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On the "Filterable Aggregates and Other Particles" Interpretation of the Slow Polyelectrolyte Mode

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Since 1978, when Lin, Lee, and Schurr[1] reported for the first time the occurrence of an extremely slow diffusive mode in low-salt poly(L-lysine) solutions by dynamic light scattering, a lot of effort was devoted to the investigation of this phenomenon. The slow polyelectrolyte mode was detected in a wide variety of synthetic and biological polymers in solutions of low ionic strength.[2−6] While it was found quite common for polymers with different chemical structures, a strong dependence on numerous physical factors such as charge density, ionic strength, polymer concentration, molecular weight, etc. was reported.[5−10] On the basis of pronounced angular dependencies of the apparent slow diffusion coefficient and scattering intensity, it was interpreted as the dynamics of large multichain domains (temporal aggregates, clusters) which arise as a result of charge interactions.[3,5,6] Dimensions of these structures were roughly estimated as ~100 nm.[5,8]

An alternative explanation was published by Reed and his collaborators.[11−15] According to them, the slow mode is identified with the presence of a small population of impurities introduced into solution during preparation or by stable permanent aggregates/particles which already exist or are at least nascent in the dry polyelectrolyte material. These aggregates/particles give weak but autocorrelable signals at low ionic strengths where the well-dispersed polyelectrolyte chains scatter very little light of their own. When the ionic strength of the medium increases, the scattering from the well-dispersed chains increases dramatically and is strong enough to bury the feeble intensity from aggregates. Hence the slow mode becomes undetectable at higher ionic strengths. The analogy was made that the aggregates/particles in low ionic solutions are similar to the stars in the night sky, which can no longer be seen when the sun rises (i.e. when the ionic strength increases and the single chain polyelectrolytes scatter brightly). The aggregates/particles were claimed to be completely removable from solution by a filter with sufficiently small pore sizes.

This "filterable aggregates and other particles" interpretation of the slow polyelectrolyte mode was later criticized in papers entitled "On the Filterable Aggregates and Other Particles Interpretation of the Extraordinary Regime of Polyelectrolytes"[16] and "Domain Structure of Polyelectrolyte Solutions: Is it real?".[17] The first paper[16] claims that the filterable aggregate model (FAM) fails to account for the established characteristics of the ordinary−extraordinary transition and is inconsistent even with the FAM author's own experimental data. The second paper[17] contains experimental data on well-defined and previously thoroughly investigated samples of sodium poly(styrenesulfonate) and poly(methacrylic acid). A 0.1 μm membrane filter was used instead of routinely used 0.2 μm filters, as it was claimed in an early paper of Reed[11] that a 0.1 μm filter was sufficient to "remove the slow mode". These experiments did not confirm the FAM, and also important examples of literature data not explainable by the FAM were given. Other experimental data inconsistent with the FAM were reported in refs 18 and 19.

Table 1. Values of Total Scattering Intensity *I* for NaPSS Solutions (M_w = 5000, c_p = 5 g/L) with Different NaCl Concentrations c_s[a]

c_s, M	0	0.0001	0.001	0.01	0.1	1.0
I	0.72	0.75	0.72	0.67	0.89	0.79

[a] Intensities were measured at $\theta = 90°$ [b] and normalized by the scattering intensity of a benzene standard. All solutions were filtered through a 0.2 μm filter. [b] When intensities are extrapolated to $\theta = 0°$, even a slight increase in scattering intensity due to angular dependencies is observed upon decreasing ionic strength.

Recently, comments on "Domain Structure of Polyelectrolyte Solutions: Is it real?" were published,[20] trying to explain experimental data in ref 17 again on the basis of the FAM.

The aim of the following communication is to show that the "filterable aggregate model" is incorrect and so are the attempts to explain some *particular* features of light scattering literature data on low-salt polyelectrolyte solutions by the FAM.

A direct experimental proof is given in Table 1 which shows total scattering intensities for the sodium poly(styrenesulfonate) of M_w = 5000 in aqueous NaCl solutions (polymer concentration c_p = 5 g/L). This sample was thoroughly investigated before[8,9] by quasielastic light scattering at salt-free conditions where the slow mode fully dominates (almost all of the scattering is coming from the slow mode). Here we supplement data on integral light scattering upon bringing the polymer from high-added salt conditions where, oppositely, the fast mode dominates, to zero-added salt conditions. As can be seen from Table 1, the total scattering intensity is almost constant in the whole range of ionic strengths. The slow mode develops without decreasing the total scattering intensity upon lowering the ionic strength. Hence "no sunset is necessary to observe the slow mode".

