Dynamics in polyelectrolyte solutions : the counterion effect

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Samples of 6,9-ionene polyelectrolytes [Malikova12,Malikova15], with either F- or Br- counterions, were measured on IN15 in solution of D_2O, at two different ionene monomer concentrations, c_p=0.4 and 2.0M (no additional salt present). The coherent neutron scattering signal arises from the contrast between the hydrogen-rich ionene chains and the deuterated solvent. A background of incoherent scattering is present due to the hydrogen-rich chains.

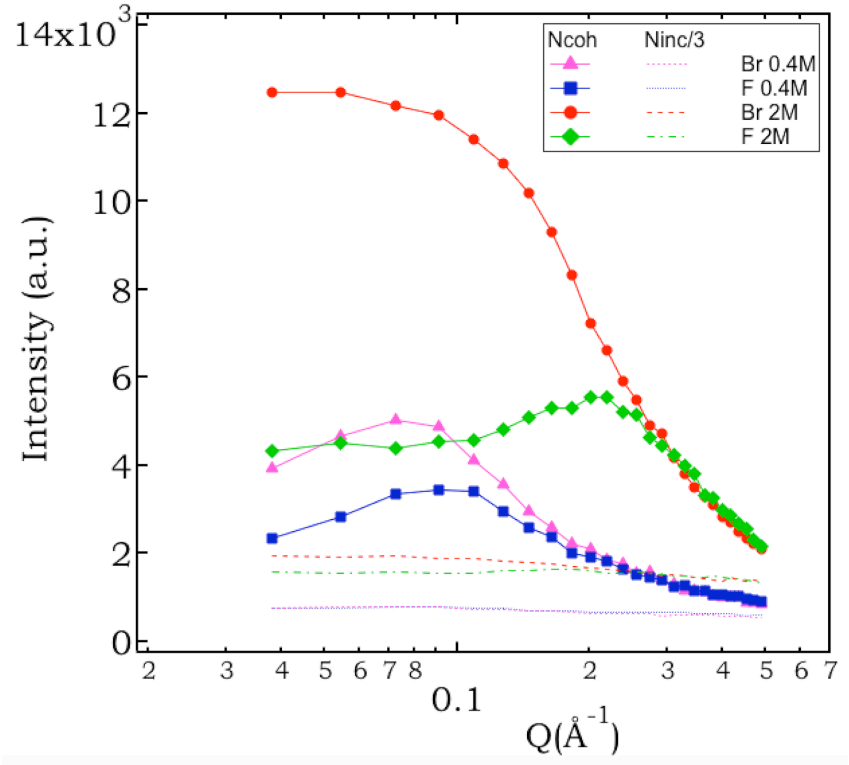

Figure 1. Scattered intensity as a function of the wave-vector Q, decoupled into the coherent (Ncoh) and incoherent (Ninc) contributions. The latter is presented with an intensity pre-factor of 1/3, to reflect its effective contribution in the dynamic signal measured by the neutron spin echo technique. Four samples are considered: ionene chains with F and Br counterions, each at a low and a high monomer concentration, 0.4M and 2M respectively.

The S(Q) signal of the four ionene samples measured is presented in Figure 1 (curves labelled Ncoh). The coherent signal dominates, especially at Q values below 0.5 $Å^{-1}$. Furthermore, the relative importance of the incoherent scattering is diminished in the dynamic measurements by a factor of 1/3, due to the spin flip process occurring for incoherent neutron scattering from hydrogen nuclei. As seen already in the previous small angle neutron scattering (SANS) data [Malikova12, Malikova15], we observe a very similar S(Q) signal for the two diluted ionene samples (F 0.4M and Br 0.4M), both featuring a broad structural peak centred on 0.08-0.09 $Å^{-1}$. At high Q, the two curves superimpose, suggesting that the local environment of the chains, as seen by neutron scattering, is identical for the two counterions. The concentrated ionene solutions show a marked difference: while above 0.3 $Å^{-1}$ the two curves superimpose (as for the diluted samples), below 0.3 $Å^{-1}$ the situation is radically different. A structural peak remains in the case of F counterions and as expected its position is now shifted towards higher Q values in comparison to the diluted system, peak centered on 0.2 $Å^{-1}$; while for Br-ionene a significant increase in the coherent signal is observed in the entire Q region below 0.2 $Å^{-1}$, no structural peak as such is observed any longer. Across the Q range shown in Figure 1, we carried out dynamic neutron scattering measurements using the neutron spin echo technique, leading us to the intermediate scattering function, I(Q,t) measured on the dominating coherently scattered signal.

