



Experiment title: Structural Changes in Thin Films of Surfactant Encapsulated Clusters (SEC) upon Annealing	Experiment number: SC 829
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Report:

Our general research interests are the wetting properties of complex fluids. In this study, we have concentrated on two systems: Surfactant Encapsulated Clusters (SEC) and liquid crystals from the *n*CB series.

SECs are a supramolecular assembly of a polyoxomolybdate spherical hollow shell (“giant fullerene”) enclosed by a layer of surfactant [1], hydrophobic, spherical particles with a diameter of 4.5 nm. Thin SEC films can be produced by LB techniques or spin coating and are thought to act as model systems for the dewetting behaviour of simple liquids. The SEC would represent an “atomic liquid” that can be detected individually by e.g. AFM.

Heating such a film to temperatures of ca. 200 °C leads indeed to dewetting and growth of holes, easily observable by optical microscopy and similar to what has been observed in e.g. polystyrene films.

AFM imaging of such films shows a roughening of the initially flat surface at temperatures near 100 °C. Further heating to about 180 °C leads to the formation of terrace-like structures of approximately monolayer height and shows small holes opening at the edges of the resulting facets, see Fig. 1. This represents the onset of the dewetting process, only visible by AFM and precedes the large scale dewetting observable by optical microscopy.

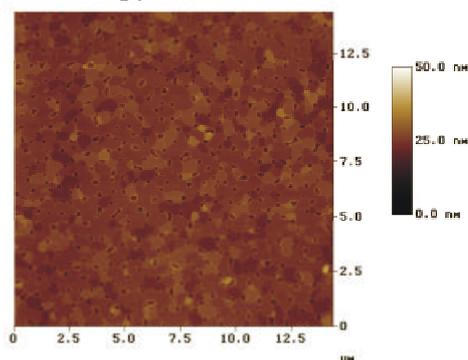


Fig. 1: SEC-film after annealing at 180 °C for 5 min. (AFM image)

We studied this unique dewetting pathway by SAXS and GID while heating our samples in situ. This allows us to understand exactly which changes in the film structure lead to this surface topography. We have worked with a standard setup for both types of measurements at a X-ray wavelength of 1.5576 Å. Our samples were mounted horizontally on a commercial heat stage (Linkam THMSG 600) in a self made helium flow chamber. A linear PSD detector was mounted horizontally for the SAXS measurements and vertically for GID.

Reflectivity measurements of thin films of SEC on silicon wafers with varying thickness were recorded. Upon heating, significant changes in the film structure with temperature can be observed, see Fig. 2 left for an example of a monolayer of SEC: at room temperature the features representing the calculated diameter of the SEC can be seen. During heating sharp peaks appear that can be attributed to the formation of terraces of multilayers with a layer thickness of 2.7 nm, which corresponds to the diameter of the molybdate core of the SEC. The GISAX data, shown in Fig. 2 right, reveal at room temperature a maximum corresponding to a structure of dimension 4.7 nm which can be attributed to the diameter of a single SEC (4.5 nm according to molecular modeling [1]) and a less pronounced peak corresponding to 3.1 nm. At temperatures close to 200 °C, where dewetting can be observed optically, the films show only a very broad peak corresponding to an in plane ordering with a structural length of ca. 3.5 nm and an additional feature corresponding to 1 nm can be observed on some scans (Fig. 2 right, inset). This leads us to the conclusion that the material degrades while heating, the 1 nm peak being due to aggregates of free surfactant molecules while the terraces are formed by multilayers of bare molybdate shells. The dewetting of the films would then proceed while the SEC break up into their constituents, resulting in a structure consisting of aggregates of molybdate shells ordered in terraces and free surfactant.

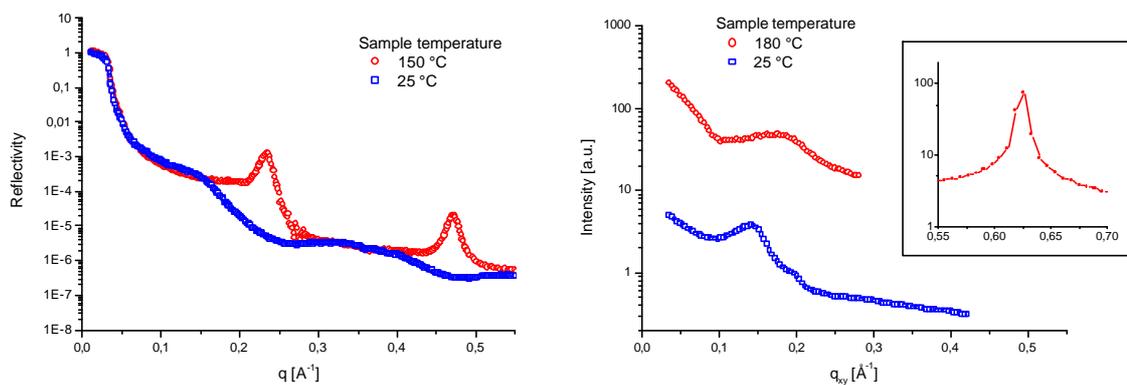


Fig. 2: left: Changes in reflectivity while annealing a SEC film, right: GID data taken while annealing a SEC film

Our SAXS measurements on thin films (20-200 nm) of liquid crystals from the *n*CB (4'-*n*-alkyl-4-cyanobiphenyl) series on Silicon substrates were aimed to study the transient instability in film thickness, which these materials exhibit while changing from the nematic to the isotropic phase. This process starts below the transition temperatures of the bulk material (T_{NI} 35 °C for 5CB and 40.5 °C for 8CB); see Fig. 3 [2]. The lateral wavelength of this instability is dependent on the heating rate, varying from 0.01 K/min to 10 K/min. The heat stage setup for the SEC made it possible to observe the change in film thickness quantitatively in real time by SAXS.

