Domain Structure of Polyelectrolyte Solutions: Is It Real?

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Received August 18, 1992

ABSTRACT: Static and dynamic light scattering experiments were performed on salt-free solutions of sodium poly(styrenesulfonate) (M_w = 5000) and partially ionized solutions of poly(methacrylic acid) (M_w = 30 000). Prior to measurements, solutions were filtered through 0.1- and 0.2-μm pore-size membrane filters. Attention was focused on the comparison of two sets of data obtained with 0.1- and 0.2-μm filters, respectively. Recently it was reported[30-34] that the slow mode, which is typical for salt-free polyelectrolyte solutions, is caused by the presence of impurities or entanglements in solution and is "removable" by filtration through a 0.1-μm filter. Our results contradict these conclusions and show that the slow mode arises as a result of electrostatic interactions in solution. Filtration through a 0.1-μm filter has only relatively small, quantitative influence on light scattering data. The observed effects are interpreted as a small distortion of multichain domains, which are forced to pass through pores smaller than their dimensions. Domains in solution are considered to give rise to the slow mode.

Introduction

The structure and dynamics of polyelectrolyte solutions with low salt concentrations currently belong to the least understood parts of polymer physics. Both theoretical treatment and experimental research meet many difficulties. Consequently, this issue is partly controversial.

Problems in theoretical approaches and interpretations of experimental data arise from the complexity of a system consisting of several components: polyions, counterions, co-ions, and solvent. The multicomponent nature of polyelectrolyte solutions is reflected in many types of interactions which should be taken into account: intramolecular interactions between segments of the same macromolecule, intermolecular interactions between different macromolecules, interactions between polyions and counterions, electrostatic screening by low molecular weight salt, polymer-solvent interactions, and entropic forces (mainly due to the presence of counterions). Electrostatic interactions are long range and relatively strong in the low-salt limit.

Because of the complexity of the problem, various approximations and assumptions are used in theoretical treatments to simplify the situation. Consequently, different results are obtained.

A rodlike conformation of polyions which are ordered parallel in a hexagonal structure was proposed by Lifson and Katchalsky[1] on the basis of strong electrostatic repulsions between charges on chains.

According to de Gennes et al.,[2] polyions can be more flexible at higher concentrations and, similarly to neutral polymers, form entangled solutions. There is no preferential orientation of chains in the net, and hence this model is called isotropic. It was later refined by Odijk,[3] who applied scaling theory based on the concept of an electrostatic persistence length. Scaling relations were derived for a correlation length and the persistence length. Witten and Pincus[4] proposed a different approach to the isotropic model by taking into account the role of polyion screening in an entangled solution. Only one length scale was found in solution as the correlation length was equal to the persistence length.

The two-state three-dimensional model of Ise[5] is based on experimental results, mainly the naked-eye microscopic observations of charged latex particles in solution. It was reported that ordered regions with a higher density of particles can be found while the rest of the solution is relatively disordered. As a mechanism of the origin of these structures, the authors proposed an attractive interaction between charged particles through the intermediary of counterions.[6] They suggested that the situation in solutions of linear flexible polyions is very similar: Chains are in a compact conformation as a result of intramolecular attractive forces and form ordered and disordered regions. A similar idea of "temporal aggregates" was proposed by Schmitz.[7] The existence of aggregates was explained as a result of fluctuating attractive forces created by counterion dynamics.

The interpretation of experimental data obtained by various techniques is also rather controversial. In some cases even the same data are interpreted in different ways, using different models. Experimental results obtained under conditions of low salt concentration exhibit unusual features, which are qualitatively different from neutral solutions.

Viscosity measurements show pronounced maxima in plots of the reduced viscosity vs concentration.[8,9] Positions of maxima roughly correspond to molar concentrations of low molecular weight salt. The salt concentration is nonzero even under "salt-free" conditions. In thoroughly deionized water it was estimated as 4×10^{-6} mol/L.[8,9] The existence of maxima is ascribed to the screening of long-range intermolecular interactions by the residual electrolyte in solution. Positions of maxima do not depend on molecular weight,[8] and hence the same behavior is observed under conditions $c/c^* \ll 1$ and $c/c^* \sim 1$, where c^* is the crossover concentration based on the isotropic model.