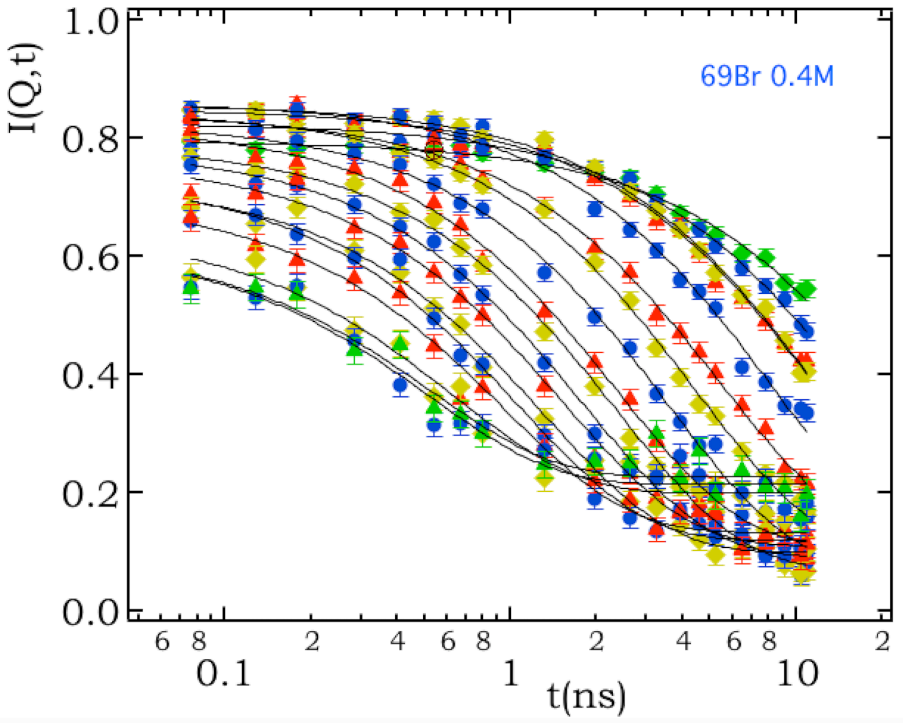

Figure 2. The intermediate scattering function, I(Q,t), measured on the 6,9-ionene sample with Br counterions. I(Q,t) curves were measured for a series of 18 Q values across the range of 0.04 to 0.4 Å^{-1}.

As an example, Figure 2 features the I(Q,t) measurements for the 6,9-ionene sample with Br counterions. The set-up allowed us to access correlations in the time-range between 0.08 and 10ns, where all the I(Q,t) curves show a significant decay, as a function of the Fourier time. The data were modelled with a single exponential decay, letting a free intensity pre-factor, as well as a free background constant. The relaxation times obtained from the exponential fits of I(Q,t) signals were converted to an effective diffusion coefficient using, $D(Q)=1/(\tau * Q^2)$. The behaviour of D(Q) for the 4 different samples is presented, along with S(Q), in Figures 3.

The left panel of Figure 3 summarizes the S(Q) and D(Q) of the low concentration ionene solutions for the two different counterions. The D(Q) for the two samples features the same behaviour: for Q values greater than the maximum of the structural peak, we observe clearly a constant behavior of D(Q), while below the structural peak an increase in D(Q) is observed [Nallet83]. The right panel of Figure 3 features the S(Q) and D(Q) for the two concentrated systems. Again at high Q, above the structural peak observed for the F-ionene sample, the D(Q) signal of the two concentrated samples is identical, featuring a constant. Below the structural peak, the behaviour of D(Q) is very different. While the D(Q) for F-ionene features a fast increase as soon as we pass onto the left of the structural peak, the D(Q) for Br-ionene remains suppressed, though slowly increases as we move towards low Qs.

Our interpretation of static (SANS) data in for Br and F-ionenes was based on increased "condensation" of Br counterions onto the chain backbone, consistent with the "disappearance" of the correlation peak [Malikova12,Malikova15]. Our main expectation was to see a different behaviour in D(Q) in the high Q region for Br and F ionenes at high concentration: a constant D(Q) for F and D(Q) increasing linearly with Q for Br-ionene, as in the case of neutral polymers [Adam77]. Obviously, the latter is not seen, both F and Br ionene have a constant D(Q) beyond the q* (position of the structural peak for the concentrated F-ionene), attesting to a charged chain (polyelectrolyte) behavior in both cases [Nallet83].