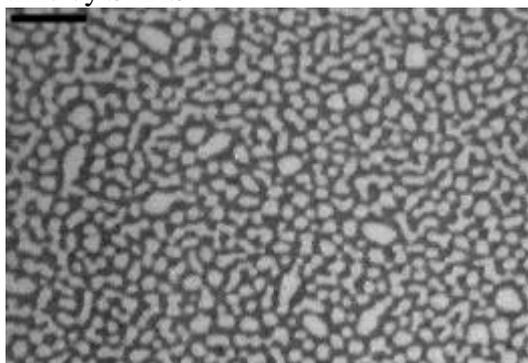


Fig. 3: 5CB film (51 nm thick) undergoing an instability at 33.5 °C (optical micrograph; black bar = 100 μm)

In order to get a high temperature resolution, we used temperature ramps with heating rates of 0,1 and 0,05 K/min in our experiments. During these ramps we could record a SAXS reflectogram every 4 minutes. Fig. 4 (left) shows typical examples for an initially 38 nm thick 5CB film. Above and below the instability the

reflectograms show a film with a distinct thickness and no internal structure. While crossing the temperature region in which the instability occurs, a more complicated structure is visible, which can be described as a superposition of the reflectivity of two films with different thickness. The curve shown for 32.5 °C, for example, can be approximated rather well by the coexistence of a 21 nm and a 55 nm thick film with a relative contribution of 75 % and 25 % respectively, confirming a recent study on 5CB [3]. The instability vanishes eventually, leading to a flat, isotropic film (red curve). Surprisingly, the same behaviour was found for 5CB films prepared on silicon wafers covered with a thin layer of the polyelectrolyte PEI (polyethylene-imine), which imposes different anchoring conditions at the solid interface.

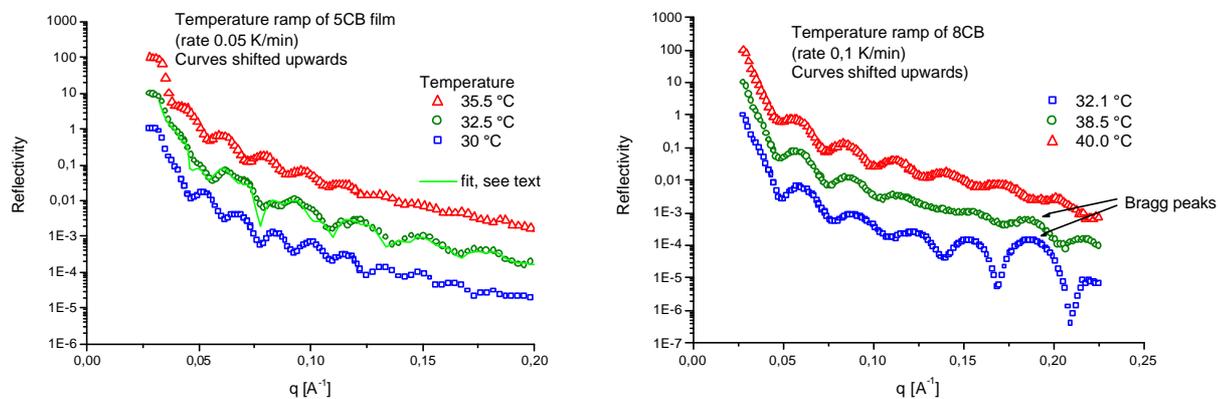


Fig. 4: LC films undergoing the thickness instability.

8CB films did show a different behaviour from 5CB:

Fig 4 (right) shows a typical example of an 8CB film consisting initially of 7 smectic layers of 8CB dimers and a 3-layer next to the substrate, giving a total film thickness of 25 nm. In contrast to 5CB, the reflectivity data on 8CB do not show a coexistence of well defined film thicknesses during the instability but only an increasing roughness (Fig. 4 right, green curve). After reaching the isotropic phase, the roughness again decreases. The Bragg-peak, indicating the smectic layering of the 8CB molecules, can be observed up to temperatures of 38 °C, well above the bulk smectic-nematic phase transition temperature of 32.5 °C, indicating residual smectic order in these films. An 8CB film on PEI covered silicon, however, did not show an increased roughness upon heating up to 40.5 °C. Only the smectic-nematic phase transition was visible [4].

In addition, some SAXS and GID measurements were performed on 8CB filled into parallel microchannels that were etched into a silicon sample. We could obtain clear data on the ordering of the LC molecules inside the channels, proving that microchannels may be a useful tool for the analysis of filamentous materials aligned in these channels.

References

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