Other frequently used techniques are small-angle X-ray and small-angle neutron scattering. The characteristic feature of these experiments is the existence of maxima in angular dependencies of scattered radiation. They were interpreted in different ways. One interpretation[10] is based on the isotropic model and explains the existence of maxima as a consequence of a correlation hole, a region around a charged chain which is impenetrable by other chains. The other interpretation[11] explains the maxima as a result of three-dimensional ordering in solution. Experiments on samples with a broad range of molecular weights suggest that the wave vectors of the maxima scale as $q_m \sim c^{1/3}$ in the dilute regime and $q_m \sim c^{1/2}$ in the semidilute.[12] The authors proposed that a three-dimensional ordering is present in the dilute regime, while in the

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semidilute, an entangled network gives the $c^{1/2}$ dependence.

Characteristic of dynamic light scattering on polyelectrolyte solutions with low salt concentrations is the occurrence of two dynamic modes with widely separated characteristic times, a relatively fast one on the order of several microseconds and a relatively slow one on the order of 10^3–10^4 μs. The fast mode is diffusive in nature and is interpreted as a coupled diffusion of polyions and counterions.[7,13-15] At higher concentrations, where an entanglement of chains can be expected, the fast mode was interpreted as a counterion-accelerated (coupled) blob diffusion[16] or as a simple gel mode of the network.[17] The phenomenon of electrostatic coupling was observed also at higher concentrations of added salt and was theoretically described by several authors.[18-20]

The occurrence of the slow mode is less understood and sometimes even referred to as "mysterious". It was observed for the first time by Lin, Lee, and Schurr[19] in poly(L-lysine) solutions at low salt concentration. A pronounced drop in diffusion coefficient was observed as the salt concentration was decreased through some critical value. This transition was called "ordinary–extraordinary", indicating that the system exhibits extraordinary (unusual) behavior, which is not typical for neutral solutions. Later it was shown[21] that it is a splitting of diffusion coefficient rather than a drop. Two diffusive modes were simultaneously observed also in salt-free or low-salt solutions of t-RNA,[22] DNA,[14] BSA, latex particles, polynucleosomes,[7] polyadenylic acid,[23] poly(acrylic acid),[24,25] poly(methacrylic acid),[15] sodium poly(styrenesulfonate),[13,16,26] and quaternized poly(vinylpyridine).[17] It seems that the main features of the behavior of salt-free polyelectrolyte solutions, especially the existence of the slow mode, are common for a very broad spectrum of charged systems.

Mainly on the basis of angular dependencies of the apparent slow diffusion coefficient, total scattering intensity, and the scattering intensity corresponding to the slow mode, it was concluded that formation of multichain domains (clusters) is responsible for the presence of the slow mode.[7,13,15] Apparent dimensions of domains were estimated as ~100 nm irrespective of molecular weight,[16] which indicates that a variable number of chains is involved in one domain. In the case of small molecular weights, this number can be on the order of hundreds or thousands. The slow-mode behavior was investigated in detail as a function of concentration,[15,17,26] molecular weight,[16,17] charge density,[15] temperature,[27] and dielectric permittivity of solvent.[28,29] On the basis of these results, it was concluded that (1) some kind of attractive interaction is necessary to give rise to domains and (2) the mechanism of domain formation is of electrostatic nature; i.e. charge interactions play an important role in this process.[15,16,28]

Recently light scattering data on solutions of proteoglycan monomers, heparin, chondroitin 6-sulfate, poly(styrenesulfonate), acrylamide/sodium acrylate copolymers, and other polyelectrolytes were presented.[30-34] It was reported[30-34] that the slow mode was not measurable when samples were filtered through a 0.1-μm pore-size membrane filter instead of conventional 0.2-μm pore-size filters, which are used in light scattering experiments to avoid dust particles. (In some cases even 0.05-μm filters were used.) It was concluded that the slow mode is caused by a small amount of large particles in solution which are "removable" by filtration through a proper size filter. The authors noted that[30] "there is a number of ways that these aggregates can form, including lyophilization prior to dispersal in solvent, and no impurities need be involved". The aggregates did not reappear after removal, at least on a time scale of days.[30-34] (On the other hand, a gradual reappearance of the slow mode after filtration was reported in other papers.[35,36]) The "loss" of the slow mode as the ionic strength of the solution increases was explained as a result of the weak scattering signal from impurities or entanglements getting buried in the sharply increasing scattering from polyelectrolyte molecules.[34]

The aim of the current work is to contribute to the solution of this discrepancy. The strategy will be to perform simultaneous measurements with both 0.1- and 0.2-μm filters and to make consequent conclusions about the nature of the slow mode.

