

The sodium salt of poly(styrenesulfonate) (NaPSS), purchased from Pressure Chemical Co. (Pittsburgh, PA), was a sample with molar mass $M_w = 650\,000$. This NaPSS batch has been prepared by the sulfonation of *well-defined samples* of polystyrene with an $M_w/M_n < 1.1$.

The poly(2-vinylpyridine) (P2VP) was purchased from Pressure Chemical Co. (Pittsburgh, PA). The sample with $M_w = 70\,000$ had a narrow molecular weight distribution, as the shapes of the ICFs under high added salt conditions were very closely single exponential.

Preparation of the Samples. The solvent of the polyelectrolytes used was deionized water purified by a Milli-Q purification system, to which *pro analysi*, NaCl was added. Before preparation of the polyelectrolyte solution, the solvent was filtered through a Millipore VM 0.05 μm pore size filter to clear it from dust particles. To clear it from air bubbles, the solvent was prepared at least 1 day before dissolving the polyelectrolytes or diluting the samples.

The degrees of charge β of P2VP and LPEI·HCl were adjusted at 80% with Titrisol 0.1 M HCl and Titrisol 0.1 M NaOH, respectively. This value of β remains unaffected upon the dilution of the polyelectrolyte solutions. The addition of NaOH to the LPEI·HCl solutions resulted in a significant NaCl concentration, approximately one-fifth of the LPEI concentration used. To adjust the NaCl concentration and to ensure a constant chemical potential upon the dilution, the polyelectrolyte solutions were dialyzed against the aqueous NaCl solution used as the solvent. Spectrapore membranes from Spectrum Medical Industries, with a molecular weight cutoff of 3500, were used for the dialysis. The membranes were purified by boiling in a solution of sodium bicarbonate (*pro analysi*; Merck) and in a solution of EDTA (Titriplex III; Merck), followed by extensive rinsing with Millipore water. The dialysis was performed in a small cask (15 mL) in which volume changes could be controlled. One side of the cask consisted of a dialysis membrane, cut out of a purified dialysis membrane tube. The small cask was suspended in a large container filled with 1 L of a suitable solvent, which was refreshed three or four times in a single dialysis experiment. During the dialysis experiment the polyelectrolyte solution in the small cask was kept under nitrogen.

We have checked that during the dialysis no large pollutants are released by the membranes treated as described. Millipore water, dialyzed against water for 1 week (the typical duration of a dialysis experiment), gave an ICF not differing significantly from that of undialyzed water. No new (slow) mode could be detected.

The concentrations of the LPEI, P2VP, and NaPSS solutions were adjusted by weight, taking into account the amounts of water in the dry polyelectrolyte batches. After dialysis the concentrations were corrected by measuring the increased weight of the total volume, which could be achieved with an error of less than 1%. The concentration of NaPSS was checked by measuring the extinction at 261-nm UV light, using an extinction coefficient of 1.92 ± 0.2 L cm^2 g^{-1}. The concentrations of LPEI and P2VP were determined using a carbon analyzer Model 1555b from Ionics and by potentiometric titration. For LPEI the latter have been performed at a temperature of 60 °C, at which the LPEI is fully soluble in water over the complete charging range.

Before every sample preparation the cylindrical quartz cuvettes of 1-cm diameter and the filtration setup without the filter were rinsed with a Titrisol 0.1 M HCl and a Titrisol 0.1 M NaOH solution. Then the cuvettes and the filtration setup with the filter were extensively rinsed with Millipore water. The efficiencies of the purification procedure of both the cuvette and the filter setup were tested by measuring in the cuvette the autocorrelation function of (Millipore) water filtered using the filter setup. This correlation function was not allowed to show any significant decay time within the typical duration of an experiment (minutes).

The polyelectrolyte samples were prepared from dialyzed stock solutions freshly obtained or kept frozen at −20 °C. The solutions were cleared of dust particles by filtering two to three times through a Millipore GS or a Durapore GV 0.2 μm pore size filter or through a Millipore VS or a Durapore VV 0.1 μm pore size filter. No distinction between the two types of filters of the same pore was found despite their differences in chemical composition.

(Millipore filters are made of a mixed ester of cellulose acetate and nitrate, and Durapore filters, of poly(vinylidene fluoride).) The decrease of the concentration due to the filtration through a filter with a 0.22 μm pore size was less than 3% and was neglected. The decrease of the concentration due to the filtration through a filter with a 0.10 μm pore size was approximately 8% and was taken into account.

Dynamic Light Scattering Measurements. The dynamic light scattering experiments were performed with a commercial apparatus consisting of a Model ALV/SP-86#042 goniometer and an ALV-3000 correlator with the extended multiple-τ option (ALV, Langen, Germany). The laser used as the light source was an argon ion laser (Spectra Physics, Model 2000) operating at a wavelength of 514.5 nm. The autocorrelation functions of the scattered light intensity were recorded in the real time multiple-τ mode with a time interval ranging from 0.8 μs to 50 s. The samples were thermostated during a measurement at a temperature of 25 °C.

Analysis of the Dynamic Light Scattering Data. If the scattered field is assumed to have Gaussian statistics, the normalized intensity autocorrelation function $g^{(2)}(\tau)$ is directly related to the normalized electric field autocorrelation function $g^{(1)}(\tau)$ through the Siegert relation.

$$g^{(2)}(\tau) = 1 + B|g^{(1)}(\tau)|^2 \qquad (1)$$

Here B is an equipment-dependent amplitude factor.[27] Two types of ICFs were measured, namely, correlation functions having one mode (monomodal) and correlation functions having two well-separated modes (bimodal).

The monomodal intensity autocorrelation functions, which only slightly deviated from a single exponential, were analyzed by fitting to a cumulant expansion.[28,29] The general cumulant expansion is given by

$$g^{(2)}(\tau) = 1 + B\exp\left(-2K_1\tau + \frac{2K_2}{2!}\tau^2 - \frac{2K_3}{3!}\tau^3 + ...\right) \qquad (2)$$

If the first moment K_1 is found to be proportional to q^2, one can determine an apparent diffusion coefficient D_{app}.

$$D_{\text{app}} = K_1/q^2 \qquad (3)$$

In the analysis of our results the first three cumulants were obtained from a third-order polynomial least-squares fit of the logarithm of the intensity autocorrelation function minus unity.

$$\log(g^{(2)}(\tau) - 1) = \log B - 2\left(K_1\tau - \frac{K_2}{2!}(\tau)^2 + \frac{K_3}{3!}(\tau)^3 + ...\right) \qquad (4)$$

The base line is thus assumed to have a *fixed* value 1. Relative values with respect to K_1 of the second cumulant are on the order $K_2/(2K_1) = 0.12$ for the LPEI and NaPSS solutions and 0.05 for the P2VP solutions. The third cumulants were even smaller.

Two criteria were used to conclude that a cumulant fit with N data points is satisfactory. The first criterium is the value of the quality factor Q of the fit, defined as

$$Q = 1 - \frac{\sum_{i=1}^{N-1}(n_i - \tilde{n}_i)(n_{i+1} - \tilde{n}_{i+1})}{\sum_{i=1}^{N-1}(n_i - \tilde{n}_i)^2} \qquad (5)$$

where n_i is the value of the ith experimental point of the autocorrelation function and $\tilde{n}_i$ is its value according to the fitted curve. Fits with $Q \geq 0.75$ were assumed acceptable. The second criterium is the absence of systematic deviations in plots of the residues.

