Hydrophobic polyelectrolytes

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Polyelectrolytes are macromolecules containing ionizable groups which in a polar solvent like water dissociate into charges tied to the polymer backbone and counter-ions dispersed in the solution. They are called hydrophobic when water is a poor solvent for the backbone. By analogy with the Rayleigh instability of a charged droplet [1], the single chain is expected to adopt an unique pearl-necklace conformation as it has been predicted theoretically [2, 3] and observed in numerical simulations (fig. 1).
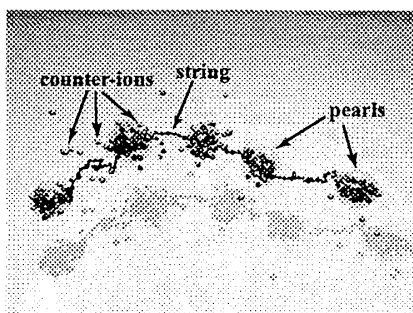

FIG. 1: The single-chain pearl-necklace conformation of hydrophobic polyelectrolyte as shown by recent numerical simulation [4, 5] with counter-ions explicitly taken into account. Strings and pearls are clearly evidenced. Courtesy from Limbach et al.

By presenting a series of experiments performed on well-defined hydrophobic polyelectrolyte molecules, this poster is an invitation into the real and mysterious world of hydrophobic polyelectrolytes.

I. Synthesis and characterization

A series of well-defined poly(styrene-co-styrenesulfonate, sodium salt), abbreviated PSS, of various chemical charge fractions f and chain lengths N have been synthesized and characterized precisely [6]. These monodisperse and randomly charged PSS can be considered as model hydrophobic polyelectrolytes.

II. Anomalously large reduction of the effective charge fraction

Osmotic pressure and freezing point depression measurements have shown [7] a strong reduction of the effective charge fraction f_{eff} as a function of f:

$$f_{eff}(\%) = 100 \frac{f - f^*}{100 - f^*} \frac{a}{l_B} = \frac{f(\%) - 18}{82} 36 \tag{1}$$

where f^* is the chemical charge fraction at which f_{eff} equals 0, a is the monomer size (0.25 nm) and l_B is the Bjerrum length (0.71 nm in pure water at 25°).

III. Structural properties in bulk

Structural properties of PSS salt-free solutions have been investigated as a function of f, N and the polymer concentration C_p. In reciprocal space, Small Angle X-ray Scattering (SAXS) experiments have allowed us to measure the correlation length ξ_c from the position q^* of the correlation peak: $\xi_c \approx 2\pi/q^*$. In real space, PSS solutions have been confined in a sphere-plane geometry and the force as a function of the sphere-plane distance z has been measured using an atomic force microscope (AFM). When z becomes of the order of ξ_c, force curves present oscillations (figure 2a), the period d of which is a measure of ξ_c. Figure 2b shows that AFM and SAXS are in remarkable agreement for the ξ_c measurement [8]. The combination of these two techniques has allowed us to establish unambiguously the following relationship [9]:
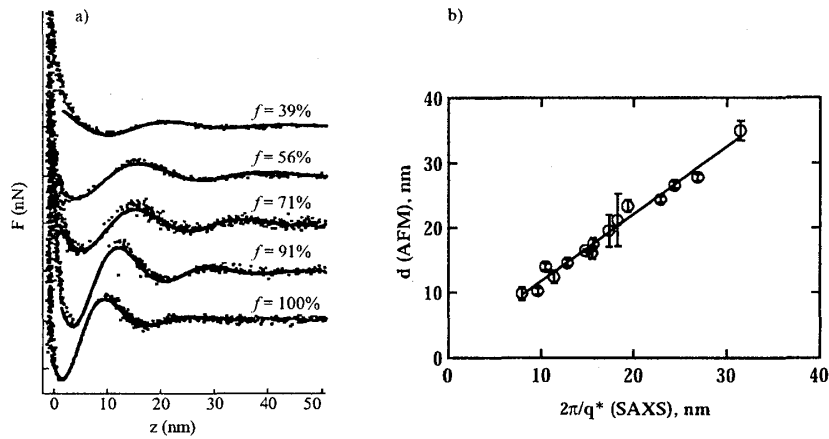
$$\xi_c \propto N^0 C_p^{-\alpha} \tag{2}$$

FIG. 2: a) AFM colloidal probe technique: force curves as a function of vertical distance z for a PSS solutions ($C_p = 0.05$ mol.L^{-1}, $N = 410$) of various charge fractions f. b) Comparison between the oscillation period d measured by AFM and $2\pi/q^*$ obtained from SAXS. The best-fit line has a slope of 1.05 and an offset of 1.2 nm.

the exponent α increasing continuously as function of f from 1/3 at $f \approx 30\%$ (3D organisation of self repelling globular chains) to 1/2 at $f = 100\%$ (classical exponent for a hydrophilic polyelectrolyte in the semi-dilute regime). This is in semi-quantitative agreement with scaling predictions [10] and recent simulations [11].

IV. Interfacial properties

In order to characterize the single chain conformation, PSS chains have been trapped by adsorption onto planar, oppositely charged solid surfaces in conditions where the bulk conformation persists in the adsorbed state [12]. The PSS layers have been characterized at the solid-liquid interface using *in situ* ellipsometry [13] and an original technique: *in situ* high energy X-ray reflectivity [14]. These two techniques have allowed us to measure the PSS layer thickness h which, in these conditions, is closely related and proportional to the pearl size D_p: $h \propto D_p$. We have found [13, 14]:

$$h \propto aN^0 f_{eff}^{-2/3} \tag{3}$$

where f_{eff} is estimated from f using equation 1. Equation 3 is in perfect agreement with the prediction of the pearl-necklace model for the pearl size [3]. It shows also that the effective charge fraction, rather than f, is controlling the electrostatic intra-chain interactions.

V. Other interfaces

Finally, we will present some interfacial properties of significant practical interest:

- hydrophobic polyelectrolytes as wetting agents
- surface gelification of soft interfaces (e.g., air-water interface, lipidic membrane) induced by the adsorption of hydrophobic polyelectrolytes

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