Materials and Methods

Poly(methacrylic acid) (PMA; M_w = 30 000) was prepared by radical polymerization and purified by ion exchange. A mixed-bed resin, Bio-Rex MSZ 501(D), from Bio-Rad was used. Sodium poly(styrenesulfonate) (NaPSS; M_w = 5000) was purchased from Pressure Chemical Co. as a molecular weight standard with polydispersity M_w/M_n = 1.05. The commercial sample was also purified by ion exchange. The acidic form of poly(styrenesulfonate) was converted to the sodium salt by titration with sodium hydroxide. Lyophilized samples were dissolved in deionized water with a resistivity of 15 MΩ·cm.

Solutions were filtered through 0.1- and 0.2-μm polycarbonate membrane filters from Nuclepore. These filters were chosen because the pores are well-defined and relatively monodispersed. They are prepared by using a two-step process of nuclear particle track-etching. During the first step, polymeric films are exposed to collimated, charged particles in a nuclear reactor. As particles pass through the material, they leave sensitized tracks. Second, the tracks left by the particles are etched into uniform, cylindrical pores. By controlling the length of the etching process, a specified pore size is produced. To check for the loss of polymer during filtration, solution concentrations were established after the measurements by freeze-drying and weighing the polymer. Because of relatively small molecular weights, no significant loss of polymer was observed.

A homodyne spectrometer consisting of a custom-built goniometer and an ALV5000/800 multibit correlator with 256 geometrically placed channels was used. An Ar laser (Carl Zeiss ILA 120-1) with 200 mW at λ = 514.5 nm was used as the light source. Correlation curves were analyzed with the CONTIN program yielding the distribution function of decay times $A(\tau)$ defined as

$$g^{(1)}(t) = \int_0^\infty A(\tau)e^{-t/\tau}\,\mathrm{d}\tau \qquad (1)$$

where $g^{(1)}(t)$ is the normalized field autocorrelation function, t is the delay time, and τ is a decay time. A transputer board ALV800 was used for CONTIN calculations. Correlation functions were typically double exponentials with two well-separated modes (fast and slow). Characteristic decay times τ_f and τ_s and relative amplitudes A_f and A_s of the two modes were evaluated through the moments of the distribution function $A(\tau)$. Diffusion coefficients were calculated as $D_f = (1/\tau_f)q^{-2}$ and $D_s = (1/\tau_s)q^{-2}$, where q is the scattering vector defined as $q = (4\pi n/\lambda_0)\sin(\Theta/2)$, with n the solution refractive index, λ_0 the laser wavelength, and Θ the scattering angle.

Static light scattering experiments were performed with the same goniometer. To achieve a better quality of data, the laser beam was not focused during these measurements. Scattering intensities were measured by photon counting. Doubly distilled and filtered benzene was used as a standard to evaluate absolute scattering intensities.

Results and Discussion

The choice of the two polymers for our experiments was motivated by several factors: (1) Well-defined samples can be prepared with sufficient purity. (2) Both polymers have been extensively investigated.[13,15,16,26-28] (3) The

