

Hydrophilic/Hydrophobic Nanostripes in Lipopolymer Monolayers

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The self-organization of macromolecules with a complex architecture is studied extensively in the last years, with the aim to nanostructure surfaces. Linear diblock copolymers with mutual antagonistic groups are a simple, much investigated system, since the respective block lengths determine the size of the nanostructure[1]. Yet little is known about the equilibrium structure when the forces from the two interfaces, and the intra- and intermolecular interactions are all of comparable magnitude. An active control of the domain morphology as well as the possibility to manipulate the structures in situ would obviously improve our understanding.

On a water surface the lateral density of a polymer monolayer can be externally adjusted, thus one can observe nucleation and growth of the nanostructure. We focused on lipopolymers[2, 3], the air-adjacent block consists of two lipid tails, the water-soluble block of the lipid head group and the polymer Poly(ethylene oxide) (PEO). In the highly compressed state, and at suitably low temperatures, we found a phase with ordered lipid tails, as is well known from other lipids and easily characterized by GID[4]. In that phase, the strong attractive short-ranged force of the condensed alkyl chains competes with the long-ranged repulsive entropic force of the polymers. Therefore, extremely high viscoelastic forces are theoretically expected[5] and experimentally found[6]. Furthermore, the balance of these competing forces may lead to a nanopatterned structure. Since the repulsive polymer forces decay very slowly, the size of the equilibrium nanostructure may be varied by nucleation and growth conditions, by the lateral pressure, or other external parameters.

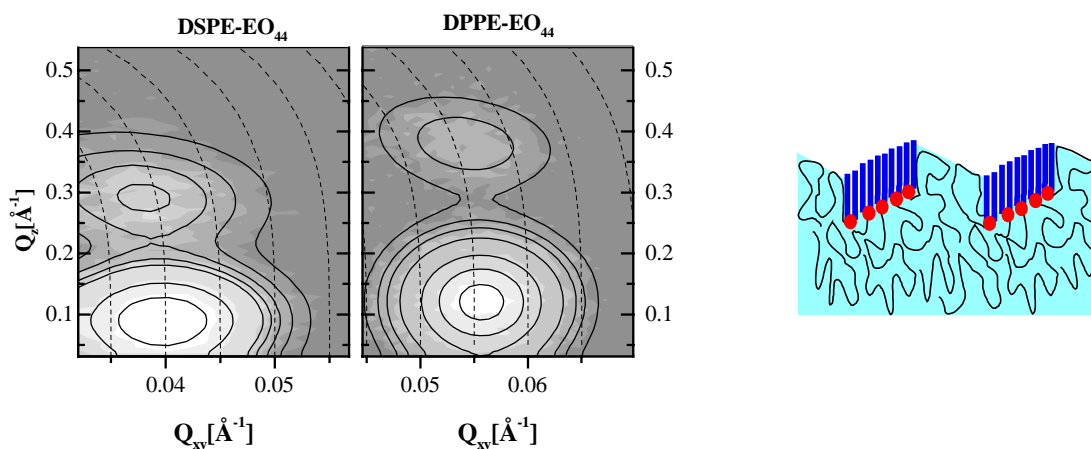


Figure 1: Superstructure peaks of DSPE-EO₄₄ (left) and DPPE-EO₄₄ (center). The molecules differ by the alkyl tail length (C₁₈ and C₁₆, respectively). Dashed lines indicate constant Q_{xy} in the non-Cartesian coordinates of the GISAXS-peaks. The measured intensity is represented by the gray scale, the lines are fits to Gaussian peaks. Right: tentative model of the lipopolymer arrangement on the water surface. Blue rods symbolizes alkyl tails, red circles the lipid head groups with their high electron density and black thin lines the polymer chains.

PEO-lipopolymers form nanostripes, as we concluded from transferred monolayers imaged with AFM[2, 3]). The nanostripe periodicity of monolayer on the water surface was successfully measured after realigning the liquid surfaces set-up at BW1 for small angles (cf. Fig. 1). Always, two peak maxima above the water surface at the same Q_{xy} -position, yet different Q_z -positions were found. The polymer length did not influence the superstructure. The only obvious effect of

decreasing polymer length was the increasing correlation length of the alkyl lattice (peak maxima at $Q_{xy} \approx 1.5 \text{ \AA}^{-1}$).

However, the nanostripe width is strongly influenced by the alkyl chain length. For DSPE-EO_N (C₁₈-alkyl chains, variable polymer length) the stripe periodicity varied between 140 and 160 Å, for DPPE-EO₄₄ (C₁₆-alkyl chains) between 110 and 120 Å. Obviously, shorter alkyl chain lengths cause a smaller short-ranged attractive force, and therefore a smaller stripe width. Generally, the stripe periodicity on the water surface is somewhat larger than for the monolayers transferred onto solid substrates, which is attributed to dehydration on transfer.

We tried to model supermolecular lateral structure, assuming polymer and lipid stripes, and the same averaged electron density profile as found in X-ray reflectivity. In this calculation, the contrast observed would be mainly due to the phospholipid head groups with their high electron density. However, we found no consistent model. The form factors describing the GISAXS peaks show unphysically long alkyl tail lengths. Therefore, we are now trying another approach. A striking fact of the experiments is that the positions of the GISAXS-peak maxima have the same ratio Q_z/Q_{xy} for the two different lipopolymers. Assuming for both molecules a similar form factor, this would indicate a tilted structure as sketched in Fig. 1. In this model, the tilt angle respective to the surface normal of both the hydrophilic and hydrophobic nanostripes would be the same[7].

The superstructure peak intensity depends mainly on the applied pressure, thus we can control the area fraction of the stripe phase. However, the stripe periodicity DSPE-EO₄₄ varies by a factor of 1.5 (12-18nm), depending on monolayer history. The smallest stripe periodicity is measured at the beginning of the first compression – then, the stripe width increases both with time and compression. This very unusual behavior is a strong indication of threshold behavior: the nanostripes of condensed alkyl chains embedded in polymer nucleate during the first order phase transition. With increasing degree of crystallization, they need to deform, reorient and/or merge. On second compression, the largest stripe periodicities were measured, which decreased with time. Obviously, the molecules were pre-aligned, facilitating the highly cooperative process of alkyl chain condensation within the nanostripe center, and, in the 2nd step, the nanostripe alignment. Exploring these effects will help us to find the equilibrium stripe distance, and, in the next step, its pressure dependence.

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