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| | Experiment title: Polyelectrolyte-surfactant films as templates for inorganic oxides | Experiment number: CH-2727 |
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Report:

Our group has an extensive research program into the formation of self-assembled silica surfactant films at the air solution interface.¹⁻³ Recently, we have also been investigating mesostructured polymer-surfactant films which were inspired by our work on the mechanisms of structure formation in silica-surfactant systems.⁴⁻⁶ In this experiment we explored synthesis of mesostructured silica films by using the highly ordered polymer-surfactant materials as secondary templates to synthesize inorganic materials. This was done by introducing silica precursors into solution along with the soluble polymer and surfactant. Silica deposits in regions of the film filled with a polymer hydrogel, surrounding the arrays of ordered micelles. This provides an easy way to introduce a polymeric species as part of the inorganic film to make it robust and mechanically strong, but also to enhance its chemical functionality which could have practical applications in catalysis and sensing.

Solid films form at the surface of silica/CTAB/PEI solutions within 30min.⁷ SAXS data showed that dried films have highly ordered 2D hexagonal structures and neutron reflectivity indicated that phase transitions occur during film assembly. Here ID10B, Trokia II, was used to measure time resolved off-specular reflectivity from films growing at the air/water interface. Once films were formed, reflectivity and grazing incidence X-ray diffraction (GIXD) measurements were used to obtain structural details of the phases within the films. We aimed to determine whether similar formation mechanisms operate in the presence of PEI at high pH compared to our earlier studies of silica films synthesized without PEI at low pH.

We used surfactant cetyltrimethylammonium bromide (CTAB) and polyethylenimine (PEI) as a template and tetramethoxysilane (TMOS) as silicate precursor to form films at the air/water interface. Two polymer molecular weights (MW~2000 SPEI and ~750 000 LPEI) were used. Films synthesized with SPEI, used a crosslinker, EGDGE to enhance the thickness of the resulting inorganic films. PEI concentrations were varied from 20g/l to 40g/l. For both polymers, the molar ratio of inorganic:CTAB varied from 3.5 to 10.5. These correspond with molar ratios used in our earlier SAXS and neutron reflectivity studies.

Film formation was observed by the appearance of diffraction peaks along with loss of the specular reflectivity peak due to surface roughening in the time resolved experiments. In both cases the diffraction peak appeared before we could start the measurement indicating

rapid accumulation of mesostructured material at the solution surface. In Figure 1, for CTAB/30SPEI templated silica films, loss of the specular peak began within 10min and the intensity continued to decline. However, for LPEI films, the specular peak was not visible by the time we started the measurement. The data suggested that silica films synthesized with long PEI form rough films quickly while films synthesized with SPEI take a longer time to form and are smoother at the interface.

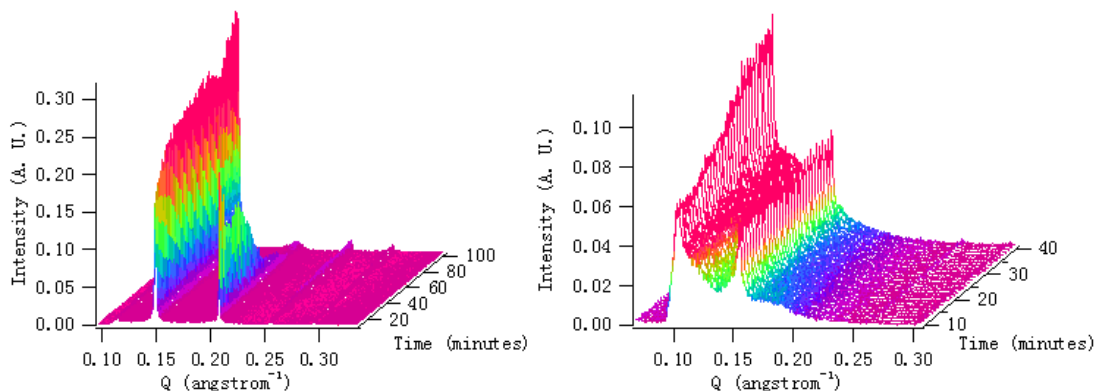


Figure 1: Time resolved off-specular reflectivity of silica films templated with (a), CTAB/30SPEI and (b) CTAB/30LPEI developing at the air-solution interface.

The final structure of silica films synthesized with CTAB/PEI have been confirmed by GIXD. As shown in Figure 2A, films synthesized with 30g/l SPEI show 2D hexagonal structure with d spacing ~ 4 nm, variation of PEI and TMOS concentration does not change film structure. However, for LPEI there is no long-range ordering when [LPEI] is lower than 20g/l. At 30g/l, (Figure 2B), final film structure is ordered 2D hexagonal. A $Pn3m$ cubic phase is observed for LPEI at 40g/l, (Figure 2C). This differs from SAXS data on dried films at the same concentrations of CTAB/LPEI/TMOS. Drying processes therefore have a significant impact upon film structure. This phase transformation probably results from evaporation of water which decreases the polar head group area, increasing the surfactant packing parameter and forcing a rearrangement of the micelles.

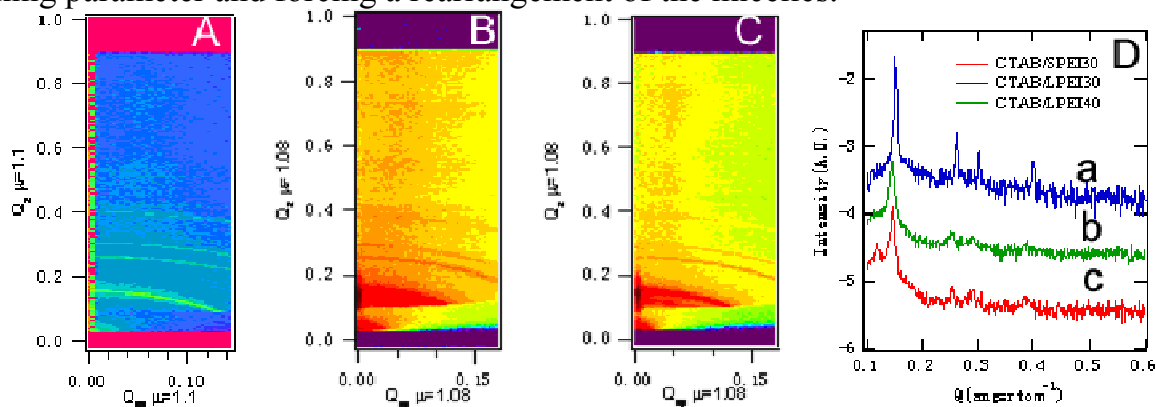


Figure 2: GID patterns: (A) CTAB/30SPEI, (B) CTAB/30LPEI, and (C) CTAB/40LPEI templated silica films at the air-solution interface; (D) Line profiles at $Q_y = 0.01 \text{ \AA}^{-1}$ from GID patterns in A, B, C.

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