Experimental report

24/05/2025

Proposal: DIR-344 **Council:** 4/2024

Title: Studying of the local crystalline structure of polymer micelles at solid-liquid interfaces under shear

Research area: Soft condensed matter

This proposal is a resubmission of 9-10-1809

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Samples: Pluronic F127

Instrument	Requested days	Allocated days	From	To
D22	3	2	21/05/2024	23/05/2024

Abstract:

Gels consisting of polymer micelles offer various possible applications in the fields of tissue engineering and drug delivery. A model example for such a system is Pluronic F127 micelles in aqueous solutions. It forms cubic crystal lattices affected by interfaces and shear forces. This experiment investigates the influence of these parameters on the ordering. Three surfaces with different energies will be prepared to study micellar behavior under shear and temperature variations to investigate their influence on micellar ordering. Grazing incidence SANS will enable us to determine scattering length density profiles. A significant finding from previous studies is the reduction in the 111 Bragg peak intensity, even at low shear rates, challenging conventional expectations
from bulk studies. It is suggested that shear induces wavy lattice planes, leading to decreased contrast in scattering length density along the surface normal and increased diffuse scattering. GISANS is well-suited to investigate these questions since it can probe the local crystalline structure close to interfaces.

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During experiment DIR-344 Grazing Incidence Small Angle Neutron Scattering (GISANS) measurements were performed to characterize the ordering processes of a soft crystalline material close to the solid-liquid interface. The sample was Pluronic F127, which is a triblock co-polymer with amphiphilic properties that self-assembles into micelles and may further assemble into crystalline structures under the right conditions. This study aimed at understanding the effect of the interface itself on the formation of crystalline structures and whether there are any notable differences to the known bulk behavior.

As such, three different interfaces were investigated by functionalizing the surface of silicon blocks differently. First, an untreated SiO surface which was just rinsed with ethanol with a contact angle (CA) of approximately 40 degrees. Second, a block with a Octadecyltrichlorosilane (OTS) coating and CA of approximately 110 degrees. Third, a block treated with RCA clean and CA of below 10 degrees. All three surfaces were measured under three different temperatures: 24, 27 and 37 degrees. In addition, the effect of shear on the ordering was investigated with every temperature-surface combination exposed to shear rates of: 0 s^{-1}, 0.01 s^{-1}, 10 s^{-1}, 100 s^{-1}. To achieve this, an Anton Paar rheometer was placed on the sample stage and the silicon blocks mounted on an aluminium plate to achieve a cone-plate rheological setup.

An example of a recorded pattern is shown in figure 1. One can see a number of strong

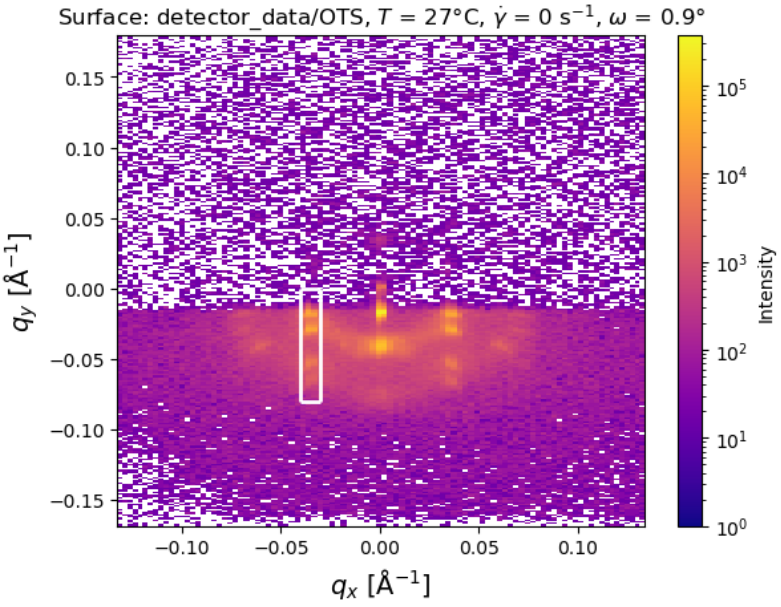

Figure 1

reflections that are excited which are corresponding to different Miller indices as well as hcp and ccp stacking. For further analysis, a cut was made for all patterns along the white box as marked in figure 1. One such cut is presented in figure 2. To investigate how the structure of the soft crystal changes, the intensities of a number of peaks were investigated by determining their intensity with Gauss fits. This can give information about the prevalence of certain phases in the different in the material and how the experimental conditions influence

the phase changes. To get a better understanding of this, such a cut was repeated for every experimental condition.

