Counterion associative behavior with flexible polyelectrolytes

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At low ionic strength, organic counterions dress a flexible charged polymer as measured directly by small-angle neutron scattering and neutron spin-echo spectroscopy. This dressed state, quantified by the concentration dependence of the static correlation length, illustrates the polymer-counterion coupled nature on the nanometer length scale. The counterions, made visible by selective hydrogen and deuterium labeling, undress from the polymeric template by addition of sodium chloride. The addition of this electrolyte leads to two effects: increased Debye electrostatic screening and decoupled organic counterion-polymer correlations. Neutron spin-echo spectroscopy measures a slowing down of the effective diffusion coefficient of the labeled counterions at the length scale of 8 nm, the static correlation length, indicating the nanosecond counterion dynamics mimics the polymer. These experiments, performed with semidilute solutions of tetramethylammonium poly(styrene sulfonate) $[(h\text{-}TMA^+)\,d\text{-}PSS]$, apply to relevant biopolymers including single and double stranded DNA and unfolded proteins, which undergo orchestrated dynamics of counterions and chain segments to fold, unfold, and assemble. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1776556]

I. INTRODUCTION

Small molecule and polymer associations are crucial in drug design and biological processes. The docking of low molecular weight polyamides to the minor groove in DNA (Ref. 1) or motor protein motion along microtubules must overcome Brownian motion to carry out their function.[2] These examples rely on intermolecular forces including hydrogen bonding and electrostatics which are balanced by an entropic loss. For biopolymers such as DNA and proteins, the association between counterions and chain is electrostatic in origin. The length scale and time scale of the association has been the subject of fundamental research.[3] In particular for charged polymers the importance of the counterion distribution and correlations to polyions on the static and dynamic properties remains experimentally and theoretically challenging. Recently simulations of dilute and semidilute polyelectrolyte solutions have considered the role of counterions and added salt on the solution structure and dynamics.[4–6]

Measurements of the local counterion distribution around flexible and semiflexible polyelectrolytes were performed by van der Maarel *et al.*[7,8] and Guilleaume *et al.*[9] using neutron and x-ray scattering methods, respectively. van der Maarel *et al.* measured the counterion partial structure factor to exhibit a static correlation peak. A Poisson-Boltzmann cell model (PBCM) was used to model high scattering wave vectors, $Q > 0.1\,\text{Å}^{-1}$, length scales of order of the chain persistence length. In both studies the PBCM could not quantify the correlations on the order of the static correlation length (ξ), as the polymer topology and spatial corre-

lations are not included in the model. Such a model remains a challenge to construct for flexible polyelectrolytes and compare quantitatively with experimental data.

The concentration dependence of the counterion self-diffusion coefficient (D_{self}) was measured by Schipper *et al.*,[10–12] using pulsed-field gradient nuclear magnetic resonance, spanning the dilute to semidilute regimes. Their results show D_{self} increases with added salt, while a nonmonotonic decrease in D_{self} versus polymer concentration is observed; the presence of a maximum was concluded to have origin in the change of counterion distribution about the polyion. These experiments were quantified using the PBCM without reference to the interchain correlations known by small-angle neutron scattering (SANS). Measurements of the counterion diffusive behavior and partial structure factor as a function of added salt and polymer concentration are necessary to interpret the influence of interchain correlations on the measurements of Schipper *et al.*

The local counterion distribution properties also influence the collective diffusion coefficient as measured by dynamic light scattering (DLS). This method reveals multimode relaxations; a fast-mode associated to coupled polyion-counterion motions and a slow-mode diffusion of multi chain domains.[13] With the addition of excess electrolytes the fast mode is eliminated suggesting a decoupled polyion-counterion dynamics. Neutron spin-echo (NSE) spectroscopy provides a high resolution experiment which complements DLS extending to shorter length scales and faster time scales. In this paper, a direct measurement of the counterion partial static structure factor (S_{cc}) in low and high ionic strength was completed using SANS, while the counterion dynamics at low ionic strength were probed by NSE spectroscopy.

