Comments on “Domain Structure of Polyelectrolyte Solutions: Is It Real?”

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There has been some debate about whether the “slow mode” of diffusion often reported for dynamic light scattering experiments on polyelectrolyte solutions at low added salt $C_p$ corresponds to the formation of domains, fleeting entanglements, long-range order, etc., or merely to a small population of entangled or aggregated polymers and other particles, which already exist or are at least nascent in the dry polyelectrolyte material. The latter explanation, concluded from extensive experiments in refs 9–13, holds that these polyelectrolyte aggregates and/or other particles (A/P) which are not completely eliminated by centrifugation and filtration procedures give weak but autocorrelatable signals at low ionic strengths where the well-dispersed polyelectrolyte chains themselves are osmotically very incompressible and scatter very little light of their own. When the ionic strength of the medium increases, the scattering from the polyelectrolytes increases dramatically, a long-known and well-documented fact, and the aggregate/particle explanation asserts that this signal is often strong enough to bury the feeble intensity from the aggregates, thus leading to the “loss” of the slow mode. (Experimental results and theoretical considerations, pp 1117 and 1120 of ref 13, respectively, indicate that the scattering from the aggregate population does not change appreciably with $C_p$.) The analogy was made that the A/P in low ionic strength solutions are similar to the stars in the night sky, which can no longer be seen when the sun rises (i.e., when $C_p$ increases and the polyelectrolytes scatter brighty).

The work mentioned in the title of this paper, hereafter referred to as “Domain Structure...”, takes specific issue with the aggregate/particle explanation of refs 9–13 and offers data to refute it. It seems, however, that the data in “Domain Structure...” are fully consistent with the data of refs 9–13 and provide further evidence for the aggregate/particle explanation.

Comments on Sodium Poly(styrenesulfonate) (NaPSS) Data. For filtrations through 0.1- and 0.2-$\mu$m filters, respectively, Tables 1 and 2 in “Domain Structure...” compare the fast and slow modes of diffusion $D_f$ and $D_s$, the ratio of slow to fast scattering amplitude $A_s/A_f$, the apparent radii of gyration $R_G_{eff}$, and the total scattering intensity $I$.

At all concentrations $R_G_{eff}$ decreases and $D_s$ increases when the solutions are filtered through 0.1-$\mu$m filters instead of 0.2-$\mu$m filters. Interestingly, at the lower concentrations (where refs 9–13 were done) the “slight” differences in $D_s$ and $R_G_{eff}$ reported between 0.1- and 0.2-$\mu$m filtration amount almost neatly to a factor of 2, the ratio of the pore sizes. The apparent Stokes–Einstein diameters corresponding to the filtrations through 0.1- and 0.2-$\mu$m filters for 2 g/L solutions of NaPSS are roughly 0.063 and 0.11 $\mu$m, respectively. The statement is also made that the 0.1-$\mu$m measurements were not considerably different after a couple of hours. These results are consistent with ref 13 and the interpretation that the filtration is removing A/P down to roughly the pore size of the membrane used and that there is no evolution in time of the slow mode.

If the slow mode is eliminated and does not reappear or it is altered quantitatively in character by different filtrations and does not regain a definite well-characterized state, the physical state corresponding to it is not a reversible, equilibrium state on the time scales appropriate to electrostatic, steric, and hydrodynamic forces that govern most solution dynamics. According to an experiment described in the Note Added To Proof in ref 13, no evidence was found for the notion of a strong Coulomb barrier hindering the reassociation of the domains after they were eliminated by filtration.

Figure 4 in “Domain Structure...” gives the scattering intensity vs polymer concentration, $C_p$, for 0.1- and 0.2-$\mu$m-filtered NaPSS solutions. According to $A_s/A_f$ in Tables 2 and 1, the majority of the scattering is from the slow mode in both cases. The slope of Figure 4 is virtually unity, which is what the simple model from the A/P explanation in ref 13 predicts (eqs 8 and 14) when the A/P scattering dominates and the concentration of A/P varies directly with the net concentration of the sample solution. According to that simple model, this slope should also be independent of the pore size used as long as there is still a slow mode whose amplitude dominates the scattering.

The amplitude of the scattering of the slow mode should depend both on the distribution (polydispersity) of the A/P and on their mass scaling with $R_G$. While these factors, and how they are quantitatively affected by filtration, are unknown, the qualitative trend should be for $I$ to decrease with decreasing filter pore size, while the proportionality should still hold. This is substantiated at all concentrations in Table 1 and in Figure 4 in “Domain Structure...”.

Figure 3 shows the type of concentration dependence usually found for $D_s$ in most reports. This behavior is accounted for by the model in ref 13 (Figure 6b), at least for the range of $C_p$ studied there. Additionally, at higher $C_p$ the A/P may well act as probes of the increasing solution viscosity, leading to a further decrease in $D_s$ with $C_p$.

