

# Phase Transition of Flatly Adsorbed Polyelectrolytes: From Disordered to Two-dimensional Lamellar Phase

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We study experimentally the adsorption of polyelectrolytes onto an oppositely charged surface. Theoretical calculations predict that the polyelectrolytes may order in a two-dimensional lamellar phase, the polymer chains run parallel and do not overlap [1]. Until recently, for polyelectrolytes with a persistence length of a few nanometers, only a laterally disordered flat adsorption layer has been observed [2]. Recently, we observed the two-dimensional lamellar phase [3].

An insoluble monolayer at the air/water interface is used as a charged surface, since in this case the surface charge and the lipid phase (fluid or ordered) can be controlled by adjusting the molecular area. In this work we use monolayers of the saturated double-chain amphiphiles DODA (dioctadecyldimethylammonium bromide) interacting with the strong polyelectrolyte PSS (poly(styrene sulfonate)). The two-dimensional lamellar phase is studied with GID (Grazing Incidence Diffraction) experiments at BW1, in the liquid surfaces set-up (cf. Fig. 1). Varied is the molecular weight of the PSS (i.e. the length of the stretched chain, the contour length is varied between 50 and 16,500 Å). We are interested in the energy necessary to align the chains.

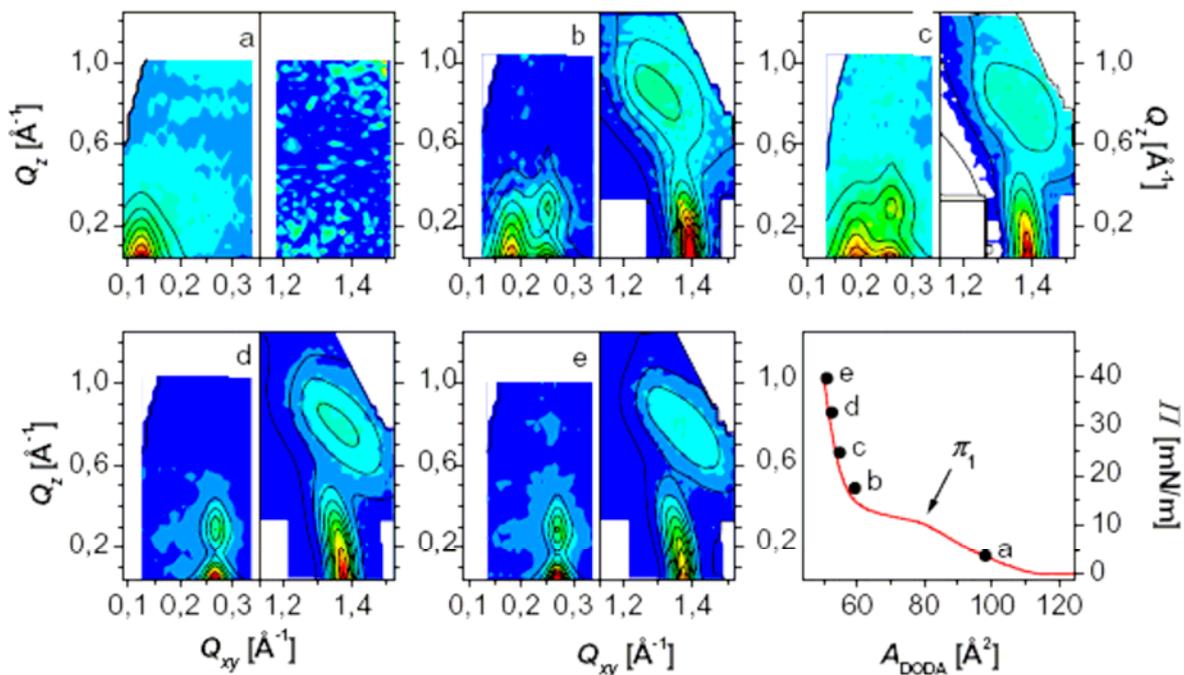


Figure 1: Wide and small angle GID study of a DODA monolayer on a subphase containing  $10^{-4}$  mol/L PSS (with respect to the monomer concentration). The measurements are taken at the DODA molecular areas indicated in the isotherm. The peaks at low  $Q_{xy}$  measure the separation of the aligned PSS chains, those at high  $Q_{xy}$  the structure of the alkyl tails of the lipid monolayer. Measurement (a) is taken in the fluid phase (no ordered alkyl tails), (d) and (e) are taken in the phase with ordered alkyl tails. (b) and (c) are taken in the coexistence region: two different low angle peaks are observed, one attributed to the aligned PSS chains beneath the fluid lipids, the other (with a second maximum at high  $Q_z$ ) beneath the ordered lipids [3].