The intensity autocorrelation functions showing two well-separated modes, which both slightly deviated from a single-exponential behavior, were fitted of a double-exponential model,

$$g^{(2)}(\tau) - 1 = A + (B_f\exp(-\Gamma_f\tau) + B_s\exp(-\Gamma_s\tau))^2 \qquad (6)$$

which has as fit parameters A, the deviation of the base line from unity, the amplitudes B_f and B_s, the fast decay rate Γ_f, and the slow decay rate Γ_s. A *Marquardt Levenberg* algorithm was used for the nonlinear least-squares fit of the correlation function to the model in eq 6. The biexponential fit was found satisfactory if the fitted A value was less than 5% of the sum of $(B_f + B_s)^2$ and if the decay rates Γ_f and Γ_s differed by at least a factor 10.

Table 1. Γ/q^2 Values and Amplitude Ratios of P2VP (M_w = 70 × 10^3, 80% Charged) in 10 mM NaCl at a Scattering Angle of 90°

conc P2VP (×10^3 mol/L)	D_{app} (×10^7 cm^2/s)	Γ_f/q^2 (×10^7 cm^2/s)	Γ_s/q^2 (×10^9 cm^2/s)	B_f/B_s
104		21	9.5	1.2
56.9		20	7.4	1.2
31.8		12	18	3.7
12.6	4.6			

For a better comparison of the results $c(\tau)$ functions have been represented in some figures, where $c(\tau)$ is the ICF normalized to its value at $\tau = 0$.

$$c(\tau) = \frac{g^{(2)}(\tau) - 1}{g^{(2)}(0) - 1} \qquad (7)$$

The value of $g^{(2)}(0)$ was obtained from the fit.

All samples dissolved in a solution with a concentration of added NaCl $c_s \geq 10$ mM were measured several times over the angular range 40–140°, resulting in about 150 to 250 intensity autocorrelation functions. The samples were purified until at least 70% of the correlation functions measured were not distorted by excessive fluctuations of the total scattering intensity. The apparent diffusion coefficients were determined by the extrapolation of the fitted K_1/q^2 values as a function of q^2 to zero angle. The values of the reduced decay rates Γ_i/q^2 for samples dissolved in solutions with concentrations of added NaCl $c_s \leq 1$ mM were determined from ICFs measured at a scattering angle of 90° only, because of the difficulties in measuring ICFs with an acceptable amount of noise within a reasonable duration of the experiment.

Experimental Difficulties. The data included in this work were measured with samples giving reproducible relaxation rates and amplitude values at a given angle. However, not all samples prepared gave reproducible fit parameters. With some LPEI and P2VP solutions, which gave bimodal ICFs after filtration through a 0.22 μm pore size filter, variations of B_s up to a factor 2 were observed by changing the position with respect to the laser beam of the measuring cell in its holder. For these samples the values of B_s could also differ when measured at the same scattering angle but at different time periods (minutes). An increase of B_s was always accompanied by an increase of the total scattering intensity. The data of such samples have not been included in the results presented, despite the small influence of the variations of B_s on the mean values of Γ_f and Γ_s. Another noteworthy point is that the study of polyelectrolyte solutions in 1 × 10^{-3} and 1 × 10^{-4} M NaCl was sometimes hampered by an unpredictable time evolution of the samples, as for many of these samples the scattering intensity became unstable some hours or days after the filtration.

Results

Polyelectrolyte and Salt Concentration Dependence of the Intensity Correlation Functions. Intensity autocorrelation functions (ICFs) of aqueous solutions containing P2VP (M_w = 70 × 10^3) with an 80% degree of charge in 10 mM NaCl have been measured at four different polyelectrolyte concentrations at a scattering angle of 90°. The fit parameter of these functions are given in Table 1, with $D_{\text{app}} = K_1/q^2$ for the monomodal correlation functions and Γ_f/q^2 and Γ_s/q^2 the reduced decay rates of the fast and slow modes, respectively, for the bimodal correlation functions. A change from the monomodal correlation function to a bimodal one upon an increase of the polyelectrolyte concentration c in moles of monomer per liter is shown. At the lowest concentration

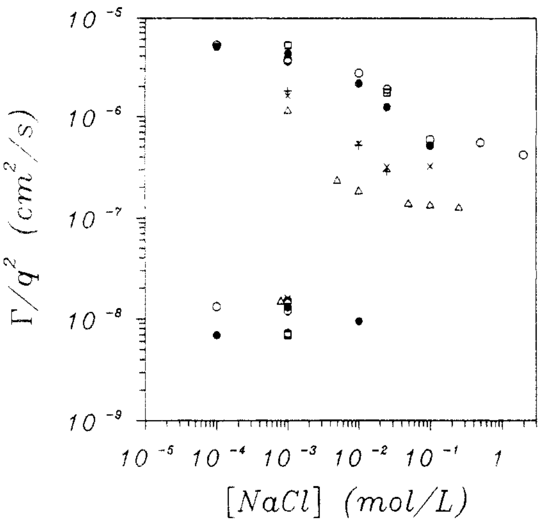

Figure 1. NaCl concentration dependence of Γ/q^2 at a scattering angle of 90° (D_{app} for the monomodal correlation functions) for six different polyelectrolyte solutions at a constant polyelectrolyte concentration: LPEI ($M_w = 42.0 \times 10^3$) of 0.104 mol/L (○) and of 12.6×10^{-3} mol/L (+); LPEI ($M_w = 88.2 \times 10^3$) of 0.104 mol/L (□) and of 12.6×10^{-3} mol/L (×); P2VP ($M_w = 70 \times 10^3$) of 0.104 mol/L (●); NaPSS ($M_w = 650 \times 10^3$) of 4.9×10^{-3} mol/L (△).

Table 2. Γ/q^2 Values, Amplitude Ratios, and Ionic Strengths μ of P2VP ($M_w = 70 \times 10^3$, 80% Charged) Solutions with a Polyelectrolyte Concentration of 0.104 mol/L and Different Concentrations of Added NaCl (Scattering Angle = 90°)

conc NaCl ($\times 10^3$ mol/L)	D_{app} ($\times 10^7$ cm^2/s)	Γ_f/q^2 ($\times 10^7$ cm^2/s)	Γ_s/q^2 ($\times 10^9$ cm^2/s)	B_f/B_s	μ ($\times 10^3$ mol/L)
100	5.1				118
25	1.2				43
10		21	9.5	1.2	28
1		43	13	2.8	19
0.1		50	6.9	0.8	18

Table 3. Γ/q^2 Values, Amplitude Ratios, and Ionic Strengths μ of LPEI ($M_w = 42 \times 10^3$ and 88.2×10^3, 80% Charged) Solutions with Polyelectrolyte Concentrations of 0.104 and 12.6×10^{-3} mol/L and Different Concentrations of Added NaCl (Scattering Angle = 90°)

conc NaCl ($\times 10^3$ mol/L)	D_{app} ($\times 10^7$ cm^2/s)	Γ_f/q^2 (10^7 cm^2/s)	Γ_s/q^2 ($\times 10^9$ cm^2/s)	B_f/B_s	μ ($\times 10^3$ mol/L)
a. Polyelectrolyte Concentration 0.104 mol/L					
2000	4.2				2020
500	5.5				520
100	5.89				120
25	19				46
10	27				31
1		36	7.2	0.7	22
1		37	12	0.7	22
1		36	15	1.4	22
0.1		52	13	0.7	22
25[a]	17				46
1[a]		52	6.9	2.4	22
b. Polyelectrolyte Concentration 12.6×10^{-3} mol/L					
100	3.2				102
25	3.2				27
10	5.4				12
1		16	16	0.7	4.0
25[a]	2.9				27
10[a]	5.2				12
1[a]		18	13	0.6	4.0

[a] $M_w = 88.2 \times 10^3$.

