| ESRF | **Experiment title: Mesostructure in functionalised polymer-surfactant films** | **Experiment number**: SC-2707 |
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| **Beamline**: ID10B | **Date of experiment**: from: 08/07/2009 to: 14/07/2009 | **Date of report**: 31/08/2009 |
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**Names and affiliations of applicants** (* indicates experimentalists):

Dr Karen Edler*, Department of Chemistry, University of Bath
Mr James Holdaway*, Department of Chemistry, University of Bath
Mr Matthew Wasbrough*, Department of Chemistry, University of Bath

**Report:**

This experiment aimed to investigate the mesostructure in functionalised polymer-surfactant films. Our group is currently investigating the design, formation and characterisation of surfactant templated polymer-surfactant films that form spontaneously at the air-water interface upon mixing of water soluble polymer and surfactant solutions. This method of structured film formation offers a compelling alternative to more labour intensive methods such as layer-by-layer deposition or spin coating.

Our initial film forming system comprised mixtures of cationic surfactant hexadecyltrimethylammonium bromide (CTAB) and polyethylenimine (PEI). We found it possible to cross-link the PEI within the films using ethylene glycol digylcidyl ether (EGDGE) to enable robust film removal and determined that the film structure was 2D hexagonal close packed (CH2281 Dec 06)[1]. More recent experiments showed that it was possible to form films from mixtures of cationic surfactant CTAB and the anionic surfactant sodium dodecyl sulfate (SDS) and a wider variety of biocompatible polymers such as polyacrylamide (PAAM). In these experiments we found it possible to achieve bicontinuous 3D cubic structures by variation of the surfactant ratios and electrostatic architecture of the polymer (SC2452, Jul 08)[2].

To introduce functionality to our mesostructured polymer-surfactant films we have been investigating films formed from mixtures of phenylboronic acid (PBA) containing polyacrylamides, CTAB and SDS. PBA has been chosen as it reversibly binds saccharides[3]. We intend to use these mesostructured PBA films as glucose sensors with controllable properties. The PBA containing polyacrylamides have been synthesised by co-polymerisation of acrylamide and methacrylamidophenylboronic acid (MAAMPBA) to produce polyacrylamide-co-polymethacrylamidophenylboronic acid (PAAM-PBA); to introduce cross-linking functionality to the polymer acrylamide and MAAMPBA were co-polymerised with acrylic acid (AA) to produce polyacrylamide-co-polymethacrylamidophenylboronic acid-co-polyacrylic acid (PAAM-PBA-AA).

To investigate the control of mesostructure in films formed from PBA containing PAAM, CTAB and SDS three variables were investigated; CTAB to SDS ratio, total PBA content of the polymer and the amount of EGDGE used as cross-linker. The surfactant ratios

investigated were CTAB and SDS in ratios of 9:1, 8:2 and 7:3 at a total surfactant concentration of 0.05M. PBA content in PAAM-PBA was investigated at 1%, 2% and 3% molar content of PBA. EGDGE concentration present as an electrophilic cross-linker when used with PAAM-PBA-AA was investigated at ratios of 1:2, 1:1 and 2:1 compared to polyacrylic acid content in the polymer-surfactant mixture. We used off-specular time-resolved reflectivity to investigate film formation, and reflectivity and grazing incidence x-ray diffraction (GIXD) to probe structure.

Variation of surfactant ratios in the film forming systems manifested as different film structures. At a ratio of 7 CTAB: 3 SDS with PAAM-PBA (1% PBA) a possible *Im3m* cubic structure is present, suggested by the GIXD pattern (Fig 1A) whereas when a ratio of 9 CTAB: 1 SDS are used with the same polymer, a distinctly different phase is formed, which is possible a *Pn3m* phase (Fig 1B). Variation of PBA content in the polymer also causes variation in the mesostructure of the film. For PBA content at 1% and formed with 7 CTAB: 3SDS a possible *Im3m* cubic structure is formed (Fig 1A) whereas when PBA content is at 3% at the same surfactant ratios a possible *Fd3m* cubic structure is formed (Fig 1C). Cross-linking of the films manifests in structural changes; when the EGDGE is present in a 1:1 ratio with the AA monomers in PAAM-PBA-AA films formed with 7 CTAB: 3 SDS a lamellar structure is present (Fig 1D) compared to the cubic in the non-cross-linked analogue (Fig 1A). Definite indexing of the film structures in on-going.