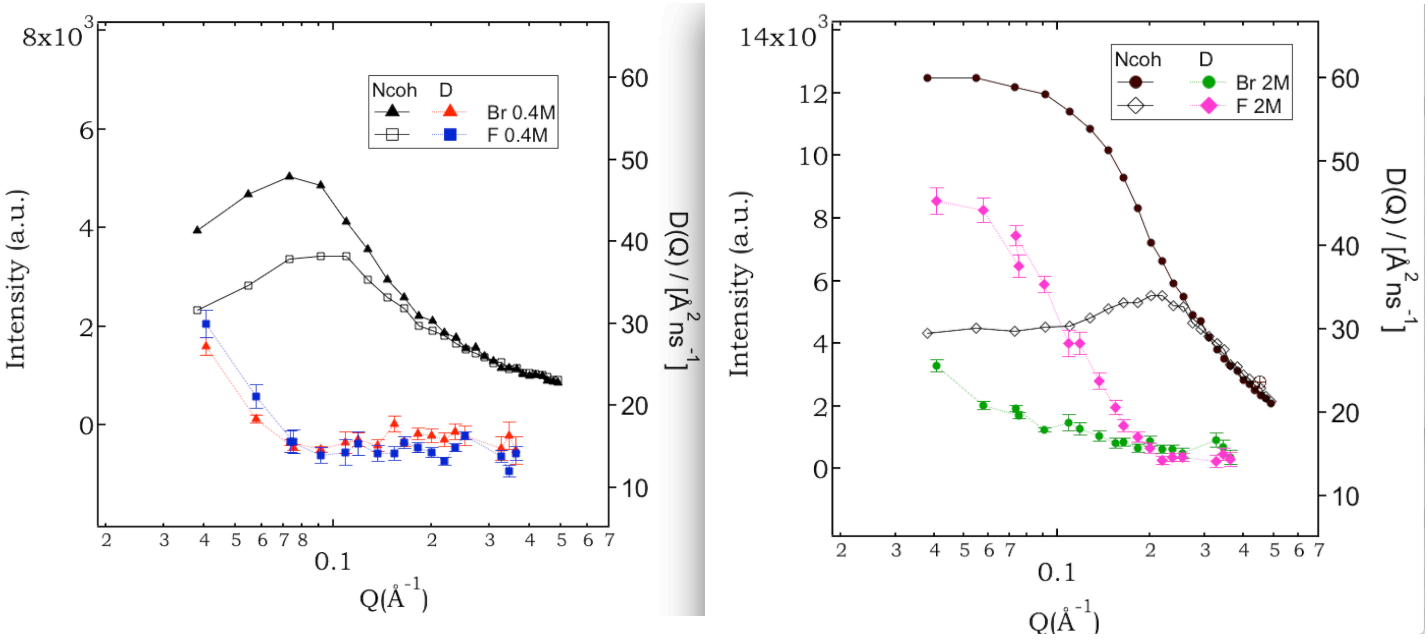

Figure 3. The structure factor, S(Q) (labelled Ncoh), and effective diffusion coefficients, D(Q) (left y-axis and right y-axis respectively) are presented for ionene samples with Br counterions (left panel) and F counterions (right panel), each time at a low and a high ionene concentration, as indicated in the legend.

An interesting comparison is to consider the rigidity of the chains as we go from diluted to concentrated chains (for a given counterion). The most rigid behaviour (i.e. D(Q) remaining a constant over a large range of Q) is for the diluted samples. From an electrostatic point of view, this is indeed understandable, we have a solution at a low ionic strength, screening is inefficient, the chains are extended and rigid. As we concentrate the two solutions, in both cases we decrease the rigidity (the Q domain over which D(Q) is constant decreases), and in the F-ionene system this effect is much more pronounced. While we have been interpreting the "disappearance" of the polyelectrolyte peak in Br-ionenes at high concentrations to counterion condensation on the chain, this does not lead to a decreased rigidity of the ionene chains, as seen through D(Q) here, on the contrary. Overall, we observe the Br-ionene solution at high concentration as less repulsive than F-ionene and with a much slower (suppressed) dynamics at low Q-values (lower than the position of the F-ionene polyelectrolyte peak, i.e. below 0.2 $Å^{-1}$).

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