Table 4. Γ/q^2, Amplitude Ratios, and Ionic Strengths μ of NaPSS ($M_w = 650 \times 10^3$) Solutions with a Polyelectrolyte Concentration of 4.9×10^{-3} mol/L and Different Concentrations of Added NaCl (Scattering Angle = 90°)

conc NaCl ($\times 10^3$ mol/L)	D_{app} ($\times 10^7$ cm^2/s)	Γ_f/q^2 ($\times 10^7$ cm^2/s)	Γ_s/q^2 ($\times 10^9$ cm^2/s)	B_f/B_s	μ ($\times 10^3$ mol/L)
250	1.29				250
100	1.36				100
50	1.40				51
10	1.88				11
5	2.38				5.9
1		11.6	15	0.84	1.9

of the P2VP investigated the ICF was monomodal and nearly monoexponential, with $K_2/(2K_1)$ only 0.05. At the three higher P2VP concentrations the ICFs are clearly bimodal and characterized by two decay rates which for a given solution differs at least 2 order of magnitude. Both reduced decay rates Γ_f/q^2 and Γ_s/q^2 depend on the polyelectrolyte concentration. *The former increases with increasing c, as can be seen from Table 1. The dependence of the latter is, however, less clear in the relatively small concentration range studied.*

At a constant polyelectrolyte concentration the NaCl concentration dependence of Γ_f/q^2 and Γ_s/q^2 has been studied with 80% charged P2VP solutions in the range $0.1 \le c_s \le 0.0001$ M. A fixed value of $c = 0.104$ mol/L has been chosen because at this concentration and at the scattering angle of 90° the ICF in 10 mM NaCl is characterized by two well-separated modes of comparable amplitude. Results are given in Table 2. The two decay rates of the bimodal correlation functions at relatively low c_s show a different dependence on the salt concentration, *with Γ_f/q^2 definitely increasing with decreasing NaCl concentrations and a less clear dependence of Γ_s/q^2, which is rather insensitive or perhaps slightly decreasing on decreasing c_s*. It can also be seen that the ICF changes from a monomodal to a bimodal type in the range between 25 and 10 mM NaCl at a constant P2VP concentration of 0.104 mol/L.

Both the increase of the P2VP concentration at a constant, low salt concentration and the decrease of the salt concentration at a constant, relatively high polyelectrolyte concentration thus induce a change from a monomodal ICF toward a bimodal correlation function. For LPEI solutions it has not been possible to determine the ICFs at sufficient low concentrations to detect the transition between the bimodal and the monomodal correlation functions with decreasing polyelectrolyte concentration in 10 mM NaCl, because of the much lower scattering intensity of the LPEI solutions compared to that of the P2VP solutions under comparable conditions. For NaPSS solutions in the absence of salt a transition from a monomodal to a bimodal ICF has been observed however with increasing *c*.[12]

The salt concentration dependence of the ICFs of P2VP has been compared to that of solutions containing 80% charged LPEI (of two different molar masses, $M_w = 42.0 \times 10^3$ and $M_w = 88.2 \times 10^3$, respectively) at the same concentration $c = 0.104$ mol/L, the lower concentration $c = 12.6 \times 10^{-3}$ mol/L, and of solutions containing NaPSS of a much higher molar mass ($M_w = 650 \times 10^3$) at $c = 0.0049$ mol/L. (The latter polyelectrolyte was chosen because it had been investigated previously in this laboratory by Koene *et al.*[4,5,6,13]) The corresponding results are collected in Tables 3 and 4. In Figure 1 the decay rates as given in Tables 2–4 are shown. In all cases upon decreasing c_s the change of the monomodal toward bimodal ICFs can be observed, albeit in different NaCl concentration ranges. The K_1/q^2 values of the monomodal correlation functions are seen to increase with decreasing c_s and smoothly link up with the Γ_f/q^2 values of the bimodal-shaped ICFs. On the contrary no significant change with

Table 5. Angular Dependence of the Γ/q^2 and Amplitude Ratios of 63 × 10^{-3} and 0.104 mol/L LPEI (M_w = 42.0 × 10^3, 80% Charged) Solutions in 1 mM NaCl

scattering angle (deg)	Γ_f/q^2 (×10^7 cm^2/s)	Γ_s/q^2 (×10^9 cm^2/s)	B_f/B_s
40	40	7.1	0.56
60	47	8.0	0.80
90	35	8.1	0.91
120	39	7.5	0.99
60[a]	43	5.0	0.55
70[a]	43	6.4	0.67
90[a]	36	7.2	0.67
120[a]	37	8.0	0.74

[a] 0.104 mol/L LPEI.

salt concentration is observed for the Γ_s/q^2 values in the polyelectrolyte systems with bimodal ICFs presently investigated. Typical values for Γ_f/q^2 and K_1/q^2 are in the range (0.1–6) × 10^{-6} cm^2 s^{-1} and in the range (4–20) × 10^{-9} cm^2 s^{-1} for Γ_s/q^2.

The angular dependence of the reduced fast and slow decay rates for LPEI with bimodal ICFs is rather weak (see Table 5 and Figure 2). For the fast mode, given the experimental accuracy, it is not clear if the reduced decay rate has any angular dependence at all. For the fast mode Γ_f/q^2 at an angle of 90° may thus be considered to represent an apparent diffusion coefficient. For the slow mode an angular dependence was found at least at the higher LPEI concentration, and extrapolation of several Γ_s/q^2 values to zero angle remains necessary.

For samples of LPEI solutions in 1 mM NaCl, when taken from the same stock solution, the fit parameters of the ICFs were found to be identical within experimental accuracy. However, for samples obtained from separately prepared LPEI solutions in 1 mM NaCl with the same LPEI concentration, a large scatter in the amplitude and the decay rate of the slow mode was observed. An example is shown in Table 3a where the fit parameters for three different solutions of 0.104 mol/L LPEI (M_w = 42 × 10^3) in 1 mM NaCl are given.

Another interesting point is the remarkable observation that for some solutions of the lower molar mass LPEI the slow mode *disappeared spontaneously* a few months after the initial filtration through 0.22-μm filters (see Figure 3). In the first days after filtration the decrease of the amplitude was the fastest, with a decrease in B_s/B_f of approximately 25% in 1 day. The complete disappearance of the slow mode took, however, about 6 months! To check if degradation of the molar mass has occurred in the 6 months old 0.104 mol/L LPEI solution at 1 mM NaCl, it was diluted to a 2.9 × 10^3 mol/L LPEI solution in 100 mM NaCl which gave a monomodal ICF. From this ICF a D_{app} value of 2.9 × 10^{-7} cm^2 s^{-1} was derived which compared well to the value of 2.7 × 10^{-7} cm^2 s^{-1} of a freshly prepared solution of the same composition, thus ruling out degradation as the cause of the slow mode disappearance.

