Bundle Formation in Polyelectrolyte Brushes

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Polyelectrolytes, solved in dilute solutions, show a large persistence length l_τ due to electrostatic repulsion between their chain segments. Given l_0 as the persistence length of the uncharged chain, the self-repulsion of the polyion chain leads to an increase of the persistence length, which is dependent on the extent of salt screening, resulting in $l_\tau = l_0 +$ const. $\times (f/a)^2/I$, with f/a as the charge density per unit length, calculated from f as the fraction of charged monomers along the chain, a as the monomer length. I is the concentration of monovalent salts. (Here, Manning condensation, which occurs at high charge densities on the chain, is neglected.) Thus, the rigidity of the chain increases with decreasing ionic strength.[1]

Due to chain stiffening, at low ion concentration, polyelectrolyte chains are predicted to form structures of ordered rods with a nearest neighbour distance $d: \sqrt{c_{polymer}}$. Light scattering could support the appearance of partially ordered rods, however, the distance d was found to be larger then expected.[2] One explanation is the formation of bundles consisting of two or more rodlike polyelectrolyte chains induced by short range attraction. Because of lack of suitable approach there is no experimental evidence for polyelectrolyte bundles in bulk solution. Our approach is to study polyelectrolyte brushes anchored at the air-liquid inter-face. We used amphiphilic diblock copolymers consisting of a hydrophobic anchor (PBA, poly butyl acry-late) and a polyelectrolyte block (PAMPS, poly acrylamido-methyl-propane sulfonic sodium salt, Fig. 1), where the brush thickness corresponds to at least 50% of the contour length (data not shown).[3]
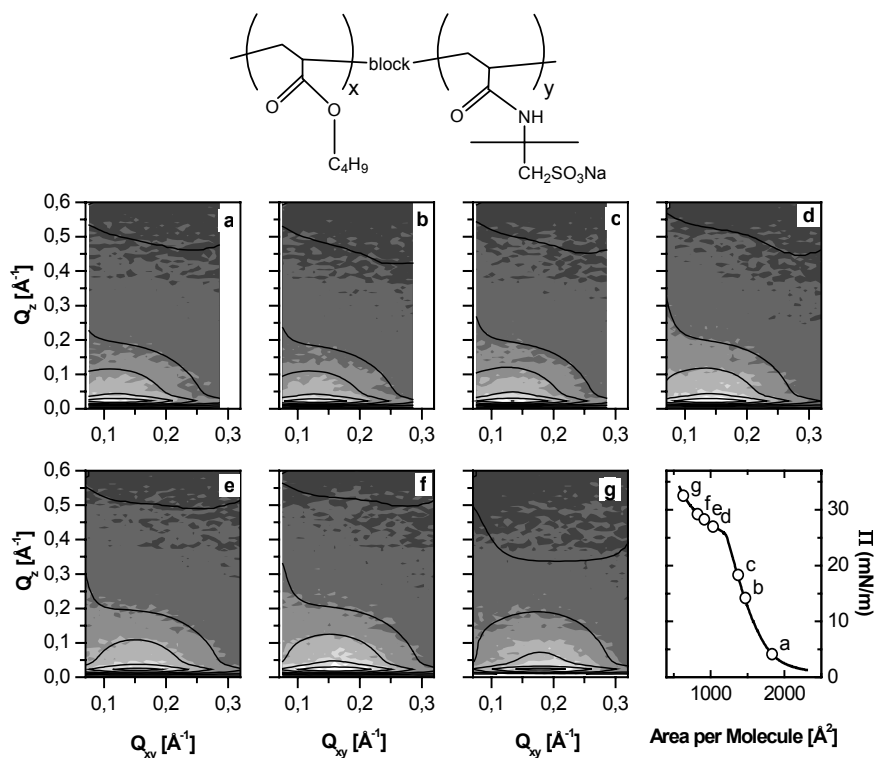

Figure 1, top: Structure formula of diblock copolymer $PBA_{76}PAMPS_{158}$. Bottom: In-plane X-ray diffraction measurements of $PBA_{76}PAMPS_{158}$ on 1 mM $CaCl_2$ solution along the isotherm.

