Correlation length of hydrophobic polyelectrolyte solutions

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Abstract. – The combination of two techniques (Small Angle X-ray Scattering and Atomic Force Microscopy) has allowed us to measure in reciprocal and real space the correlation length $\xi$ of salt-free aqueous solutions of highly charged hydrophobic polyelectrolyte as a function of the polymer concentration $C_p$, charge fraction $f$ and chain length $N$. Contrary to the classical behaviour of hydrophilic polyelectrolytes in the strong coupling limit, $\xi$ is strongly dependent on $f$. In particular a continuous transition has been observed from $\xi \sim C_p^{-1/2}$ to $\xi \sim C_p^{-1/3}$ when $f$ decreased from 100% to 35%. We interpret this unusual behaviour as the consequence of the two features characterising the hydrophobic polyelectrolytes: the pearl-necklace conformation of the chains and the anomalously strong reduction of the effective charge fraction.

Introduction. – Polyelectrolytes are polymers containing ionisable groups which, in a polar solvent like water, dissociate into charges tied to the polymer backbone and counter-ions spread in the solution. Polyelectrolytes are called hydrophobic when water is a poor solvent for the backbone. Their single chain properties (conformation and effective charge density) are very different from those of hydrophilic polyelectrolytes. Theories \[123\], simulations \[45\] and experiments \[67\] are all consistent with a pearl-necklace description of the single chain where low dielectric constant nanoregions (the pearls) are connected by narrow elongated strings. Another important feature is the charge renormalisation. By osmometry Essafi et al. measured the effective charge fraction $f_{eff}$ as a function of the chemical charge fraction $f$ for partially sulfonated polystyrene (PSS) \[8\]. In a range of charge fractions where hydrophilic polyelectrolytes followed rather well the so-called Manning-Oosawa condensation theory \[910\], they found for PSS a further strong reduction of $f_{eff}$ \[11\].

What happens for a large number of interacting chains in solution is still a largely open question. Indeed in the framework of the theoretical pearl-necklace model two semi-dilute

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Table I – PSS samples of various chain lengths \(N\), chemical charge fractions \(f\) and effective charge fractions \(f_{\text{eff}}\). \(f_{\text{eff}}\) is calculated from \(f\) according to [11].

| \(N\)  | \(f\)(%) | \(f_{\text{eff}}\)(%) | \(N\)  | \(f\)(%) | \(f_{\text{eff}}\)(%) | \(N\)  | \(f\)(%) | \(f_{\text{eff}}\)(%) |
|-------|----------|------------------------|-------|----------|------------------------|-------|----------|------------------------|
| 120   | 34       | 3.4                    | 1320  | 36       | 4.3                    | 2520  | 37       | 4.8                    |
| 410   | 39       | 5.8                    | 1320  | 53       | 12                     | 2520  | 54       | 13                     |
| 410   | 56       | 14                     | 1320  | 71       | 21                     | 2520  | 89       | 30                     |
| 410   | 71       | 21                     | 1320  | 91       | 31                     | 5800  | 57       | 14                     |
| 410   | 91       | 31                     | 5800  | 90       | 30                     |

Regimes have been predicted [3]. As long as the pearl size is much smaller than the correlation length \(\xi\) which characterises the transient network of overlapping chains, a classical polyelectrolyte behaviour is expected, i.e. \(\xi \sim C_p^{-1/2}\) where \(C_p\) is the polymer concentration (string-controlled regime). However when the pearl size becomes of the order of \(\xi\), a transition to \(\xi \sim C_p^{-1/3}\) is predicted (bead-controlled regime). Experimentally two regimes have only been observed for an atypical polyelectrolyte soluble in polar solvents other than water, the scaling exponents being -1/2 and -1/7 respectively [12].