Such a disappearance of the slow mode was *not found* for LPEI of the higher molar mass nor for the solutions of the two other polyelectrolytes in 1 mM NaCl during the same time interval. One sample solution of 4.9 × 10^{-3} mol/L NaPSS in 1 mM was even kept for more than *one year* but still gave essentially the same ICF as measured directly after filtration through a filter with a 0.22-μm pore size.

Removal of the Slow Mode by 0.1-μm Filtration. LPEI and NaPSS solutions, with bimodal ICFs when filtered through 0.22-μm filters, showed monomodal correlation functions without a slow mode after filtration through 0.1-μm filters. This complete removal of the slow mode by filtration is in agreement with the observations by Gosh *et al.*[23] For solutions of P2VP the removal of the slow mode could not be established as filtration through 0.1-μm filters—both Durapore and Millipore—turned out to be impossible due to plugging of the filters used. The origin of this plugging is not clear; it is probably not due to adsorption of the polyelectrolyte to the filter material. Filtration of a P2VP solution in 1 mM NaCl through 0.22-μm filters of the same chemical composition resulted only in a decrease of the P2VP concentration of less than 3%, while the solutions exhibited a bimodal ICF.

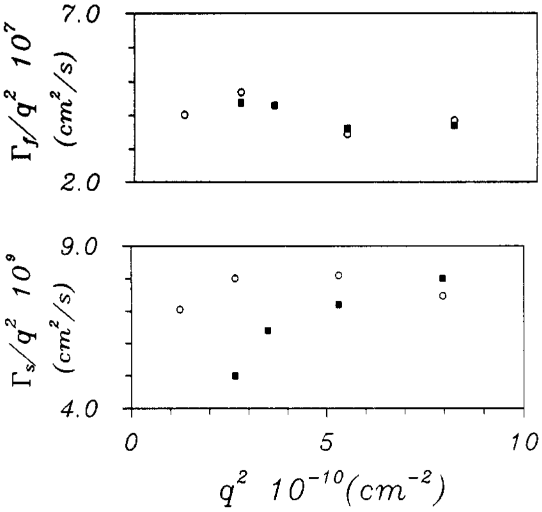

Figure 2. q^2 dependence of Γ/q^2 for a 63 × 10^{-3} mol/L (○) and a 0.104 mol/L (■) LPEI (M_w = 42.0 × 10^3) solution in 1 mM NaCl.

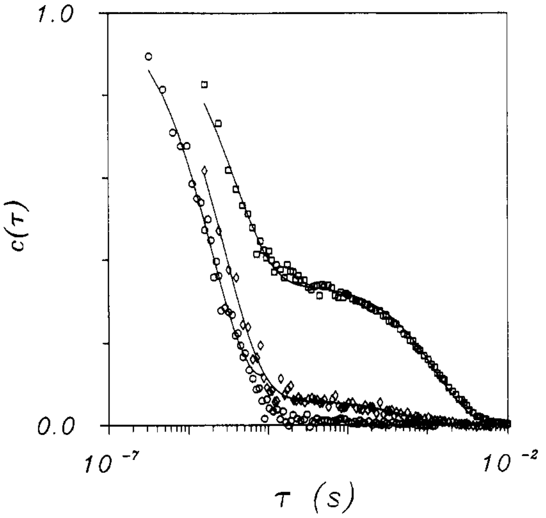

Figure 3. Disappearance of the slow mode in the normalized intensity correlation function of a 0.104 mol/L LPEI (M_w = 42.0 × 10^3) solution in 1 mM NaCl, measured (a) directly after filtration (□), (b) 2 months after filtration (◊), and (c) 6 months after filtration (○). The fit parameters are for (a) Γ_f/q^2 = 3.6 × 10^{-6} cm^2/s, Γ_s/q^2 = 7.2 × 10^{-9} cm^2/s, and B_f/B_s = 0.67; for (b) Γ_f/q^2 = 3.8 × 10^{-6} cm^2/s, Γ_s/q^2 = 1.7 × 10^{-8} cm^2/s, and B_s/B_f = 0.07; and for (c) K_1/q^2 = 4.3 × 10^{-6} cm^2/s.

Figure 4 illustrates the disappearance of the slow mode for a solution of 0.104 mol/L LPEI in 1 mM NaCl in the ICF measured at an angle of 90°. The ICF of the sample filtered through a 0.22 μm pore size filter is definitely bimodal, whereas for an identical solution filtered through a 0.1 μm pore size filter a monomodal ICF is found. For the bimodal ICF the fit parameters are Γ_f/q^2 = 3.63 × 10^{-6} cm^2 s^{-1} and Γ_s/q^2 = 1.52 × 10^{-8} cm^2 s^{-1}, with B_f/B_s = 1.4. The decay rate for the monomodal correlation function is Γ/q^2 = 3.79 × 10^{-6} cm^2 s^{-1}, which agrees well with the decay rate of the fast mode of the bimodal ICF. This indicates that the removal of the slow mode does not

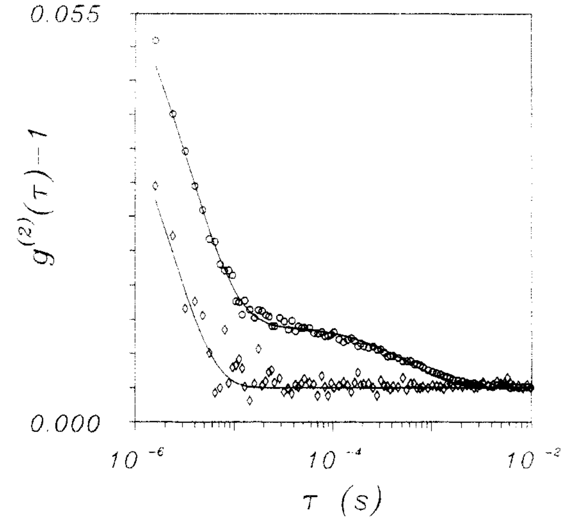

Figure 4. Two intensity correlation functions measured at a scattering angle of 90° on two LPEI ($M_w = 42.0 \times 10^3$) of 0.104 mol/L dissolved in 1 mM NaCl. One solution was filtered through a GV filter with a pore size of 0.22 μm (○); the other solution was filtered through a VC filter with a pore size of 0.1 μm (◇). The fit parameters are for the first solution: $\Gamma_f/q^2 = 3.63 \times 10^{-6}$ cm²/s, $\Gamma_s/q^2 = 1.52 \times 10^{-8}$ cm²/s, and $B_f/B_s = 1.4$. For the second solution, $K_1/q^2 = 3.79 \times 10^{-6}$ cm²/s.

significantly affect the remaining mode. (Note that the decay rate of the monomodal ICF has been estimated by fitting it to an exponential function because the cumulant analysis turned out to be less accurate.) Once removed by filtration the slow mode did not reappear, at least not within 2 *weeks*.

Filtration through a 0.1 μm pore size filter reduced the LPEI concentration by about 8% at the most. This decrease of the polyelectrolyte concentration cannot fully account for the disappearance of the slow mode. This is evidenced by comparison of the ICFs of the 0.104 mol/L LPEI solution in 1 mM NaCl with that of a LPEI solution with the much lower concentration of 0.063 mol/L (see Table 5). The latter, when filtered through a 0.22 μm pore size filter, also has a bimodal ICF notwithstanding a polyelectrolyte concentration which is about 60% lower than that of the former.