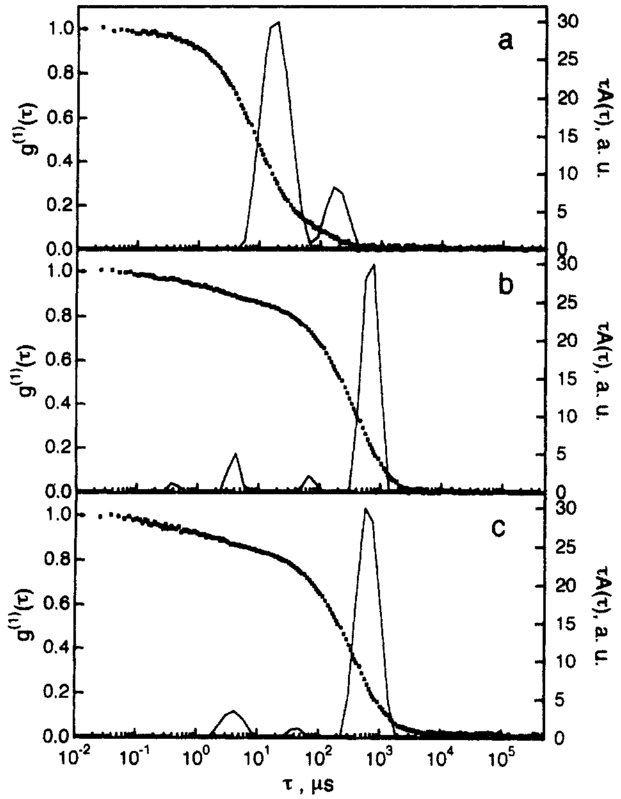

Figure 1. Composite correlation functions and spectra of relaxation times for solutions of PMA (M_w = 30 000): (a) sample with $\alpha = 0$, filtered through a 0.1-μm filter; (b) sample with α = 0.4, neutralized by adding an aliquot amount of NaOH through a 0.1-μm filter; (c) sample with $\alpha = 0.4$, filtered once more through a 0.1-μm filter.

NaPSS sample with extremely low molecular weight (M_w = 5000) was chosen to minimize the influence of relatively small filter pores on single chains during filtration. Our aim was to investigate only the influence on domains (aggregates). Individual molecules should pass freely through the filter. (4) PMA is a weak polyelectrolyte with very low self-ionization. Various degrees of ionization can be reached by neutralization with a proper alkali. This was the basis for our previous experiments,[15] where solutions of PMA neutralized to different degrees were investigated by dynamic light scattering. Samples were prepared from a stock solution with $\alpha = 0$ (uncharged polymer) by adding aliquot amounts of NaOH solution. Afterward, samples were filtered and sealed. The "intensity" of the slow mode was proportional to the degree of neutralization. At $\alpha = 0$, the correlation function was almost single exponential and hence the slow mode almost "invisible". With increasing α, the slow mode gained quickly in influence. Oppositely, addition of HCl suppressed a slight natural ionization at $\alpha = 0$. The correlation curve was then clearly single exponential. This experiment has demonstrated by itself that the slow mode is due to the charging of chains, not to the presence of impurities or entanglements.

To exclude the possibility of the presence of impurities or entanglements in the neutral stock solution and to investigate the influence of filtration through a 0.1-μm pore-size filter on the slow mode, a similar experiment was performed with the 0.1-μm filter. Figure 1a shows the correlation function and the spectrum of characteristic times for the solution with $\alpha = 0$, which was filtered through a 0.1-μm filter. Figure 1b corresponds to the sample with $\alpha = 0.4$. This sample was prepared by adding several drops of NaOH through a 0.1-μm filter to the scattering cell with the original solution with $\alpha = 0$. Clearly, the addition of thoroughly purified NaOH results in a pronounced slow mode, as can be seen from the comparison of parts a and b of Figure 1.

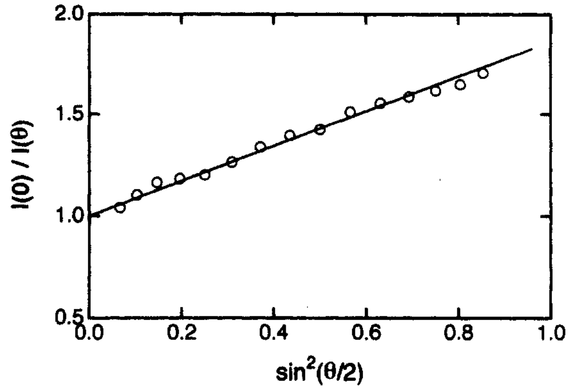

Figure 2. Dependence of the normalized reciprocal excess scattering intensity on scattering angle: PMA (M_w = 30 000), α = 0.4. Sample was prepared by adding an aliquot amount of NaOH to the stock solution with $\alpha = 0$. Both the stock solution and NaOH were filtered through a 0.1-μm filter.