For the model hydrophobic polyelectrolyte PSS in water, Essafi et al. found by Small Angle Scattering measurements (SAXS and SANS) that the position of the so called polyelectrolyte peak, \(q^*\), which is a measure of the inverse of \(\xi\), scaled as \(q^* \sim C_p^\alpha\) in the whole \(C_p\) range with \(\alpha\) depending qualitatively on \(f\) [8, 13, 14]. This behaviour was later observed for more complex systems like concentrated polyelectrolyte stars [15]. On the other hand, using thin film balance technique, Théodoly et al. measured the wavelength \(\lambda\) of the oscillating disjoining pressure isotherms of various polyelectrolytes confined in thin liquid films [16]. They found for hydrophobic PSS the same concentration dependence as for hydrophilic polyelectrolytes: \(\lambda \sim C_p^{-1/2}\).

In such an unclear situation it seemed essential to measure systematically the correlation length as a function of \(f\), chain length \(N\) and \(C_p\). For this purpose well defined model hydrophobic polyelectrolytes, PSS’s, have been prepared [17] and \(\xi\) has been measured by two different techniques: SAXS for a classical measurement in reciprocal space and Atomic Force Microscopy (AFM) in real space. In the SAXS experiment \(\xi\) has been taken as \(2\pi/q^*\) where \(q^*\) is the position of the polyelectrolyte peak. AFM has been used to provide force-distance measurements of the polyelectrolyte solution confined in a sphere-plane geometry. The period \(d\) of this oscillating force has been assumed to be a direct measurement of \(\xi\).

**Experimental details.** – Well defined monodisperse \((M_W/M_N < 1.3)\) PSS’s (poly(styrene-co-styrene sulfonate, sodium salt) of various chemical charge fractions \(f\) and chain lengths \(N\) (Table I) have been prepared and characterised according to a method described elsewhere [17]. Salt-free water was produced by a milli-Q system (Millipore co.) feded with triply-distilled water. PSS solutions were prepared by weight and left under stirring for a few days in airtight plastic bottles before use.

For the SAXS experiments cylindrical capillaries of 2 mm internal diameter were filled with the PSS solutions and sealed by Teflon tape. Measurements were performed at the European Synchrotron Radiation Facility (ESRF, Grenoble, France) on BM26 beamline. We used the highly monochromatic (\(\Delta \lambda/\lambda \approx 2 \times 10^{-4}\)) X-ray beam at \(\lambda = 0.124\) nm (10.0 keV). The detector was a 1D quadrant gas-filled detector situated at 7.8 m from the sample. The scattering vectors \(q (q = 4\pi/\lambda \sin(\theta/2), \theta\) is the scattering angle) ranged from 0.1 to 0.9 nm\(^{-1}\).

Force-Distance measurements were carried out using a commercial Atomic Force Micro-
Fig. 1 – SAXS Intensity (arbitrary units) as a function of the wavevector $q$ for PSS at $C_p = 0.1$ mol/L, $N = 410$ monomers and various chemical charge fractions $f$.

scope (Molecular Force Probe, Asylum Research, USA) equipped with an inductive sensor (LVDT sensor). We used the colloidal probe technique [18] in which the usual sharp AFM tip was replaced by a colloidal silica particle of 7 µm diameter (Bangs Laboratories Inc.) that was glued to a tipless cantilever ($\mu$Mash, CsCl2). Clean silicon wafers (Wacker, Germany) were used as substrates. Particles glued to the cantilevers were cleaned directly before the measurement by plasma cleaning for 20 minutes (Plasma cleaner PDC-32G, Harrick Scientific, USA). Then a drop of the PSS solution was put onto the substrate and the probing head (the silica particle) was also immersed in the solution. Force-distance curves were obtained at a pulling frequency of 0.2 Hz, corresponding to piezo speed from 200 nm/s to 800 nm/s, depending on the range of the pulling distance. Variation of the pulling speed in this range showed no change in force-distance data. For each solution, the force-distance curves were measured at 3-5 different locations on the same substrate as well as on 2-4 different substrates.