Filtration through a 0.1 μm pore size filter decreased the total scattering intensity of the 0.104 mol/L LPEI solution in 1 mM NaCl at an angle of 90°, corrected for the solvent scattering, by about 36% as compared to the total, corrected scattering intensity for the same solution filtered through the 0.22 μm pore size filter. This decrease in the scattering intensity must be related to the removal of large scatterers responsible for the slow mode by the 0.1 μm pore size filter.

Hysteresis in LPEI Solutions. We have observed a hysteresis of the slow mode for LPEI solutions upon increasing and decreasing the NaCl concentration. Two LPEI solutions of the same concentration in 10 mM NaCl were prepared in two different ways. In the first (direct) method a 12.6×10^{-3} mol/L solution was prepared by dissolving a given amount of polyelectrolyte directly into aqueous 10 mM NaCl. In the second (indirect) way the LPEI was first dissolved into aqueous 1 mM NaCl and the NaCl concentration was subsequently increased to 10 mM. This was achieved by dilution of a 0.104 mol/L solution in 1 mM NaCl with a mixture of 100 and 10 mM NaCl generating a solution of 12.6×10^{-3} mol/L in 10 mM NaCl. Both solutions have been filtered after preparation through 0.22 μm pore size filters.

The LPEI solution prepared in the direct way gave a monomodal ICF at an angle of 90°, as shown in part a of Figure 5 and more clearly in part b. The reduced decay rate of this ICF is $K_1/q^2 = 5.5 \times 10^{-7}$ cm² s⁻¹. In the same figures is also represented the ICF of a solution prepared in the indirect way which is clearly not monomodal, with reduced decay rates $\Gamma_f/q^2 = 6.4 \times 10^{-7}$ cm² s⁻¹ and $\Gamma_s/q^2 = 2.9 \times 10^{-8}$ cm² s⁻¹ ($B_f/B_s = 0.7$). The total scattering intensity, after correction for the scattering of the solvent, of the LPEI solution prepared indirectly is about twice as large as that of the solution obtained by the direct method. This must be due to the contribution of the scatterers responsible for the slow mode present in the indirectly prepared solution.

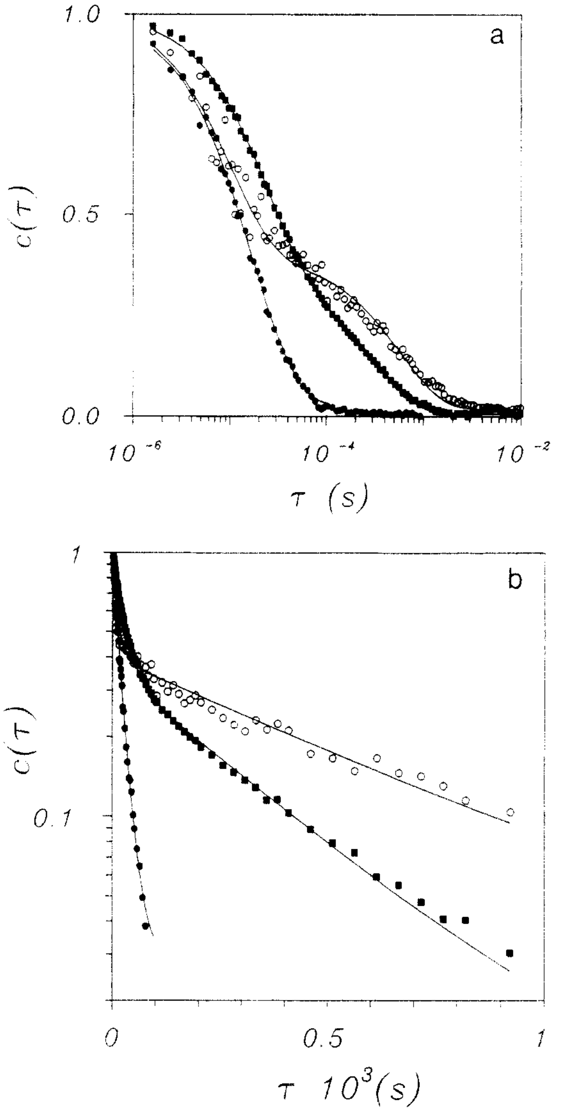

Figure 5. (a) Three normalized intensity correlation functions, measured at a scattering angle of 90° on three 12.6×10^{-3} mol/L LPEI ($M_w = 42.0 \times 10^3$) solutions. One correlation function is measured with a solution of LPEI directly dissolved in 10 mM NaCl (●) and is monomodal with $K_1/q^2 = 5.5 \times 10^{-7}$ cm²/s. One correlation function is measured with a solution LPEI dissolved in 1 mM NaCl (○); it is bimodal with $\Gamma_f/q^2 = 1.6 \times 10^{-6}$ cm²/s, $\Gamma_s/q^2 = 1.6 \times 10^{-8}$ cm²/s, and $B_f/B_s = 0.6$. The last correlation function obtained with a LPEI solution in 10 mM NaCl concentration prepared from LPEI in 1 mM NaCl as explained in the text (■) showed two modes as well, with $\Gamma_f/q^2 = 6.4 \times 10^{-7}$ cm²/s, $\Gamma_s/q^2 = 2.9 \times 10^{-8}$ cm²/s, and $B_f/B_s = 0.7$. (b) Same normalized intensity correlation functions as shown in part a represented as log[$c(\tau)$] *versus* τ.

To complete the hysteresis cycle, a 0.104 M LPEI solution in 10 mM NaCl prepared in the direct way (with monomodal ICFs[7]) was subsequently dialyzed to reduce the NaCl concentration to 1 mM and diluted to an LPEI concentration of 12.6×10^{-3} mol/L in 1 mM NaCl. The