Table I
Values of Fast Diffusion Coefficient D_f, Slow Diffusion Coefficient D_s, Ratio of Scattering Amplitudes of the Two Modes A_s/A_f, Apparent Radius of Gyration of Domains $R_{G,app}$, and Total Scattering Intensity I for Different Concentrations of NaPSS (M_w = 5000, 0.1-μm Filter)[a]

c, g/L	D_f, 10^{-6} cm²/s	D_s, 10^{-9} cm²/s	A_s/A_f	$R_{G,app}$, nm	I
2	5.52	80.0	8.3	26	0.31
4	5.77	70.1	6.9	34	0.72
8	5.60	66.2	6.5	37	1.44
16	5.79	51.5	9.2	62	2.90
22	6.27	48.0	7.5	75	4.20

[a] All samples were filtered through a 0.1-μm filter. Scattering intensities are extrapolated to zero angle and normalized by the scattering intensity of a benzene standard.

The excess scattering intensity shows an angular dependence for $\alpha = 0.4$ (Figure 2), contrary to the case with $\alpha = 0$. An apparent radius of gyration of scatterers responsible for this dependence $R_{G,app}$ = 40.5 nm was calculated according to the formula

$$I(0)/I(\Theta) \cong 1 + C(R_{G,app})^2 \sin^2 \Theta/2 \qquad \Theta \to 0 \qquad (2)$$

where $I(\Theta)$ is the scattering intensity corresponding to the scattering angle Θ and $C = {}^1/_3(4\pi n/\lambda_0)^2$. This value is close to results of previous experiments,[15,16] where the scatterers were identified as multichain domains (clusters).

The sample with $\alpha = 0.4$ was filtered again through a 0.1-μm filter and measurements were repeated. The corresponding correlation function and the spectrum of characteristic times are shown in Figure 1c. Parts b and c in Figure 1 differ very little, and the values of diffusion coefficients calculated from these spectra are relatively close ($D_f = 4.90 \times 10^{-6}$ cm²/s, $D_s = 31.0 \times 10^{-9}$ cm²/s for Figure 1b, and $D_f = 4.80 \times 10^{-6}$ cm²/s, $D_s = 37.3 \times 10^{-9}$ cm²/s for Figure 1c). It can be concluded that the repeated filtration of the sample had no pronounced effect on the results of these measurements.

A more detailed investigation was performed with the NaPSS sample. Solutions with concentrations ranging from 2 to 22 g/L were filtered through 0.1- and 0.2-μm filters. Static and dynamic light scattering measurements were performed on both sets of samples. Results are summarized in Tables I and II and Figures 3 and 4. Absolute excess scattering intensities I are evaluated as

Table II
Values of Fast Diffusion Coefficient D_f, Slow Diffusion Coefficient D_s, Ratio of Scattering Amplitudes of the Two Modes A_s/A_f, Apparent Radius of Gyration of Domains $R_{G,app}$, and Total Scattering Intensity I for Different Concentrations of NaPSS (M_w = 5000, 0.2-μm Filter)[a]

c, g/L	D_f, 10^{-6} cm²/s	D_s, 10^{-9} cm²/s	A_s/A_f	$R_{G,app}$, nm	I
2	5.67	46.0	40	48	1.50
4	5.89	42.1	36	64	3.51
8	5.64	38.2	36	72	7.20
16	6.01	35.9	45	87	14.5
22	6.05	34.0	40	105	21.0

[a] All samples were filtered through a 0.2-μm filter. Scattering intensities are extrapolated to zero angle and normalized by the scattering intensity of a benzene standard.

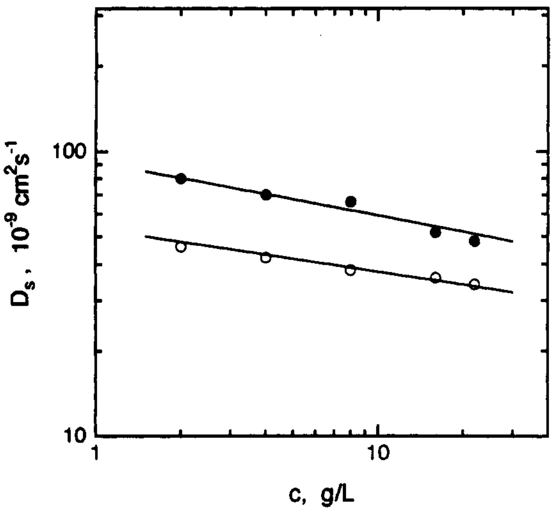

Figure 3. Dependence of slow diffusion coefficient D_s on concentration: NaPSS, M_w = 5000. Samples were filtered through a 0.1-μm filter (●) and through a 0.2-μm filter (○).