**Results and discussion.** A series of typical SAXS spectra $I(q)$ are presented in fig. 1 for salt-free solutions of PSS as a function of $f$, all other parameters remaining constant. One notes the presence of the classical broad maximum also called the polyelectrolyte peak. In the case of hydrophilic polyelectrolytes in salt-free water, it is independent of $f$ as long as $f$ is above the onset of the Manning-Ooasawa condensation (about 35% in the case of vinylic polyelectrolytes) [19]. Here the situation is very different. When $f$ decreases, i.e. when the hydrophobicity increases, this broad maximum becomes sharper, more intense and the maximum moves to smaller $q$ values. In other terms the characteristic correlation length $2\pi/q^*$ increases (in this example from 11.4 nm to 18.3 nm) with fluctuations decreasing. Assuming that the correlation length is related to an inter-chain electrostatic repulsion, its size should be of the order of the Debye screening length $\lambda_D$. In salt-free solutions electrostatic screening comes from the residual ions in water (on the order of $10^{-5}$M) and the free polyelectrolyte counter-ions at a concentration $C_p f_{eff}$. In our experimental conditions the former contribution can be neglected and we have:

$$\lambda_D \approx \left( \frac{e^2}{\epsilon k_B T} C_p f_{eff} N_A \right)^{-1/2}$$  \hspace{1cm} (1)

where $e$ is the elementary charge, $\epsilon$ the dielectric constant of water, $k_B$ the Boltzman constant, $T$ the temperature and $N_A$ the Avogadro number. $f_{eff}$ has been calculated from $f$ assuming that the empirical renormalisation law established by Essafi et al. [11] is valid here. $2\pi/q^*$ is plotted in fig. 2 as a function of $\lambda_D$ for all PSS samples. For clarity of presentation points have been grouped in four average charge fractions $\langle f \rangle$: 35%, 55%, 70% and 90%. First of all $2\pi/q^*$ is an increasing function of $\lambda_D$. This means that the solution is organised on a
length scale of the order of the screening length; therefore it is strongly related to the free counter-ion concentration. This confirms indirectly that the anomalously strong reduction of $f_{\text{eff}}$ observed in the dilute regime \([11]\) also occurs in this moderately concentrated regimes. However the proportionality between $2\pi/q^*$ and $\lambda_D$ is only observed at the highest charge fraction ($\langle f \rangle = 90\%$). In this case PSS behaves as a hydrophilic polyelectrolyte in the semi-dilute regime and obeys the expected scaling law: $2\pi/q^* \sim \lambda_D^{1/2}$. Then when $\langle f \rangle$ decreases and hydrophobicity increases, $2\pi/q^*$ progressively deviates from the hydrophilic behaviour ($\xi$ proportional to $\lambda_D$, the straight line in fig. 2). This means that for hydrophobic polyelectrolytes the solution structure is not solely controlled by electrostatic interactions. It depends also on the hydrophobicity of the chain and conformational properties will have to be taken into account.

In order to ascertain that the observed deviation from the classical hydrophilic polyelectrolyte behaviour was not due to some artifacts of the SAXS technique \([20]\), we have also measured $\xi$ by AFM. Following the pioneering work of Milling with fully charged PSS \([21]\), we have analyzed the force distance curve of various hydrophobic PSS solutions confined in the sphere-plane geometry. The polymers were the same as those used for the SAXS measurements for one chain length only ($N = 410$). Oscillatory forces were systematically observed and their characterisation will be described in detail in a forthcoming paper. We focus here on $d$, the period of oscillation, which has been shown to be the characteristic length of the solution structure in real space \([22, 23]\). The comparison between $d$ measured by AFM and $2\pi/q^*$ as measured by SAXS is presented in fig. 3. The two techniques are in remarkable agreement and within experimental errors we have found:

$$d = 1.05 \frac{2\pi}{q^*} + 1.2 \text{ nm}$$  \(2\)

A detailed comparison between the techniques will be presented elsewhere.

