



	Experiment title: Structure development and structural studies in mesostructured silica films templated with nonionic and polymeric surfactants	Experiment number: CH-1443
Beamline: ID10B	Date of experiment: from: 9 th July to: 15 th July 2003	Date of report: 28 th August 2003
Shifts: 18	Local contact(s): Dr Leide Cavalcanti	<i>Received at ESRF:</i>
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Report:

The aim of these experiments is to study the structure and growth mechanisms of surfactant-templated silica films at the air/solution interface. These materials are formed by the polymerization of silica around surfactant micelles in solution to form composite solids containing a channel system that has the dimensions and connectivity of a surfactant liquid crystalline phase.¹ Removal of the surfactant results in a solid containing open nanoscale channels with potential applications as high surface area materials in chromatographic separations, heterogeneous catalyst supports and in patterned structures for nanotechnology. Under certain conditions thin films of these materials form at the air-solution interface forming a solid mesostructured membrane which can be removed from the surface. The intensity available on ID10B allows us to follow the growth process by making diffuse reflectivity measurements in the z-direction; a pattern is collected in 60 seconds so the evolution of diffraction peaks corresponding to ordered mesophases within the film, can be followed over time.² As a result of our experiments using cetyltrimethylammonium bromide (CTAB) as the templating surfactant we put forward a model of silica-surfactant interaction that suggested the polymerising silicate in this acidic system acts in a similar fashion to a branched polyelectrolyte interacting with surfactant micelles.³ Mesostructured film formation occurs at the solution surface for a wide range of concentrations, however the mesostructure development follows either a surface-driven or a bulk-driven pathway.^{4,5} Under a narrow range of concentrations mesostructured particles form in the subphase and rise to the surface to form the film. At concentrations outside this range, the mesostructure develops more slowly at the surface by accumulation of silica coated micelles. This behaviour is similar to coacervation formation in polyelectrolyte-surfactant solutions.

In the current experiment we replaced the cationic surfactant CTAB with the nonionic polymeric surfactant Pluronic P123, (EO)₂₀-(PO)₇₀-(EO)₂₀. This surfactant is more industrially attractive than CTAB since it is cheap, more environmentally friendly and

produces mesostructured silicates that are more hydrothermally stable, with larger pores, and the thicker walls. Films formed with P123 contrast with films templated with CTAB since now the surfactant itself is a form of polyelectrolyte, so the interaction is between two polyelectrolytes rather than between polyelectrolyte and a small molecule surfactant. Also in this case interactions between the two species must be due in greater part to hydrogen bonding, rather than electrostatic interactions, as the polymer does not carry a formal charge.

The experiments proved to be technically difficult due to the larger d-spacing of the diffraction peaks forcing us to use a lower incident angle to collect the data, increasing the sensitivity of the measurement to height changes due to evaporation. Also, although film formation is observed over a wide range of concentrations, ordered films with sharp diffraction peaks were observed only at a narrow range of concentrations. Interestingly, SAXS experiments conducted simultaneously on BM26B on the same system showed development of mesostructured particles in solution over the entire range of concentrations investigated, despite the apparent lack of mesostructure observed in the films at the surface.

In those films where peak development was observed the peaks grew in rapidly after long induction periods, appearing and growing to their maximum intensity within 2-3

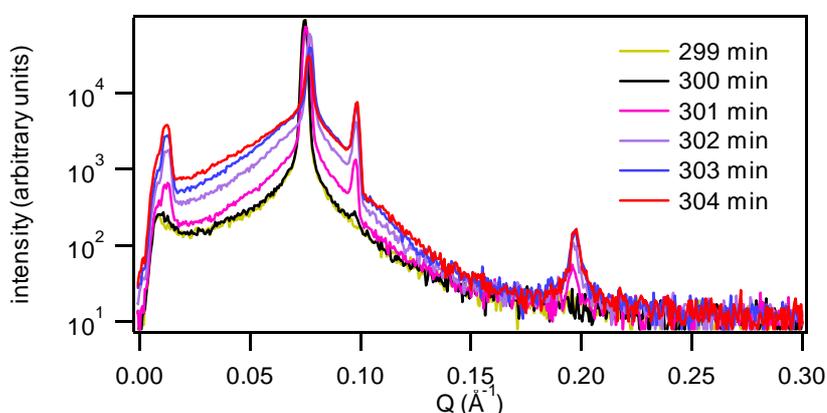


Fig 1: Rapid development of diffraction peaks at 0.1 and 0.2 \AA^{-1} in a P123/TMOS film accompanied by surface roughening causing a drop off in specular intensity.

minutes (Fig. 1) unlike the CTAB case where peak intensity developed over several tens of minutes. The peaks had a constant, narrow width suggesting the mechanism in this case is bulk-driven, corresponding with the observed development of mesostructured particles in the subphase. It is also possible that in this case a non-ordered film at the surface undergoes a rapid ordering transition independently to subphase processes. In films which

did not form sharp peaks, broad bumps in the position of the first order were observed, similar to those seen in silica-surfactant films containing a glass of spherical rather than cylindrical micelles. In many cases, broad features under the specularly reflected peak were also observed to develop during the induction period, possibly due to small angle scattering from surface domains. Brewster angle microscope images of these films show the presence of large non-continuous structures hundreds of microns across at the interface for long periods before the development of diffraction peaks was observed in the reflectivity profiles.

References:

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