Comments on Poly(methacrylic acid) (PMA) Data. The data provided by Figures 1a–c in “Domain Structure...” may be the paper’s most novel demonstration of the A/P explanation. In Figure 1a the PMA is neutral so that scattering intensity due to well-dispersed polyelectrolyte chains is dominant, similar to that of charged PMA at high ionic strength. The $D_s$ in Figure 1a corresponds to these well-dispersed, small ($M = 30,000$) neutral polymers. The slower mode in Figure 1a which was described as “almost invisible” is actually a significant peak in the CONTIN relaxation spectra. This slower mode may correspond to a population of A/P existing in the $\alpha = 0$ solution. Then, as $\alpha$ increases by adding NaOH, the well-dispersed chains become charged, their scattered intensity diminishes drastically as their $A_s$ increases, and the slow mode which was almost invisible at $\alpha = 0$ predominates at higher $\alpha$, and the $D_s$ corresponds to the A/P, now much more visible against the dark polyelectrolyte background (“the stars have come out”). The further decrease in $D_s$ may be related to the decreased diffusion of the A/P in the PMA solution, whose viscosity has increased as the chains are charged. Figures 3–5 in ref 4, an earlier work in which the author of “Domain Structure...” was involved, also show behavior for $D_s$, $D_n$, and $A_s/A_f$ consistent with the A/P explanation of the slow mode.
In connection with Figure 1a, the PMA solution of "Domain Structure..." may actually contain more A/P than most polyelectrolyte solutions investigated; if the slower mode in Figure 1a at \( \alpha = 0 \) corresponds to the A/P, then this is one of the few instances where the slow mode was resolvable at the equivalent of high ionic strength (i.e., at \( \alpha = 0 \) in this case), where scattering from the well-dispersed polyelectrolyte chains \( (A_i, D_i) \) dominates (Figure 2a in ref 10 may be another example). The author mentions that samples were lyophilized, a technique demonstrated to produce large aggregate populations in polyelectrolytes.3,10

The statement in "Domain Structure..." in reference to the experiments associated with Figures 1 and 2 that "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" might better read "This experiment has demonstrated that the detectability of the slow mode, whose origin is most likely the already existing A/P, is due to the suppression of the scattering from the well-dispersed polyelectrolyte chains as they are charged".

Summary. The behavior of \( D_r \), in both the domain and A/P explanations is ultimately electrostatic in origin, with a fundamental, nonsemantic difference: The domain explanation claims that electrostatic effects cause reversible clustering/domain formation. The aggregate/particle explanation claims that it is the extreme sensitivity of \( A_2 \) to the ionic strength of the well-dispersed polyelectrolyte phase which allows the slow mode due to already existing A/P (already existing or at least nascent in the dry polyelectrolyte) to be detected at low \( C_p \) when the well-dispersed polyelectrolyte scatters weakly, but which renders detection of the slow mode far more difficult, or even impossible, when \( C_p \) increases and the well-dispersed polyelectrolyte scatters brightly. The A/P are irreversible, and do not re-form after removal by filtration.

It is worth repeating the cautions in ref 13 that this explanation was developed for the polyelectrolytes in that work under the \( C_p \) and \( C_s \) conditions studied (in refs 9–13 \( C_p \) rarely exceeded 2 mg/mL). Although ref 11 clearly demonstrated that angular scattering peaks of both \( I(q) \) and \( 1/D(q) \) for proteoglycan monomers are unrelated to \( D_r \) (i.e., such peaks were observable with \( D_r \) present and also after it was removed by filtration), no conclusions have been extrapolated to the case of qualitatively different systems, such as latex spheres. These latter particles, for example, have radically different densities, and charge and mass distributions from semiflexible linear polyelectrolytes, and can form genuine crystalline-type structures in low ionic strength solutions at relatively low hard volume fractions.15,16

Recent work has also shown that the membrane filter material is important, in addition to the pore size, in removing the aggregates: Polyelectrolyte succinoglycan solutions at \( C_s = 0 \) and at low \( C_p \) showed pronounced angular static and dynamic scattering peaks, with single, rapid decay times when filtered through 0.1-μm cellulose nitrate membranes. When filtered through 0.1-μm poly(vinylidene fluoride) membranes (or 0.2-μm cellulose nitrate), however, the scattering was dominated by incompletely removed aggregates, with scattering peaks of diminished contrast, and a second, slow mode in the autocorrelation function corresponding to the aggregates.17

"Domain Structure..." provides several experimental demonstrations of slow mode phenomena, all of which are consistent with A/P explanation of the slow mode. The A/P explanation of the slow mode is currently the simplest explanation which is consistent with all published dynamic light scattering data on the effect.

References and Notes

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