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II. EXPERIMENT

A purified sample of perdeuterated sodium-poly(styrene sulfonate) (Na$^+$ d-PSS), with degree of polymerization 553,[14] was dissolved in D$_2$O followed by ion exchange to the acidic form using Dowex 650C H$^+$ ion-exchange resin.[15] The resin was purified and rinsed with heavy water to reduce the H$_2$O content prior to use. The acidic solution was titrated with tetramethylammonium hydroxide in D$_2$O to the end-point. This solution was then filtered with a Gelman Laboratory 1 μm poly(tetrafluoroethylene) filter unit, frozen and lyophilized. The purified (h-TMA$^+$) d-PSS sample was then dissolved in D$_2$O and the final concentration determined using ultraviolet spectroscopy. Samples containing added sodium chloride at 0.1, 0.4, and 1.0M (Ref. 16) levels were prepared by adding known quantities of analytical grade NaCl directly into a controlled volume of the salt free polymer solution.

Small-angle neutron scattering was performed on the NG 3 30 m instrument at the NIST Center for Neutron Research (NCNR). The neutron wavelength (λ) was 6.0 Å with wavelength spread ($\Delta\lambda/\lambda$) of 0.15. The scattered intensity is measured as a function of the wave vector (Q) defined by $Q = 4\pi\lambda^{-1}\sin(\theta/2)$, where θ is the scattering angle. Two configurations were used, a 13 m and 2 m, in the experiments involving added salt only a 2 m configuration was used. The details with regards to data collection and reduction can be found elsewhere.[17] Quartz banjo-type scattering cells of 2 mm path were used for all experiments.

Neutron spin-echo spectroscopy measurements were performed on the NG 5 instrument at the NCNR. The Fourier times explored were 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 10.0, 20.0, 30.0, and 40.0 ns using a neutron wavelength of 8.24 Å, leading to a Q range between 0.0586 and 0.10 Å^{-1}. The instrument is based upon the NSE spectrometer at the Forschungszentrum, Jülich and details of the measurement method and theory can be found elsewhere.[18–20] Titanium NSE scattering cells with path length of 4 mm contained the samples between quartz windows. All SANS and NSE measurements were performed at (25.0±0.1) °C.

The uncertainties in scattered intensity are calculated as the estimated standard deviation of the mean. In presented figures the uncertainty is smaller than the plotted symbols, the limits are left out for clarity. Fits of the scattering data are made by a least-squares minimization and the associated error to the regression parameters corresponds to one standard deviation.

III. RESULTS AND DISCUSSION

A. Scattering contrast variation

Neutron scattering methods used here are able to measure dynamics covering 45 ps to 100 ns and length scales from 10 to 1000 Å. The current problem of counterion statics and dynamics, investigated with neutron scattering, provides a direct local measurement which would not be possible using an inorganic counterion such as Na, due to low contrast. Organic counterions provide an opportunity to measure the pair correlations even in a multicomponent solution directly by suitably choosing the hydrogen and deuterium contrast

TABLE I. Neutron scattering lengths and partial specific molar volumes.

	$b_i [10^{-13}\text{ cm}]$	$v_i [\text{cm}^3\text{ mol}^{-1}]$
(CH$_3$)$_4$N$^+$	−8.94	84.2(Ref.32)
D$_2$O	19.2	18.1
d-PSS$^-$	120.1	114.8

variation. This can be designed following the algebraic notation for multicomponent scattering,[21] using the incompressibility hypothesis,

$$I(Q) = \sum_i^p (b_i - b_0)^2 S_{ii}(Q)$$
$$+ 2\sum_{i<j} (b_i - b_0)(b_j - b_0)S_{ij}(Q). \quad (1)$$