To explore the lateral order, in-plane diffraction experiments were performed at BW1 in the liquid surfaces set-up (Fig. 1, bottom). In-plane peaks were observed for different kind of counterions (monovalent Cs^+ and divalent Ca^{2+}) and different ion concentrations in the subphase. On monolayer compression, the peak shifts

to larger Q_{xy} values, indicating smaller lattice distances. The lattice constant d, is expected to decrease according to $A^{-1/2}$, which is approximately true (with A the area per molecule). However, the lattice constant from the measurements exceeds the one calculated from the known molecular area (assuming a hexagonal lattice) by a factor of 1.3 to 2 (Fig. 2), suggesting that we do not measure the separation between single chains but rather between bundles. The fact that the lattice constant obtained from diffraction experiments is larger than the one calculated from the molecular area is seen as an indication of chain aggregation or bundle formation. In principle, chain clustering is caused by a balance of a short range attraction (possibly hydrophobic interaction), caused by the polymer backbone, and a long-ranged electrostatic repulsion. Furthermore, the lattice distance is larger (indicating more chains per bundle) when divalent ions are in the subphase than the same concentration monovalent ions. Actually, molecular dynamic simulations suggest that divalent counterions and stiff chains are necessary conditions for bundle formation, furthermore the chains must be sufficiently long and stiff.[4]
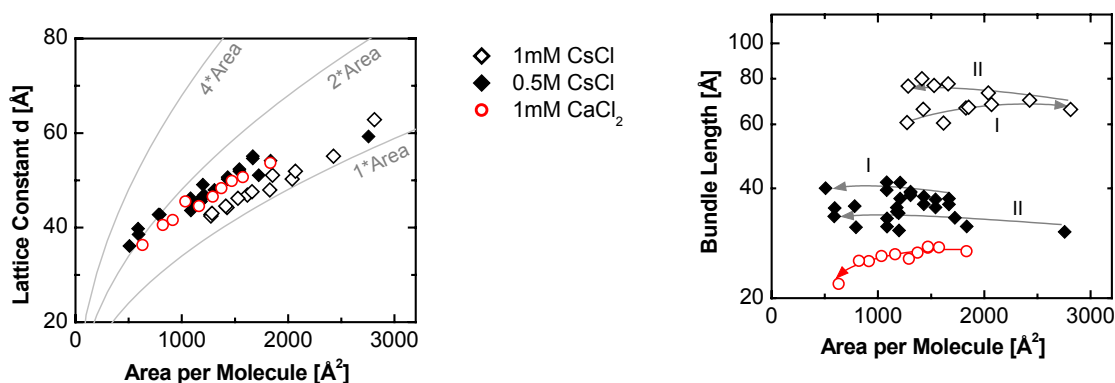
Figure 2: Results from in plane measurements. Left: Measured lattice constant d (assuming hexagonal lattice) vs. the area per molecule. Right: Length of the bundles deduced from the vertical coherence length of the rod-scans. "I" indicates the first, "II" the second compression or expansion, respectively.

In agreement with this model, the bundle thickness is roughly proportional to the persistence length: at low salt (1mM CsCl) it is 60-80Å, about twice the thickness found at high ion concentration (0.5M CsCl). Varying the grafting density by a factor of 2-3, it is constant within error. With divalent ions (1mM $CaCl_2$) the bundle length is smallest, and even shrinks slightly on compression, from about 30 to 22Å.
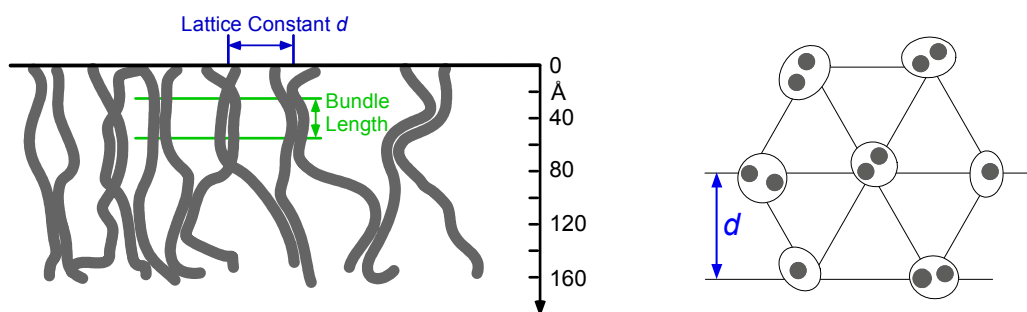
Figure 3: Model of clustered polyelectrolyte chains. Left: side view. Right: Top view.

References

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