Different surfactant concentrations were also to be investigated however due to the block allocation of this experiment with SC-2706, time constraints meant this was not possible.

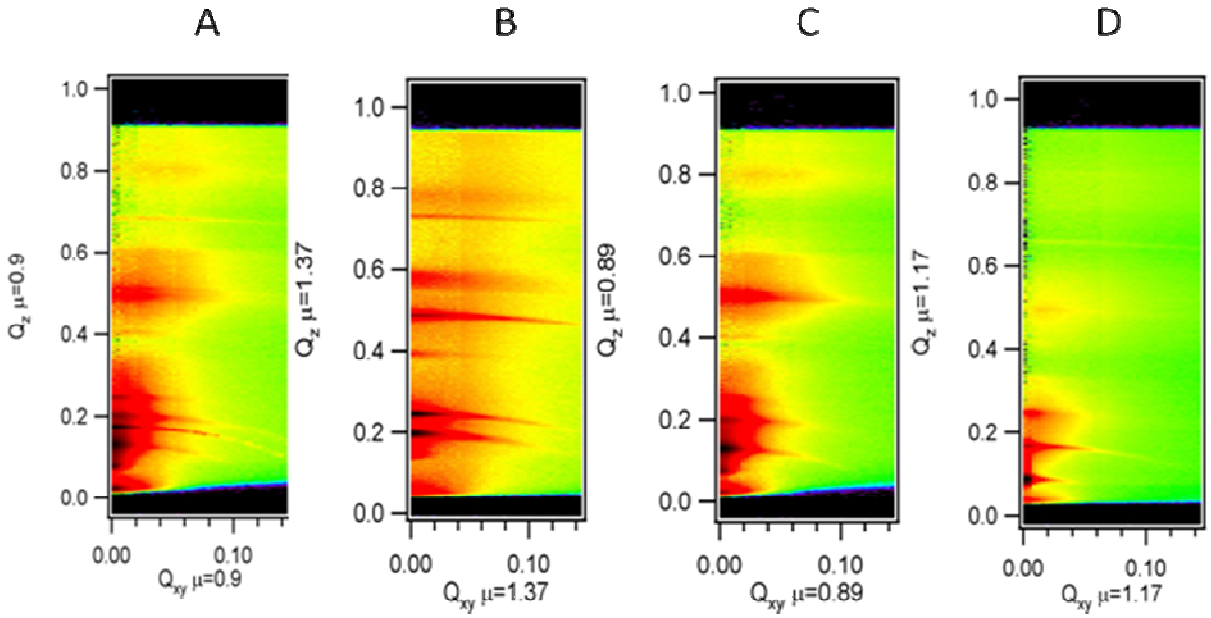


**Fig 1. GIXD of films. 7 CTAB: 3 SDS 0.05M PAAM-PBA (1% PBA) 0.1%wt (possible Im3m cubic structure) (A), 9 CTAB: 1 SDS 0.05M PAAM-PBA (1% PBA) 0.1% wt (possible Pn3m cubic phase) (B), 7 CTAB: 3 SDS 0.05M PAAM-PBA (3% PBA) 0.1% wt (possible Fd3m cubic) (C) and 7 CTAB: 3 SDS 0.05M PAAM-PBA-AA (1% PBA, 1% AA) 0.1% wt (lamellar structure).**

## References


1. O'Driscoll, B. M. D., Fernandez-Martin, C., Wilson, R. D., Knott, J., Roser, S. J. and Edler, K.J., *Langmuir*, 2007, 23, 4589-4598.
2. Edler, K. J., Wasbrough, M. J., Holdaway, J.A. and O'Driscoll, B. M. D., *Langmuir*, 2008, 25, 4047-4055.
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