Supporting Information for Publication: Probing the mesh formed by the semirigid polyelectrolytes

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Scattering intensity curves for HA

In the Fig.S1 we compare our SAXS results for HA with the similar measurements observed by other authors.[1,2] We note that the lack of the polyelectrolyte peak is not specific to our results and this lack has been a common observation for HA. Indeed, a shoulder could be identified as a characteristic scattering feature for HA in the concentration range 10-100 g/L.

Villetti *et al.*[2] proposed that the peak was not observed because of the weak polyelectrolyte character of HA, its small intrinsic persistence length or weak scattered signal. The first reason seems to be the most probable because the polyelectrolyte peak reflects the local ordering of polyelectrolyte segments due to the Coulombic repulsion between them. Already Koyama[3,4] has simulated scattered intensity of a polyelectrolyte and showed that the simulated curves lacked the peak and featured only a shoulder if the repulsive interaction between the polyion chain segments was reduced. Suppression of the repulsion may come naturally for HA, a weakly charged polyelec-

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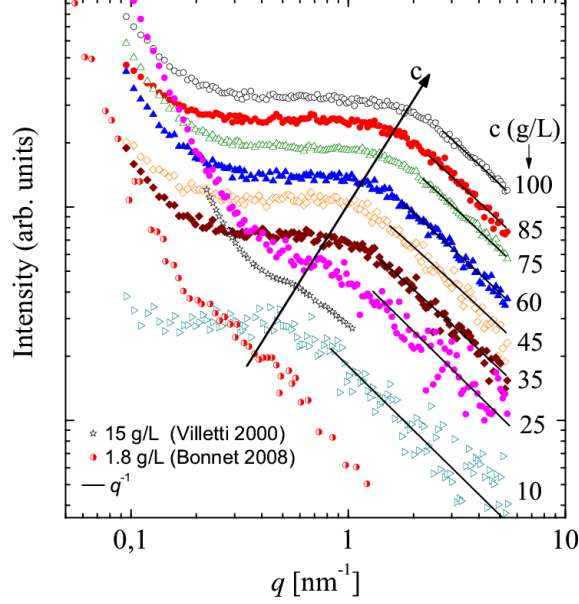
Figure 1: S1. Common features of scattering intensity curves for HA observed by us and by other authors: absence of the polyelectrolyte peak , q^{-1} dependence at high q, an upturn at low q.[1,2] A shoulder may appear between the upturn and the q^{-1} features. The data for 1.8 g/L are obtained by neutron scattering and for 15 g/L by synchrotron X-ray scattering.

trolyte. We distinguish HA as such according to the Manning theory of counterion condensation.[5] HA has one charge per monomer of the size $b_{HA} = 1$ nm, which is longer than the Bjerrum length $l_B = 0.72$ nm.[6,7] Thus, the Manning charge density parameter $\eta = l_B/b = 0.7$ for HA is smaller than 1 and its counterions do not condense, but remain in a diffuse atmosphere around the polyion. For DNA, there are two charges per monomer and $b_{DNA} = 0.34$ nm, thus $\eta = \frac{l_B}{b/2} = 4.2$ and the case is opposite, about 75% counterions are condensed. Even with condensation the effective linear charge is $1e^-/l_B$ for DNA (and other strong polyelectrolytes) and it is 50% higher than for HA with $0.7e^-/l_B$. Thus, in case of HA the electrostatic interaction can be considered as reduced and screened due to the reduced linear charge density on the chains and large fraction of non-condensed counterions.

Interestingly enough, when Villetti *et al.* have sheared their HA solution they did observe a peak arising in place and position of the shoulder. Their interpretation was that the peak arises due to the electrostatic interactions magnified by the effect of shear. This corroborates our proposition that the shoulder in HA scattering has reduced electrostatic interaction as origin.

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Further in this analysis of the features of SAXS curves for HA, we note that the strength of the shoulders in Fig.S1 depends on the fact that the low-q upturn appears only below 0.2 nm^{-1} in our data and already below 0.7 nm^{-1} for 15 g/L curve by Villetti *et al.* but also in one of our curves, for 25 g/L sample. For the later two curves, the stronger upturn seems to cover the shoulder. The upturn is common in polyelectrolytes and has been related to the *slow mode* observed in dynamic light scattering (DLS). A possible, however not yet established, origin could be locally ordered clusters of chain segments (domains). Aggregates would be a misnomer as the chains within the domain should still maintain relatively large distances, more comparable to the correlation length than the chain diameter. Conceivably such domains would account for the *slow modes*.[8–10] Borsali *et al.*[9] found it acceptable to apply the Guinier equation to the low q scattering intensity (for DNA). This provided a gyration radius for the presumed clusters. The cluster size decreased with the addition of salt. The above scenario however does not lead us to propose any scenario for a different (steeper) upturn and thus different R_g of clusters for our 25 g/L sample - preparation routine and the sample stock was the same for all HA samples studied by SAXS.