The result in Table 1 and the consequent conclusion are not so surprising after all. Data on total scattering intensities for other (usually higher molecular weight) polyelectrolyte samples do show a decrease upon lowering the ionic strength; however, this decrease is anyway small (not sufficient to account for the appearance of the slow mode according to the FAM). The decrease in total scattering intensity over the whole range of accessible ionic strengths is proportional to the molecular weight of the sample: the lower the molecular weight, the smaller the decrease. For instance the ratio of total scattering intensities measured in 1 M NaCl and zero-added salt NaPSS solutions at $\theta = 90°$ and c_p = 5 g/L is 39.0 (M_w = 1 200 000), 7.1 (M_w = 47 000), and 1.1 (M_w = 5000).[21] The author of the FAM reported the ratio 20 for a 1 g/L solution of NaPSS with M_w = 780 000.[15] All NaPPS samples were from the same supplier (Pressure Chemical, Pittsburgh, PA).

Further we would like to present new experimental data concerning the above mentioned paper "Domain Structure...".[17] In the experiment described in ref 17, a neutral aqueous solution of poly(methacrylic acid) (PMA) was filtered through a fine 0.1 μm filter to remove possible impurities. Then several drops of NaOH were added through a 0.1 μm filter directly to the scattering cell to charge the PMA chains. While before addition of NaOH the correlation curve was

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dominated by the fast mode, after addition it was dominated by the slow mode and a strong angular dependence of scattering intensity developed. This experiment clearly showed that in contradiction to the FAM the slow mode and related angular dependencies have an electrostatic origin. In "Comments on Domain Structure..."[20] the author speculates that maybe the 0.1 μm filter is not good enough to remove all aggregates/particles from the neutral solution and therefore they become visible after charging chains and lowering the scattering intensity (the author of "Comments on Domain Structure..."[20] reported previously that sometimes a 0.1 μm filter is not sufficient to remove completely the slow mode and a 0.05 μm filter has to be used). We repeated "the PMA experiment" with a 0.05 μm filter. The same result was obtained as for the 0.1 μm filter. An aqueous solution of PMA ($M_w = 13\,000$, $c = 39$ g/L) filtered through a 0.05 μm Nuclepore filter showed a pronounced slow mode after addition of NaOH ($A_s/A_f > 30$, $D_s = 37.0 \times 10^{-9}$ cm^2/s). In addition to the result that A_s/A_f was again clearly non-zero, the striking fact is that it was not even lower than A_s/A_f ratios obtained upon using 0.2 or 0.1 μm filters. This also contradicts the FAM.

Another failure of the FAM can be documented on the basis of the FAM author's own experimental data. He reported[15] that the excess scattering (normalized to the scattering by a toluene standard) was 0.05 and 0.19 for salt-free 1 g/L poly(L-lysine) solutions filtered through 0.05 and 0.22 μm filters, respectively. It was further stated[15] that there was no slow mode detectable after the filtration through a 0.05 μm filter and that all the scattering was due to the well-dispersed phase. Oppositely, the measurement on the solution containing both the well-dispersed phase and aggregates/particles (filtered through an 0.22 μm filter) yielded the slow mode only.[15] The excess scattering from aggregates/particles can then be calculated according to the FAM as (the excess scattering intensity of the sample filtered through an 0.22 μm filter) $-$ (the excess scattering intensity of the well-dispersed phase) $= 0.19 - 0.05 = 0.14$. Hence the ratio of the excess scattering intensity of the well-dispersed phase to the excess scattering intensity of aggregates/particles was $0.05/0.14 = 0.36$. This is in contradiction with the FAM conclusion that the well-dispersed phase in a solution filtered through a conventional 0.22 μm filter was invisible at zero salt conditions and therefore only the slow mode due to aggregates/particles was observed.

According to the FAM, impurities and/or aggregates have an inherent, relatively broad distribution of sizes and their dimensions in solution are given by the cutoff of the filter used. Changes in the slow diffusion coefficient with polymer concentration were explained as a decreased or increased diffusion of these particles due to changes in solution viscosity. However, apparent radii of gyration obtained from angular dependencies change appreciably with polymer concentration, too. It was reported[8] that the apparent radius of gyration obtained in solutions of NaPSS at zero-added salt conditions changes from ~100 nm to zero upon dilution (simply by adding drops of filtered water directly to the scattering cell). This is another fundamental argument against the FAM. According to the FAM, the apparent radius of gyration obtained in a salt-free solution in the polymer concentration range where the slow mode fully dominates (all the scattering is coming from aggregates/particles) should be given by the cutoff of the filter used and should not change from 100 nm to zero upon a decrease in polymer concentration.

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