$I(Q)$ is the absolute coherent elastic scattered intensity in units cm^{-1}, p is a general index of the number of components, b_i is the coherent elastic scattering length of the ith component, b_0 is the average scattering length of the solvent normalized to the volume of the contrast-paired molecule, and S_{ij} refers to the partial structure factor; the Fourier transform of the pair correlation function between components i and j. For the case of quantifying the scattering by a three-component system ($p=3$) of polymer (m), counterion (c), and solvent (0), Eq. (1) takes on the following form,

$$I(Q) = (b_m - b_0)^2 S_{mm}(Q) + (b_c - b_0)^2 S_{cc}(Q)$$
$$+ 2(b_m - b_0)(b_c - b_0)S_{mc}(Q). \quad (2)$$

The typical case for high contrast labeling, or zero average contrast, decomposes S_{mm} into the interpair and intrapair structure functions. To measure the counterion dynamics and statics through S_{cc}, the contributions of S_{mm} and S_{mc} need to be reduced, or eliminated.

The basis for the current work rests on the observation that the contrast leading to the polymer pair correlations can be tuned; perdeuterated poly(styrene sulfonate) (d-PSS) in D$_2$O yields an effective contrast factor $(b_m - b_0)^2 = 0.00668$ cm^2, whereas protonated PSS in D$_2$O provides high contrast of 32.9 cm^2 calculated from the scattering lengths and partial molar specific volumes provided in Table I. Thus the deutero-polymer is neutron optically invisible in the former experiment. This allows the measurement of the organic counterion pair correlations, via contrast variation, with a counterion that has sufficient contrast with the solvent.

The organic counterion, protonated tetramethylammonium (h-TMA$^+$), has a calculated contrast with D$_2$O of 57.4 cm^2. Hence, an experiment of d-PSS in D$_2$O using h-TMA$^+$ provides a system for studying counterion density-density correlations by SANS and the coherent dynamic structure factor with NSE spectroscopy. The ratio of contrast amplitudes between the polymer-solvent and counterion-solvent is 0.00668/57.4, a 0.01% contribution to the measured scattering, while that arising from the counterion-polymer is 0.67%. Thus, the pure heavy water effectively contrast matches the
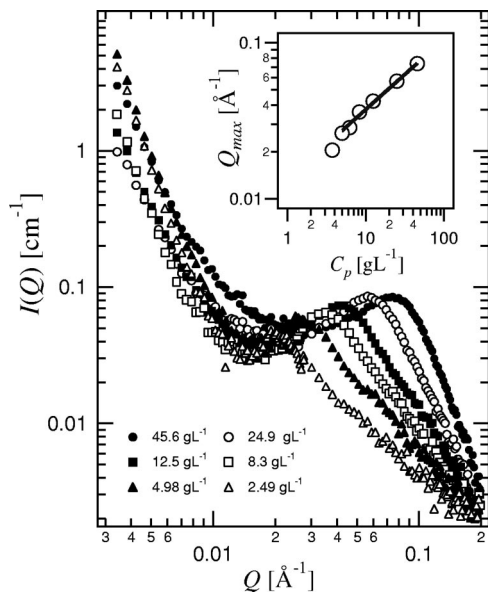
FIG. 1. Small-angle neutron scattering from (h-TMA) d-PSS in D_2O as a function of polymer concentration. The inset provides the scaling of the peak position as a function of concentration with dependence $Q_{max} = (0.0133 \pm 0.001)C_p^{0.45 \pm 0.02}$; systematic deviations occur near the dilute solution limit.

scattering arising from the polyion-polyion correlations. In this case $(b_m - b_0)^2$ and $(b_m - b_0)(b_c - b_0)$ are negligible, simplifying Eq. (2) yields

$$I(Q) = (b_c - b_0)^2 S_{cc}(Q). \tag{3}$$

The measurement of S_{cc} was observed before for model polyelectrolyte systems,[7,8,22] but the influence of polymer concentration (C_p) and added salt concentration (C_s) in semidilute solutions were not completed. In contrast, the total static scattering features and scaling dependencies within semidilute polyelectrolyte solutions are well known.[3]