Within this experimental framework we have then systematically measured $\xi$ as a function of $N$, $f$, and $C_p$. The classical logarithmic plot $q^*$ as a function of $C_p$ is presented in figure \(4\) for chain lengths ranging from 120 to 5800 monomers and various $f$ per chain length. First there is clearly no dependence on $N$ as expected for semi-dilute solutions of overlapping chains. However there is a strong influence of $f$ even though these polymers are highly charged strong polyelectrolytes with $f$ above the onset of Manning-Oosawa condensation ($f \geq 35\%$). In the
case of hydrophilic polyelectrolytes we should expect \( q^* \sim C_p^{1/2} \) for all \( f \). This behaviour is only observed for the highest charge fraction (at \( \langle f \rangle = 90\% \) we have \( q^* \sim C_p^{0.46} \)) i.e. only when PSS almost behaves as a model hydrophilic polyelectrolyte. When \( f \) decreases, the linear density of hydrophobic moieties along the chain (styrene monomer) increases and the intrinsic hydrophobicity of the backbone is enhanced. The consequence is a progressive deviation towards \( q^* \sim C_p^{1/3} \) at the lowest \( f \) (\( \langle f \rangle = 35\% \)). Having a \( C_p \) exponent different from 1/2 is highly unusual for polyelectrolyte and this clearly results from hydrophobic effects. In the framework of the pearl-necklace model two limit behaviours have been predicted (\( q^* \sim C_p^{1/2} \) in the string-controlled regime and \( q^* \sim C_p^{1/3} \) in the bead controlled regime) on each side of a crossover occurring when the pearl size becomes of the order of \( \xi \). In this study such a

Fig. 3 – Direct comparison between \( d \) the period of the oscillating force as measured by AFM and the correlation length \( 2\pi/q^* \) obtained from SAXS. The best fit line has a slope of 1.05 and an offset of 1.2 nm.

Fig. 4 – Position of the correlation peak \( q^* \) depending on the polymer concentration \( C_p \). Data have been grouped in four average chemical charge fractions: 35%, 55%, 70% and 90%. From the top to the bottom straight lines have slopes of: 0.46, 0.42, 0.38, and 0.33 and the dashed lines have slopes of 1/2 and 1/3, respectively.
transition has never been observed. However it may appear out of the $C_p$ range that is narrow in this study [24]. To sum up, in this regime where no transition has been observed, a general law for the position of the peak has been found:

$$q^* \sim N^0 C_p^{\alpha}$$  \hspace{1cm} (3)

This leads for the correlation length $\xi$:

$$\xi \sim N^0 C_p^{-\alpha}$$  \hspace{1cm} (4)

$\alpha$ is plotted in fig. 5 as a function of $f$ or $f_{\text{eff}}$ as calculated from $f$ using [11]. It has been determined by SAXS and using AFM as well (the oscillation period that is a measure of $\xi$ scales as: $d \sim C_p^{-\alpha}$). Both techniques show that $\alpha$ depends on $f$ and continuously decreases from $\alpha = 0.50$ at $f = 100\%$ to reach $\alpha = 0.33$ at $f = 35\%$. At $f = 100\%$ PSS behaves as a hydrophilic polyelectrolyte and obeys the classical power law for hydrophilic polyelectrolytes in the semi-dilute regime $\xi \sim C_p^{-1/2}$. At the lowest charge fraction ($f = 35\%$), PSS is very hydrophobic and is thus in very poor solvent condition. The chains are compact, slightly charged ($f_{\text{eff}} = 3 - 5\%$) globules that electrostatically repel each other. In this case we thus have $\xi \sim C_p^{-1/3}$. The two limit exponents 1/2 and 1/3 can be physically interpreted: a hydrophilic polyelectrolyte behaviour when fully charged and a self repelling colloidal organisation at very low $f$. The intermediate situation when $\alpha$ differs from 1/3 or 1/2 is very delicate to interpret and it has never been predicted by any theory. However very recently Limbach et al. made molecular-dynamics simulations on strongly charged polyelectrolytes in poor solvent which is the situation of PSS in water. At $f = 50\%$, they found that the position of the peak in the structure factor scaled as: $q^* \sim C_p^{0.35}$ for all investigated $C_p$ [3]. This value for $\alpha$ is reported in fig. 5. Their result is in quantitative agreement with the continuous transition that we have experimentally observed.

**Conclusion.** – The correlation length $\xi$ of well defined hydrophobic polyelectrolyte has been determined using two very different techniques: SAXS and AFM. $\xi$ obeys a general
power law: $\xi \sim N^0 C_p^{-\alpha}$. Contrary to the case of hydrophilic polyelectrolytes, $\alpha$ depends strongly on $f$, decreasing from 1/2 at $f = 100\%$ to 1/3 at $f = 35\%$ in the vicinity of the solubility limit.

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