STRUCTURE FUNCTIONS OF STAR-BRANCHED POLYELECTROLYTES

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Unusual structure functions have been measured for salt-free aqueous solutions of sodium sulfonated polystyrene (NaPSS) star-branched polyelectrolytes. Whatever the concentration, they display two kinds of maxima (figure 1). The first is related to a position order between star cores. It covers a main maximum at q_1^* and a further harmonic at $\sqrt{3}\,q_1^*$ for the lower concentrations in the dilute regime. The second comes into sight at higher q values. It involves one maximum at q_2^*, quite similar to the broad halo observed in the scattering pattern of a semidilute aqueous solution of NaPSS linear polyelectrolytes. It is therefore associated with a correlation hole of electrostatic character.
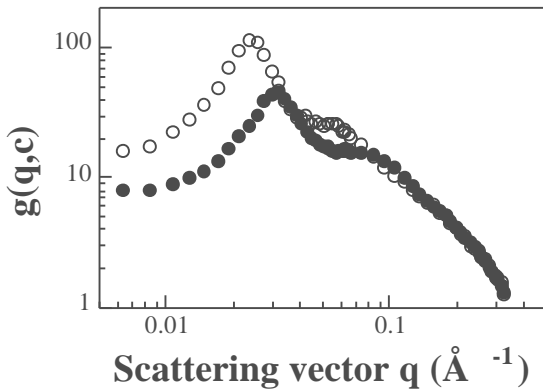

Figure 1 : Structure functions of NaPSS star solutions obtained on the spectrometer PACE at LLB
The NaPSS star sample corresponds to f=12, N_a=100 and t_S=1. Two concentrations are considered : c=0.102 mol.l^{-1} (open circles) ; 0.258 mol.l^{-1} (dark circles)

The variations of q_1^* and q_2^* with the monomer concentration c allow to stress the difference in nature of these maxima (Figure 2).
q_1^* almost scales as $c^{1/3}$ with prefactors depending on the star functionality f and the arm degree of polymerization N_a. No dependence upon the arm degree of sulfonation τ_S, has been found in the τ_S-range providing solubility of the NaPSS stars. Obviously, such results support the close relation between q_1^* and the mean distance between star cores (d = $2\pi/q_1^*$), i.e.

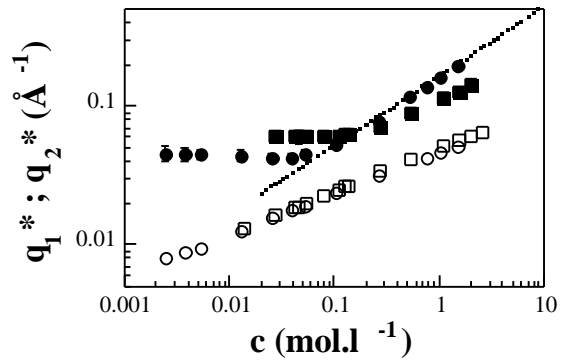the short or long range order character of the first maximum.

Figure 2 : Scattering vectors q_1^* and q_2^* associated with the main maxima of the NaPSS star structure functions
Two NaPSS star samples are considered. They have the same functionality (f=12) and arm degree of polymerization (N_a =100), but distinct t_S values. Open circles and squares correspond to q_1^* values measured for t_S=1 and 0.65, respectively. Dark circles and squares correspond to q_2^* values measured for t_S=1 and 0.65, respectively. The scaling law related to the electrostatic peak of NaPSS linear polyelectrolytes in semidilute aqueous solutions is also reported for t_S=1 (dotted line)

The c-dependence of q_2^* is quite different (q_1^* and q_2^* are therefore not commensurate). In the dilute regime (c<c*), q_2^* is found to be constant, only depending on N_a and τ_S. On the other hand, in the semidilute regime (c>c*), q_2^* scales as c^α with α in between 1/3 and 1/2, according to the τ_S value. Moreover, it is unaffected by any change in N_a. Such scaling laws fit those associated with the position q* of the broad peak characterizing the structure functions of NaPSS linear polyelectrolytes in semidilute aqueous solutions. The second maximum of the NaPSS star structure functions is therefore primarily due to the existence of a correlation hole (or tube) surrounding each polyion, from which the others are expelled by the electrostatic repulsion. For c>c*, it mainly corresponds to the semidilute solution formed by the interpenetration of stars and q_2^* yields its mean mesh size ξ or the Debye-Hückel screening length κ^{-1} (isotropic model). For c<c*, it still represents the

electrostatic repulsion between arms. However, in that case, it is exclusively concerned with arms belonging to the same star. It is indeed a simple intramolecular feature, as demonstrated by using the zero average contrast method. Then q_2^* yields an effective screening length κ^{-1}, through the relation $q_2^* \propto \kappa$, which gives an information about the condensation of couterions inside each star. From this point of view, it is not really

surprising that q_2^* is almost constant in the dilute regime. However, the results presented in figure 2 also show that the counterion condensation inside each star increases as τ_S decreases. On the other hand, the variation of q_2^* with N_a is in agreement with the existence of an internal screening length distribution. Finally, the distinct behaviours of q_2^* in both the dilute and semidilute regimes provide a way to estimate the overlap concentration c*.