B. h-TMA$^+$ counterions static partial structure factor

1. Polymer concentration dependence

Using the previously defined contrast scheme, the SANS results for the polymer concentration dependence of the scattered intensity, arising from the counterion partial structure factor, for C_p ranging from 45.6 to 2.5 gL^{-1} are shown in Fig. 1. It should be emphasized that the pair correlations measured display the typical low ionic strength polyelectrolyte peak. However, this peak is made visible by the counterions. Such strong scattering provides a direct view on how counterions are strongly correlated to the main chain as to mimic the pair correlations typical for the polymer. In Fig. 1, two features are observed, the broad peak at high Q typically arising from interchain correlations and the increase in scattered intensity in the low-Q region. The concentration dependence of the peak maxima, Q_{max}, shown in the inset, leads to a scaling dependence of $(0.013 \pm 0.001)C_p^{0.45 \pm 0.02}$. This result agrees with data obtained under full contrast conditions when the scattering arises from polymer-polymer pair correlations, when the counterions are neutron optically invisible. The expected crossover from a scaling of 1/2 to 1/3, the semidilute to dilute regime, should occur near the overlap

concentration of 0.7 g L^{-1}, estimated using the radius of gyration of an extended chain conformation. This result demonstrates without resort to counterion condensation mechanisms or quantification by Poisson-Boltzmann models for counterion distribution that the long-ranged electrostatic interactions present in polyelectrolyte solutions are visible with either polyion or counterions.

One physical interpretation is that the counterions are spatially correlated with the main chain. However, these correlations are better described by an apparent counterion dressing of the chain such that the connectivity of the monomers is also emulated by the counterions. This would then purport that within the no added salt semidilute limit the counterions are not randomly distributed within the system, but maintain strong correlations with the oppositely charged polymer as viewed by the scaling results. Our static results are not in complete agreement with recent simulation findings by Chang and Yethiraj.[5] They properly recover the S_{mm} polyelectrolyte peak scaling with concentration, but do not observe the peak in S_{cc} for the semidilute solutions, as measured in Fig. 1; only dilute solutions show a peak in S_{cc}. The fraction of ions that are correlated cannot be addressed here, but is the subject of osmotic pressure measurements. The comparison of scattering results with osmotic pressure would provide a quantification of the osmotic coefficient. However, due to the low-Q scattering such a separation is not directly possible. This low-Q upturn indicates that large scale multichain domains are also visible by the counterions. A power law behavior is typically observed in the total scattering experiment as described previously, however, for the current case the power law scaling is not observed.[14] Forcing a power law leads to exponents different from the total scattering results; the highest concentration (45.6 g L^{-1}) yield an apparent power of 3.4 ± 0.1, while the lower C_p reveals exponents between 4.4 and 5.3, over a limited Q range. This behavior, typically associated with compact domains, illustrates that at the length scale ($1/Q \sim 100$ Å) of the domain size the counterions reveal additional structural information, possibly weakly associated counterions spanning multichain domains. Polydispersity effects observed in true fractal aggregates cannot be ruled out.[23,24]