Bragg peaks are caused by flatly adsorbed, aligned PSS chains are observed, when DODA is in the fluid and also when it is in the condensed phase (cf. Fig. 1). The molecular DODA area and the area per PSS monomer are compared. We find that charge compensation in the two-dimensional lamellar phase is never achieved, in agreement with theoretical predictions [1].

Isotherms are measured with the same PSS concentration in the subphase (cf. Fig. 2). It is interesting to note that the PSS chain with the shortest length  $L_K$  (50 Å) leads to the highest surface pressure, the system appears fluidised. On increase of the contour length of the PSS the surface pressure decreases, for contour lengths exceeding 960 Å saturation is achieved. By measuring the isotherms at different temperatures, the transition enthalpy of the fluid/condensed phase transition of the lipid can be determined (the alkyl chain ordering transition). It is found that it exhibits a maximum for contour lengths of 80 Å (cf. Fig. 2, centre). This maximum can be understood by considering the GID diffraction peaks such as those shown in Fig. 1. For PSS chains with the contour length 50 and 80 Å no diffraction peak is observed when the DODA is in the fluid phase. However, always the two-dimensional lamellar phase is observed when the DODA is in the condensed phase. This can be understood if the separation of the aligned PSS chains is considered: for DODA in the fluid phase the PSS separation is big, on monolayer compression it decreases from 65 to 40 Å. However, for the DODA in the condensed phase, much more PSS is adsorbed and the chain separation decreases from 28 to 24 Å.

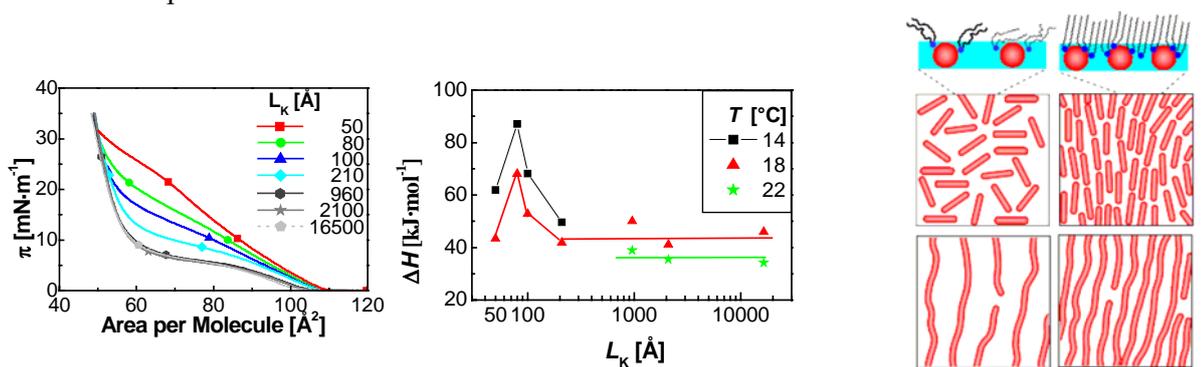


Figure 2, left: Isotherms of DODA with flatly adsorbed PSS ( $T = 18^\circ\text{C}$ , PSS concentration is  $10^{-5}$  mol/L, with respect to the monomer concentration), varied is the contour length  $L_K$  of the PSS. Centre: Transition enthalpy of the liquid/condensed phase transition of the lipid as function of the contour length  $L_K$ . Right: Schematic of the changes in the conformation of the flatly adsorbed PSS chains when the DODA undergoes its fluid/condensed phase transition: top: if the chains are short ( $L_K = 50$  or  $80$  Å), they are stretched and disordered, and are only aligned on monolayer compression. If the chains are long (100 to 16 500 Å), they are already in the two-dimensional aligned phase even if their surface coverage is low. The maximum in the transition enthalpy is attributed to the disorder/order transition of the longest PSS chains which undergo this transition.

For the very short PSS chains at low surface coverage (i.e., when the DODA is in the fluid phase), the chain separation (45 to 60 Å) is very similar to the chain length (50 to 80 Å). Obviously, at this low surface coverage the rotation entropy of the electrostatically stiffened chains [1] favours a flatly disordered adsorbed phase (cf. Fig. 2, right). Only when the surface coverage is increased, it is energetically more favourable to form the two-dimensional lamellar phase. Therefore, the maximum in the transition enthalpy observed with the isotherms, is attributed to the disorder/two-dimensional lamellar phase of the longest PSS chains ( $L_K = 80$  Å) which undergoes this transition. If the chains are longer, only the chain separation decreases on monolayer compression, this needs much less energy. Probably, for chains with a length exceeding 200 Å, some sort of equilibrium is achieved, because the isotherms show no longer a dependence on the contour length. Furthermore, the transition enthalpy is constant for PSS lengths exceeding 200 Å.

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## References

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