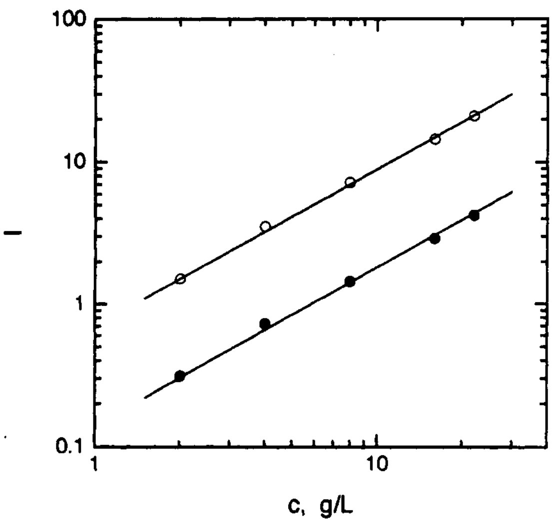

Figure 4. Concentration dependence of excess scattering intensity: NaPSS, M_w = 5000. Samples were filtered through a 0.1-μm filter (●) and through a 0.2-μm filter (○). Intensities are extrapolated to zero angle and normalized by the scattering intensity of a benzene standard.

a ratio of the scattered light intensity to the intensity scattered by a distilled and filtered benzene standard. All values are extrapolated to zero angle.

The following conclusions can be made from the comparison of the two sets of data: In the case where a 0.1-μm filter is used (Table I) instead of a 0.2-μm filter (Table II), (1) the fast diffusion coefficient is the same, (2) the slow diffusion coefficient is systematically slightly higher, (3) A_s/A_f ratios and absolute scattering intensities are lower, and (4) the apparent radii of gyration of domains are slightly smaller. As can be seen from Figures 3 and 4, slopes of concentration dependencies of D_s and I are independent of the filter size.

The fast diffusive mode is interpreted as a coupled diffusion of polyions and counterions. As individual molecules are not altered by filtration, D_f is independent of the filter size. On the other hand, apparent radii of gyration of domains in PMA and NaPSS solutions were estimated as 50–100 nm[15,16] and hence diameters of domains correspond to 100–200 nm. It follows that in the case of a 0.1-μm pore-diameter filter, domains are forced to go through pores smaller than their dimensions. This has a weak disrupting effect on domains. They are smaller in size and scatter less light, and the slow diffusion coefficient is consequently higher.

However, the presence of domains is still very pronounced. Also slopes of concentration dependencies of the slow diffusion coefficient and the absolute scattering intensity are not altered by using different filters (Figures 3 and 4). A relatively large slope of the concentration dependence of the absolute scattering intensity is typical for the presence of domains in solution.[26]

Repeated measurements on samples filtered through a 0.1-μm filter have not shown considerably different results after a couple of hours. However, repeated measurements on a scale of longer times might be a task for further investigation.

Problems in filtration occurred with higher molecular weights and concentrations. For instance, a solution of NaPSS with M_w = 47 000 at c = 45 g/L either did not flow through a 0.1-μm filter or aggregated under higher pressures. The aggregation was accompanied by a visible turbidity and a 10-fold increase in the scattering intensity.

Other problems in using small pore-size filters may occur as well. The retention of polymer molecules can be relatively high and hence the actual concentration much lower. Therefore it is necessary to check concentrations after filtration. It was shown[26] that the slow mode is less pronounced at lower concentrations. In addition to the retention, it is very difficult to predict the influence of filtration on individual polyions when a smaller pore size than the radius of a single chain is used.[30,33]

Current experiments have shown that the origin of the slow mode is electrostatic in nature and that it is not possible to explain it as a result of the presence of impurities or stable entanglements in solution. Impurity- or aggregate-free solution of neutral PMA exhibits a pronounced slow mode after several drops of clean (impurity- or aggregate-free) solution of NaOH are added. The only change introduced into the solution by this procedure is charging of the PMA chains.