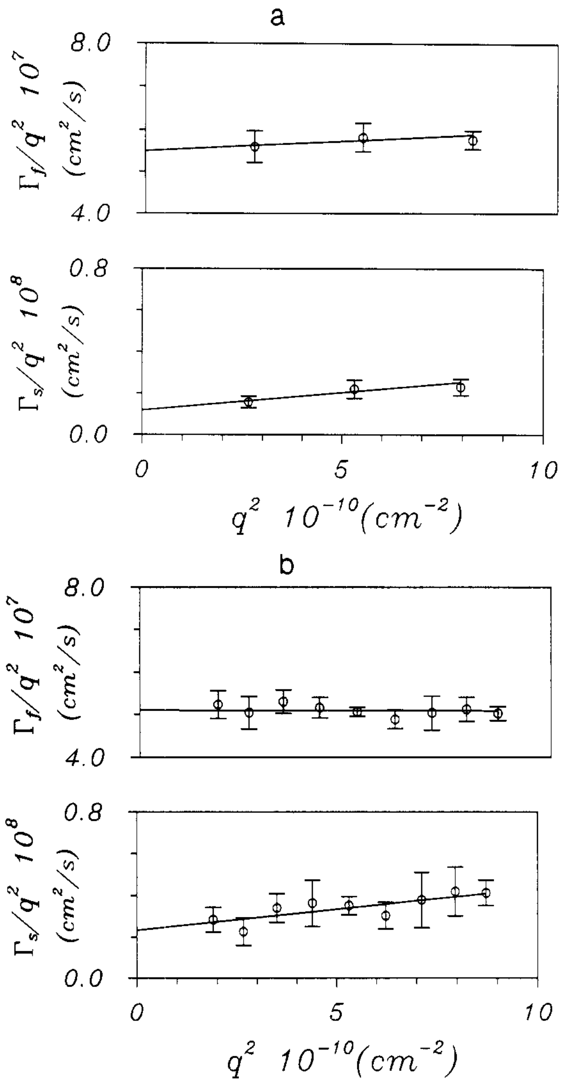

Figure 6. (a) Angular dependence of the fast and slow reduced decay rates of a 12.6×10^{-3} mol/L LPEI ($M_w = 42.0 \times 10^3$) in 10 mM NaCl, prepared from a 0.104 mol/L solution in 1 mM NaCl, measured at the scattering angles 60, 90, and 120°. The values extrapolated to zero angle are $D_f = (5.4 \pm 0.4) \times 10^{-6}$ cm^2/s and $D_s = (1.18 \pm 0.2) \times 10^{-8}$ cm^2/s. (b) Angular dependence of the fast and slow reduced decay rates of a 12.6×10^{-3} mol/L LPEI ($M_w = 88.2 \times 10^3$) in 10 mM NaCl, prepared from a 0.104 mol/L LPEI in 1 mM NaCl, measured at the scattering angles 60, 90, and 120°. The values extrapolated to zero angle are $D_f = (5.1 \pm 0.1) \times 10^{-6}$ cm^2/s and $D_s = (2.33 \pm 0.1) \times 10^{-8}$ cm^2/s.

ICF of this indirectly prepared 1 mM NaCl solution is also represented in Figure 5. It has the usual bimodal shape of LPEI solutions observed on decreasing the NaCl concentration below 10 mM, when filtered through a 0.22 μm pore size filter.

To allow for a better comparison between the solutions of 12.6×10^{-3} mol/L LPEI in 10 mM NaCl prepared by the two methods, the angular dependence of the reduced decay rates was determined and the values were extrapolated to $q = 0$. In parts a and b of Figure 6 the values of Γ_f/q^2 and Γ_s/q^2 are reported obtained at several different angles for LPEI solutions of respectively $M_w = 42.0 \times 10^3$ and 88.2×10^3 in 10 mM NaCl prepared in the indirect way. For both molar masses, Γ_f/q^2 has a very weak angular dependence and extrapolates to $(\Gamma_f/q^2)_{q=0} = (5.4 \pm 0.4) \times 10^{-7}$ cm^2 s^{-1} for the lower and $(\Gamma_f/q^2)_{q=0} = (5.1 \pm 0.1) \times 10^{-7}$ cm^2 s^{-1} for the higher molar mass LPEI. These are in good agreement with the values of $D_{app} = (K_1/q^2)_{q=0}$ determined for solutions prepared in the direct way, which are $(5.4 \pm 0.3) \times 10^{-7}$ and $(5.2 \pm 0.3) \times 10^{-7}$ cm^2 s^{-1} for respectively the lower and higher molar masses. It can thus be concluded that D_{app} and $D_{app,f} = (\Gamma_f/q^2)_{q=0}$ are identical and molar mass independent for this polyelectrolyte concentration. (Values of the reduced decay rates extrapolated to zero angle have not been determined for LPEI in 1 mM NaCl, because of the unreasonable duration of experiments determining ICFs with such weakly scattering samples at several angles.)

On the other hand, for the LPEI solutions in 10 mM NaCl, prepared in the indirect way, the values of the reduced decay rates of the slow mode extrapolated to zero angle [$(\Gamma_s/q^2)_{q=0}$ are $(1.2 \pm 0.2) \times 10^{-8}$ cm^2 s^{-1} and $(2.3 \pm 0.1) \times 10^{-8}$ cm^2 s^{-1} for respectively the lower and higher molar mass LPEI] are significantly different. These results could point to a molar mass dependency of $(\Gamma_s/q^2)_{q=0}$, although it is rather unexpected that the lower molar mass has also the lowest value of $(\Gamma_s/q^2)_{q=0}$.

A similar hysteresis was also observed with LPEI solutions in 25 mM NaCl prepared either directly or indirectly starting from a solution in 1 mM NaCl. The indirectly prepared solutions with bimodal ICFs also have a higher total scattering intensity than the directly prepared solutions with monomodal ICFs, probably caused by the contribution to the total scattering intensity of the scatterers responsible for the slow mode. For the LPEI solution of 12.6×10^{-3} mol/L prepared in the indirect way the correlation times of the fast and the slow modes in the ICFs at an angle of 90° differed, however, not more than a factor of 10. Such a difference is too small to be reliable in the two-exponential fit, taking into account the deviations of both contributions from a pure exponential function.

A slow mode in the ICF of LPEI in 10 mM or higher NaCl concentrations, prepared in the *direct* way, was also observed if the dry-frozen LPEI·HCl was first heated to 100 °C before preparing the solutions. This heating causes the LPEI·HCl samples to lose their water (approximately 10%) content.[7] The correlation time of the fast mode is, however, again identical to the correlation time of the monomodal ICF obtained with the solution prepared directly from the unheated LPEI at the same polyelectrolyte and salt concentration. The slow mode of solutions made of the heated LPEI filtered through a 0.22 μm pore size filter *disappeared* spontaneously after a few weeks. This was checked, *i.e.*, for a 0.104 mol/L LPEI solution, in 100 mM NaCl. No results obtained on solutions prepared with preheated LPEI are included in this work.

Discussion

Single Mode of the Monomodal ICFs and the Fast Mode of the Bimodal ICFs. The ICFs of the light scattered by LPEI, NaPSS, and P2VP solutions show a monomodal decay at high added NaCl concentrations and a bimodal decay with fast and slow modes at low added NaCl concentrations. As shown in Figure 1 the reduced decay rates of the single mode of the former and the fast mode of the latter smoothly link up and increase with decreasing concentrations of added NaCl, in agreement with earlier results.[10,14] From this behavior a comparable origin of both modes may be asserted. This assumption is supported by the observation that the slow mode may be removed by filtration without affecting the fast one and also by the observed hysteresis of the slow mode for LPEI solutions again without a significant interference with the faster mode. Thus a fast mode of a bimodal ICF can become a single mode of a monomodal ICF, and *vice versa*, depending on the preparation method of the samples.

The decay rates of the fast mode and of the single mode of the LPEI solutions were identical to those of the P2VP

Table 6. Calculated Values of c^* in mol/L ($\times 10^3$) at Different NaCl and Polyelectrolyte Concentrations, Taking into Account the Contribution of the Noncondensed Counterions According to Eq 9

	100 mM NaCl	10 mM NaCl	1 mM NaCl
NaPSS, 4.9×10^{-3} mol/L, $M_w = 650 \times 10^3$	6.2	0.88	0.18
P2VP, 104×10^{-3} mol/L, $M_w = 70 \times 10^3$	28.6	12.4	10.9
LPEI, 104×10^{-3} mol/L, $M_w = 42.0 \times 10^3$	31.8	14.2	12.4
LPEI, 104×10^{-3} mol/L, $M_w = 88.2 \times 10^3$	17.5	7.7	6.7
LPEI, 12.6×10^{-3} mol/L, $M_w = 42.0 \times 10^3$	27.9	9.9	4.9
LPEI, 12.6×10^{-3} mol/L, $M_w = 88.2 \times 10^3$	15.5	5.5	2.8

solutions for the same polyelectrolyte (0.104 M) and NaCl concentrations. This agreement indicates that the decay rates of these modes do not significantly depend on the specific chemical composition of these highly charged flexible polyelectrolytes. This was already observed by Smits *et al.*[7] for the light scattering data of LPEI and NaPSS solutions in the semidilute regime with identical polyelectrolyte and added salt concentrations at higher ionic strengths.

