Interactions of Soft crystalline materials with solid-liquid interfaces studied by neutron scattering

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Soft crystalline materials are used in many applications that improve human life, like tissue engineering [1] or in photonic crystals in optical devices [2]. The ability to tune the optical or mechanical properties of such materials easily through changes in temperature, pressure, composition as well as the exact type of interface they are in contact with, paired with the usually low toxicity, makes them frequently used in the industry today. Understanding the structural mechanisms and surface effects on the molecular scale of these materials has, however, remained challenging to study, especially in the near surface region. The sample in this study is a triblock co-polymer from polyethylene-glycol(PEG)-polypropylene-glycol(PPG)-PEG, which self-assembles into micelles. At higher polymer concentrations or temperatures, the spherical micelles form close-packed superstructures whose viscoelastic and optical properties are highly tunable. The hydrated crystals can experience beam-damage in X-rays and cryo-methods exclude the study of dynamic shear and pressure-effects on the sample. The buried interface of interest only allows for highly-penetrating probes. As such, neutron scattering methods, mainly neutron reflectometry and Grazing incidence small angle neutron scattering (GISANS) [3], with their high-penetration power and the ability to harness the high hydrogen-deuterium contrast in nuclear scattering, have been used to study the solid-liquid interface in some detail.
We employ *in situ* -Rheo-Near-surface-SANS (NSSANS) to study the effects of mechanical deformation on the ordering of polymer micelles close to interfaces of varying surface energies. An increasing shear rate is observed to reduce the order of cubic stacking in the near surface region, which is in contrast to previous bulk studies, where shear has generally improved ordering of dense layers in out-of-plane direction. At the same time, the near surface crystallite size decreases. We propose that close to the interface, the shear-induced transitioning to hexagonal states may be explained by stress-induced deformation faults in the stacking sequence. Fault probabilities of a few percent are sufficient to derive the observed intensity distributions in the NSSANS patterns. Further surface scattering experiments showed that even pressure can be used as an excitation to obtain rich structural behavior in the interfacial region for this sample. A pressure of 500 bar was observed to destroy any close-packed order at room temperature, while a higher temperature could overcome this high hydrostatic pressure to reform the crystal.

Keywords:
polymers, micelles, self assembly, soft crystals, rheology, neutron scattering

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