

Bundle Formation of Polyelectrolyte Brushes with Divalent Counterions

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Bundles between charged chains form due to short-ranged attraction between the polyelectrolyte molecules, the number of chains in a bundle 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. Recently, we found bundle formation in polyelectrolyte brushes [1]. The electrostatic repulsion was reduced by increasing the salt concentration in the solution, leading to more and shorter bundles. Bundle size and length are investigated using the vertically aligned and oriented chains of polyelectrolyte brushes. Polyelectrolyte brushes show two distinctly different regimes called “osmotic brush” and “salted brush,” respectively. In both phases, the ions compensating the polymer charges are found in the brush [2-4].

To test the idea that divalent counterions in the solution also promote bundle formation, experiments are performed. 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) [1,2], PEE₁₄₄PSS₁₃₆. The hydrophilic block forms polyelectrolyte brushes [1,2]. To explore the lateral order, grazing incidence diffraction experiments (GID) were performed at BW1 in the liquid surfaces set-up.

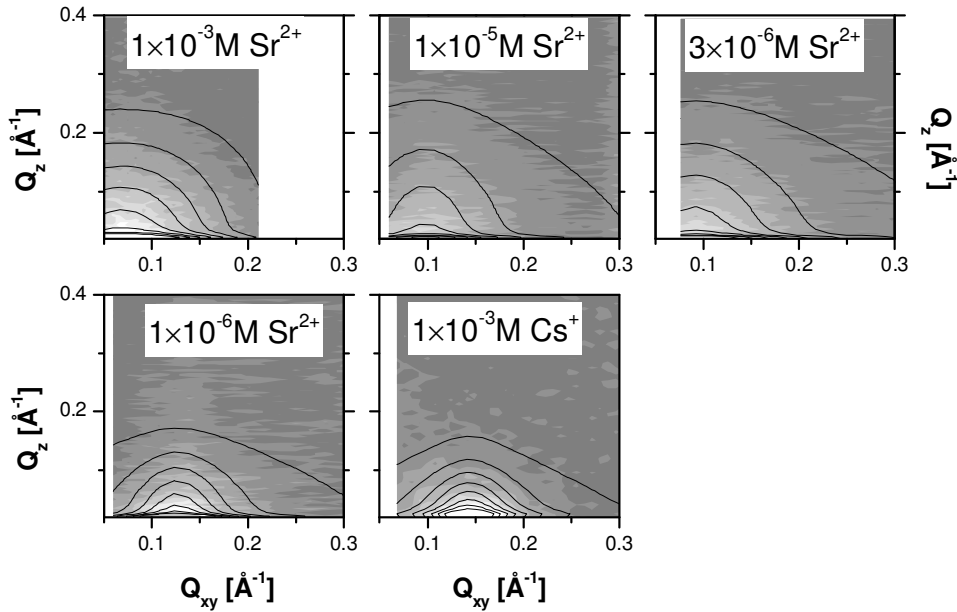


Figure 1: Small angle GID measurements of PEE₁₄₄PSS₁₃₆ brushes on subphases with divalent counterions Sr²⁺, measured at 1000 Å²/molecule. Also a diffraction peak on 1 mM CsCl is shown.

Diffraction peaks measured with different concentrations of SrCl₂ in the subphase are shown in Fig. 1. On monolayer compression, a shift to larger Q_{xy} -values occurs, indicating a decrease of lattice distances. 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 GID measurements exceeds the molecular area A_{Mol} as determined from the isotherm, even assuming a close-packed two-dimensional lattice ($A_{\text{cell}} = (2/\sqrt{3})d^2$ with d the distance deduced from the Bragg peaks). 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 Cs^+ counterions, cf. Fig. 2 and [1]) to a factor of about 8 (1 mM SrCl_2), 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.

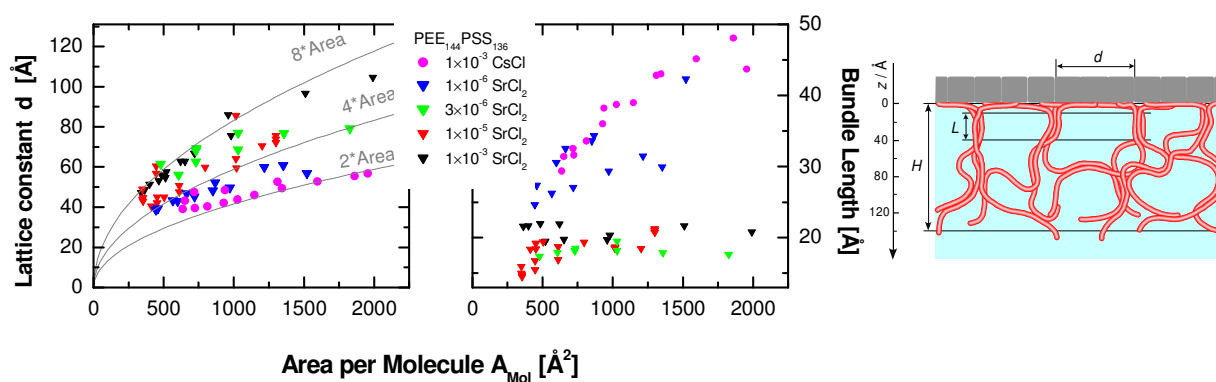


Figure 2: Derived parameters – lattice constant (left) and bundle length (centre) from GID measurements of $\text{PEE}_{144}\text{PSS}_{136}$ brushes on subphases with divalent cations Sr^{2+} (cf. Fig. 1). Also plotted are values for the polyelectrolyte in the osmotic brush phase with monovalent counter ion Cs^+ as reference. Right: Schematic of PSS bundles

Already a concentration of 1 μM SrCl_2 increases the number of chains per bundle slightly beyond two, the value obtained for a pure water subphase, and also for a subphase concentration of 0.1 M monovalent ions [1]. On further increase of the concentration of the divalent salt up to 1 mM, the number of chains per bundle increases, up to eight, a value obtained also with 0.2 or 0.3 M monovalent salt.

The pronounced sensitivity to extremely small concentration of divalent ions is also found when the bundle length L is considered. At 1 μM divalent salt, the behaviour is very similar to salt-free solutions or 1 mM monovalent salt: on increase of the grafting density of the brush, the bundle shortens from 40 to 25 Å, an effect which is attributed to the increased counterion concentration which reduces the chain stiffening. However, already at 3 μM divalent salt, the bundle length is almost constant, and about 20 Å. It is no longer influenced by changes of the grafting density, or further increase of the divalent salt concentration. This value is assumed to be the minimum value, the persistence length is reduced to the value found for neutral polymers, no electrostatic intrachain repulsion induces chain stiffening.

Concluding, the bundles observed with divalent ions causing the attraction between the chains is similar as found with monovalent salt, both concerning the number of chains per bundle, and the bundle length. However, the concentration of divalent salts is much reduced compared to monovalent salts, bundles formed in 1 mM divalent and 0.2 M monovalent salt are very similar.

References

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