Bundle Formation in Poly(styrene) sulfonate Brushes


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Linear polyions in solution repel each other and form strongly structured fluids. Thus, Bragg peaks are detected with scattering methods [1]. At high polyion concentrations \( c_p \), their nearest neighbor distance \( d \) scales with the square root of \( c_p \). To explain this relationship, de Gennes et al. [2] proposed a detailed model of flexible polyelectrolytes at low ionic strength and high polyion concentrations \( c_p \). Different chains overlap each other, and several arrangements were discussed: (a) a lattice of rigid rods and (b) an isotropic phase of entangled and thus partially flexible chains. The latter case is assumed the most probable structure. Each chain consists of connected, randomly oriented segments. Within one segment, electrostatic effects dominate and induce an elongated segmental conformation (i.e., an increased persistence length), whereas between different segments, the interactions are completely screened. For this model, the average distance as derived from the Bragg peaks is \( d = \sqrt{2f_c}^{-1/2} \), where \( f \) depends on the lattice geometry (hexagonal, square, etc.) [3]. Therefore, an exponent of -1/2 does not necessarily indicate an ordered array of rigid rods, but may also originate from an isotropic network of entangled chains [1]. Experimentally, in the semidilute concentration regime, all experimental points obtained from various polyelectrolytes fall onto a common line, with the predicted power law dependence. However, the measured lattice distance in dilute solutions is larger than expected for aligned rods, a phenomenon yet unexplained.

Bundle formation would explain those scattering data. Bundles form because of a short-ranged attraction between the polyelectrolyte molecules, their number is limited by the electrostatic repulsion between the aggregated chains. On salt addition, the amplitude and range of the electrostatic force decreases, and more chains are expected in a bundle. Bundle size and length is investigated using the vertically aligned and oriented chains of polyelectrolyte brushes. The brush thickness \( H \) is 30 - 50% of the contour length [4]. Polyelectrolyte brushes show two distinctly different regimes called “osmotic brush” and “salted brush,” respectively. In both phases, the ions compensating the polymer charges are incorporated into the brush [4-6].

Monolayers at the air/water interface are prepared from amphiphilic diblock copolymers, consisting of a fluid hydrophobic (PEE, poly ethylene) and a polyelectrolyte block (PSS, poly styrene sulfonate) [4], PEE\(_{144}\)PSS\(_{136}\). The hydrophilic block forms polyelectrolyte brushes [4]. To explore the lateral order, in-plane diffraction experiments were performed at BW1 in the liquid surfaces set-up.

![Figure 1: Grazing incidence diffraction peaks of PEE\(_{144}\)PSS\(_{136}\) monolayers at the molecular areas indicated in the isotherm. The aqueous solution contains 1 mM CsCl.](image-url)
Diffraction peaks measured along the isotherm are shown in Fig. 1. On monolayer compression, a shift to larger $Q_{xy}$-values occurs, indicating a decrease of lattice distances. The correlation length deduced from in-plane peak width is slightly less than twice the lattice constant, typical for a structured fluid. Always, the peak maximum occurs at $Q_z=0$, suggesting a vertical alignment of the brushes. On compression, the out-of-plane peak width increases, indicating that the vertical length $L$ of the ordered fraction of the chains within the brush decreases, even though the brush thickens [4].

The unit cell area $A_{cell}$ deduced from the distance measurements exceeds the molecular area $A_{Mol}$ as determined from the isotherm, even assuming a close-packed two-dimensional lattice ($A_{cell} = (2/\sqrt{3})d^2$). With increasing salt concentration in the subphase, the deviation between $A_{cell}$ and $A_{Mol}$ gets more pronounced, from a factor 2 (osmotically swollen brush with Na$^+$ counterions) to a factor of about 15 (salted brush with 1 M CsCl subphase), cf. Fig. 2. Obviously, not the separation between single chains is measured but the distance between bundles consisting of at least 2 and up to 15 chains, depending on salt conditions.

The bundle length $L$ as deduced from the out-of-plane peak width is smaller than the brush thickness $H$ (cf. Fig. 2). The polymer chains experience electrostatic stiffening due to chain charges [1]. On increase of the salt concentration, the chains get more flexible and the persistence length shrinks, leading to shorter bundles with constant length $L$. In the osmotic brush phase (mM salt concentration), on monolayer compression the counterion concentration and the monomer density increase (from 0.5 to 2.5 M). In this phase, compression causes a slight increase in brush thickness $H$ while the brush length $L$ shrinks simultaneously. In the salted brush phase (0.2 or 1 M salt concentration), the increased salt concentration leads to the minimum bundle length, independent of $A_{Mol}$.

![Figure 2. The area per unit cell as deduced from the GID peaks (left), the bundle length $L$ (centre) and the brush thickness $H$ [4] (centre) vs. the molecular area $A_{Mol}$ derived from the isotherms. The ion concentrations in the subphase are indicated. Right: Schematic of PSS bundles.](image)

References