

Experimental report

12/02/2025

Proposal: 9-10-1809

Council: 10/2023

Title: Re-orientation of polymer micelles under shear at the liquid solid interface

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: Pluronic F127

Instrument	Requested days	Allocated days	From	To
FIGARO	3	3	22/03/2024	25/03/2024
D22	3	0		

Abstract:

We request beamtime at ILL to explore the effects of surface energy and shear on the ordering in polymer micellar crystals. Utilizing Neutron Reflectivity (NR) and Grazing Incidence Small Angle Neutron Scattering (GISANS), we aim to understand how different surface termination, shear rates and temperatures impact the crystalline structure vertically and horizontally. This will be able to connect bulk effects with much less studied surface effects.

Our study investigates the surprising reduction in specular reflected intensity of Bragg peaks at low shear rates, possibly due to surface-induced lattice alignment. We will deposit self-assembled monolayers on silicon wafers to create controlled surfaces. Data will be collected across various temperatures and shear rates using an Anton Paar rheometer, focusing on the region of small shear rates.

Combining NR and GISANS measurements, our experiment will shed light on the complex behavior of F127 micellar crystals, which is a material frequently used across a variety of applications, including tissue engineering, drug delivery systems or lubrication.

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During experiment 9-10-1809 neutron reflectometry (NR) 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 preparing 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: 25, 26 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} .

Looking at specular reflection, it becomes apparent that it is very challenging to properly reduce the data because of significant off-specular contributions to the scattering pattern. In addition, there is small angle scattering leaking around the beam stop which influences the specular reflection, see figure1.

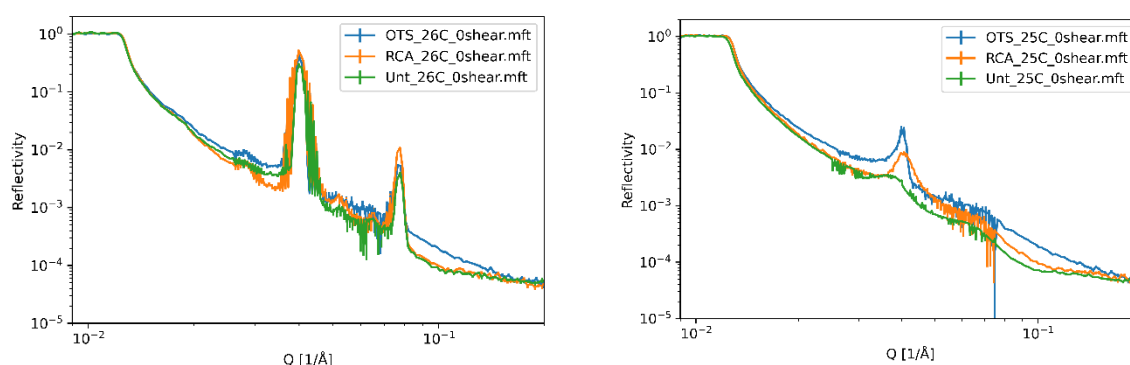


Figure 1

Due to the inhomogeneous layering and limited correlation length of the soft micelles, a large off-specular scattering component could be observed. To analyze this, the Bragg rod was fitted row for row for every Q (wavelength) and as such a cut along the rod plotted. From the shape of the Bragg rod one can deduce information about the ordering processes. In Figure 2, three cuts are presented for the three different surfaces at 26 degrees and no shear. A higher peak height can be interpreted as a higher degree of order.

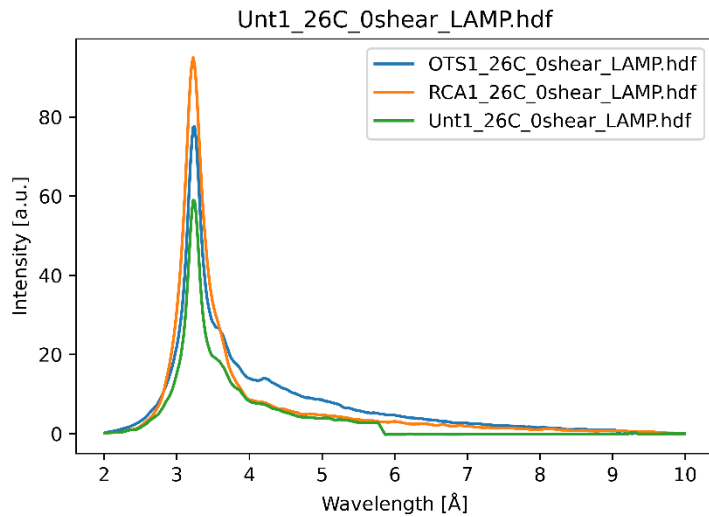


Figure 2

In figure 3, the maximum value of the Bragg peak is plotted against the applied shear rate for all surfaces. One interesting feature that can be observed is the strong decrease of order for the OTS-coated surface, compared to the untreated surface with increasing shear rate.

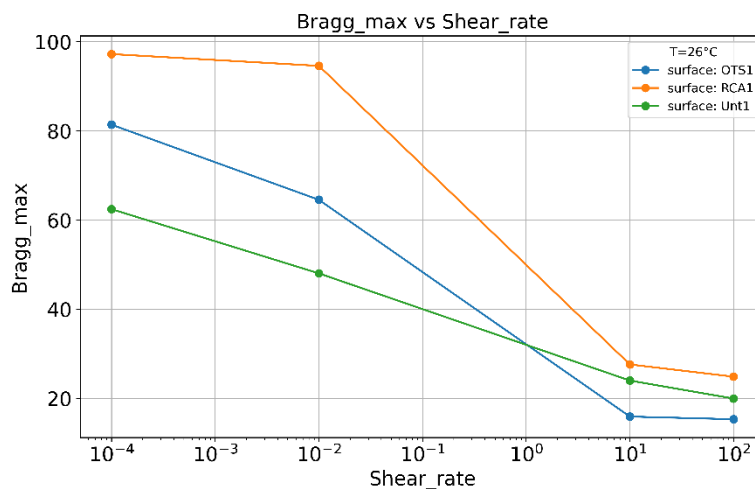


Figure 3