The practically independent behavior of the K_1/q^2 and Γ_f/q^2 values on the scattering angle, as shown in Figure 2, allows for these reduced decay rates to be interpreted as apparent diffusion coefficients. The dependence of K_1/q^2 and Γ_f/q^2 on the NaCl concentration, the polyelectrolyte concentration, and the molar mass of LPEI can then be understood by considering the semidilute nature of the polyelectrolyte solutions studied. Polyelectrolyte solutions may be considered as semidilute when the polyelectrolyte concentration is higher than the overlap concentration c^*, which is defined for neutral flexible polymer solutions by[2]

$$c^* = \left(\frac{1}{AN_A}\right)\frac{1}{\frac{4}{3}\pi R_{\mathrm{g},0}{}^3} \tag{8}$$

with l the contour length of the polyelectrolyte, A the length of a monomeric unit, N_A Avogadro's constant, and $R_{g,0}$ the radius of gyration at infinite dilution of the polymer coils. For polyelectrolyte solutions the ionic strength dependence of their $R_{g,0}$ must be taken into account, as pointed out earlier.[3]

For most polyelectrolyte solutions measured in the present investigation the equivalent polyelectrolyte concentrations are rather high compared to that of the added NaCl. In such solutions the contribution of the polyelectrolyte counterions to the ionic strength becomes important. This is taken into account by defining the ionic strength μ as follows.

$$\mu = c_s\left(1 + \frac{a}{Q}\frac{\beta c}{2c_s}\right) \tag{9}$$

Here β is the degree of charge of the polyelectrolyte chain, a the average contour length per unit charge, and Q the Bjerrum length, and counterion condensation according to Manning[30] has been assumed to occur if $Q > a$. The distance between successive charges on the chain a is 0.25 nm for NaPSS, 0.31 nm for 80% charged P2VP, and 0.35 nm for 80% charged LPEI. They are all smaller than the value of the Bjerrum length Q, which is equal to 0.71 nm in aqueous solutions at a temperature of 298 K.

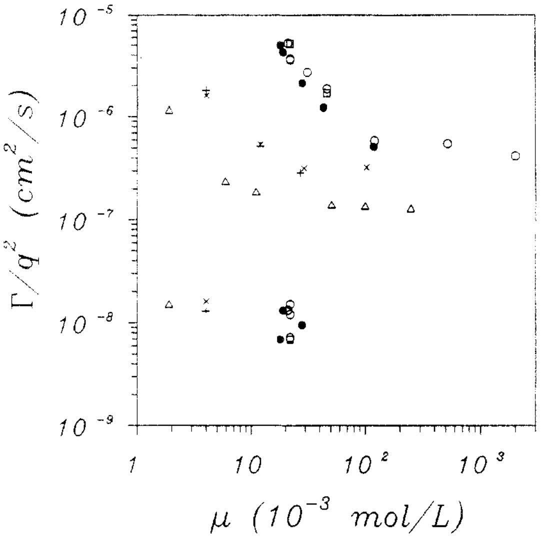

Figure 7. Ionic strength dependence of Γ/q^2 at a scattering angle of 90° (D_{app} for the monomodal correlation functions) of six different polyelectrolyte solutions at constant polyelectrolyte concentration: LPEI ($M_w = 42.0 \times 10^3$) of 0.104 mol/L (○) and of 12.6×10^{-3} mol/L (+); LPEI ($M_w = 88.2 \times 10^3$) of 0.104 mol/L (□) and of 12.6×10^{-3} mol/L (×); P2VP ($M_w = 70 \times 10^3$) of 0.104 mol/L (●); NaPSS ($M_w = 650 \times 10^3$) of 4.9×10^{-3} mol/L (△).

In Table 6 the c^* values of the polyelectrolyte solutions investigated are shown for three concentrations of added NaCl, using eq 9 to evaluate the ionic strengths influencing $R_{g,0}$ and assuming that under all conditions the contour length of the chain is much larger than the total persistence length including its electrostatic part.[3,7] From these calculated c^* values it may be asserted that the polyelectrolyte solutions studied were all semidilute at the lower NaCl concentrations as $c > c^*$. Note that the c^* values calculated for ionic strengths without taking into account the contribution of the noncondensed counterions would even be lower, thus not affecting the conclusion that polyelectrolyte solutions are in the semidilute regime. At very low concentrations of added salt several overlap concentrations may occur due to the increased local stiffness,[3] but at the polyelectrolyte concentrations studied at transient network as assumed above may be expected.

This semidilute nature of the polyelectrolyte solutions explains the molar mass independence of the apparent diffusion coefficients of the LPEI solutions.[3] It is in agreement with the molar mass independence experimentally determined for semidilute polyelectrolyte[4,5,7] and polymer[31] solutions. Similarly, the way K_1/q^2 and Γ_f/q^2 depend on the polyelectrolyte and NaCl concentration may be explained by the dependence of the cooperative diffusion coefficient on the average mesh size of the polyelectrolyte network, as suggested for semidilute solutions.[2,3] This mesh size significantly decreases with increasing polyelectrolyte concentrations and increases with increasing ionic strength.[3–7]

In Figure 7 the reduced decay rates already shown in Figure 1 are now represented as a function of μ as calculated according to eq 9. As the influence of the noncondensed counterion concentration $(a/Q)(\beta c)$ on the ionic strength μ is the larger, the lower the concentration c_s of the added NaCl, the dependence of reduced decay rates on μ is different from that on c_s. In particular, the dependence of Γ_f/q^2 on the NaCl concentration at the lowest NaCl concentrations is considerably affected. The quasi negligible influence of c_s on μ in the NaCl range 1–0.1 mM at the much higher LPEI and P2VP concentration of 0.104 M manifests itself by an accumulation of the reduced decay rates for these solutions at the lowest NaCl concentrations, which tend to the value of the apparent diffusion coefficient in solutions without added salt. This effect is, however, less visible for the LPEI and NaPSS solutions at a much lower polyelectrolyte concentration. The displacement of the three curves in Figure 7 is attributable to the influence of the polyelectrolyte concentration and the molar mass on c^*.

The effect of c on μ could perhaps also explain the quasi independence of the reduced fast decay rate on the polymer concentration in polyelectrolyte solutions without added salt at relatively high concentrations ($c > 10^{-2}$ mol/L), as measured by Förster *et al.*[14] with quaternized P2VP and Koene and Mandel with NaPSS.[1,6] The expected decrease with c of the mesh size in the semidilute solution is counteracted by the increase due to the increase with c of the ionic strength of the solution.

Slow Mode of the Bimodal ICFs. The existence of a slow mode at relatively low salt concentrations is not yet well understood. It has lead various authors to propose different models to explain its origin. The metastability of the slow mode (as revealed, e.g., by its disappearance, either spontaneously or after filtration, and by the hysteresis effect) may help to discriminate between the different models. The models based on collective modes and reptation can hardly be applied to solutions in which the slow mode disappears after filtration. It seems unlikely that reptation and collective modes can be removed *irreversibly* from a solution by filtration. Neither can these models explain why the slow mode should depend on the establishment history of the NaCl concentration of the solution.

