The Internal Interface of a PEO$_{432}$-PEE$_{484}$ Diblock Copolymer Monolayer

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The phases and internal interfaces of diblock copolymers are understood in three dimensions [1]. The choice of a particular pair of monolayers (in our case ethyl etylene, EE, and ethylene oxide, EO) establishes the sign and magnitude of the energy of mixing between the blocks, which can be approximated by the Flory-Huggins segment-segment interaction parameter $\chi$. When $\chi>0$, a decrease in PEE-PEO segment contacts reduces the system enthalpy. Yet PEE-PEO segregation is opposed by a loss in entropy, which is increased by (i) the PEE-PEO joints localised at an interface and (ii) the confinement and stretching of the chains (i.e., a loss in configurational entropy). Compression of a PEE-PEO monolayer promotes the chain stretching further, and therefore, it is possible to explore the internal interface as function of grafting density.

To investigate PEO brushes at different anchoring densities, we chose a hydrophobic, fluid anchoring block (poly (ethyletylene), PEE), and prepared monolayers at the water surface. Both neutron and X-ray (cf. Fig.1) reflectivity experiments were performed (some of the latter at BW1, in the liquid scattering set-up). The contrast for X-rays is inferior to the one for neutrons, yet due to the higher incoming X-ray intensity larger $Q_z$ values are accessible. The combination of the two methods provides insights not possible with one method alone. Fitting the X-ray reflectivity curves, the PEE thickness can be determined very well. Also, one finds a thin (1-3 nm) interfacial layer between the PEE and the PEO/water blocks, and sees a bit of the PEO brush. Yet, because of the better contrast, the density profiles of the PEO brushes are determined from neutron reflectivity [2].

Figure 1: Left: Normalized X-ray reflectivity curves at the molecular areas indicated in the isotherm shown in the inset of the bottom plot. The lines are fits with the simplest model leading to satisfactory results: one layer PEE exhibiting PEE bulk density, however a thin and a thick layer PEO were necessary. Bottom: The electron density profile as deduced from the fits. Right, top: The thickness of the hydrophobic PEE-layer as derived from the neutron (open symbols) and the X-ray (filled symbols) measurements vs. the grafting density (the inverse molecular area). The solid line is calculated assuming a nm-thin PEE layer with the mass density of the bulk phase. Bottom right: The thickness of the PEO brush as calculated from the 1$^{st}$ moments of the respective density profiles. The straight line is a power law with the exponent 0.45, fitted to the neutron data (open symbols).
Fitting the X-ray reflectivity curves, one finds a thin (1-3 nm) interfacial layer between the PEE and the PEO/water blocks. This layer was introduced in the scattering length density profile, to which the neutron reflectivity measurements are fitted. According to the neutron reflectivity results, the scattering length density of the interfacial layer decreases on film compression, indicating removal of water, or addition of PEO [2]. According to the X-ray results for the expanded monolayer, the electron density of the interfacial layer is very high, suggesting an adsorbed PEO monolayer, as described often in the literature [3, and references quoted therein]. However, on monolayer compression, the electron density in the thin interfacial layer decreases dramatically, indicating removal of PEO or addition of water. This contradiction between neutron and X-ray results is obtained by assuming a binary mixture (PEO/water) in the thin interfacial layer. The incorporation of additional PEE in the interfacial layer allows to explain both neutron and X-ray results self-consistent (cf. Fig. 2).

![Graph showing volume fractions of PEO (open squares), PEE (filled circles) and water (filled triangles) in the thin interfacial layer between the PEE and PEO blocks as function of the grafting density, as calculated from both X-ray and neutron experiments. Right: Schematics of the molecular arrangement of the PEE-PEO monolayer and its changes on compression.](image)

The broadening of the interface between the two blocks reduces the entropy loss which is caused by chain stretching in the two compressed brushes. Such a broadening was theoretically considered possible, but to our knowledge was not observed before.

**References**