ESRF	**Experiment title:** Surfactant and crosslinking effects on polyelectrolyte-surfactant films at the air-solution interface	**Experiment number**: CH-2064
Beamline: ID 10B	**Date of experiment**: from: 7 September 2005 to: 13 September 2005	**Date of report**: 12 October 2005
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Report:

This work forms part of our program of experiments investigating the formation and evolution of structure in thin films which form spontaneously at the air-solution interface. In this experiment we measured, on the Troika II beamline, reflectometry profiles and grazing incidence X-ray diffraction (GID) patterns from a series of surfactant templated polymer films. These transparent films, which form at the air/water interface, are often up to 100 microns thick and previous experiments show that such films can possess a relatively high degree of liquid crystalline ordering. Our previous experiments show that the ordering is dependent on the polymer molecular weight,[1] the charge on the polymer and the charge on the micelle.[2] The purpose of the current experiment was to study the effect of crosslinking the polymer on the mesoscale organisation within the films. Crosslinking introduces permanent bonds between polymer molecules making the films sufficiently robust to remove from the solution surface and form continuous membranes with the ordered micellar array trapped within the film.

Primarily our experiments examined the tetradecyltrimethylammonium bromide (C_{14}TAB) or dodecyltrimethylammonium bromide (C_{12}TAB)/polyethylenimine (PEI) and the cetyltrimethylammonium bromide (C_{16}TAB)/PEI/ethyene glycol diglycidyl ether (EGDGE) mixed systems. The C_{16}TAB concentration was constant at 0.04M, while the concentration of the PEI (expressed as molar concentration of monomer units, so that the two molecular weights can be directly compared) was varied from 1.4M to 0.088M. Previously we have examined films of C_{16}TAB, C_{14}TAB, and C_{12}TAB with PEI (MW = 750,000 Da and 2000 Da) using neutron reflectometry and observed that the length of the alkyl chain does affect the position of the diffraction peaks in the reflectometry profile.[1] To determine whether the ordering within the film is also changed (ie are diffraction rings or spots produced from the films and under what conditions) we have performed, GID measurements on films of PEI and C_{12}TAB or C_{14}TAB surfactants at a range of concentrations (eg Figure 1a).

The effect of the addition of EGDGE, a cross-linking agent, to the C_{16}TAB/PEI films was also examined at several PEI and EGDGE concentrations. EGDGE concentrations were adjusted to give ratios of PEI monomer :EGDGE of 3.5, 35 & 350 for the different concentrations of PEI used. Importantly the GID patterns that were obtained for the EGDGE containing films are similar to those of the non-EGDGE containing films for similar concentrations and polymer molecular weights, indicating that the cross-linking of the film does not significantly disrupt mesoscale ordering or the film formation process (Figure 1b).

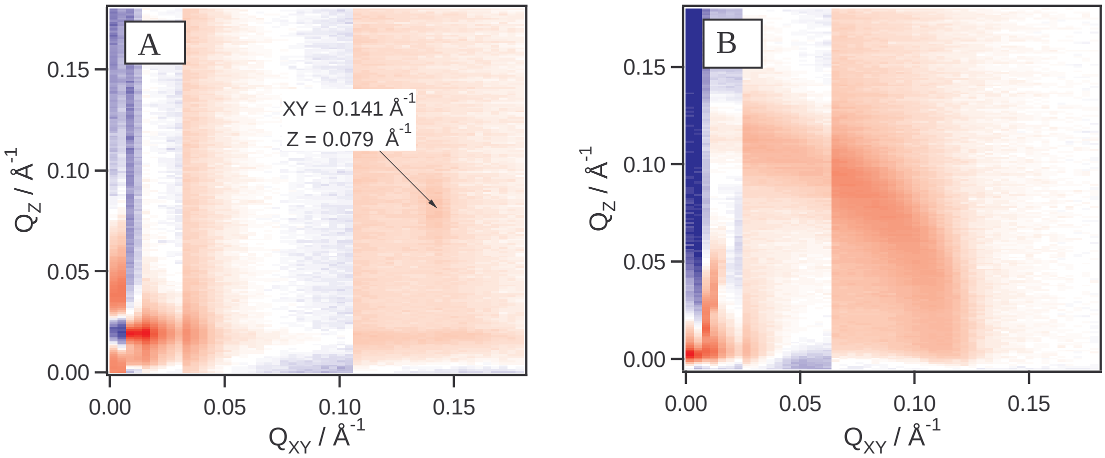

Figure 1 – (a) C_{12}TAB/PEI (750,000 Da), (b) C_{16}TAB/PEI (750,000 Da)/EGDGE. No absorber correction has been made to the patterns.

A series of secondary experiments were also performed on films of C_{12}TAB with DNA, cetyltrimethylammonium bromide (CpB) with PEI, and C_{16}TAB and sodium dodecyl sulfate (SDS) with polyacrylamide (PAA). Whilst no significant structure was collected in either the reflectometry or GID patterns for the DNA films, the patterns for the CpB/PEI and C_{16}TAB/SDS/PAA films both gave good structure (Figure 2). In particular the C_{16}TAB/SDS/PAA film patterns suggest that multilamellar vesicles are incorporated into the film which raises the exciting possibility of encapsulating water-soluble species within the films for slow release applications. Work on confirming the structures in these films is proceding.

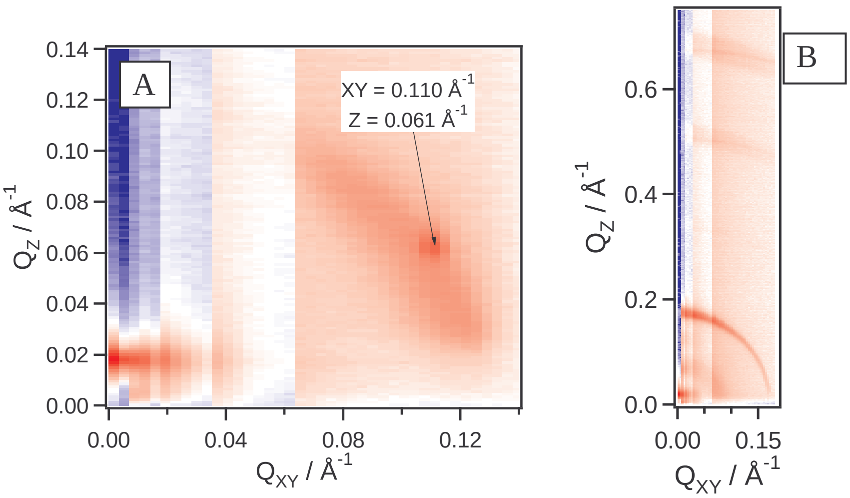

Figure 2 – (a) CpB/PEI (750,000 Da), (b) C_{16}TAB/SDS/PAA. No absorber correction has been made to the patterns.

References

1. O'Driscoll, B. M. D. et al. Thin Films of Polyethylenimines and Alkyltrimethylammonium Bromides at the Air/Water Interface. *Macromolecules* **38**, 8785-8794 (2005).
2. O'Driscoll, B. M. D., Fernandez-Martin, C., Wilson, R. D., Roser, S. J. & Edler, K. J. The Effect of Micelle Composition on the Formation of Surfactant-Templated Polymer Films. *J. Phys. Chem. B*, submitted (2005).