2. Salt concentration dependence

For low ionic strength polyelectrolyte solutions, the long-ranged electrostatic interactions reveal unique structural correlations. With the addition of salt, the range of the electrostatics becomes screened, quantified by the Debye screening length, and the structural features in the polyelectrolyte solution closely resemble neutral polymer solutions[25] using the unique contrast scheme presented here, the role of this Debye screening on the coupled counterion-polyion correlations via S_{cc} as a function of 0, 0.10, 0.40, and 1.0 M NaCl is shown in Fig. 2, for a fixed polymer concentration of 24.9 g L^{-1} (0.13 M). At an added NaCl level of 0.10 M, the peak is absent, but a rise in $I(0)$ is observed within the measurement range. This 0.10M result is compared to those obtained under full contrast conditions using SANS or small-angle x-ray scattering in which with the addition of salt, the peak position shifts to lower Q and a rise in $I(0)$ is observed due
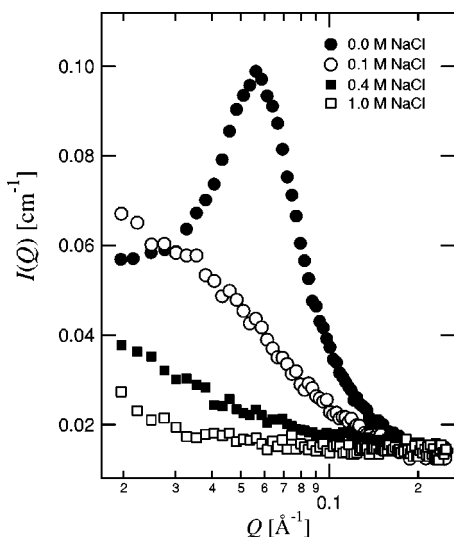
FIG. 2. Elimination of the polyelectrolyte peak and decrease in amplitude in the small-angle neutron scattering due to the displacement of h-TMA$^+$ counterions with added NaCl for $C_p = 24.9$ gL^{-1}.

to screening of long-ranged electrostatic interactions;[26,27] at high added salt the scattered intensity decays monotonically with Q and becomes independent of the added salt concentration for systems far from phase transitions.

The results presented in Fig. 2 do not follow the trends when the scattering arises from the polymer-polymer density correlations.[26,27] In the present case, by extending to higher added salt, 0.4M and 1.0M NaCl, the scattered intensity is further reduced and nearly eliminated. To explain this observation the modification of the structural features are observed through the structure factor, S_{cc}, not the scattering contrast prefactor $(b_c - b_0)^2$. The unique labeling has allowed the observation from the point of view of the initial h-TMA$^+$ counterion species. The strong correlations to the chain, exhibited by the correlation peak and scaling dependence, illustrate that throughout the semidilute solution the counterions are highly correlated to the chain. The influence of adding NaCl, which is not contrast visible, to the solutions leads to a loss in the structural features provided by the counterions mediated by the polyelectrolyte.

A simple equilibration between native cations with added Na$^+$ could lead to a loss in observed scattering. The presence of counterion correlations is strongest with the no added salt condition. Upon adding salt, the additional Na$^+$ cations in solution appear to equilibrate with the h-TMA$^+$ associated with the chain. The structure is due to the template nature of the polyelectrolyte dressed by organic counterions. Apart from ion-specific affinity or binding, the exchange of counterion species at equilibrium should occur. The extent of this equilibration may be quantified by considering the change in the concentration (C) of cations available to the chain as (C_{Na+}/C_{TMA+}). Initially, the molar concentration of h-TMA$^+$ cations and monomer anions are equal, at the no added salt condition. Upon adding NaCl, the presence of Na$^+$ serves as an equivalent counterion to the chain and there will be a redistribution of these two species. As the salt concentration is increased from 0.0, 0.10, 0.40, and

1.0M, the cation ratio ($C_{Na+}/0.13M$) becomes 0, 0.77, 3.1, and 7.7, respectively. So, at the lowest level of added salt, the fraction of h-TMA$^+$ cations in the solution is reduced by 57% $[C_{TMA+}/(C_{Na+} + C_{TMA+})]$, thus we expect h-TMA$^+$ ions to be displaced, assuming cation mixing; the chain remains partially dressed as observed from the $I(Q)$ dependence. At the highest added salt concentration the h-TMA$^+$ cation fraction is reduced to 11%, expecting the displacement of nearly 89% of the original h-TMA$^+$ dressed ions. The few remaining h-TMA$^+$ ions that decorate the chain, may be responsible for the scattering at the lowest Q. Structural correlations are absent as viewed through the Q-independent scattering above 0.05 Å^{-1} or length scales smaller than 125 Å. This displacement effect does not state that sodium ions are not correlated, it states that the measurable h-TMA$^+$ are now less correlated (decoupled) to the chain by exploring the volume of the solution. Such a view is not inconsistent with the predictions of simulation results in which an enhanced salt density near the chain is observed.[4,6] The equilibration of the Na$^+$ ions with the visible TMA$^+$ ions cannot rule out this observation. An experiment in which a TMA$^+$ salt was added to enhance the visibility can test this simulation result. The essential physics remains in the behavior of S_{cc}, not through the scattering contrast prefactor. This counterion undressing is the unexplored physics in flexible polyelectrolytes. The data, shown in Fig. 2, provide direct evidence for the structural contributions to the osmotic pressure through the counterion displacement.