The removal of the slow mode by filtration for different polyelectrolyte solutions including NaPSS solutions, first reported by Gosh *et al.*,[23] has led to the claim that the slow mode is due to large particles (parasitic scatterers) *already* present in the dry polyelectrolyte sample or originating in the dialysis bags used. These conclusions were based on the absence of a slow mode in *some* salt-free Heparin solutions, dependent on the manufacturer of the polyelectrolyte, and dependent on the observation of a slow mode in dialyzed water to which no polyelectrolyte was added. The absence of the slow mode at higher added salt concentrations was explained by the larger scattering intensity of these solutions.

To check this hypothesis, we have duplicated the water dialysis experiment of Gosh *et al.*[23] For this experiment we have dialyzed water against water for 1 week, which was the typical duration time of a dialysis experiment. Contrary to the results of Gosh *et al.*,[23] we have not observed a slow mode in the ICFs of this water after filtration through a 0.22 μm pore size filter. This difference might be due to our purification procedure of the membranes (see Preparation of the Samples). As we observed for bimodal ICFs of polyelectrolyte solutions at relatively low salt concentrations the origin of the slow mode cannot in our case be sought in impurities introduced by the dialysis procedure.

The hysteresis effects observed in the present investigation exclude the possibility that the slow mode is due to large particles already present in the dry polyelectrolyte salt, as suggested by Gosh *et al.*[23] According to that hypothesis, a slow mode should always or never be present in ICFs of LPEI in the presence of 10 mM NaCl and should not depend on the establishment history of the NaCl concentration as observed for LPEI. This hypothesis concerning the origin of the slow mode is also contradicted by the fact that for P2VP in 10 mM NaCl, which gives bimodal ICFs at polyelectrolyte concentrations $c > 3 \times 10^{-2}$ mol/L, a monomodal ICF has been observed at a much higher dilutions (see Table 1).

The argument that the absence of a slow mode in solutions at the higher salt concentration end is due to a higher scattering intensity is incompatible with our observation that for solutions of identical P2VP and LPEI concentrations bimodal ICFs were observed at already a higher NaCl concentration for the former (10 mM; see Table 2) than for the directly prepared LPEI solutions (1 mM NaCl; see Table 3), despite the much stronger light scattering of the P2VP solutions.

A plausible explanation for the origin of the slow mode is the presence of large "structures" in solutions of relatively low NaCl concentrations. It must then be assumed that these structures either have an average size large enough to be filtered out or are disrupted by the filtration through a 0.1-μm pore size. Moreover, they should not immediately break down in LPEI solutions upon an increase of the NaCl concentration (hysteresis).

Our results indicate that, whatever these structures are, they must *originate* in the polyelectrolytes themselves. Possibly they are due to the clustering of the polyelectrolytes at low added salt and high polyelectrolyte concentrations. This is supported by the hysteresis in the appearance of the slow mode in the ICFs of LPEI solutions (see Figure 5). Once appearing at low salt concentrations (1 mM NaCl) these clusters apparently persist under metastable conditions when the NaCl concentration is increased.

Another argument for the large clusters to originate in the polyelectrolyte chains may be found in the disappearance of the slow mode upon dilution, as shown in Table 1 for the P2VP solutions in 10 mM NaCl. The *disappearance* of the slow mode upon dilution cannot only be due to a lowering of the concentration of these clusters, as the faster mode does remain detectable. Rather it must be assumed that the clusters tend to disappear or deform upon the dilution, which is *a priori* not expected for parasitic scatterers. The disappearance of only the slow mode upon the dilution was reported before for NaPSS[12] and quarternized P2VP[14] in solutions without added salt.

The formation of such structures or clusters in the polyelectrolyte solutions with low added salt concentrations is also supported by the measurements of Sedlak *et al.*[32] They have measured for solutions of 36 g/L of charged poly(methacrylic acid) without added salt a strong reduction of the amplitude ratio B_f/B_s up to a factor of 10 by increasing the temperature from 60 to 90 °C and a hysteresis of the B_f/B_s ratio by the variation of the temperature. This can only be explained by an intrinsic change within the polyelectrolyte solutions. It is rather unlikely that particles already present in the polyelectrolyte salt or introduced into the solutions by, for example, the use of the dialysis membranes, can be responsible for such a systematic concentration and molar mass dependence of the slow mode of salt-free NaPSS solutions as reported by Sedlak *et al.*[12,20]

We have observed important dissimilarities in the appearance of the slow mode for the different polyelectrolyte samples studied. Thus the NaCl concentration ranges at which the slow mode appears are different for the three polyelectrolytes P2VP, LPEI, and NaPSS studied in this investigation. For P2VP solutions a slow mode was already observable in 10 mM NaCl, whereas for LPEI (directly dissolved) in 10 mM NaCl no slow mode could be detected. The behavior of the LPEI solutions was similar to that of NaPSS solutions as no slow mode was detected in 10 mM NaCl even at much higher NaPSS concentrations than the LPEI concentrations we used.[5] It is not possible to relate these dissimilarities to differences in the chain lengths or the linear charge density only. A difference between the different polyelectrolytes was also observed regarding the possibility to eliminate the slow mode by filtration. Plugging of the 0.1 μm pore size filters was observed for P2VP solutions in 1 mM NaCl, which did not occur for analogous LPEI and NaPSS solutions. This plugging corresponds to the plugging reported by Sedlak[32] for filtration through a 0.1-μm filter of a 45 g/L NaPSS (M_w = 47 000) solution. Only partial removal of the slow mode by filtration was observed for NaPSS (M_w = 5000) solutions without added salt by Sedlak *et al.*[24] They also reported that in solutions of poly(methacrylic acid) (M_w = 5000) without added salt the slow mode could not be eliminated by filtration through 0.1 μm pore size filters.

The origin and the composition of the structures in the polyelectrolyte solutions at low ionic strengths as well as the nature of the slow mode still remain, however, *a subject of discussion.*[33] It is tempting to relate the formation of these structures to the entangling of polyelectrolytes as was concluded for neutral polymer solutions showing a slow mode.[22] For polystyrene in toluene these clusters were found to disappear in time,[21] indicating that the situation without a slow mode is the true thermal equilibrium. Such a hypothesis seems to be attractive for polyelectrolyte solutions too, since it explains the disappearance of the slow mode in time as we found for the lower molar mass of LPEI and as is also reported for poly(adenylic acid) by Mathiez *et al.*[21] It could also account for the permanent removal of the slow mode by filtration assumed to break the structures. For low molar mass DNA a *reversible* disappearance of the slow mode by filtration has already been observed previously.[9] For other polyelectrolyte solutions at low ionic strengths it may take a very long time (perhaps even infinitely long) before a true equilibrium state is reached. At the moment, the question may even be raised whether the origin of the slow mode is an interesting property to study or whether it is an artifact indicative of the difficulties to obtain polyelectrolyte solutions at equilbrium depending on the previous history of the sample and the preparation method used. In this respect it should be recalled that water-free LPEI samples gave already ICFs with a slow mode at higher ionic strengths than the corresponding unheated ones containing about 10% water.

To clarify this unsatisfactory situation, more *systematic* investigations are necessary on well-characterized polyelectrolyte solutions, with careful and *detailed* information on the preparation methods used. This could lead to a meaningful comparison of the results obtained in different laboratories and, perhaps, a better understanding of the phenomena underlying the origin of the slow mode.

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