Correlation length obtained by the dielectric spectroscopy

We provide further arguments for the length scale obtained by DS to be the correlation length, as well as that it attains realistic values when rescaled by 2π.

Without added salt, at very low concentrations (< 0.1 mM in monomers) DNA dissolved in pure water starts to denature, as the strong Coulomb repulsion, tears the strands apart.[11] The counterions alone do not provide sufficient screening of the Coulomb interaction between the strands. Consequently, the DNA, originally in a double stranded form, produces a denser mesh of ssDNA molecules for the same concentration. Correspondingly, the correlation length should decrease. That is, the number of monomers doubles for ssDNA and monomer size b is also somewhat larger for ssDNA (0.43-0.5 nm instead of 0.34 nm[12]). Therefore $(bn)_{\text{dsDNA}}^{-1/2} \approx 1.7(bn)_{\text{ssDNA}}^{-1/2}$. Indeed, the factor 1.7 appears in Fig.S2, where the values for L_{DS} deviate from the $L_{\text{DS}} = (bn)^{-1/2}$ line due to

DNA denaturation.

Further, in Fig.S3 we combine, for DNA146, L_{DS} *vs. c* (slope 1/3 on a log-log plot) obtained for the dilute solution combined with ξ *vs. c* (slope 1/2 on a log-log plot) obtained by SAXS[13] in the semidilute concentration range. These data sets define, experimentally, a dilute-semidilute crossover for 50 nm rod-like DNA146 fragments. Theoretical concentration for these fragments is at an order of magnitude lower concentration. We remind, at the theoretical crossover concentration the volumes swept by the rotation of neighbouring fragments start to overlap. This crossover has been demonstrated for other systems. There, the authors[14,15] also noted that the experimental crossover concentration appears at an order of magnitude higher than the theoretical one. The position of the crossover in Fig.S3 depends on the scaling factor for L_{DS}. Only with the factor 2π the crossover is positioned in accordance with data for other systems.
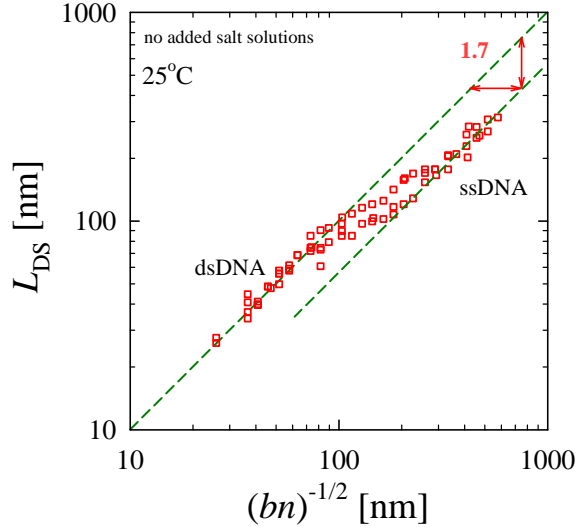

Figure 2: S2. Correlation length L_{DS} obtained by dielectric spectroscopy of long DNA.[16] The deviation from $L_{DS} = (bn)^{-1/2}$ line for a factor 1.7 is due to DNA denaturation. Presumed DNA forms are denoted.
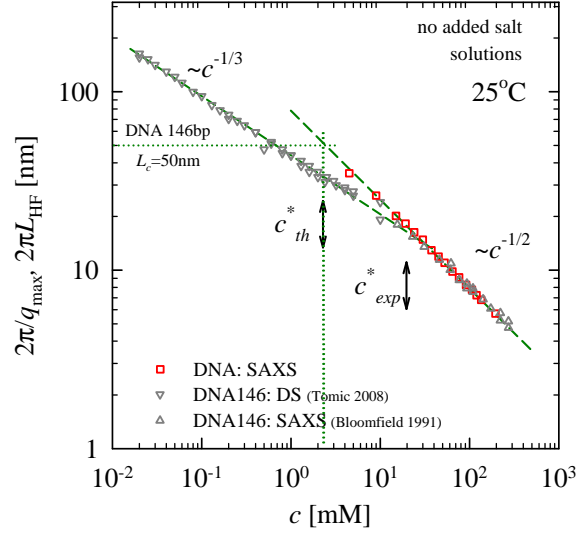
Figure 3: S3. Correlation length $\xi = 2\pi/q_m$ obtained by SAXS (DNA - data from this work, DNA146 - data from [13]) and the length scale $L_{DS} = 2\pi l$ obtained by dielectric spectroscopy of DNA146.[17] The concentration dependence of the characteristic length scale for the dilute solution is $c^{-1/3}$, while for the semidilute it is $c^{-1/2}$.

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