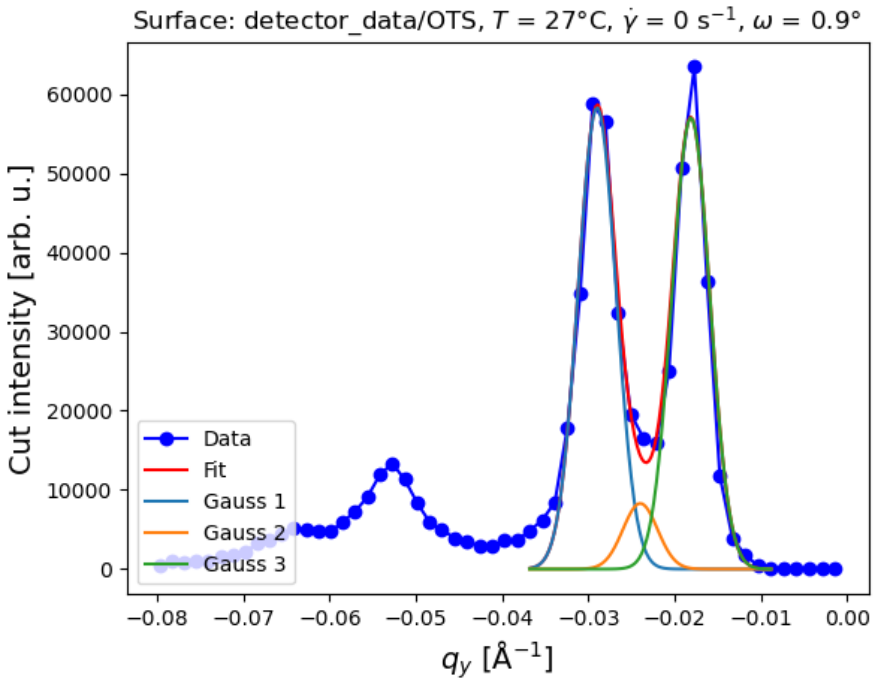

Figure 2

In figure 3 the intensity of the 002 peak of the cubic close packed phase is depicted for 27 C and all three surfaces as well as for increasing shear rates. The angle of incidence is 0.9 degrees which is above the critical angle of 0.6 degrees. Interestingly, it can be observed that the highly hydrophobic (OTS) and highly hydrophilic (RCA) surfaces show similar influence on the near surface ordering. The surface with an intermediate surface energy on the other hand shows, especially a lo shear rates, very different behavior. One potential explanation for this may be that the strongly functionalized surfaces cause a layer of surface micelles to adsorb which screens the true surface energy to the rest of the near surface region. An experiment with lower polymer concentration is planned to help understand these effects.

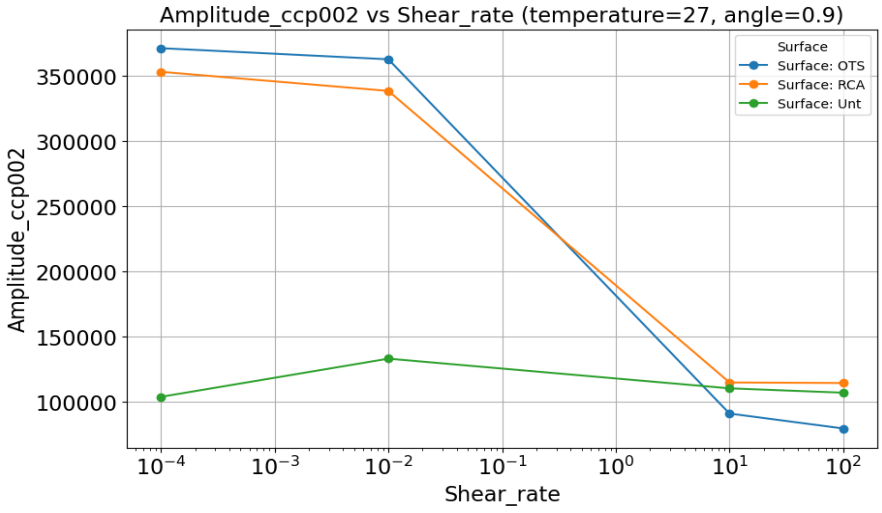

Figure 3