C. h-TMA$^+$ counterions dynamics: no added salt

The counterion coherent dynamic structure factor $S_{cc}(Q,t)$ was measured using NSE spectroscopy for a polymer concentration of 45.6 gL^{-1} using the previously described labeling scheme. Figure 3 shows the results of the normalized intermediate scattering function $[S(Q,t)/S(Q,0)]$ for five Q values. The relaxation of counterion concentration fluctuations demonstrates the nanosecond dynamics in these semidilute polyelectrolyte solutions. This coherent scattering spectroscopy quantifies the relaxation of h-TMA$^+$ pair correlations.

The spectra were fit to a single exponential with amplitude prefactor (A),[28]

$$\frac{S(Q,t)}{S(Q,0)} = A e^{-\Gamma(Q)t}. \tag{4}$$

From the decay rate (Γ), an effective diffusion coefficient was defined, $D_{eff} = \Gamma/Q^2$. With diffusive behavior, D_{eff} should be Q independent. We plot the *inverse* effective diffusion coefficient versus Q in Fig. 4 against the left axis. The right axis displays the corresponding SANS data in filled circles. The Q-dependent diffusion coefficient resembles that of the low ionic strength polyelectrolyte solution near the polyelectrolyte peak, measured under full contrast conditions.[29] This dynamical slowing down,[22,30] made visible with the dressed counterions, illustrates the h-TMA$^+$ *dynamically* coupled to the polyion. The relaxations of the counterion resemble the relaxation of the polymer,[29] even in the nanosecond time scale, and appear in agreement with the Q-dependent coun-
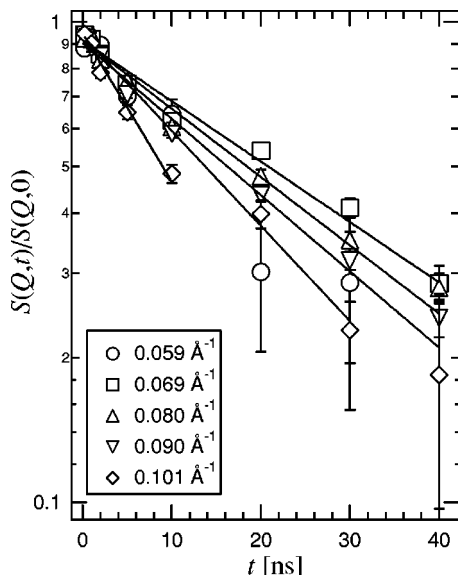
FIG. 3. Decay of the normalized coherent dynamic structure factor as a function of the Fourier time for (h-TMA) d-PSS solution at C_p $=45.6$ g L^{-1} measured by neutron spin-echo spectroscopy. The experimental data are fit by an exponential decay.

terion collective diffusion coefficient predictions of Chang and Yethiraj.[5] We observe a slight shift to higher Q of the D_{eff}^{-1} peak indicating the polyelectrolyte peak and the counterion dynamics occurs at slightly different length scales, distinguishing the results from the polymer concentration fluctuation relaxations in which the dynamic slow down occurs at the peak position.

