Two-dimensional lamellar phase of poly(styrene sulfonate) adsorbed onto an oppositely charged monolayer

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Polystyrene sulfonate adsorbed onto oppositely charged dioctadecyldimethylammonium bromide (DODA) monolayers at the air/water interface is investigated with isotherms, X-ray reflectivity and grazing incidence diffraction [1]. Bragg peaks caused by flatly adsorbed, aligned PSS chains are observed, when DODA is in the fluid and also when it is in the condensed phase. The two-dimensional lamellar phase is only found at intermediate PSS bulk concentrations (0.001-1 mmol/L, with respect to monomer concentration). In this phase, the PSS coverage can be varied by a factor of 3, depending on DODA molecular area and polymer bulk concentration. The net charge of the DODA monolayer and the adsorbed PSS in the two-dimensional lamellar phase is positive; charge compensation is almost achieved at 1 mmol/L. At larger bulk concentrations, PSS adsorbs flatly yet without chain alignment. Presumably, a necessary condition for a two-dimensional lamellar phase is a pronounced electrostatic force which causes a large persistence length as well as repulsion between the aligned chains.

The PSS chain length is varied, the PSS concentration is kept constant (0.01 mmol/L). If the DODA monolayer is in the fluid phase (distance between two chains in the 2-dim lamellar phase: 3-6 nm), aligned PSS chains are only found if the contour length exceeds 10 nm. For DODA in the solid phase, the distance between the chains is reduced (2-2.5 nm) and no chain length dependence is observed. Also, the isotherms depend strongly on PSS chain length in a nonmonotonic way. A maximum of the latent heat of the liquid/condensed phase transition of DODA is observed at 8 nm PSS contour length. Presumably, for very short PSS chains and large chain separations found beneath the lipid monolayer in the fluid phase, the rotational entropy of the short PSS chains hinders alignment, and needs to be overcome when the DODA undergoes its phase transition.

![Fig: DODA isotherm with schematics of the lipids and the aligned PSS chains beneath for DODA in the fluid and in the condensed phase. Also shown is the X-ray diffraction pattern observed when DODA is in the coexistence region, two peaks assigned to the aligned PSS chains are observed simultaneously. The peak at large $Q_{xy}$ is attributed to the aligned PSS chains beneath the DODA in the condensed phase, similarly the peak at small $Q_{xy}$ is assigned to the PSS beneath the lipid monolayer in the fluid phase.](image)