Other simple arguments may be advanced as well. Apparent radii of gyration of domains are dependent on solution ionic strength, degree of ionization, and polymer concentration.[7,17,25,26] Domains grow in size with increasing charge interactions given by increasing degree of ionization and/or decreasing ionic strength. Similarly, they grow in size with polymer concentration. Thus a simple dilution of solution can "destroy" domains. With decreasing concentration, apparent dimensions of domains decrease and the slow diffusion coefficient increases and finally merges with the fast diffusion coefficient. At some critical concentration, the slope of the concentration dependence of total scattering intensity changes, also indicating the dissolution of domains.[26] All these results cannot be explained by the presence of fixed-size impurities or entanglements, which are removable by filtration through a proper size filter.

The slow mode is specifically dependent on molecular weight.[16] The slow diffusion coefficient sharply decreases with molecular weight, whereas apparent dimensions of domains are rather molecular weight independent. In the case of stable, filterable aggregates or impurities, a different relationship between the size and the diffusion coefficient is expected. In addition, hydrodynamic radii calculated from the slow diffusion coefficient according to the Stokes–Einstein formula appreciably exceed dimensions of filter pores (e.g., $R_H = 3\ \mu m$ for a solution of NaPSS, $M_w = 780\,000$, $c = 45.6$ g/L, filtered through a 0.2-μm filter[16]).

The intensity of the slow mode and the tendency to form domains are also dependent on dielectric permittivity of solvent,[28,29,37] as this quantity strongly influences effective charges and charge interactions.

Numerous arguments can be also found in ref 38. The most convincing are that the ordinary–extraordinary transition is fully reversible (some samples have undergone three or more complete cycles from extraordinary to ordinary regime and back[19]) and that the extraordinary regime can be disrupted by applying a sinusoidal electric field.[39]

Our preliminary experiments on salt-free NaPSS solutions[40] show that the slow mode is observable also when samples are not filtered before measurements (dust and other large contaminants are removed by centrifugation of solutions directly in scattering cells). This contradicts the suggestion that polymer aggregates may form just from a buildup in polymer concentration at the membrane or from other surface effects.[34] It is shown[40] that the slow mode is most pronounced when no filter is used. Filtration of solutions suppresses the slow mode. This effect is stronger for 0.1-μm filters than for 0.2-μm filters.

Finally, a few comments can be made on results presented in ref 34. The authors investigated several polyelectrolytes (heparin, chondroitin sulfate, NaPSS, poly(L-lysine), sodium polyacrylate, and BHA) from different manufacturers. They used different pore-size filters from 0.45 to 0.05 μm. The general trend was that they observed the slow mode when using a larger pore size and no slow mode when using a smaller pore size. The threshold pore size was different from case to case. Samples from certain manufacturers did not even show the slow mode at all. Unfortunately, not all samples were dialyzed before measurements. The authors stated that their samples had generally "undetectably low excess salt levels, as measured by conductivity before and after dialysis". As the conductivity of salt-free or low-salt polyelectrolyte solutions is a rather complex quantity, it would be preferable if each sample were dialyzed instead of relying on this conclusion. Additionally, our experience is that even dialyzed grades of polyelectrolytes from some manufacturers have rather high salt levels, which strongly influence the relative amplitude of the slow mode.[16] Second, to make correct conclusions from the data, information on the relative amplitude of the slow mode (e.g., as an A_s/A_r ratio) would be more helpful than the "yes and no" classification. Information on polymer concentration (Table I, ref 34) is also necessary.

Our conclusion is that although the slow mode cannot be filtered out in the sense of removing stable particles from solution, a small quantitative difference in data is observed when a 0.1-μm filter is used instead of a 0.2 μm filter. Generally, pressure filtration through a 0.1-μm filter corresponds to applying mechanical forces on domains. Investigation of the influence of these forces on the stability of domains can be a new challenging task on the way toward understanding the behavior of low-salt polyelectrolyte solutions.

Acknowledgment. We are grateful to Professor Norio Ise for bringing refs 30–33 to our attention.

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Registry No. PMA, 9080-79-9; NaOH, 54193-36-1; NaPSS, 25087-26-7.