These results suggest that in proximity to the static correlation length ($\xi \sim Q_{max}^{-1}$) in polyelectrolyte solutions the counterions are static and *dynamically* correlated to the chain. Thus, measurements of the self-diffusion of counterions by methods such as pulsed-field gradient nuclear magnetic resonance require the knowledge of the static structure factor to interpret the concentration dependence of the self-diffusion coefficient.[10–12] This is due to the coupled nature of
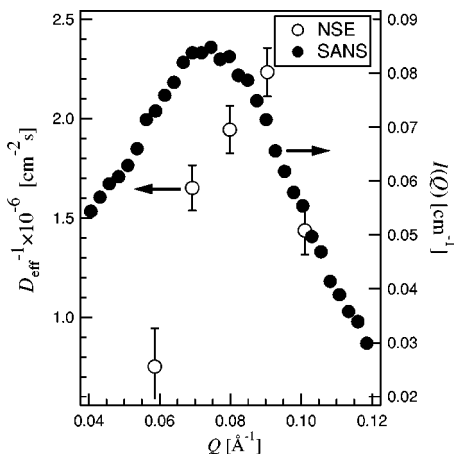

FIG. 4. Inverse effective diffusion coefficient $D_{eff}(Q)$ obtained by NSE, compared to the polyelectrolyte peak measured by SANS, for a (h-TMA) d-PSS solution at $C_p=45.6$ g L^{-1}. The difference in the peak position indicates the dynamic slowing down of the counterions at shorter length scale, in contrast to what is observed for polymers.

polyelectrolyte diffusion. Measurements of ion diffusion depend upon both the time scale and length scale of the experiment. The molecular interpretation of diffusive transport refers to hopping distances of ions with characteristic frequency. In the polyelectrolyte system, the hopping distance may have its origin within the polyion correlation length which is a function of concentration. In the presence of added electrolytes the h-TMA$^+$ ions are essentially undressed from the chain as interpreted from Fig. 2. Thus, the counterion diffusion is decoupled from the chain with added salts. The decoupled diffusion from the large polyion then leads to faster self-diffusion of the ions.[31] This behavior was recently observed by Schipper *et al.*[12] The static decoupling, as observed in Fig. 2, complements DLS in which in the limit of high salt the fast and slow modes merge reflecting the decoupled cooperative diffusion coefficient.[31] In the low salt regime DLS measures independent modes in which the fast mode is interpreted as the coupled polyion-counterion motions. This paper suggests that the fast-mode origin can be directly measured from the counterion statics and dynamics within the present model system. The experimental data do not plateau at high Q, however, if a plateau occurs it will be at values of diffusion coefficient larger than (4.6 ± 0.6) $\times10^{-7}$ cm^2 s^{-1}. Experiments are underway to explore the value of the diffusion coefficient in comparison to the fast mode, obtained from DLS, which is (6.0 ± 0.1) $\times10^{-6}$ cm^2 s^{-1}, for NaPSS, at similar concentration conditions.[14]

IV. CONCLUSIONS

The counterion partial structure factor reveals a scattering peak resembling that observed under full contrast conditions. This measurement illustrates the coupled nature between counterion and polyelectrolyte. The polymer concentration dependence of the structure peak, made visible by the protonated TMA$^+$ ions, leads to a scaling dependence of $Q_{max}=(0.013\pm0.001)C_p^{0.45\pm0.02}$ which is equivalent to the full contrast result demonstrating the coupled nature extends even into the semidilute solution. The counterion species are observed to become decoupled from the chain upon addition of added NaCl due to the dual influence of Debye screening that leads to the elimination of the structure peak and loss in scattered intensity due to the equilibration of visible TMA$^+$ ions with Na$^+$ ions. The counterion dynamic structure factor was measured for a polymer concentration of 45.6 g L^{-1} without added salts. The interpreted Q-dependent diffusion coefficient leads to a slowing down near the static structure factor peak similar to the polymer relaxations previously reported. The implication of these results provides a clear measurement of the counterion static and dynamic coupling to the polyion.

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